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The synthesis of novel homochiral polymers derived from amino acids

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THE SYNTHESIS OF NOVEL HOMOCHIRAL POLYMERS DERIVED FROM AMINO ACIDS.

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Abstract

Several series of novel acrylate and methacrylate monomers have been prepared from dipeptides. These monomers were derived from the (*S*)-Ser-(*S*)-Ala, (*S*)-Ser-(*S*)-Phe, and (*S*)-Ser-(*S*)-Pro dipeptides and contained a polymerisable group in the side chain of the serine residue. The polymerisation of the dipeptide monomer by free radical polymerisation provided a route to novel poly(peptides). The amino acid derived monomers were found to copolymerise with methyl methacrylate to provide copolymers with non-linear correlations between the percentage incorporation of chiral monomer and the value of specific rotation. The protecting groups present in the poly(peptide) were then removed in one step, to provide polymers and copolymers with significantly different solubility properties to the parent polymers.

Furthermore, a series of novel acrylate and methacrylate monomers were prepared from a tripeptide. These monomers were derived from the (*S*)-Ala-(*S*)-Ser-(*S*)-Phe tripeptide and contained a polymerisable group in the side chain of the serine residue. The tripeptide was polymerised under free radical conditions to provide novel polymeric materials which again displayed non-linear correlations between the percentage incorporation of chiral monomer and the value of specific rotation.

In a separate project, the combination of multifunctional initiators and the use of lysine residues to introduce branch points into poly(amino acids) has enabled the synthesis of novel highly branched poly(amino acids).

Contents

Abbreviations

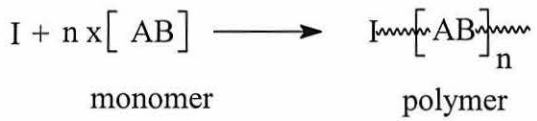
Ac	Acetyl
Ala	Alanine
Boc	*tertiary*-Butyloxycarbonyl
^{t}Bu	*tertiary*-Butyl
c	Concentration, grams per 100ml
C.I.	Chemical ionisation
cm^{-1}	Wavenumbers
d	Doublet
dd	Double doublet
δ	Parts per million
DCM	Dichloromethane
DMF	*N*, *N*-Dimethylformamide
DMSO	Dimethyl sulfoxide
E.I.	Electron impact
Et	Ethyl
F.A.B.	Fast atom bombardment
g	gram
^{1}H	Proton
Hz	Hertz
IR	Infrared
J	Coupling constant
K	Absolute temperature in Kelvin

Leu	Leucine
m	Multiplet
Me	Methyl
MeCN	Acetonitrile
mg	Milligram
MHz	Megahertz
ml	Millilitre
MMA	Methyl methacrylate
m.p.	Melting point
nm	Nanometre
nmr	Nuclear magnetic resonance
Ph	Phenyl
Phe	Phenylalanine
q	Quartet
s	Singlet
Ser	Serine
Su	Succinimide
t	Triplet
THF	Tetrahydrofuran
TMS	Tetramethylsilane
w / v	Weight per volume
Z	Benzyloxycarbonyl

1 Introduction

1.1 Macromolecules

Traditional polymer chemistry has evolved around the use of reactive modules (monomers) that can be engaged in multiple covalent bond formation to produce single molecules.[1] The multiple bond formation is driven either by a chain reaction or by a polycondensation scheme. In a single chain reaction, the average length of the chain is determined by the monomer : initiator ratio **(Scheme 1)**.



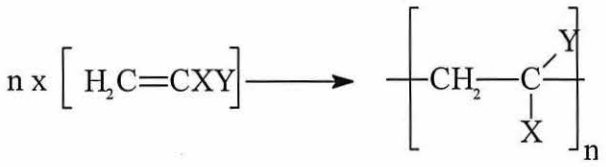
Scheme 1. n = number of monomer uni

This type of polymer chemistry gives rise to three macromolecule architectures: linear (*e.g.* plexiglass and nylon); cross-linked (*e.g.* rubbers and epoxy resins) and branched (*e.g.* low density polyethylene). In these types of polymers, there is no precise control over size, atom positions, molecular shape, or covalent connectivity (other than the linear topology).

1.2 Chain reaction type polymerisation

Addition or chain reaction polymerisation usually occurs amongst molecules containing double or triple bonds; but in certain cases, it can also occur between bifunctional compounds that result from the opening of ring structures, *e.g.* ethylene oxide. There is no liberation of small molecules during addition polymerisation.

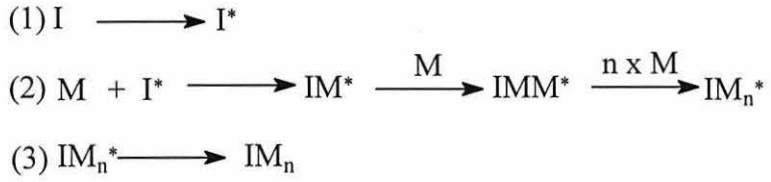
A very important group of olefinic compounds that undergo addition polymerisation are the 1-substituted and 1,1-disubstituted alkenes, $H_2C{=}CXY$, where X may be H or Me and Y may be a halogen, CO_2R, or CN **(Scheme 2)**.[2]



Scheme 2. n = number of monomer units

In theory, there are three possible ways in which this polymerisation can occur: head to tail, -CH_2CXY-CH_2XY; head to head and tail to tail, -$CXYCH_2$-CH_2CXY-$CXYCH_2$-CH_2CXY and a random combination of head to head and head to tail alignments. However, experimentally the polymerisations usually proceed through head to tail polymerisation due to steric and electronic effects.[2]

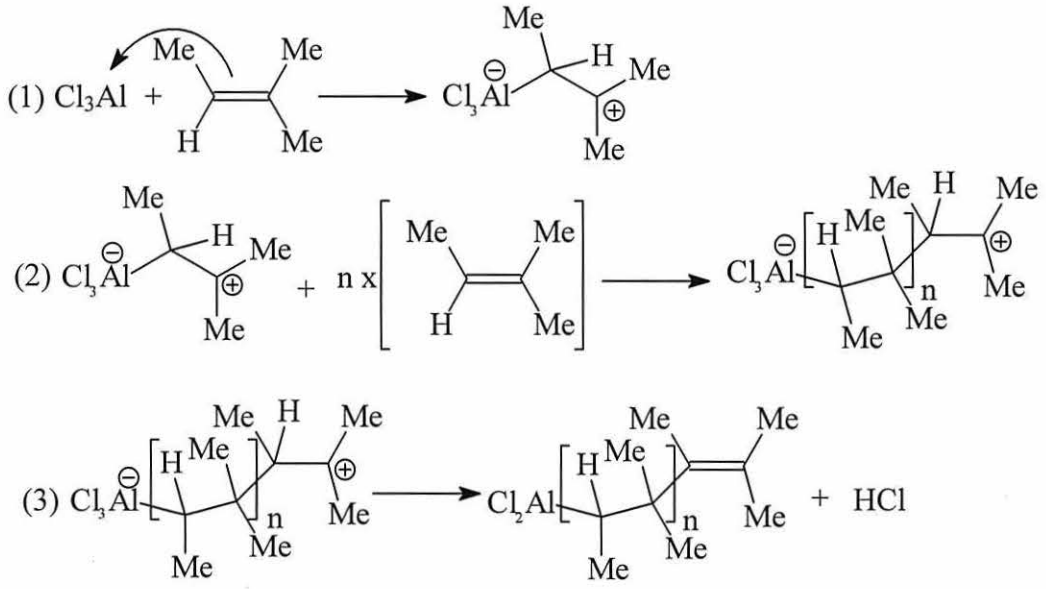
Polymerisations are carried out in the presence of catalysts or initiators and the polymerisation of olefins can be accelerated by ionic-type catalysts or radical initiators.[2-5] Both types of reaction consist of a number of steps, which follow one another consecutively and rapidly. The first step involves the generation of a short lived initiator species, which subsequently reacts with the first monomer to create an ion, or radical, this is termed initiation. In the second step of the polymerisation, this ion or radical reacts intermolecularly with the monomer in a process termed propagation. During this process, a stereocentre may be formed in the polymer backbone. In the final step of the polymerisation, two units react intermolecularly destroying the ion or radical, in a process known as termination **(Scheme 3)**.



Scheme 3. I = initiator; I* = initiator ion or radical; M = monon
M* = ion or radical; (1) initiation; (2) propagation; (3) terminati

1.3 Cationic polymerisation

Cationic polymerisation occurs in the presence of Lewis acids such as $AlCl_3$, $SnCl_4$, or BF_3.[4,5] In certain cases, H_2SO_4 can also catalyse polymerisation. Ionic catalysts are usually electrophilic reagents and the chain initiating action of these catalysts depends on their electrophilic nature and occurs through the catalyst acquiring a share in a pair of electrons (π-electrons) from the double bond of the monomer. In step three of the mechanism shown in **Scheme 4**, a proton is lost producing a double bond at the end of the chain so that the molecule becomes deactivated and ceases to grow.

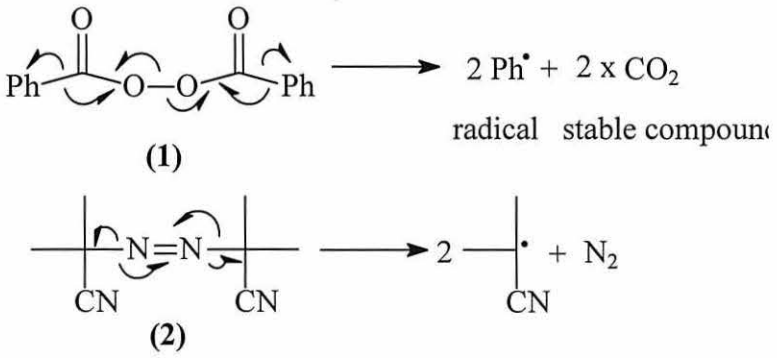


Scheme 4. n = number of monomer units; (1) initiation; (2) propagation; (3) termination.

1.4 Radical polymerisation

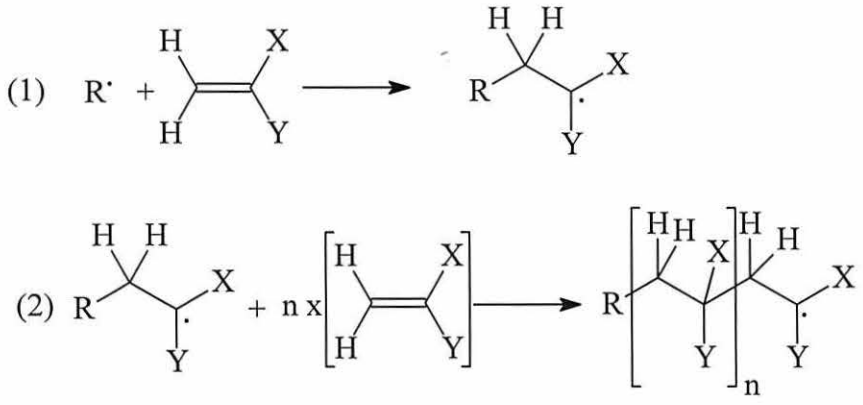
The most important cases of addition polymerisation are those which occur by a chain reaction and are brought about by radical initiators.[3-7] The initiator is usually a symmetrical molecule possessing a weak bond, which can be split through exposure to UV light or heat to form a stable radical. In most cases, when the initiator molecule is split a stable compound is formed along with the radical, *e.g.* AIBN[8] gives, N_2 and a

radical whilst benzoyl peroxide gives, CO_2 and a radical **(Scheme 5)**.

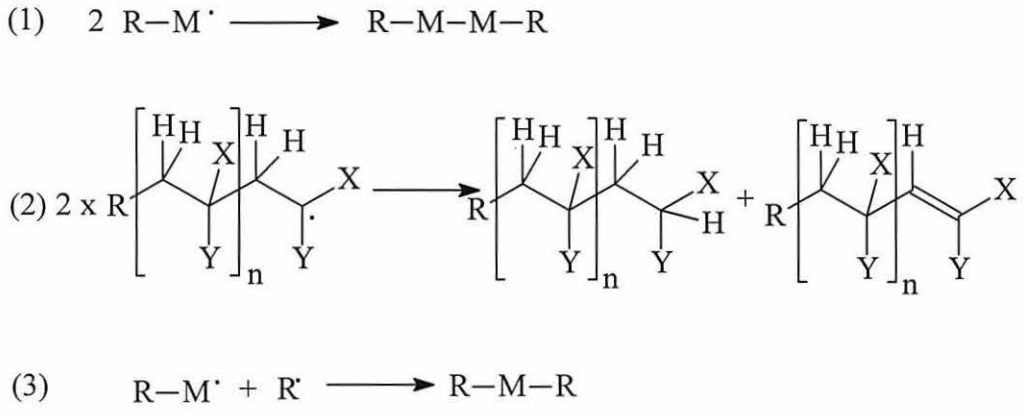


Scheme 5. (1) Benzoyl peroxide; **(2)** AIBN.

The radical then initiates polymerisation of a monomer and propagation proceeds **(Scheme 6)**. Termination occurs either through collision between two growing chains which unite to form a deactivated molecule[9]; disproportionation, by proton abstraction from another growing polymer chain[9,10]; or through collision between a growing chain and a catalyst radical **(Scheme 7)**[9].



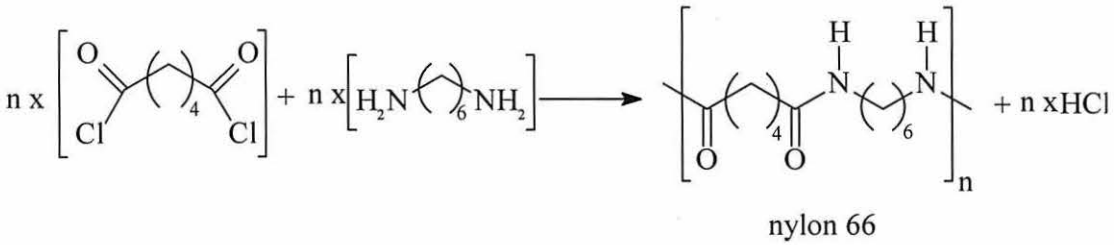
Scheme 6. (1) initiation; (2) propagation.



Scheme 7. (1) collision between two growing chains; (2) disproportionati (3) collision between growing chain and catalyst.

1.5 Condensation polymerisation

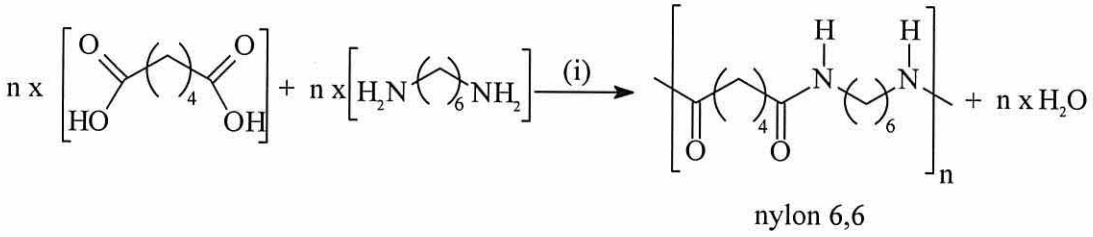
In condensation polymerisation, bi- or polyfunctional molecules condense with one another and in this process repeatedly eliminate a small molecule, such as water, HCl, or CO_2, as the reaction proceeds.[2-5] Consequently, both polymer size and the amount of polymer increase with time. The preparation of nylon (6,6) is a typical example of condensation polymerisation.[3] Nylon is often prepared by the reaction of adipoyl chloride and hexamethylenediamine **(Scheme 8)**.



nylon 66

Scheme 8.

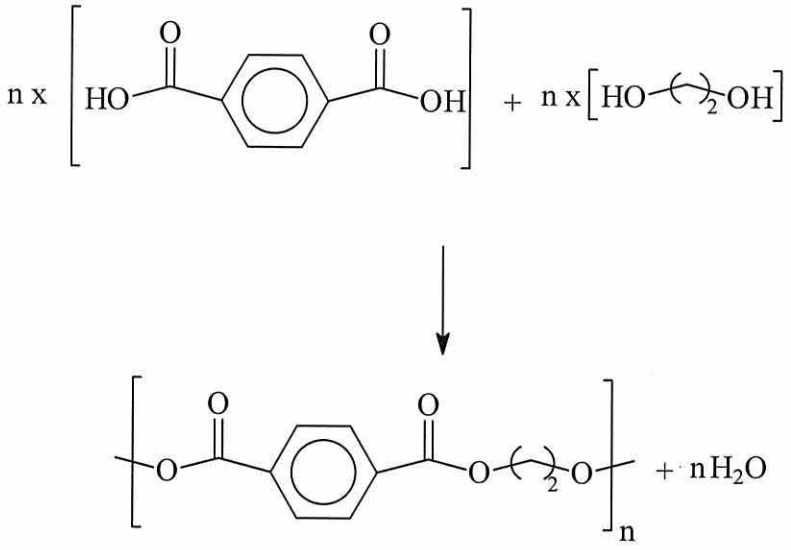
The reaction can be regarded as a nucleophilic substitution by the amine upon the acyl chloride, liberating HCl. Industrially, nylon 6,6 is produced by heating adipic acid and hexamethylenediamine at 280 °C under vacuum **(Scheme 9)**. Instead of HCl, water is liberated during the polymerisation process. The high temperature is required because the ^-OH group is not as good a leaving group as Cl^-.



nylon 6,6

Scheme 9. (i) 280 °C, vacuum.

Other examples of condensation polymers include polyesters. Polyesters are formed by the condensation of a diol and a diacid. For example, poly(ethane-1,2-diyl benzene-1,4-dicarboxylate) (terylene) is formed by heating ethylene glycol and terephthalic acid **(Scheme 10)**.[3]



Terylene

Scheme 10. n = number of monomer units.

1.6 Plastics

Plastics form a group of polymers, which have a fair range of deformability and mouldability at high temperatures. In plastics, the polymers formed do not have the same molecular weight and since the polymers are not amenable to the ordinary methods of separation, the molecular weight of a polymer is the average molecular weight.[2-5] Polymerisation is carried out with the object of building up compounds with predicted properties and since the properties of a plastic depend on the degree of polymerisation (DP), it is necessary to stop the polymerisation when the desired average molecular weight is reached. This may be achieved by various means, for example variation of the concentration of the catalyst. The average molecular weight of plastics varies from about 20,000 (*e.g.* nylon) to several hundred thousand (*e.g.* polyvinyl chloride, 250,000).

Plastics are generally tough, resistant to the action of acids and alkalis and not affected by a change of temperature. They can also be moulded to any desired shape or form. Plastics are of two main types, thermoplastic and thermosetting.[2-5] Thermoplastics are linear polymers which are soluble in many organic solvents and which soften on heating and become rigid on cooling. The process of heat softening, moulding and cooling can be repeated as often as desired, with only minor defects to the properties of the plastic. Typical thermoplastics are cellulose acetate and vinyl polymers, such as polythene and perspex.

Thermosetting plastics are cross-linked polymers which are insoluble in solvents and which can be heat-treated only once (*i.e.* during their formation) before they set, subsequent heating results in decomposition. Typical thermosetting plastics are phenol-formaldehyde resin, melamine-formaldehyde resin and silicones.[3]

In thermoplastics the chains are not chemically bound, but are held together by van der Waals' forces. It is possible to form a thermosetting plastic from a thermoplastic through the cross-linking of the polymer chains. An example is in the vulcanisation of rubber where the sulphur cross-links the hydrocarbon chains.

Furthermore, such thermosetting plastics may be reconverted into thermoplastics by opening the cross-links.

Plastics which do not soften much with a rise in temperature are made soft and readily workable by the addition of compounds known as plasticisers. For example, polyvinyl chloride is extremely stiff and hard, but addition of tricresyl phosphate makes it soft and rubber like.

1.7 Gel Permeation Chromatography

Gel permeation chromatography is a size exclusion technique, which uses hydrophobic beads to separate macromolecules.[11] As such, it is an effective tool for polymer characterisation and molecular weight determination. A sample of the polymer is dissolved in a suitable solvent and passed through a column containing hydrophobic beads, which have pores of fixed diameter. Separation occurs because large molecules cannot enter many of the pores and are consequently eluted first. Smaller components of the polymer are able to enter the pores and therefore retained on the column for longer. Intermediate-size molecules can penetrate some pores but not others, this retards their progress and they exit at intermediate times **(Figure 1)**.[12,13]

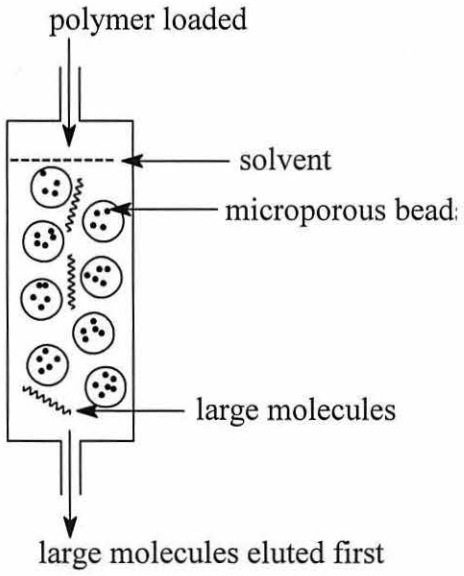


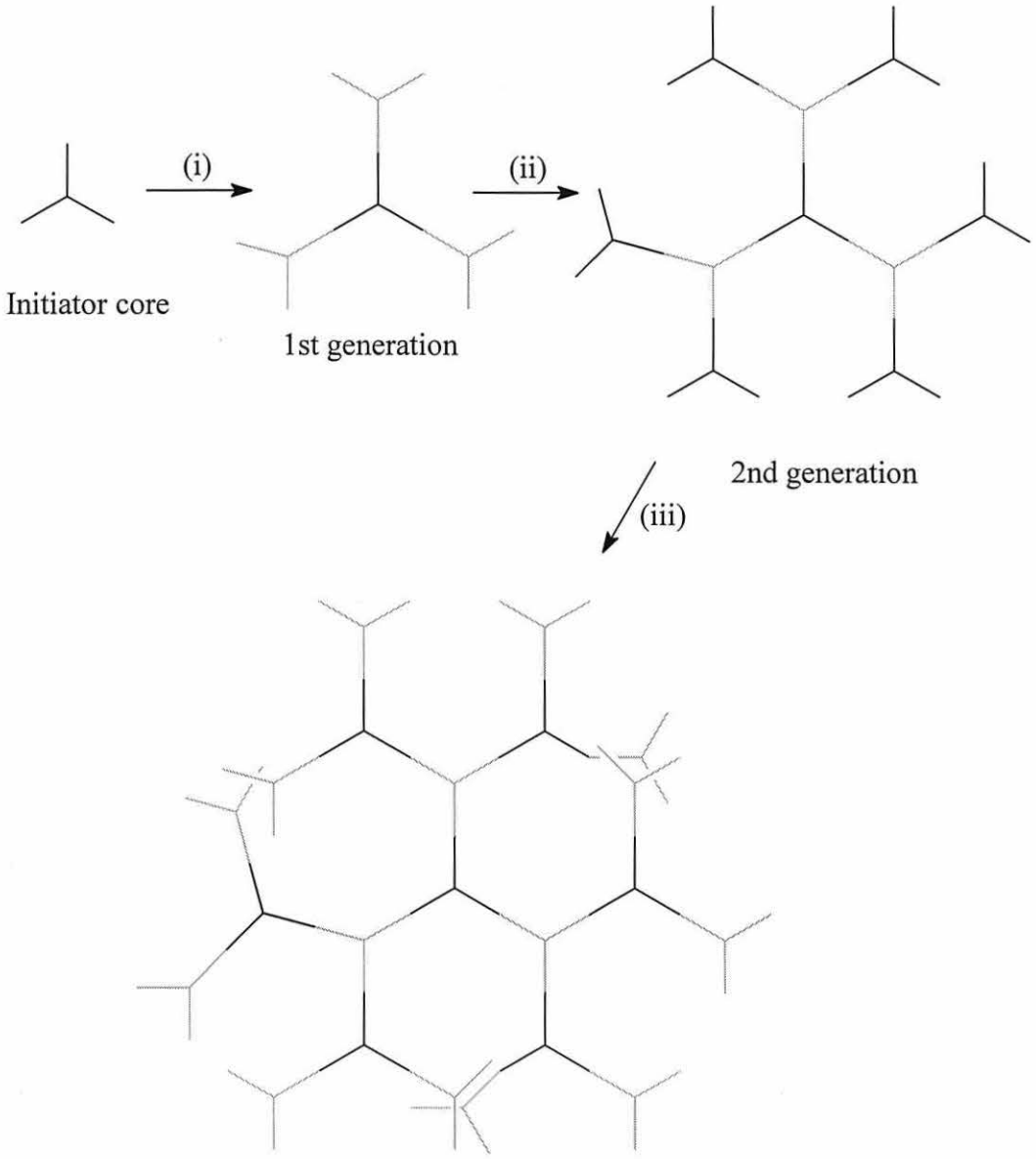
Figure 1.

The molecular weight of the polymeric material is determined by loading the column with various calibrants of known molecular weight (usually three different polymers: one with low; one with moderate and one with high molecular weight material) and timing how long it takes for these polymers to elute from the column. Hence, the molecular weight of an unknown polymer can be determined by comparing its elution time with the elution time for the calibrant polymers. This provides information on the molecular weight of the unknown polymers expressed as molecular weight equivalents of the calibrant polymer. Examples of column packings include bio-gel P, cross-linked polyacrylamide, sephadex, cross-linked dextran and bio-beads S (styragel), polystyrene gels.[11]

1.8 Dendrimers

Modern polymer chemistry has given rise to a fourth macromolecular architecture known as dendritic macromolecules (dendrimers).[14-16] Unlike traditional polymers, dendrimers are a structurally and topologically defined monodisperse species. They are extremely branched molecules, mainly synthesised from identical building blocks that contain branching sites. Dendrimers are constructed in stages in repeatable synthetic steps; each reaction cycle creating a new generation of the dendrimer and increasing the branching of the molecule by a factor n (n>1).

If n = 2, a core with three reactive functional groups will react with three equivalents of monomer to form a first generation dendrimer with six reactive groups. Subsequently, this will be able to react with six equivalents of monomer to form a second generation dendrimer with twelve reactive groups. The second generation dendrimer can react with twelve equivalents of monomer to form the third generation dendrimer with twenty four reactive groups **(Scheme 11)**.

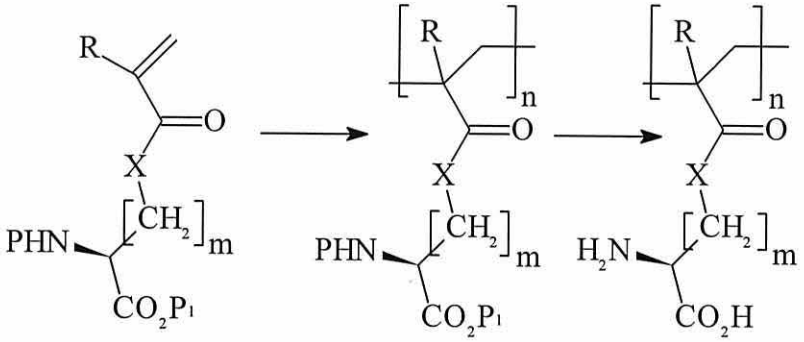


Scheme 11. (i) monomer (3eq.); (ii) monomer (6eq.); (iii) monomer (12eq.).

The branching provides the higher generations with an increasingly three-dimensional structure that is characterised by a growing number of cavitites within the molecule. Dendrimer syntheses incorporate protecting group strategies[17,18] and coupling chemistry[19] in order to obtain these successive generations. Hence, as the synthesis utilises a stepwise iterative reaction procedure, it is important that the synthetic sequence is short in terms of its number of steps, easy to perform and high yielding.

1.9 Synthesis of novel poly(peptides)

The synthesis of condensation polymers derived from amino acids by the ring opening of Leuch's anhydrides is a well established process for the synthesis of biomimetic polyamides.[20-25] However, this type of polymerisation destroys the amino and acid functional groups that were present in the amino acid starting material. The synthesis of radical induced addition polymers derived from amino acids through utilisation of alkene functionalities attached to the free amino group has also previously been reported.[26-28] However, polymerisation of this type of monomer destroys the amino functionality that was present in the amino acid starting material. Therefore, initial investigations have been undertaken on the synthesis of a different type of polymer derived from amino acids. This was achieved by the radical induced polymerisation of amino acid derivatives bearing alkene functionalities in their side chain, **(Scheme 12)**.[29]



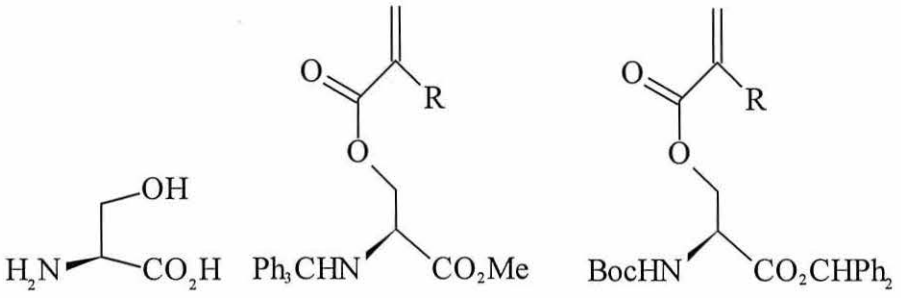
X = O, N, S, C
R = H, Me
P, P1 = protecting groups

Scheme 12.

The synthesis of condensation polymers utilising amino acid side chains has also previously been reported.[30-31] This approach has the advantage of retaining the amine and acid functional groups within the polymer, which should provide the resulting polymers with a number of useful properties including: optical activity, solubility in aqueous and highly polar solvents, electrical conductivity through ion

movement and applications to templated polymers.[32,33]

The synthesis of a different type of poly(amino acid) with the retention of both the amine and acid functionalities through utilisation of (*S*)-serine **(1)** **(Figure 2)** has previously been reported.[29] Selective protection of the amine and acid functionalities enabled an acryloyl group or methacryloyl group to be introduced onto the alcohol functionality to furnish the monomers **(2)** and **(3)** respectively **(Figure 2)**. The use of protecting groups has the effect of leaving the inherent chirality of (*S*)-serine **(1)** untouched during monomer preparation and subsequently during polymerisation.



(1)

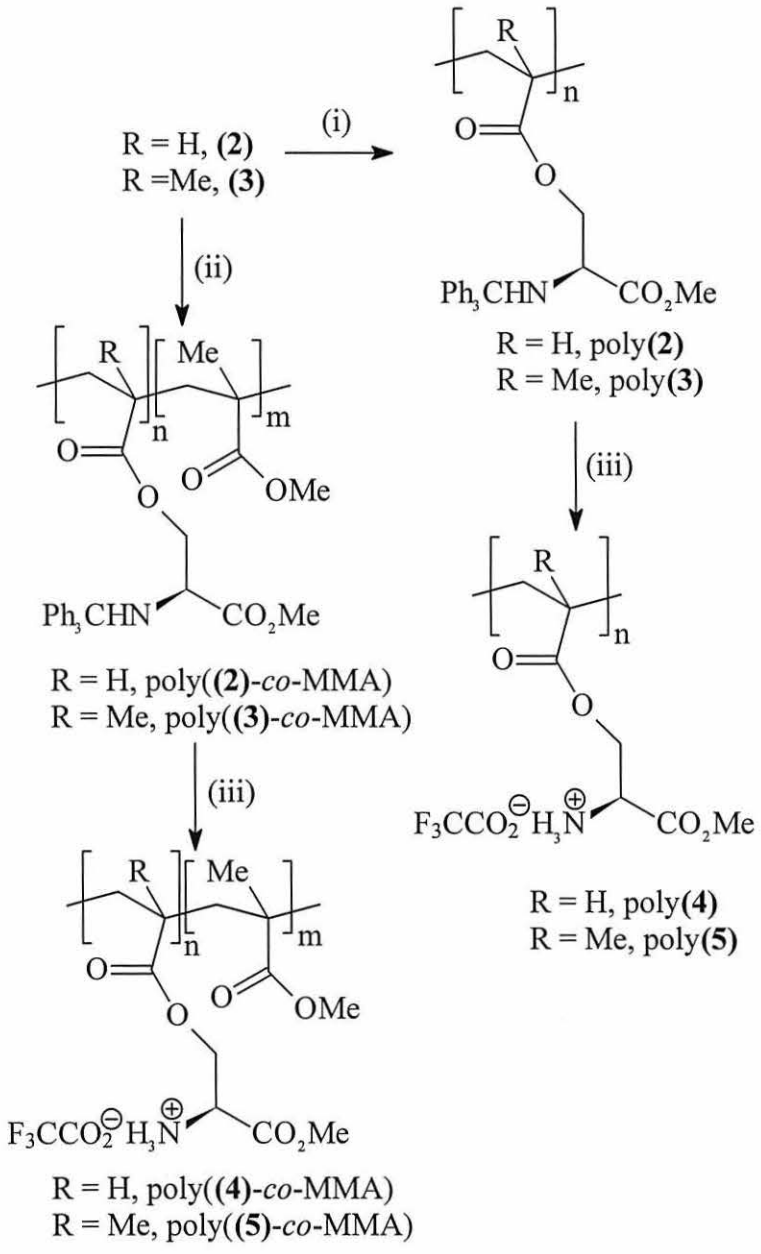
R = H, **(2)**
R = Me, **(3)**

R = H, **(6)**
R = Me, **(7)**

Figure 2.

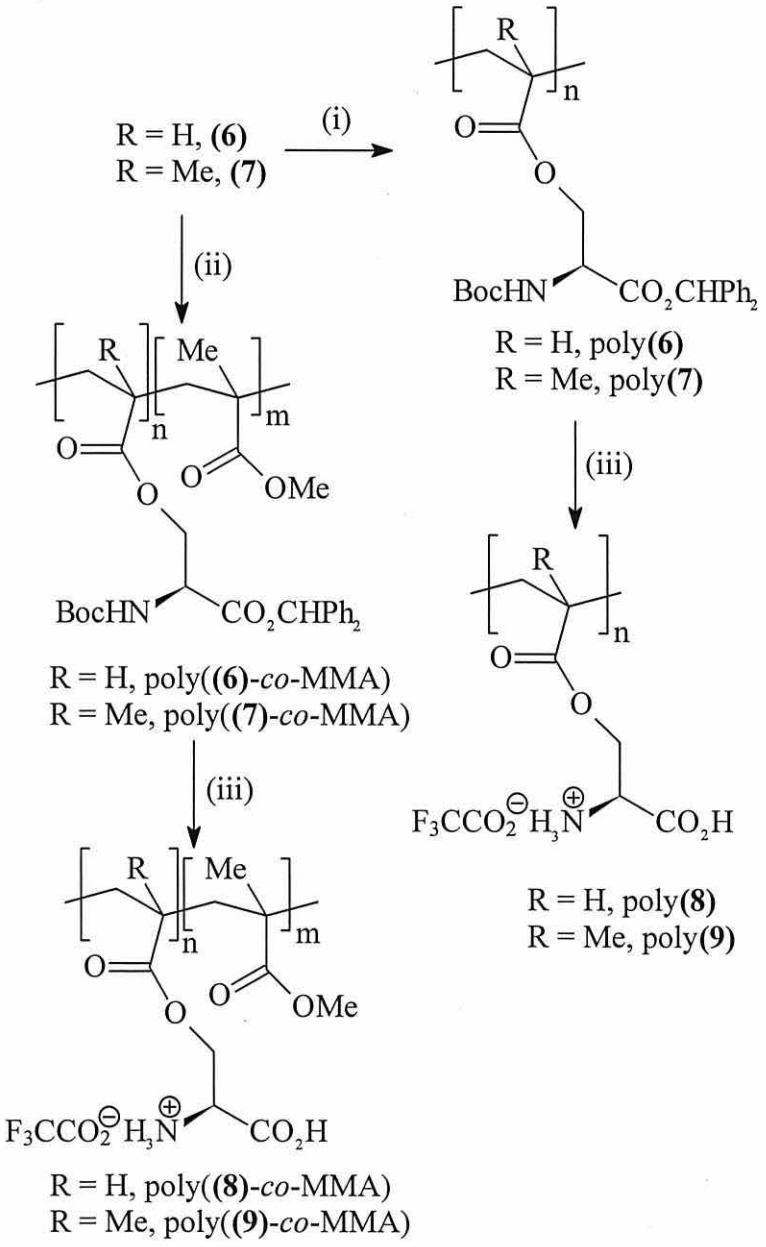
1.10 Polymerisation of the (S)-Ser derivatives

Monomers **(2)** and **(3)** were homopolymerised and copolymerised with different ratios of MMA to provide two polymer series. Deprotection of these polymers in the presence of trifluoroacetic acid yielded the partially deprotected polymers poly**(4)** and poly**(5)** **(Scheme 13)**.



Scheme 13. Reagents: (i) $(PhCO_2)_2$, PhMe;
(ii) $(PhCO_2)_2$, PhMe, $H_2C{=}C(Me)CO_2Me$;
(iii) F_3CCO_2H, CH_2Cl_2.

Further investigations led to the synthesis of monomers, **(6)** and **(7)** that have acid labile protecting groups **(Figure 2)**. These were again homopolymerised and copolymerised with varying ratios of MMA to provide two polymer series. Simultaneous removal of the Boc and diphenylmethyl ester protecting groups was achieved using trifluoroacetic acid to furnish the fully deprotected polymer series, poly**(8)** and poly**(9)**, retaining the amine and acid functionalities present in (*S*)-serine **(1) (Scheme 14)**.[34]



Scheme 14. Reagents: (i) $(PhCO_2)_2$, PhMe;
(ii) $(PhCO_2)_2$, PhMe, $H_2C{=}C(Me)CO_2Me$;
(iii) F_3CCO_2H, CH_2Cl_2.

1.11 Optical activity

All of the polymers derived from monomers (**2**, **3**, **6**, and **7**) were optically active, though the specific rotation of the polymers did not vary linearly with the percentage of chiral monomer incorporated. Rather, the specific rotation initially increased rapidly as the percentage of chiral monomer incorporated increased from 0 % to 10 %, then the rate of increase of specific rotation slowed down and continued to rise approximately linearly to 100 % incorporation. This non-linear variation is not due to differences in the molecular weight or polydispersities of the polymers, as the same effect is observed for the specific rotation of polymers with similar molecular weights and polydispersities. There are two possible reasons for this non-linear variation of specific rotation with percentage composition of the polymer; asymmetric induction from the enantiomerically pure serine α-centre to the new chiral centres which are created within the polymer backbone during the polymerisation; or a change in the conformation of the polymer from random coil to ordered, a process which would be essentially complete once the polymer contained about 10 % of the chiral monomer.

A similar non-linear variation of specific rotation has been reported for copolymers (radically or anionically initiated) derived from *N*-substituted maleimides and other monomers such as other maleimides,[35,36] styrenes, or methacrylates in which one of the components was enantiomerically pure, with both positive[37-40] and negative[41-45] deviations from linearity having been observed, as well as more complex cases in which the specific rotation increases linearly for a period followed by a deviation from linearity.[46,47] Similar non-linear effects have also been reported for polymers derived from a chiral styrene unit and a variety of styrene or methacrylate based comonomers.[48] In these cases, asymmetric induction into the polymer backbone was reported to be the cause. However, a non-linear relationship between polymer composition and specific rotation is not always observed, as the radical copolymerisation of an enantiomerically pure norbornyl ester of methacrylate or

styrene gave a series of copolymers in which the specific rotation was directly proportional to the percentage of chiral monomer incorporated into the polymer.[49,50]

Sterically hindered esters of methacrylates such as triphenylmethyl methacrylates are known to form helically chiral polymers which can be separated into left and right handed forms,[51-55] and this could provide the alternative explanation for the non-linear variation of specific rotation. In these cases, no asymmetric induction into the polymer backbone is observed, since removal of the triphenylmethyl esters gives an optically inactive polymer. Rather, the optical activity of the polymer is due solely to its conformation, which is maintained by the bulky triphenylmethyl groups. A similar effect has also been observed in the copolymerisation of amino acid derived isocyanates or other chiral isocyanates.[56,57] In this case, the specific rotation decreased as the amount of chiral monomer incorporated into the polymer increased.

None of the polymers derived from monomers (**2**, **3**, **6**, and **7**) exhibited mutarotation; a property that has been observed for other polymethacrylates whose chirality is due to conformational effects,[58] and for other helical polymers.[56,57] In addition, the specific rotation of the polymer samples was unchanged after a solution of the polymer had been heated at 50 °C for 1 hour and allowed to re-cool to ambient temperature. The specific rotation was also independent of the concentration of the solution.

The specific rotation of the polymers measured in THF showed the same non-linear variation seen in $CHCl_3$ though with different numerical values. The change to a more polar solvent would be expected to diminish any ordered conformation and hence to reduce any non-linear effects due to helicity. This has been previously observed,[37-40,49,50] though using solvents more polar than THF. In this work, the use of more polar solvents was not feasible due to the solubility characteristics of the polymers. It has also previously been suggested[35] that the saturated analogues of monomers can serve as model compounds for studying the chiro-optical properties of addition polymers. The saturated monomers of compounds (**2**) and (**3**) were found to

have specific rotations 10.9° and 1.7° lower than the specific rotation of the corresponding homopolymers. This difference in specific rotation between the model compounds and the homopolymers may provide a measure of the amount of asymmetric induction or helicity in the polymers.

In order to investigate the origin of this non-linear variation of specific rotation, a selection of the polymers (containing 100, 18, 1.5 and 0.8 % of monomer **(3)**) were investigated by circular dichroism (CD) spectrophotometry. The polymers showed a characteristic CD spectrum (in CH_2Cl_2), with maxima at 267 and 275 nm. The intensity of these CD bands increased linearly as the percentage of compound **(3)** in the polymer increased, with the homopolymer showing the most intense signals. The CD spectra of the saturated monomers with absorbance normalised to one at 275 nm were also obtained and were found to be virtually identical to those of the homopolymer. Finally, a variable temperature (200-300 K) CD study was undertaken on the polymers containing 100 % and 1.5 % of monomer **(3)** as well as on the saturated monomer. In each case, the intensity of the CD was seen to decrease as the temperature increased.

The above specific rotation, CD and ultra-violet (u.v.) results are consistent with asymmetric induction into the polymer backbone during the polymerisation process, but not with the formation of a polymer with an ordered conformation. The CD spectra are dominated by the absorbance for the triphenylmethyl group with no discernible contribution from any secondary structure and the intensity of the CD is directly proportional to the amount of monomer **(3)** in the polymer. As such, they do not mirror the non-linear variation seen in the specific rotation measurements. Furthermore, since the CD spectra of the polymers and the saturated monomer show the same temperature dependence, this temperature dependence must be related to conformational changes within the monomer unit and not to changes in the conformation of the polymer backbone.

1.12 Use of chiral water soluble polymers in the preparation of chiral conducting polymers

The fully deprotected homopolymer, poly**(8)** was found to be water soluble. Due to the acidic nature of these polymers, their use as dopants for the electrochemical polymerisation of aniline has been investigated.[60] The resulting conducting polymer, polyaniline is modified by the immobilisation of the poly(amino acid) into the polymer matrix. This has a marked effect on the electrochemical and spectroelectrochemical properties of the polymer.

The growth of doped polyaniline on a gold electrode was studied by cyclic voltammetry. This showed two redox peaks involved in the polymerisation process at α (+175 mV, -50 mV) and β (+225 mV, +175 mV). This behaviour is completely different to that previously reported for polyaniline doped with small anions, such as Cl^- or SO_4^{2-} where only one coupled polyaniline peak is observed which is broad and closely coupled.[61] Redox couple α is unusual since the peaks are narrow and a great distance apart (225 mV) while redox couple β is broad and the distance between the peaks is closer (50 mV).

The presence of two polyaniline redox peaks means that there are two types of polyanions incorporated into the polymer matrix. This behaviour is consistent with free radical type polymerisation where a broad polydispersity is observed. Redox peak α corresponds to lower molecular weight material being incorporated into the polyaniline matrix whereas redox peak β corresponds to higher molecular weight material being incorporated. After a period of time when all the lower molecular weight material has been incorporated, polyaniline is forced to start using the higher molecular weight material. This has the effect of stopping polyaniline growth, which is evidence of the poly(amino acid) being trapped in the polymer matrix. When left for 24 hours, the redox peak α had disappeared providing evidence for the incorporation of the low molecular weight material into the polymer matrix. The only observed peak corresponded to the incorporation of the high molecular weight material.

The sharp nature of peak α is unusual for polyaniline growth on a gold electrode. Normally, a polyaniline growth peak is broad and corresponds to all five oxidation states of the polymer. The low molecular weight material of the poly(amino acid) causes polyaniline to be extremely selective, polymerising in one preferred oxidation state. The large separation between the redox couple is unusual and may be due to the lower molecular weight materials freely moving in and out of the polymer matrix in a state of equilibrium, whilst the high molecular weight material becomes trapped within the polymer matrix. Subsequently, this increases the ion concentration near the polymer inducing a *Donnan* potential.[62] This separation is further increased due to the positive charge on the amino group of the poly(amino acid).

1.13 Medicinal Peptides

Synthetic peptides have been widely used to generate site specific antibodies, a fact that has stimulated considerable interest in evaluating their use as vaccine candidates.[63] The advantages of synthetic peptides include: safety, as there is no need for infectious material and the ability to chemically modify the product.

Currently only a few peptide based vaccines have been used in the field.[64,65] This is because T-cell epitopes are necessary to produce antibodies directed against β cell epitopes present in the immunogen. This results in multiple and different epitopes presented to the immune system in a single covalent structure. Consequently, large molecules are better immunogens than small peptides. Traditionally, this has been achieved by coupling a peptide epitope to a protein carrier such as a keyhole limpet hemocyanin or tetanus toxoid using chemical coupling reagents. This results in the production of high titres of anti-peptide antibodies, unfortunately anti-protein carrier antibodies are also produced. The conjugation chemistry used can also lead to changes in the peptide epitope affecting the antigenic and immunogenic properties.[66] Additionally, carrier induced epitope specific suppression can reduce the antibody response to the peptide of interest, if the recepient has had prior exposure to the protein carrier.[67-69]

Alternative strategies have included the tandem assembly of helper T cell and β cell peptide epitopes;[70] and the multiple antigenic peptides (MAP) approach.[71] Both strategies have utilised DCC and HOBt chemistry to produce multiple peptide repeats of protected peptides.[72] The tandem synthesis of β and T cell epitopes may not produce the desired immune response because the relative positions of the epitopes can drastically affect the constructs immunogenicity,[73] and the linkage of one peptide epitope to another can create novel determinants at the junction inducing inappropriate immune responses.[74,75]

The MAP strategy enables several copies of the peptide epitopes to be simultaneously synthesised onto an oligolysine support. The problem is that MAP's are often heterogeneous. This has been overcome through ligation chemistry,[28,71,76] in which peptides are functionalised with a weak nucleophilic base and subsequently reacted with an oligolysine derivatised with aldehyde groups (forming oxime and hydrazone linkages). However, the valency and number of different peptides that can be incorporated into MAP constructs is limited.

Recently a new strategy was devised utilising *N*-acryloyl peptides.[27] In general, 6-aminohexanoic acid was introduced at the *N*-terminus of the peptide and this was subsequently acrylated. The 6-aminohexanoic acid functioned as a spacer to distance the acryloyl group from the peptide. The polymerisation procedure used was similar to that used in the preparation of polyacrylamide gels, utilising TEMED as the initiator to provide high molecular weight water soluble polymers. All the monomers were copolymerised with 50 equivalents of acrylamide to allow stretches of polyacrylamide to be interspaced between the acryloyl peptide units. The aim of this copolymerisation was to minimise steric interactions between the peptide chains and to maximise water solubility of the overall polymer.

In order to test their antigenicity, the synthetic polymers were coated on plastic microtitre trays.[77] The results demonstrated that antibodies were capable of binding efficiently to determinants within the polymers, indicating that the epitopes remain antigenically intact despite exposure to free radicals. The advantage of

polymerising synthetic peptides is that multiple copies of a peptide are present in a single molecule resulting in enhanced antigenicity over the monomer.[78] This was evaluated through an inhibition ELISA, which is independent of any difference in the ability of the antigens to bind to the microtitre plate, to compare the antigenic properties of the monomeric and polymeric peptides. The results demonstrated that polymerised peptides not only retain antigen integrity but are more antigenic than the corresponding peptide monomer because multiple copies of the same antigenic determinant allows high avidity interaction with the antibody.[27]

1.14 Poly(amino acids) via condensation polymerisation

The synthesis of poly(amino acids) from Leuch anhydrides is a well documented process.[20-25,79] Polymerisation occurs through condensation polymerisation, evolving carbon dioxide, to form a linear polymer where the degree of polymerisation (DP) is determined by the monomer : initiator ratio.

1.15 Mechanism of polymerisation

Initiation can occur through two different mechanisms. The primary amine mechanism involves nucleophilic attack at the CO-5 position and subsequent evolution of CO_2 **(Figure 3).**[79-85]

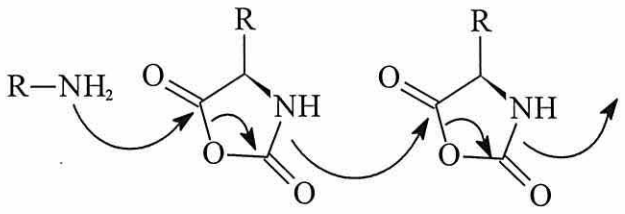


Figure 3.

The primary amine mechanism leads to polymers with a broad molecular weight distribution.[79,87] Evidence supports the theory that each amine initiates one polymer chain and this is the reason why the number-average degree of

polymerisation is given by the molar ratio of monomer : initiator.[84] This primary amine mechanism is seen in polar solvents such as DMF, *o*-nitroanisole and nitrobenzene. However, in apolar solvents the rate of polymerisation is further controlled by the conformation of the polymer.

The second mechanism involves proton abstraction from the NH of the *N*-carboxyanhydride molecules which then acts as initiator.[84,86,88] This mechanism is known as the active monomer mechanism **(Figure 4)** and applies to tertiary amines and strong bases, such as methoxide.[89] The main differences between this mechanism and the primary amine mechanism are: the amine is not incorporated into the growing polypeptide chain; reaction rates are slower and the DP value is much higher than the monomer : initiator ratio.

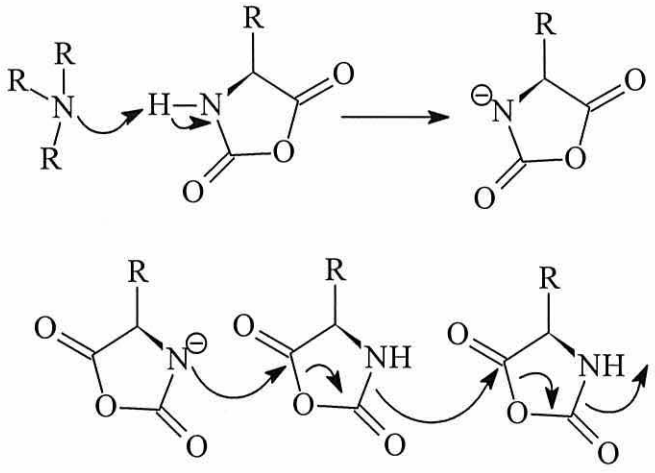


Figure 4.

For secondary amines, the mechanism is a combination of the primary amine and active monomer mechanism.[84,85] If the amine is highly hindered then it behaves as a tertiary amine and hence the active monomer mechanism predominates; but if the amine has small substituents, it will initiate preferentially by the primary amine mechanism. If the amine is present in excess this will increase the basicity of the reaction medium and will favour the formation of hydantoic acids.

1.16 Properties

The use of different types of initiators leads to traditional type polymers with inheritantly different properties, *e.g.* the polymerisation of *N*-carboxyanhydrides initiated with H_2O; primary, secondary, or tertiary amines; or alcohols will provide polymeric materials with different chain lengths and polydispersities.

1.17 IR studies

N-carboxyanhydrides exhibit strong vibrations in their IR spectrum at 1860 and 1790 cm^{-1}. Studies on the primary amine initiated polymerisation of the *N*-carboxyanhydride of (*S*)-glutamate in a monomer : initiator ratio 20 : 1 have shown that as polymerisation proceeds the vibrations at 1860 and 1790 cm^{-1} decrease whereas two new vibrations appear at 1655 and 1550 cm^{-1} due to the formation of the secondary amide bonds. The vibration at 1655 cm^{-1} is due to the stretching mode of the C=O in the CONH linkage and the vibration at 1550 cm^{-1} is due to the deformation mode of the NH group in the CONH linkage.[90,91]

1.18 Solvent effects

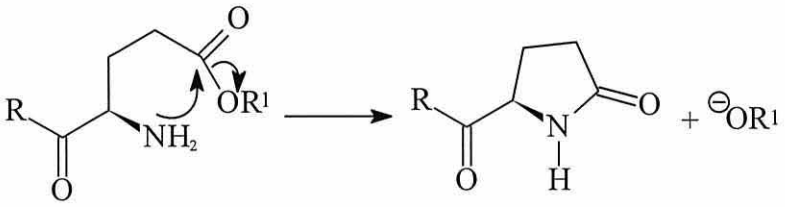
Primary amine initiated polymerisation reactions in apolar solvents such as CH_2Cl_2, ether and toluene give high molecular weight polymers with bimodal chromatograms and broad polydispersities. This is due to the conformation of the growing poly(amino acid) influencing the rate of polymerisation. Furthermore, termination steps result in a broadening of the molecular weight distribution.[23,92] Polymerisations in MeOH give high yields but cyclic products (diketopiperazines) are obtained.[88]

Polar solvents such as dioxane and DMF provide a medium for polymerisation where the molecular weight distribution is narrow.[92,93] This is because initiation is faster relative to propagation and side reactions are limited resulting in chain growth proceeding at a uniform rate producing a narrow monomodal distribution of

molecular weights. DMF provides a narrower polydispersity (PD) than dioxane, due to DMF being appreciably more polar than dioxane and as a result the growing poly(amino acids) are appreciably more soluble in DMF.

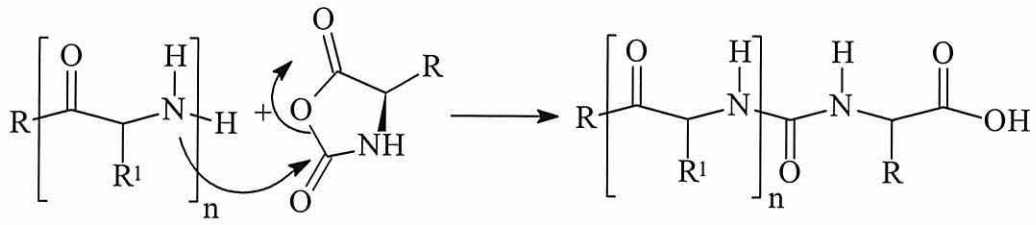
1.19 Termination reactions

In the case of poly(glutamates), the most likely termination step is the cyclisation of the chain end, by reaction of the amine of the last monomeric unit with the carbonyl group of the ester of the same unit **(Scheme 15)**.



Scheme 15. R = poly(amino acid), R^1 = alkyl group.

Investigations into the terminal groups of poly(amino acids) revealed the formation of urea end groups due to termination reactions, caused by nucleophilic attack on C2 of the *N*-carboxyanhydride monomer, leading to an inactive chain end. This has been demonstrated by the isolation of hydantoin-3-acetic acid derivatives from the hydrolysates of purified poly(amino acids) **(Scheme 16)**.[85,94,95] In particular, increasing concentrations and basicity of the primary amine favour these reactions.[96,97] Furthermore, the formation of β-sheets may cause physical death to the growing chain of non-α-helix forming poly(amino acids) through intermolecular cyclisation of the growing polymer chains. These termination reactions are responsible for keeping the molecular weights of the poly(amino acids) relatively low ($DP_n < 150$).



Scheme 16. R = initiator, n = number of monomer units, R^1 = amino acid side chain.

1.20 Block copolymers

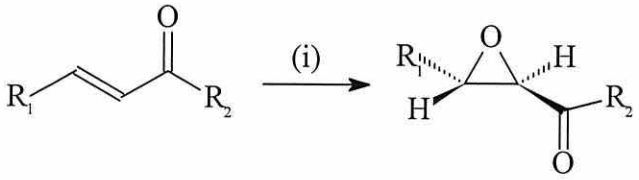
The block copolymer technique that has been used most frequently involves a sequence of non-polar amino acids [B] incorporated within sequences of a polar amino acid [A] to form a "sandwich" block copolymer of the type $[A]_m$-$[B]_n$-$[A]_o$.[91,98-102] The polar character of [A] rendered the polymers soluble in water. In all cases, the [A] block was poly((*S*)-(*R*)-Glu) or poly((*S*)-(*R*)-Lys) which are ionised at pH 7 and the [B] sequences consisted of homopolymers of (*S*)-Ala,[98,99,103] (*S*)-Phe,[100,101,103] (*S*)-Leu,[101] or (*S*)-Val.[91,102] The sandwich structure enabled studies to be undertaken on the conformational properties and the helix-coil transition of the central $[B]_n$ block in H_2O.[103] There are also reports of random copolymers and on the conformational preferences of naturally occurring amino acids.[104,105]

1.21 Uses of poly(amino acids), epoxidation reactions

The use of synthetic poly(amino acids) as stereoselective catalysts in organic reactions has been investigated.[106] The use of poly((*S*)-alanine) as a stereoselective catalyst for the enantioselective epoxidation of α,β-unsaturated ketones showed an improvement over previously reported examples using enzymes where the optical yields were low,[107] reaction times too long,[108] or the amounts of enzyme required too large.[109,110] The use of poly((*S*)-amino acid) as catalyst leads to the isolation of the epoxide with the (*S*)-configuration and the use of poly((*R*)-amino acid) as catalyst leads to the isolation of the epoxide with the (*R*)-configuration.

Further studies, utilising copolymers of the type [A]-[B], where unit [A]

consisted of poly((*S*)-Leu) and unit [B] of poly((*S*)-Ala), concluded that poly((*S*)-leucine) was a more efficient catalyst in the triphasic asymmetric epoxidation of α,β-unsaturated ketones.[111]

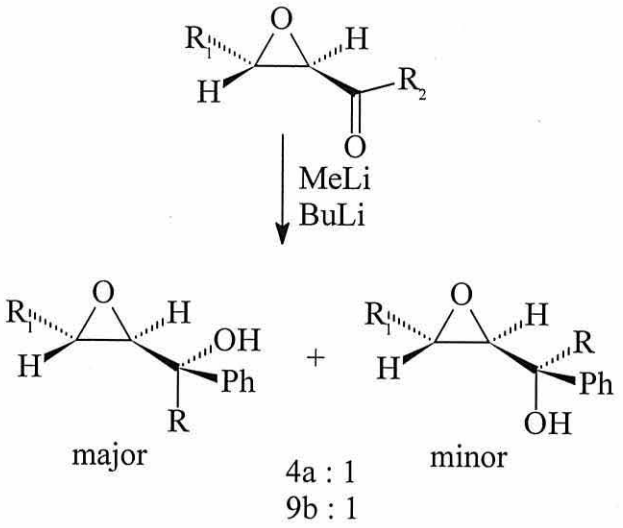


Scheme 17. R_1 = Ph, R_2 = Ph, (i) NaOH-H_2O_2, toluene, poly((*S*)-Leu), water.

The highest enantioselectivity was achieved through use of 1,3 diaminopropane as initiator with a monomer : initiator ratio of 40 : 1 **(Scheme 17)**. Not much is known about how the poly(amino acid) confers this enantioselectivity but studies on copolymers of the type [A]-[B] where the [A] unit consists of poly((*R*)-Leu) and the [B] unit of poly((*S*)-Leu) have shown that increasing the ratio of the (*R*) form to the (*S*) form from 1 : 1 to 2 : 1 decreases the enantiomeric excess from 90 % to 60 %. Therefore, the amino terminus of the poly(amino acid) dictates the configuration of the resulting epoxide and it would appear that the last 9 residues control the epoxidation.[112] Mass spectra of these poly(1,3-diaminopropane((*S*)-Leu)$_{40}$) utilising the MALDI-TOF technique showed that the peaks were separated by 113 mass units corresponding to a leucine residue.[113]

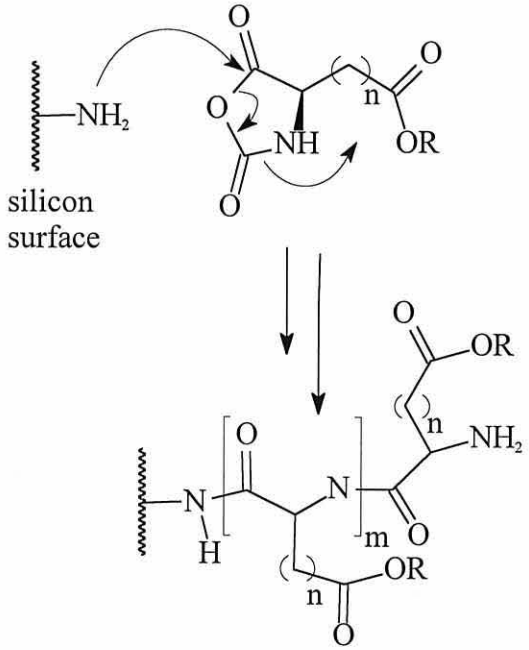
Recent work in this field has developed the asymmetric epoxidation of enones employing polymeric α-amino acids in a non-aqueous medium. The asymmetric epoxidation was conducted in a two-phase non-aqueous system made up of oxidant, non-nucleophilic base (DBU), immobilised poly(amino acid) and an organic solvent. The immobilised polymer is poly((*S*)-Leu);[114] the oxidant, urea-hydrogen peroxide complex (UHP)[115] and the reaction solvent dry THF. The new biphasic system has significantly increased selectivity and reduced reaction times, 100 % conversion in 85 % yield occurring in 30 minutes compared to 84 % conversion in 60 % yield in 28

hours with the triphasic system. Subsequent reaction of the epoxides with MeLi or BuLi has enabled access to epoxides formally derived from allylic tertiary alcohols, compounds not readily obtainable in optically active form using the Sharpless technology **(Scheme 18)**.[116]



Scheme 18. R_1 = Ph, R_2 = Ph, R = Me (a), Bu (b)

1.22 Grafting of poly(amino acids) onto Si-OH surfaces

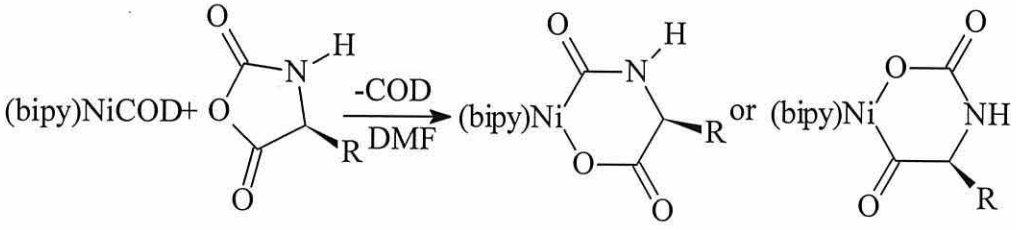


Scheme 19. n = 1, Asp; 2, Glu; m = number monomer unit

Introducing primary amino groups onto a silicon surface through the use of the amino-functional coupling agent, γ-aminopropyltriethoxysilane (γ-APS) has enabled the grafting of poly(amino acids) onto silicon dioxide surfaces **(Scheme 19)**. This has been achieved for poly((*S*)-alanine) and poly((*S*)-leucine)[117] and subsequently for poly((*S*)-asparates), poly((*S*)-glutamates) and for the copolymers, poly((γ-methyl-(*S*)-glutamate-*co*-γ-stearyl-(*S*)-glutamate) and poly(β-benzyl-(*S*)-aspartate-*co*-β-stearyl-(*S*)-aspartate).[118]

1.23 Controlling molecular weights through the use of Ni compounds

The use of a new type of initiator based on organonickel compounds, which are able to eliminate significant competing termination and transfer steps from *N*-carboxy anhydride polymerisations, has enabled the preparation of well-defined block copoly(amino acids).[119] The formation of the initiator results from the reaction of an *N*-carboxyanhydride monomer with the zero valent nickel complex bipyNi(COD); bipy = 2,2' bipyridyl, COD = 1,5-cycloctadiene. The activation and polymerisation proceeds through oxidative ring opening of the anhydride. As *N*-carboxyanhydrides are unsymmetrical anhydrides, the oxidative addition of *N*-carboxyanhydrides can yield two distinct isomeric products **(Scheme 20)**.



Scheme 20.

Isotope studies on $^{13}C_2$-(*S*)-Leu *N*-carboxyanhydride and $^{13}C_5$-(*S*)-Leu *N*-carboxyanhydride concluded that the addition of *N*-carboxyanhydrides to nickel was completely regioselective for ring opening across the O-C_5 bond. In DMF, this addition product was found to be highly active for polymerisation of additional *N*-

carboxyanhydride monomers. The efficiency of the initiator was measured through polymerisation experiments with (*S*)-Glu *N*-carboxyanhydride. The number-average molecular weight of the poly(benzyl-(*S*)-glutamate) samples formed using bipyNi(COD) was found to increase linearly as a function of the initial monomer : initiator ratios. The polymers also possessed narrow molecular weight distributions (M_w/M_n = 1.05-1.15) and were obtained in excellent yields.

This led to the synthesis of diblock copolymers of the type [A]-[B] where block [A] was poly(benzyl-(*S*)-glutamate) and block [B] was poly(ε-Z-(*S*)-lysine). Studies on the evolution of molecular weight through each stage of monomer addition using GPC showed that the molecular weight increased as expected on growth of each block copolymer whilst the polydispersity remained low, indicative of successful copolymer formation.[120] The chromatograms of the block copoly(amino acids) showed single sharp peaks illustrating the narrow distribution of chain length.

This development has enabled high molecular weight, linear poly(amino acids) to be synthesised with very low polydispersities, usually only found in dendrimer syntheses. Once the side chain protecting groups are removed, the assembly properties of these materials are expected to make them useful as tissue-engineering scaffolds, drug carriers and morphology-directing compounds in biomimetic composite formation.

1.24 Aims of the study

The aim of this project was to synthesise novel dipeptides and tripeptides containing (*S*)-serine using protecting group strategies, which incorporate a polymerisable group attached to the serine residue. Polymerisation of these dipeptides and tripeptides would allow access to a range of novel poly(peptides). Subsequent copolymerisation with MMA would enable access to a range of copolymers.

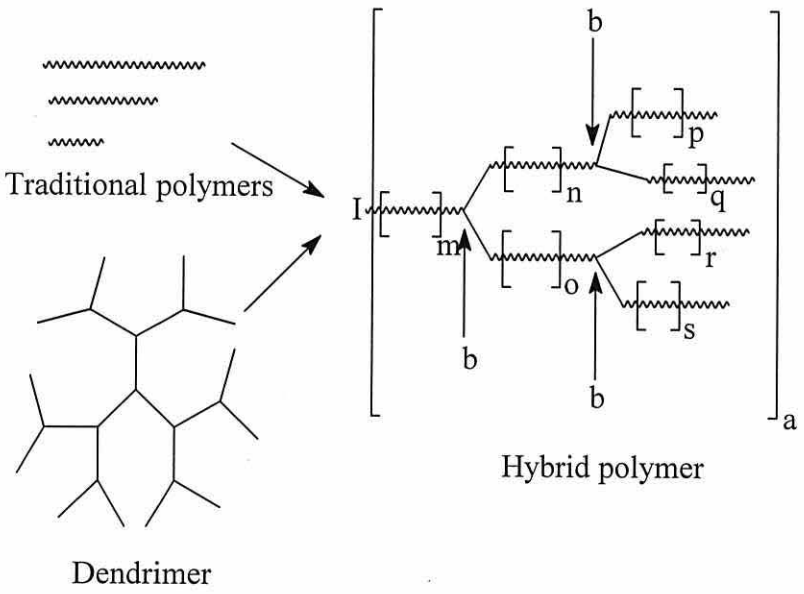
Optical activity studies were to be undertaken through polarimetry upon the homopolymers and copolymers. In this way it would be possible to investigate if the poly(peptides) derived from dipeptides and tripeptides display the same non-linear

relationship between specific rotation and percentage incorporation of chiral monomer as that which has previously been observed for poly(amino acids) prepared from (*S*)-serine.[29,34]

Deprotection of the protected polymers should provide access to the fully deprotected polymers with free amino and acid functionalities. This should enable the polymers to be soluble in water and other highly polar solvents. Subsequently this will enable their use in the preparation of chiral conducting polymers. This work will be discussed in chapter 2.

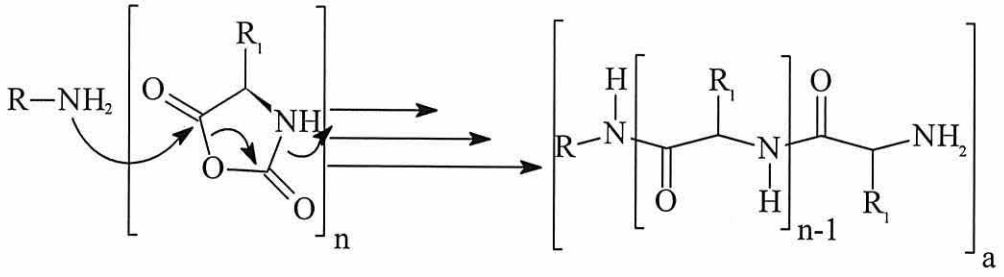
In recent years, there has been considerable interest in the synthesis of synthetic polymers with non-linear molecular architectures.[121-124] Much work in this area has concentrated on the synthesis and investigation of dendrimers,[14-16] polymers that have precisely controlled molecular weights and geometry. However, for many applications, the variety of molecular weights found in conventional synthetic polymers leads to desirable properties. Thus, there is a need for methodology which will allow the synthesis of polydisperse, highly branched polymers.

The aim of this project is to combine methodology from traditional type polymerisations with the precise branching and successive generation concepts found in dendrimer chemistry. This will lead to the synthesis of a new series of hybrid polymers **(Scheme 22)**.



Scheme 22. I = initiator core;
m, n, o, p, q, r, s = number average of monomer units in polymer ch
a = multiplicity of initiator core, *e.g.* core initiates 3 chains, a = 3;
b = branch juncture.

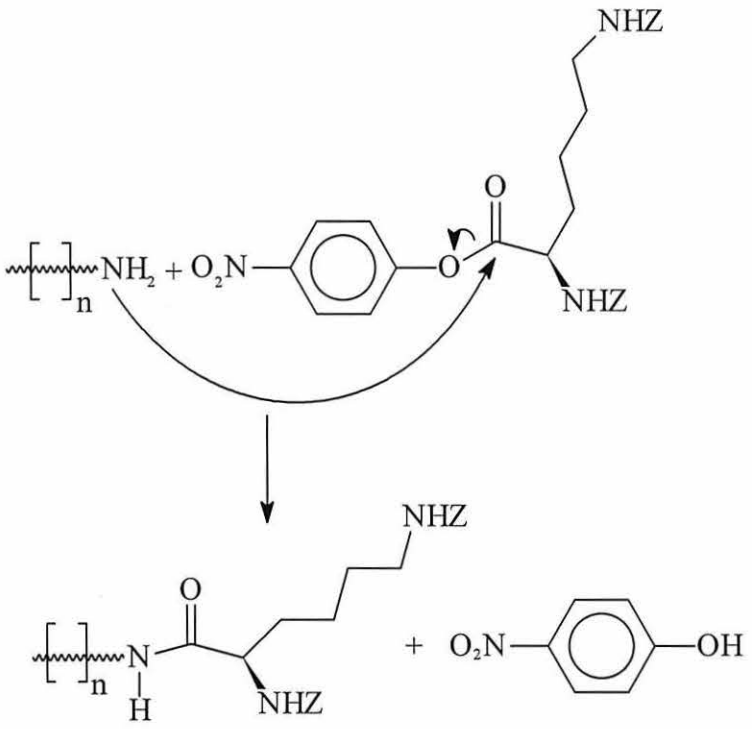
Our second aim is to utilise (*S*)-amino acids as monomers for the synthesis of these unnatural polymers which will be homochiral, highly branched and biodegradable. These novel, highly branched polymers will be prepared by utilising the well established chemistry associated with the synthesis of poly(amino acids). Poly(amino acids) are readily prepared from the corresponding *N*-carboxyanhydride by reaction with a primary amine **(Scheme 23)**.



Scheme 23. R = alkyl group initiator; R_1 = side chain of amino acid;
n = number monomer units; a = multiplicity of initiator core.

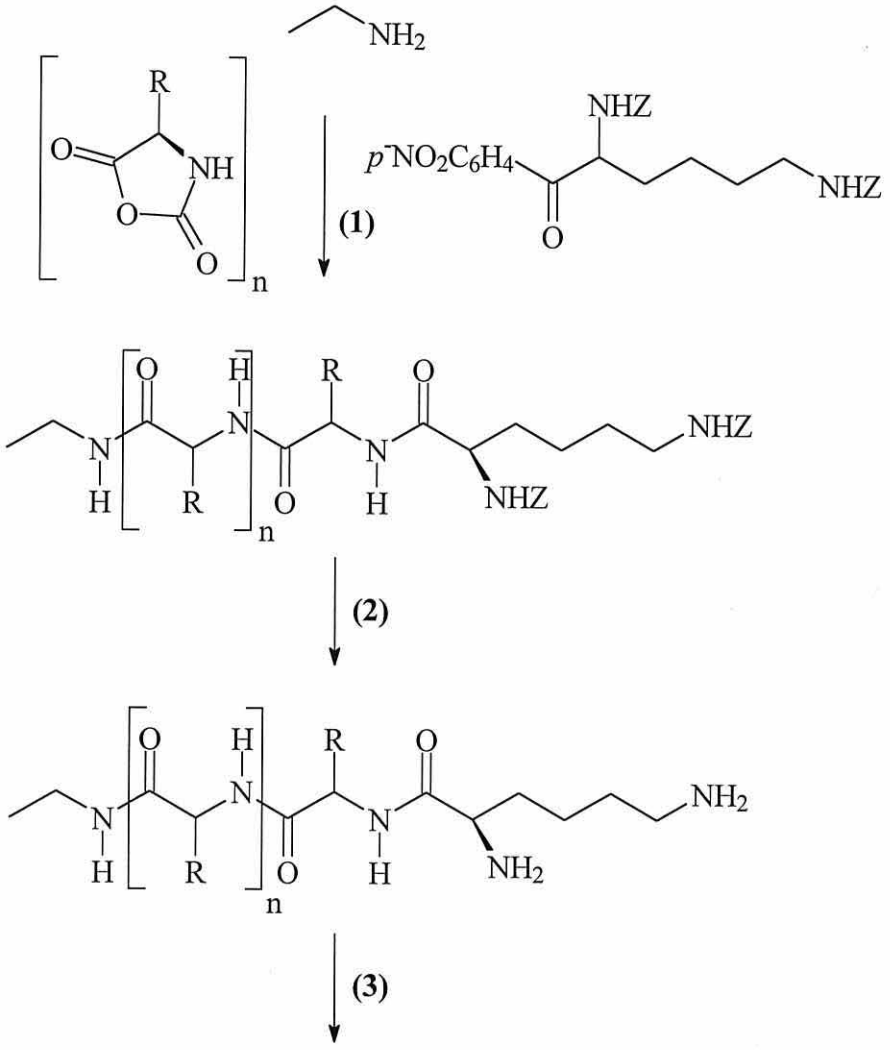
If the polymerisation is terminated by reaction with an active ester of an amino

acid which contains a second amino group in its side chain then it ought to be possible to use this methodology to introduce branching into the polymers. Protection of the amino functionalities of the diamino residues is necessary, to prevent the side chain amino group from reacting with *N*-carboxyanhydride. For example, addition of *para*-nitrophenyl-*N*-Z, *N*-Z-(*S*)-lysine to the growing poly(amino acid) chain should terminate the polymerisation **(Scheme 24)**.



Scheme 24. n = number-average monomer units

Subsequent hydrogenation of the capped polymer would reveal two primary amino groups on each chain of the initial polymer, which could be used to initiate the polymerisation of a second *N*-carboxyanhydride of an amino acid. Capping of this polymerisation by the lysine derivative would give the next generation of the polymer and the process could be repeated indefinitely to give highly branched poly(amino acids) **(Scheme 25)**.



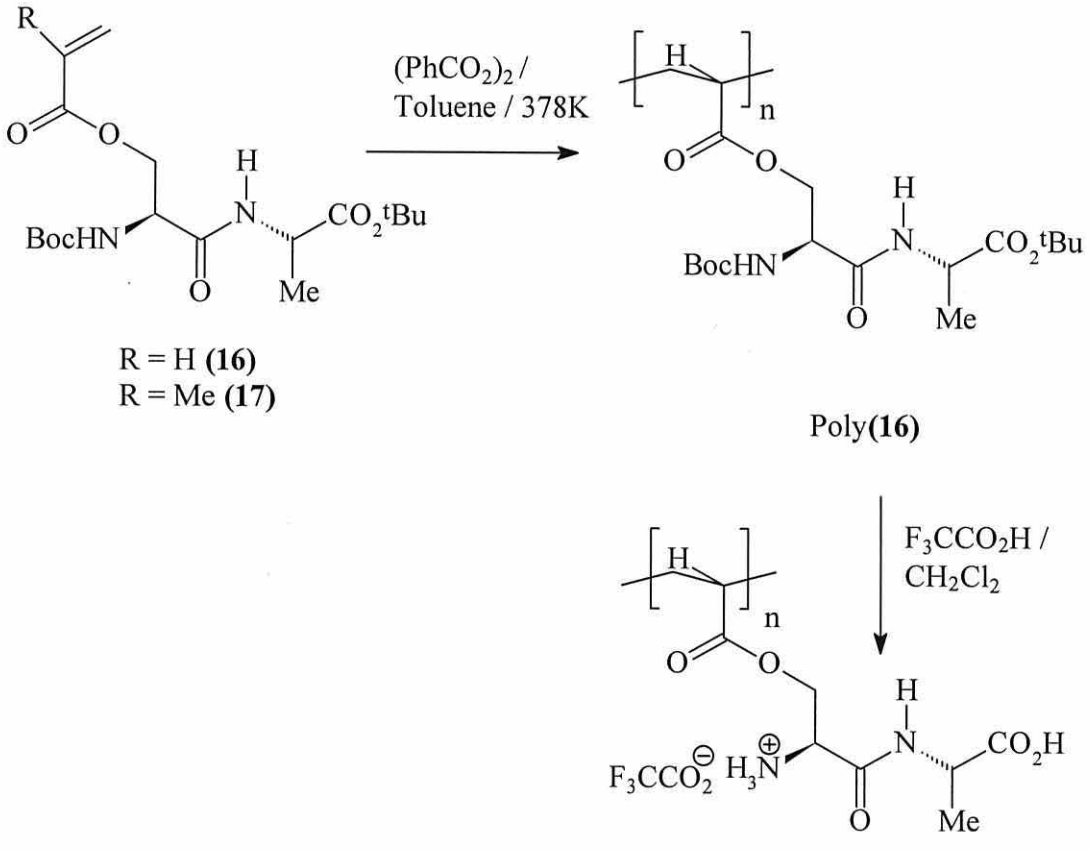
Scheme 25. **(1)** Propagation; **(2)** Hydrogenation; **(3)** Further propagation

Whilst the length of the polymer chains produced in this way will inevitably be polydisperse, the degree of branching of the polymers will be highly controlled, as exactly one degree of branching is introduced at each polymerisation stage. This will result in the synthesis of a traditional type linear polymer, which incorporates the precise branching and successive generation concept of dendrimers. This work will be discussed further in chapter 3.

2 Results and Discussion

2.1 Synthesis of dipeptide monomers with acid labile protecting groups

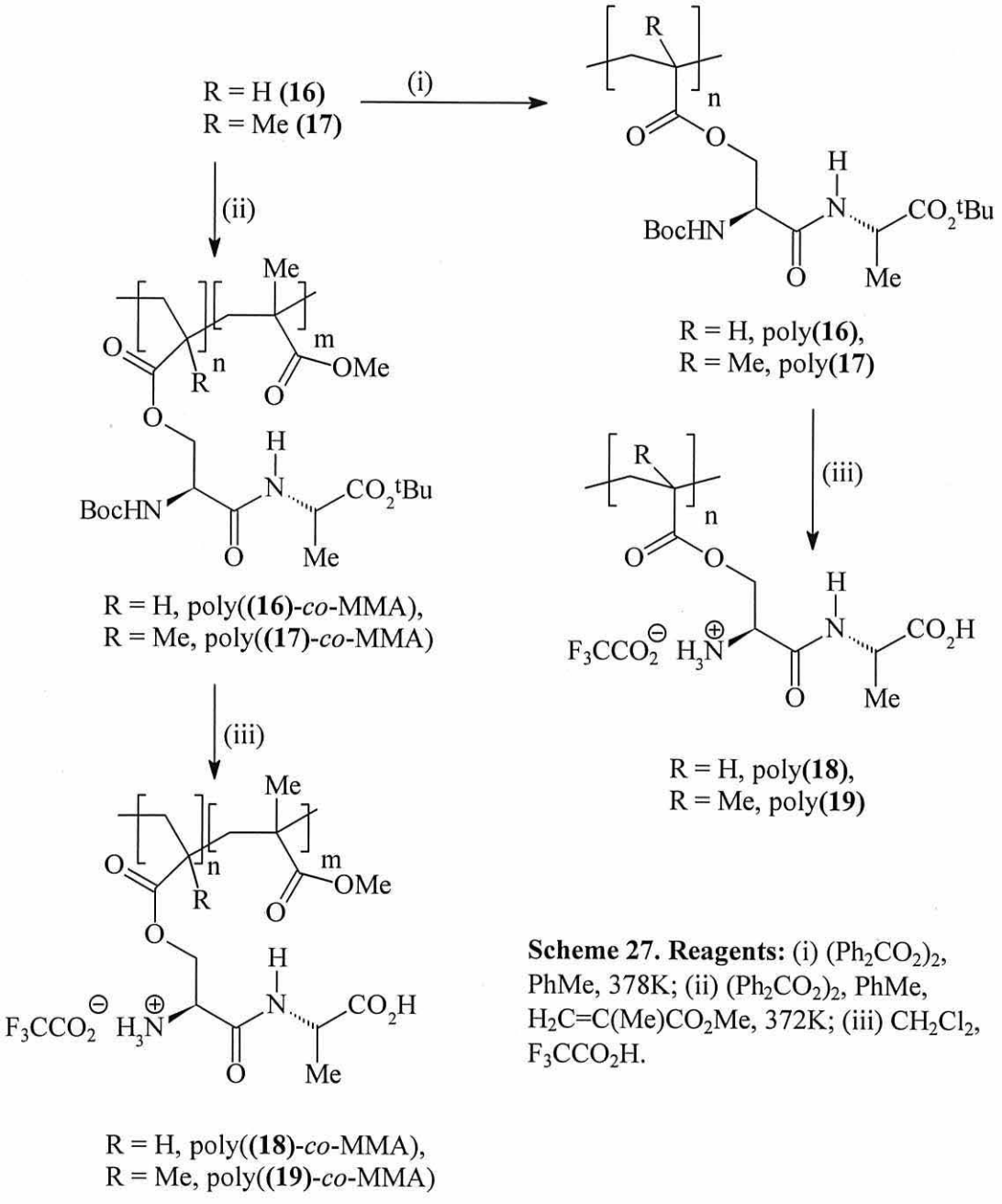
The initial investigation had led to dipeptide monomers **(16)** and **(17)** with acid labile protecting groups.[34] The dipeptide monomer **(16)** had been polymerised under free radical initiated conditions to provide poly(peptide) poly**(16)** in a moderate yield of 60 %. Furthermore, simultaneous removal of the Boc and ^{t}Bu ester groups had been achieved through acidolysis of poly**(16)** by reaction with trifluoroacetic acid in dichloromethane to furnish the fully deprotected poly(peptide) poly**(18)** in a yield of 89 %, **(Scheme 26)**.



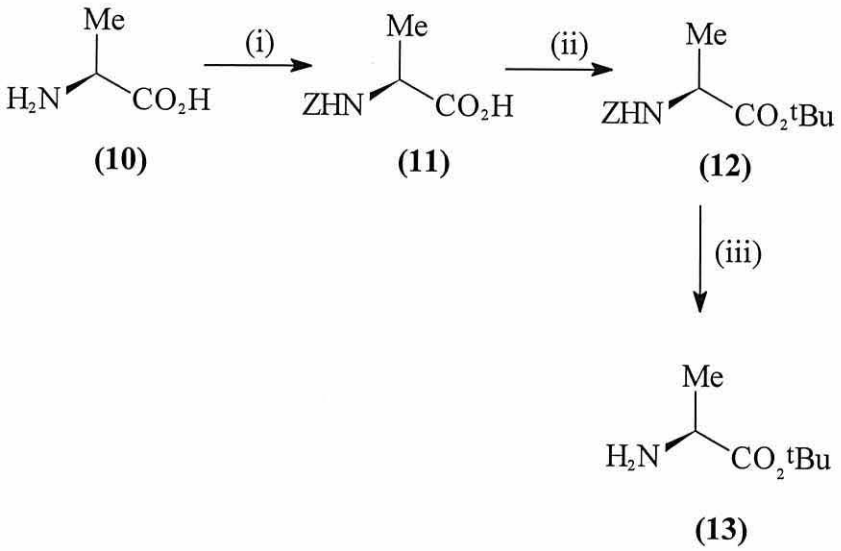
Scheme 26.

The aim of this project was to further this investigation by synthesising dipeptide monomers **(16)** and **(17)** and subsequently copolymerise them with MMA to

provide the poly(peptides), poly((**16**)-*co*-MMA) and poly((**17**)-*co*-MMA). Homopolymerisation of monomer (**17**) would provide poly(**17**). Deprotection of the above polymers should provide the deprotected homopolymers, poly(**18**) and poly(**19**) and the deprotected co-polymers, poly((**18**)-*co*-MMA) and poly((**19**)-*co*-MMA) **(Scheme27).**



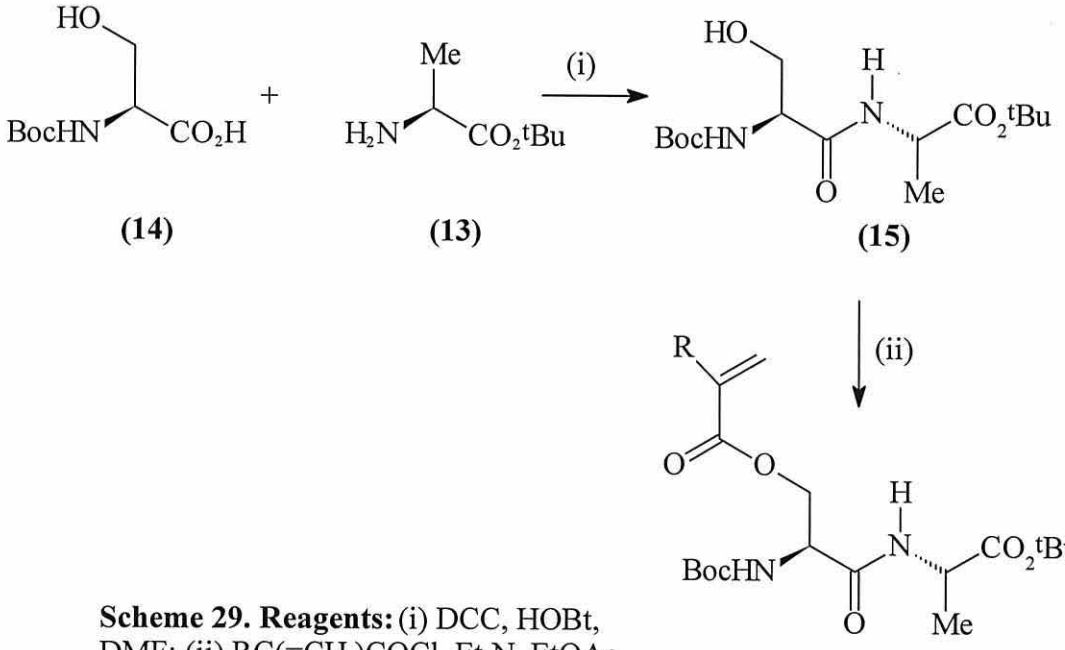
Scheme 27. Reagents: (i) $(Ph_2CO_2)_2$, PhMe, 378K; (ii) $(Ph_2CO_2)_2$, PhMe, $H_2C{=}C(Me)CO_2Me$, 372K; (iii) CH_2Cl_2, F_3CCO_2H.



(10) **(11)** **(12)** **(13)**

Scheme 28. Reagents: (i) K_2CO_3, Z-ONSu, acetone; (ii) $Me_2C{=}CH_2$, H_2SO_4, CH_2Cl_2; (iii) Pd, C, H_2, MeOH.

Protected amino acid **(13)** was synthesised in an overall yield of 93 % from the free amino acid **(10)** **(Scheme 28)**. Coupling of amino ester **(13)** to *N*-Boc-(*S*)-Ser **(14)** enabled access to the dipeptide **(15)**. This was subsequently acrylated and methacrylated to arrive at the polymerisable monomers **(16)** and **(17)** in yields of 66 % and 96 % respectively **(Scheme 29)**.



(14) **(13)** **(15)**

Scheme 29. Reagents: (i) DCC, HOBt, DMF; (ii) $RC(=CH_2)COCl$, Et_3N, EtOAc.

R = H **(16)**,
R = Me **(17)**

2.2 Polymerisation of dipeptide monomers (16) and (17)

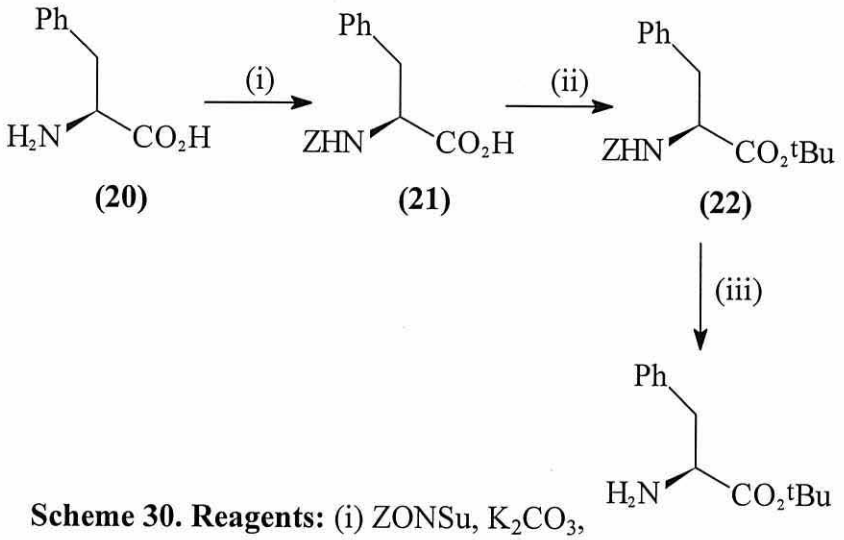
The dipeptide monomer **(16)** was polymerised under free radical initiated conditions, with benzoyl peroxide as initiator, to give the poly(peptide) poly**(16)** in a yield of 72 %. The polymeric material was separated from the starting materials by precipitation from a chloroform solution into light petrol. The polymerisation procedure was repeated for dipeptide monomer **(17)** but no evidence of poly**(17)** was detected. Dipeptide monomer **(16)** was co-polymerised with methyl methacrylate to provide poly(**(16)**-*co*-MMA) **(Scheme 27)**, however the reaction products were completely insoluble hindering further analysis. In order to obtain more soluble reaction products, MMA was substituted by methyl acrylate and styrene to obtain poly(**(16)**-*co*-methyl acrylate) and poly(**(16)**-*co*-styrene). However, the reaction products from these reactions were just as insoluble as those obtained using methyl methacrylate.

2.3 Increasing the solubility of the polymers

To overcome the problems caused by the formation of insoluble reaction products the dipeptide was changed to *N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu. This should be more soluble in organic solvents due to the presence of the hydrophobic aromatic ring. The dipeptide *N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu was also synthesised, this should be more soluble in organic solvents due to the absence of any amide NH in the dipeptide.

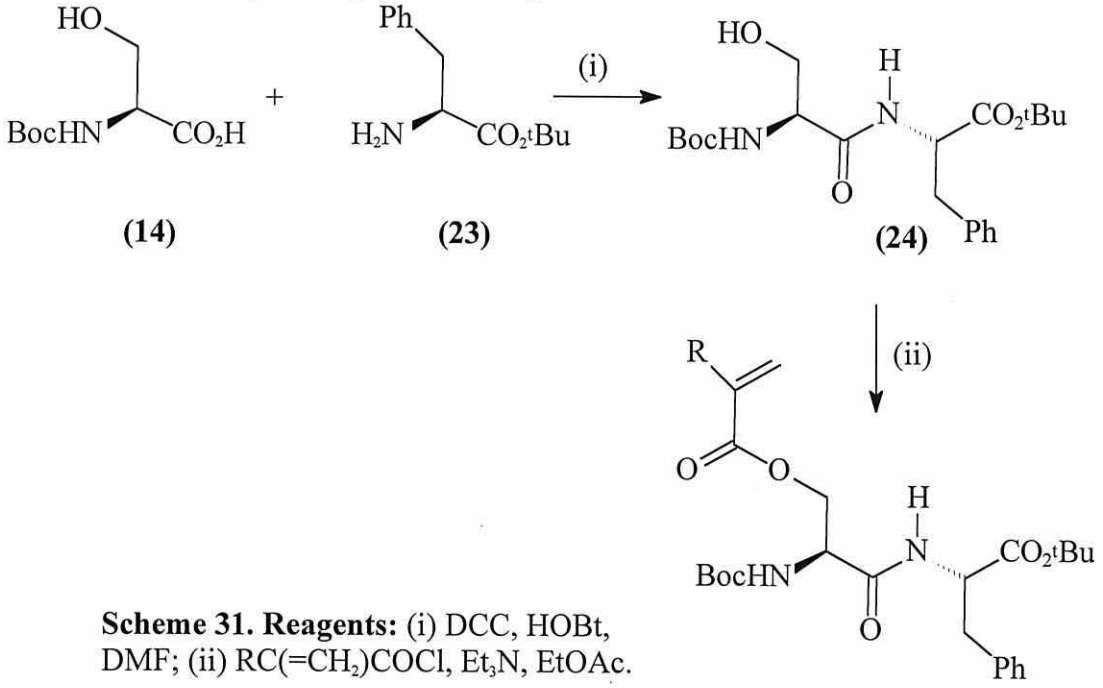
2.4 Synthesis of acid labile monomer N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu

Treatment of (*S*)-phenylalanine **(20)** with ZONSu in the presence of K_2CO_3 in a water, acetone solvent mixture gave the protected amino acid **(21)** in a yield of 99 %.[124] Carboxylate protection was achieved by treatment with isobutylene in the presence of a catalytic amount of 12M H_2SO_4, to provide the fully protected derivative **(22)** in a yield of 93 %.[125-127] Exposure to hydrogen, in the presence of a catalytic amount of Pd / carbon in methanol, yielded the free amine **(23)** in a yield of 100 % **(Scheme 30)**.[128]



Scheme 30. Reagents: (i) ZONSu, K_2CO_3, Me_2CO / H_2O; (ii) H_2SO_4, $Me_2C{=}CH_2$, CH_2Cl_2; (iii) Pd, C, H_2, MeOH.

Coupling of compound **(23)** to *N*-Boc-(*S*)-Ser **(14)** with DCC and HOBt led to the isolation of the dipeptide **(24)** in a yield of 98 %. This was subsequently acrylated and methacrylated to arrive at the polymerisable monomers **(25)** and **(26)** in yields of 90 % and 85 % respectively **(Scheme 31)**.

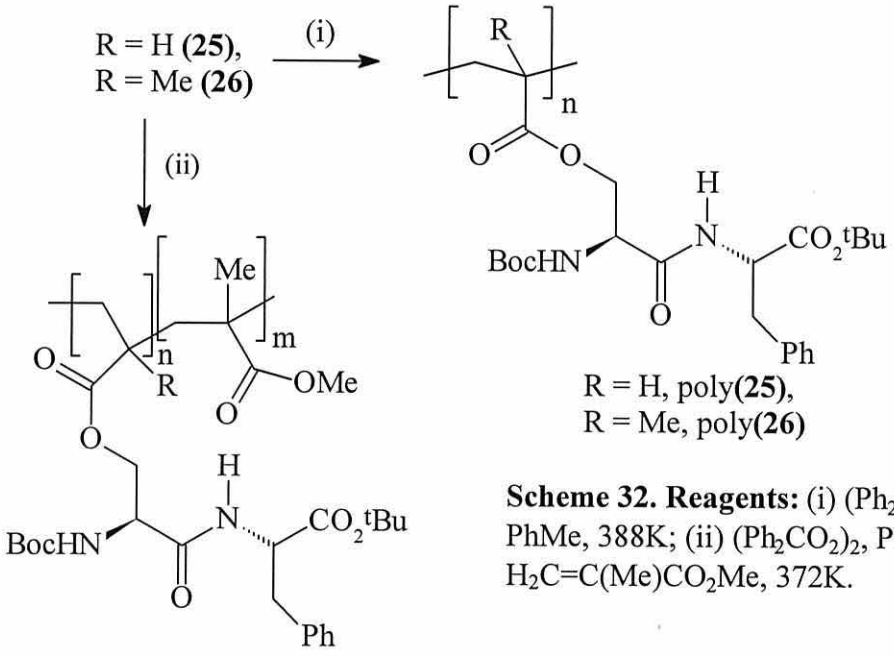


Scheme 31. Reagents: (i) DCC, HOBt, DMF; (ii) $RC(=CH_2)COCl$, Et_3N, EtOAc.

R = H **(25)**,
R = Me **(26)**

2.5 Polymerisation of dipeptide monomers (25) and (26)

Polymerisation of dipeptide monomers **(25)** and **(26)** was conducted at a concentration of *ca.* 1M in toluene, initiated by benzoyl peroxide to provide the homopolymers: poly**(25)** and poly**(26)**. The dipeptide monomers were subsequently copolymerised with MMA at a concentration between 1M and 7M in toluene, initiated by benzoyl peroxide to provide the copolymers: poly(**(25)**-*co*-MMA) and poly(**(26)**-*co*-MMA), **(Scheme 32)**.



Scheme 32. Reagents: (i) $(Ph_2CO_2)_2$, PhMe, 388K; (ii) $(Ph_2CO_2)_2$, PhMe, $H_2C{=}C(Me)CO_2Me$, 372K.

All of the crude polymers were purified by dissolving them in a small amount of chloroform (*ca.* 5 ml) and subsequently precipitating them into an excess of light petroleum (*ca.* 150 ml) to provide the polymeric material as fine white solids in all cases.

Copolymerisation of the chiral monomers **(25)** and **(26)** with different percentages of MMA resulted in the synthesis of two series of copolymers. All of these polymers were found to rotate plane polarised light and their specific rotations are recorded in **Table 1**, poly(**(25)**-*co*-MMA) and **Table 2**, poly(**(26)**-*co*-MMA).

Monomer **(25)** added(%)	Monomer **(25)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]^{28}_D$[e]
100	100	4.8	47.4	9.9	37.1
75.0	84.4	9.5	38.0	4.0	30.1
71.4	75.2	3.5	33.5	9.6	26.9
70.0	70.6	-	-	-	25.6
43.5	54.1	4.8	47.4	9.9	20.7
42.0	53.5	5.3	66.4	12.5	20.4
20.8	34.2	20.3	447	22.1	15.5
16.7	26.9	20.6	552	26.9	13.9
9.1	14.0	19.0	404	21.3	10.0
4.8	5.7	30.0	286	5.6	5.8
2.4	2.9	21.8	100	4.6	3.8
0[f]	0	11.8	29.3	2.5	0

Table 1. Physical data for the polymers derived from monomer (**25**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly((**25**)-*co*-MMA) at 301 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

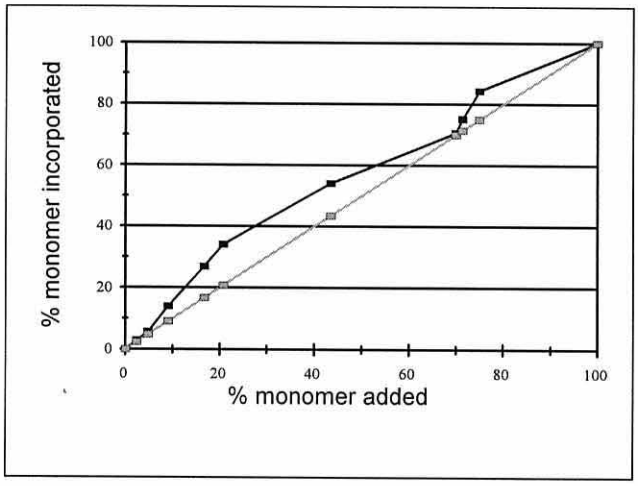
Monomer **(26)** added(%)	Monomer **(26)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]^{27}_D$[e]
100[f]	100	6.2	20.9	3.4	26.4
90.0	95.0	6.8	40.6	6.0	25.2
80.0	84.0	7.0	38.2	5.4	24.6
61.5	73.0	8.2	39.4	4.8	24.0
43.5	56.0	9.1	33.0	3.6	23.6
28.6	41.0	9.0	73.1	8.1	21.5
16.7	30.2	8.7	34.0	3.9	19.4
16.7	14.7	9.8	33.7	3.4	13.5
9.1	10.0	10.1	47.2	4.7	10.6
4.8	7.2	8.7	34.0	3.9	8.0
0[g]	0	11.8	28.3	2.5	0

Table 2. Physical data for the polymers derived from monomer (**26**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly((**26**)-*co*-MMA) at 300 K $CHCl_3$ and at 1.0 g / 100 ml. f. Polymerisation conducted in DMF. g. Homopolymer of MMA.

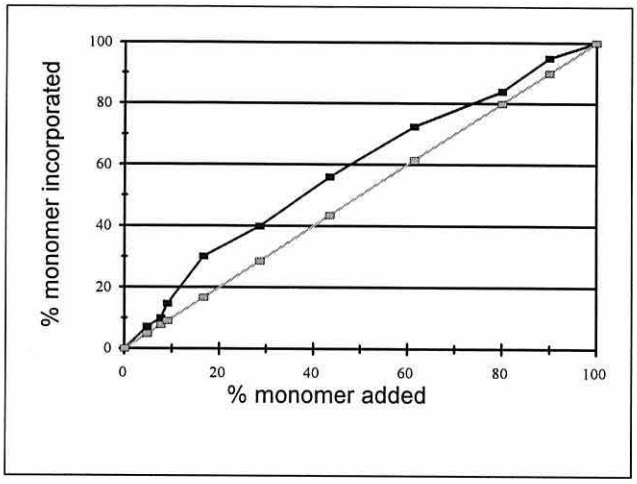
2.6 Reactivity of the monomers (25) and (26)

The reactivity of the two monomers could be expressed by plotting the ratio of monomer **(25)** or **(26)** added to the reaction, against the ratio of monomer **(25)** or **(26)** present in the polymers derived from poly(**(25)**-*co*-MMA) or poly(**(26)**-*co*-MMA), determined by ^{1}H nmr **(Graphs 1** and **2**, respectively). For monomer **(25),** these results showed there was preference between the reacting species, *i.e.* monomer **(25)** and MMA. The experimentally derived points did lie to the left of the line expected for ideal, 1:1 copolymerisation (the line derived from the equation y = x). This revealed that the chiral monomer **(25)**, derived from an acrylate, was slightly more polymerisable than the more sterically hindered and disubstituted MMA.



Graph 1. Reactivity of the chiral monomer (**25**) (% conversion between 58-100 %).

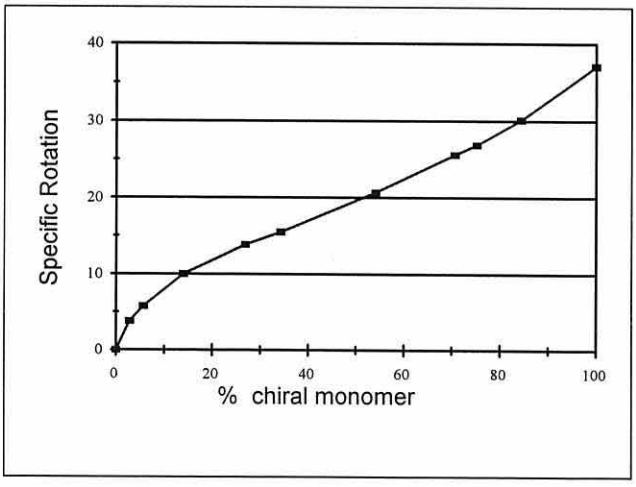
The series of polymers derived from the monomer **(26)** also showed that there was preference between the reacting species **(Graph 2)**. The experimentally derived points again lay to the left of the ideal copolymerisation situation. Since the polymerisable groups in the chiral monomer **(26)** and MMA are both methacrylate groups, this difference in reactivity may be due to the fact that MMA was evaporated from the reaction solution (reaction temperature 372 K, compared to the boiling point of MMA which is 373 K).



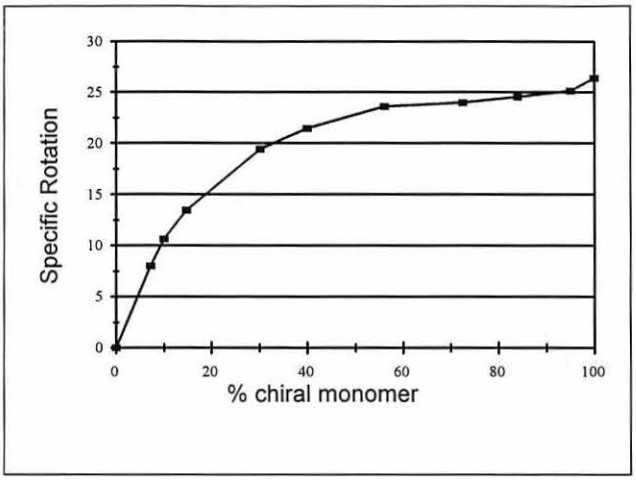
Graph 2. Reactivity of the chiral monomer (**26**) (% conversion between 70-100 %).

2.7 Polarimetry studies on the polymer series, poly(25) and poly(26)

The proportion of MMA present in each polymer was determined by comparison of the aromatic and methyl ester resonances in the ^{1}H nmr. When the specific rotation was plotted against the percentage of chiral monomer **(25)** present in the polymer, a non-linear plot was obtained for the polymers of monomer **(25)**. All values recorded were positive with the greatest rate of increase of specific rotation occurring between 0 % and 10 % chiral monomer **(Graph 3)**.



Graph 3. Specific rotation *vs* % incorporation of chiral monomer (**25**).

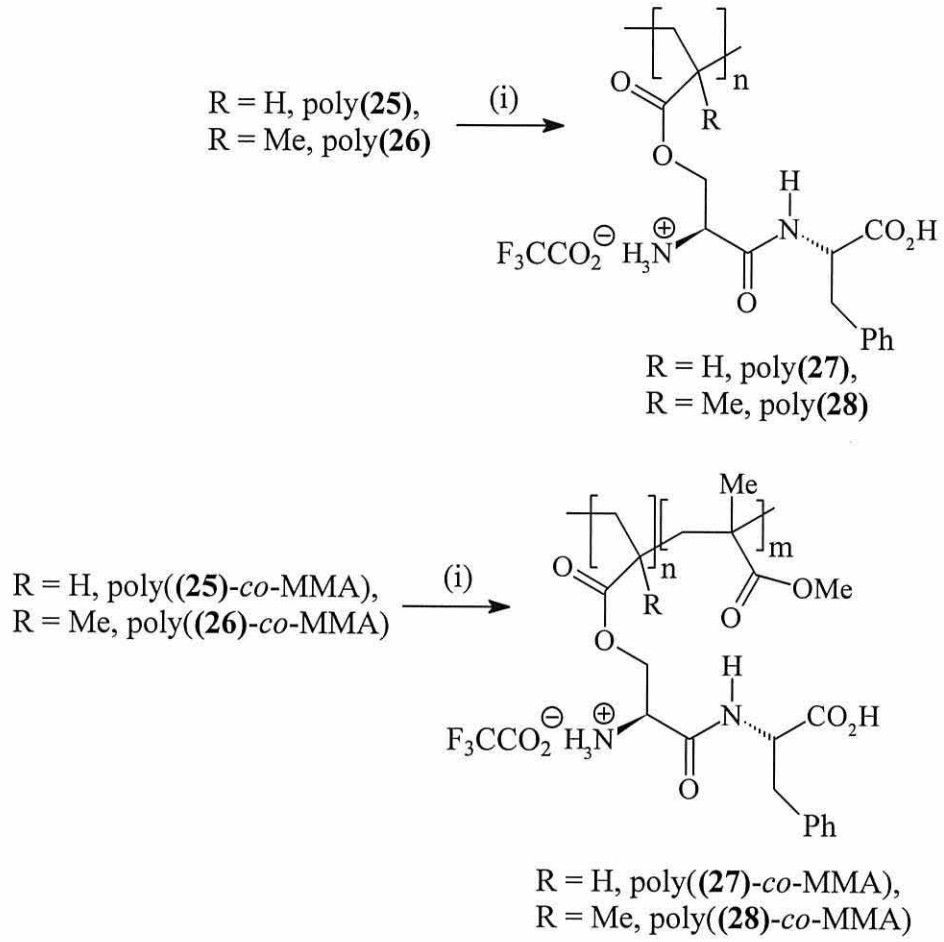


Graph 4. Specific rotation *vs* % incorporation of chiral monomer (**26**).

When the specific rotation values were plotted against the percentage of chiral monomer **(26)** incorporated into the polymers, a curved plot was again observed **(Graph 4)**. All the values observed were positive with the specific rotation values rising rapidly between 0 % and 50 % chiral monomer incorporation. The greatest rise in specific rotation value was between 0 % and 15 % chiral monomer incorporation. Between 56 % and 100 %, there was only a slight increase in the specific rotation value. The origin of these non-linear effects of specific rotation is believed to be due to asymmetric induction from the (*S*)-serine chiral centre **(see Introduction 1.11 Optical Activity)**.

2.8 Removal of the protecting groups from the poly(25) and poly(26) series

Simultaneous removal of the Boc and ^{t}Bu protecting groups was achieved through acidolysis of the fully protected polymers with an excess of trifluoroacetic acid to furnish the poly(peptides) poly**(27)** and poly**(28)** **(Scheme 33)**. Cleavage of the protecting groups was shown by ^{1}H nmr, ^{13}C nmr and IR spectroscopy. This was evidenced by the loss of the Boc and ^{t}Bu groups and the appearance of acid groups and $^{+}NH_3$ groups. Unlike their parent polymers, these deprotected polymers were only soluble in polar solvents such as DMF, DMSO and DMSO : acetronitrile mixtures.



Scheme 33. Reagents: (i) CH_2Cl_2, F_3CCO_2H.

2.9 Polarimetry on the deprotected polymer series, poly(27) and poly(28)

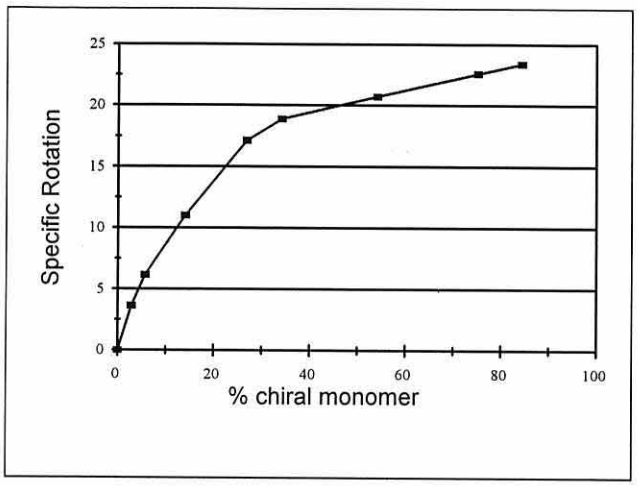
The polymers derived from the chiral monomer **(25)** gave the deprotected polymers in excellent yields, *ca.* 80 % and were found to be fully soluble in an acetonitrile : DMSO solvent mixture (1:1). The specific rotation of each of the polymers was recorded **(Table 3)**. When these values were plotted against the percentage of monomer **(25)** present in the fully protected precursor polymer, a curved plot was obtained with all the values positive **(Graph 5)**.

Monomer **(25)** added(%)	Monomer **(25)** incorporated(%)[a]	M_n[b] x10^6	M_w[c] x10^6	M_w/M_n[d]	$[\alpha]^{28}_D$[e]
75.0	84.4	11.7	16.0	1.5	24.2
71.4	75.2	5.4	13.1	2.7	22.6
43.5	54.1	-	-	-	20.7
20.8	34.2	2.5	12.7	5.4	18.9
16.7	26.9	3.8	18.0	4.7	17.1
9.1	14.0	1.8	10.5	5.8	11.0
4.8	5.7	1.6	9.1	5.6	6.2
2.4	2.9	0.3	3.8	11.1	3.6

Table 3. Physical data for the deprotected polymers derived from monomer (**25**).

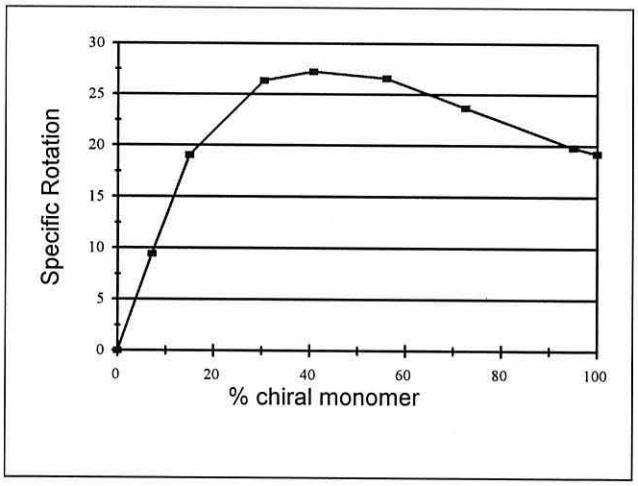
a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations of the precursor polymer. b. Determined by GPC using DMF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the deprotected polymer series poly(**(27)**-*co*-MMA) at 301 K in DMSO : AcCN (1:1) and at 0.5 g / 100 ml.

The specific rotation values were found to increase rapidly as the percentage chiral monomer incorporation was increased from 0 % to 34 %. The greatest increase in specific rotation values was observed between 0 % and 7 % chiral monomer incorporation. The specific rotation values were found to increase linearly with percentage chiral monomer incorporation from 34 % to 84 %. Again, the origin of these non-linear effects of specific rotation is believed to be due to asymmetric induction from the (*S*)-serine chiral centre (see **Introduction 1.11 Optical Activity**).



Graph 5. Specific rotation *vs* % incorporation of chiral monomer (**25**).

For the deprotected polymers derived from monomer **(26) (Table 4)**, when the specific rotation values were plotted against the percentage incorporation of chiral monomer **(26)**, a non-linear plot was obtained **(Graph 6)**. All the specific rotation values were positive.



Graph 6. Specific rotation *vs* % incorporation of chiral monomer (**26**).

The specific rotation values were found to increase rapidly as the percentage incorporation of chiral monomer **(26)** was increased from 0 % to 35 %. The greatest increase in specific rotation values was found between 0 % and 19 % chiral monomer

incorporation. The specific rotation value peaked at *ca.* 40 % monomer incorporation before decreasing linearly from 56 % to 100 % chiral monomer incorporation. The origin of this non-linear behaviour is likely to be the result of conformational effects in the polymer chain (see **Introduction 1.11 Optical Activity**).

Monomer **(26)** added(%)	Monomer **(26)** incorporated(%)[a]	$[\alpha]^{27}_{D}$ [b]	$[\alpha]^{28}_{D}$ [c]
100	100	26.4	19.2
90.0	95.0	25.2	19.9
61.5	73.0	24.0	23.7
43.5	56.0	23.6	26.6
28.6	41.0	21.5	27.3
16.7	30.2	19.4	26.4
16.7	14.7	13.5	19.1
4.8	7.2	8.0	9.5
0[d]	0	0	0

Table 4. Physical data for the deprotected polymers derived from monomer (**26**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations of the precursor polymer. b. Specific rotation of the protected polymer series poly((**26**)-*co*-MMA) at 300 K $CHCl_3$ and at 1.0 g / 100 ml. c. Specific rotation of the deprotected polymer series poly((**28**)-*co*-MMA) at 301 K in DMSO : AcCN (1:1) and at 0.5 g / 100 ml. d. Homopolymer of MMA.

2.10 GPC data for polymers derived from monomers (25) and (26)

The polydispersity (PD) values obtained by GPC for each polymerisation gave a measure of the breadth of the molecular weight distribution in the polymer. In the series of polymers derived from the chiral monomers **(25)** and **(26)** (**Tables 1** and **2**), the PD values ranged from 3.5 to 27.0. The high PD values are characteristic of

radical addition polymerisation and are attributed to the Trommsdorff-Norrish or gel effect.[4] This is supported by experimental observations where the solutions in which the polymerisations were performed became highly viscous after *ca.* 20 minutes. Subsequently the mixture became vitrified into a glassy state. When the solution becomes viscous, the ends of the polymer chains become entangled and as such are less likely to collide and terminate the polymerisation. This fall in termination rate increases the propagation rate, reflecting the high PD values.

There is a large difference between the observed M_w and M_n values of the protected polymers and the deprotected polymers **(Table 1** and **3)**. It would be expected that the deprotected polymers would have a lower molecular weight than the protected polymers. However, the observed results show the opposite. The deprotected polymer values were *ca.* 1000 times larger than the protected polymers. This suggested the occurrence of some sort of abnormal elution such as interactions between the NH groups of the polymer and the column. This was further supported by the observation that the protected and deprotected polymers with a low percentage incorporation of chiral monomer had very similar M_w and M_n values. Whereas the M_w and M_n values between the protected and deprotected polymers containing a high percentage of chiral monomer varied considerably.

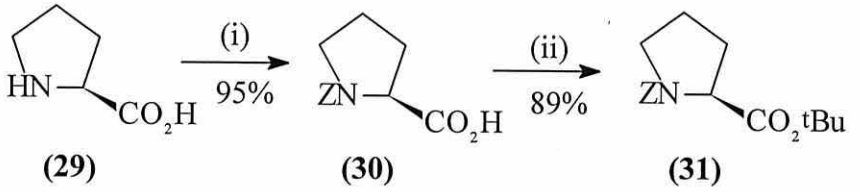
To investigate this further a combined GPC-viscosity study was performed on a range of protected polymers (82 %, 37.5 % and 5.2 % chiral monomer). The results showed that the actual M_w and M_n values were 3 times greater than the observed values obtained through calibration with polystyrene, for the polymers with a high percentage incorporation of chiral monomer. For the polymers with a low percentage incorporation of chiral monomer (5.2 %), the actual M_w and M_n values were *ca.* 2 times greater than the observed values.

Intrinsic viscosity experiments showed all the polymers to have linear plots. This proved the existence of true copolymeric materials and showed that the ratio of chiral monomer : MMA calculated from the ^1H nmr were the correct values. Deviations from this line would indicate the presence of more than one type of

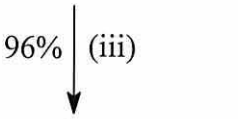
polymer, *i.e.* chiral polymer and achiral MMA.

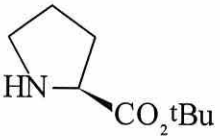
The high values recorded for the deprotected polymers are most likely incorrect and this can be attributed to abnormal column interactions such as between the $^{+}NH_3$ groups of the polymers and the column packing. Abnormal column interactions are further evidenced by the deprotected poly(**(28)**-*co*-MMA) series. All the polymers were found to be fully soluble in the sample solutions however, no significant detector response was observed when the samples were run, indicating abnormal elution. However, for the deprotected polymers derived from the chiral monomer **(25)** the GPC traces do show a broad, single resolved peak in all cases indicating the presence of polymeric material which cannot be attributed to the parent protected polymer.

2.11 Synthesis of acid labile monomer N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu



(29) **(30)** **(31)**

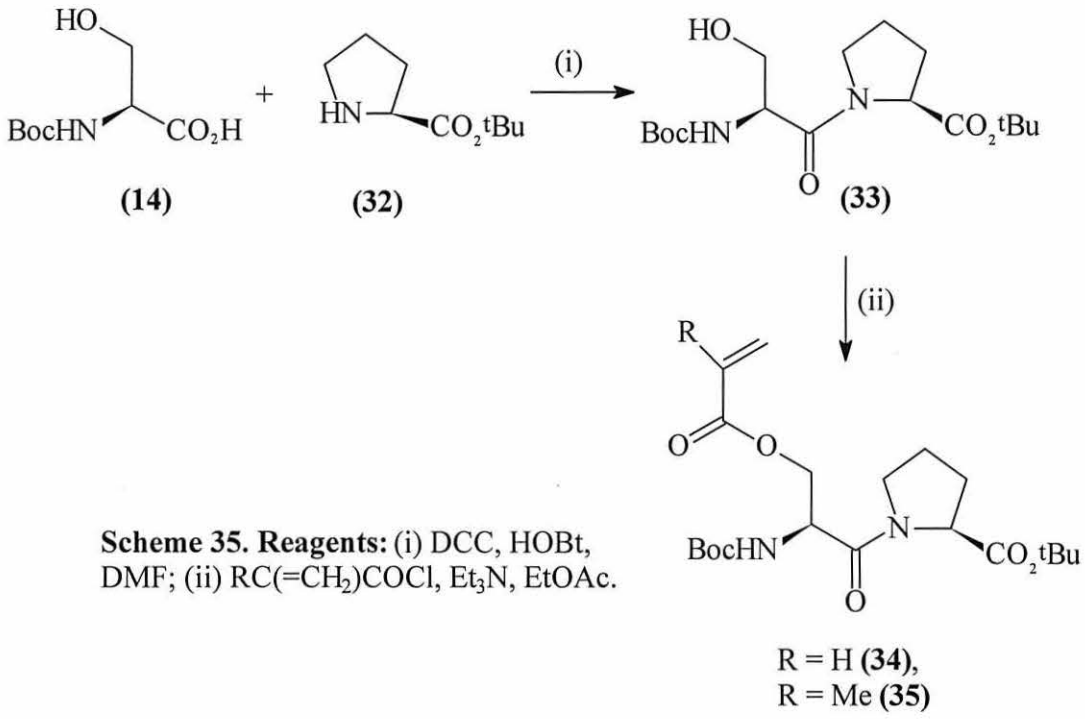




(32)

Scheme 34. Reagents: (i) K_2CO_3, ZONSu, Me_2CO, H_2O; (ii) $Me_2C{=}CH_2$, H_2SO_4, CH_2Cl_2; (iii) Pd, C, H_2, MeOH.

Proline derivative **(32)** was prepared from (*S*)-proline **(29)** **(Scheme 34)** by the same route used to prepare phenylalanine derivative **(23)**. Coupling of compound **(32)** to *N*-Boc-(*S*)-Ser **(14)** with DCC and HOBt led to the isolation of the dipeptide **(33)** in a yield of 87 %. This was subsequently acrylated and methacrylated to arrive at the polymerisable monomers **(34)** and **(35)** in yields of 89 % and 81 % respectively **(Scheme 35)**.

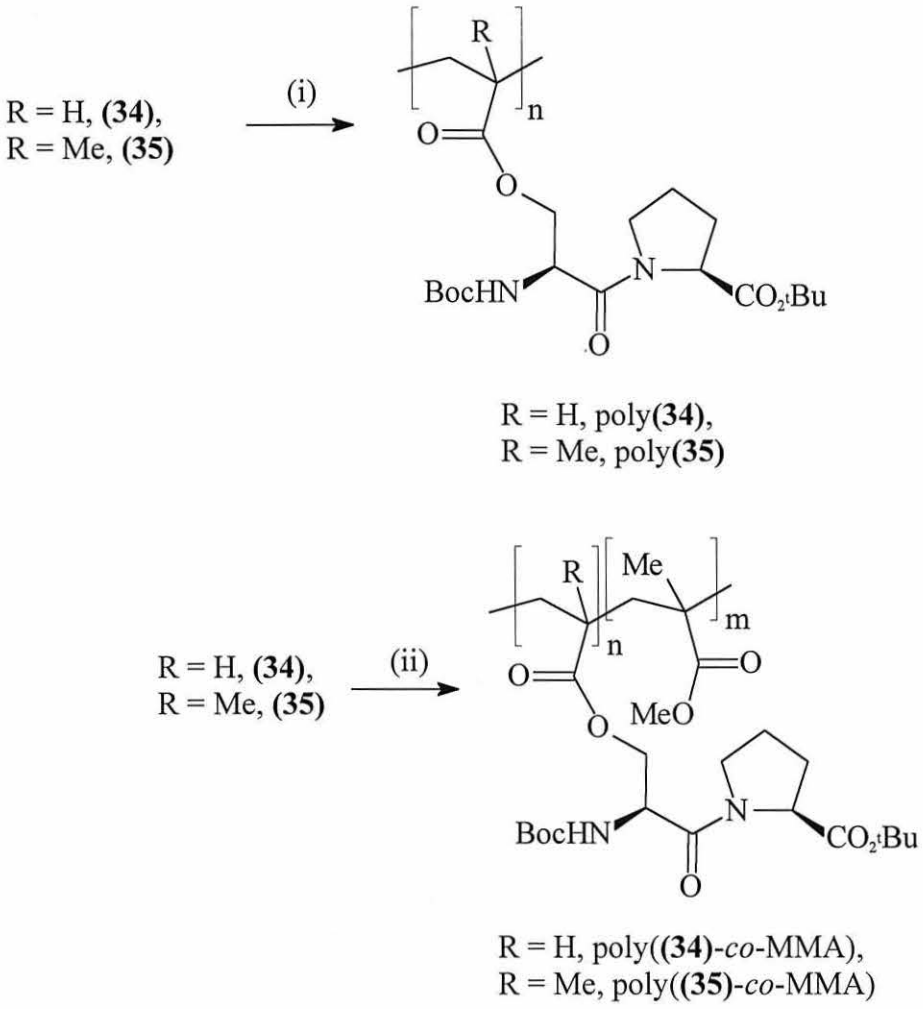


Scheme 35. Reagents: (i) DCC, HOBt, DMF; (ii) $RC(=CH_2)COCl$, Et_3N, EtOAc.

R = H **(34)**,
R = Me **(35)**

2.12 Polymerisation of dipeptide monomers (34) and (35)

Polymerisation of dipeptide monomers **(34)** and **(35)** was conducted at a concentration of *ca.* 2M in toluene, initiated by benzoyl peroxide to provide the homopolymers: poly**(34)** and poly**(35)**. The dipeptide monomers were subsequently copolymerised with MMA at a concentration between 1.5M and 8M in toluene, initiated by benzoyl peroxide to provide the copolymers: poly(**(34)**-*co*-MMA) and poly(**(35)**-*co*-MMA), **(Scheme 36)**.



Scheme 36. Reagents: (i) $(PhCO_2)_2$, PhMe, 388K; (ii) $(PhCO_2)_2$, PhMe, $H_2C{=}C(Me)CO_2Me$, 372K.

The crude polymers were dissolved in a small amount of chloroform and subsequently precipitated into an excess of light petroleum, to yield a fine white solid in all cases.

Copolymerisation of the chiral monomers **(34)** and **(35)** with different percentages of MMA resulted in the synthesis of two series of copolymers. All of these polymers were found to rotate plane polarised light and the specific rotation values are recorded in, **Table 5** (poly((**34**)-*co*-MMA)) and **Table 6** (poly((**35**)-*co*-MMA)).

Monomer **(34)** added(%)	Monomer **(34)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]^{26}_D$[e]
100	100	4.2	12.6	3.0	-38.2
85.0	85.0	6.7	17.0	2.5	-37.5
65.0	65.0	-	-	-	-35.2
60.0	48.8	10.9	149	13.7	-33.1
43.0	43.0	5.3	40.2	7.6	-32.0
38.0	38.6	7.8	32.7	4.2	-30.5
25.0	22.6	13.7	136	9.9	-23.1
20.8	16.9	10.3	222	21.6	-19.9
20.0	12.6	10.9	209	19.2	-17.1
7.1	9.1	17.7	129	7.3	-14.9
3.6	3.9	8.9	33.9	3.8	-7.3
0[f]	0	11.8	29.3	2.5	0

Table 5. Physical data for polymers derived from monomer (**34**).

a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly(**(34)**-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

Monomer **(35)** added(%)	Monomer **(35)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]_D^{26}$[e]
100	100	2.2	12.1	5.4	-44.2
85.0	82.0	6.5	35.8	5.5	-40.1
70.0	69.4	9.2	49.5	5.4	-38.3
69.7	60.0	7.3	34.8	4.7	-36.6
60.0	46.2	9.8	44.0	4.5	-34.6
43.5	37.5	5.8	22.2	3.8	-33.3
27.8	30.8	9.0	33.5	3.7	-30.5
13.5	21.4	11.7	132	11.2	-25.0
13.3	11.3	6.4	77.2	12.0	-16.1
7.1	5.2	9.1	46.1	5.1	-9.0
4.3	3.6	12.1	45.4	3.8	-5.6
0[f]	0	11.8	29.3	2.5	0

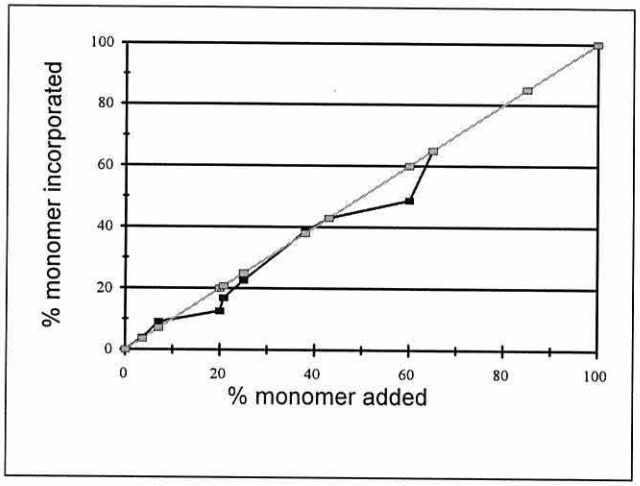
Table 6. Physical data for polymers derived from monomer (**35**).

a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly((**35**)-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

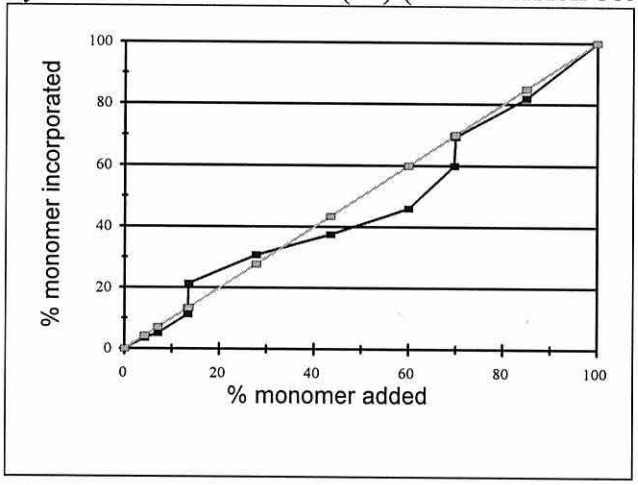
2.13 Reactivity of the monomers (34) and (35)

Analysis of the ^{1}H nmr spectra of the polymers allowed the percentage composition to be calculated. For each polymer sample, the percentage of chiral monomer incorporated into the polymer was plotted against the percentage of chiral

monomer added to the reaction. The results **(Graph 7**, monomer **(34)** and **Graph 8**, monomer **(35)**, showed that both series of polymers lay exactly on the line y = x within experimental error.



Graph 7. Reactivity of the chiral monomer (**34**) (% conversion between 46-100 %).

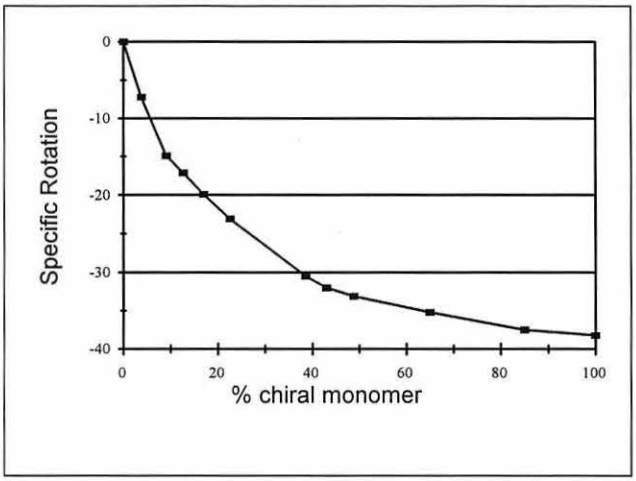


Graph 8. Reactivity of the chiral monomer (**35**) (% conversion between 48-98 %).

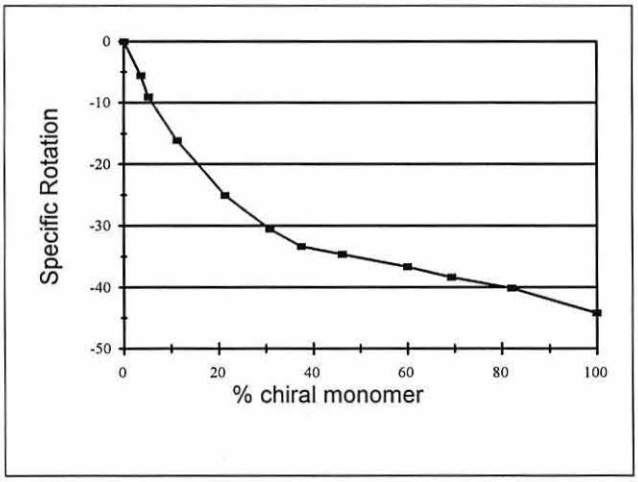
2.14 Polarimetry studies on the polymer series, poly(34) and poly(35)

When the specific rotation of the polymers was plotted against the percentage of chiral monomer **(34)** present in the polymer, a curved plot was obtained with all the values negative **(Graph 9)**. The specific rotation values decreased rapidly between 0 % and 40 % chiral monomer incorporation. The greatest decrease in specific rotation

value occurring between 0 % and 20 %. Between 40 % and 100 %, there was only a slight decrease in the specific rotation value.



Graph 9. Specific rotation *vs* % incorporation of chiral monomer (**34**).

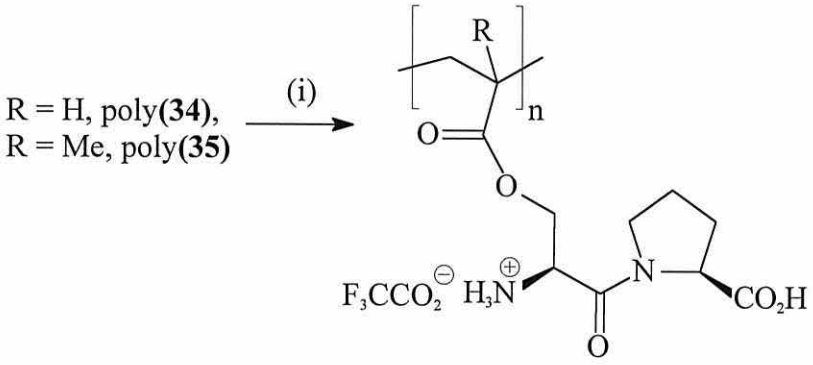


Graph 10. Specific rotation *vs* % incorporation of chiral monomer (**35**).

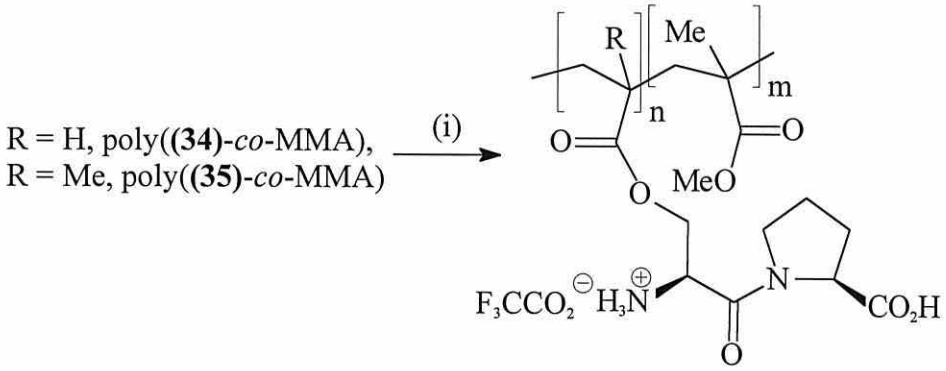
For the polymers derived from monomer **(35) (Table 6)**, when the specific rotation values were plotted against the percentage incorporation of chiral monomer **(35)**, a curved plot was obtained **(Graph 10)**. The sign of the specific rotation was

negative with the values of specific rotation rapidly decreasing between 0 % and 40 % chiral monomer incorporation. The greatest decrease in the observed specific rotation values was between 0 % and 20 %. The specific rotation values were found to decrease linearly with percentage chiral monomer incorporation from 40 % to 80 %, the homopolymer deviated from this line as it was more negative. Again, the origin of these non-linear effects of specific rotation is believed to be due to asymmetric induction from the (*S*)-serine chiral centre (see **Introduction 1.11 Optical Activity**).

2.15 Removal of the protecting groups from the poly(34) and poly(35) series



R = H, poly(**36**),
R = Me, poly(**37**)



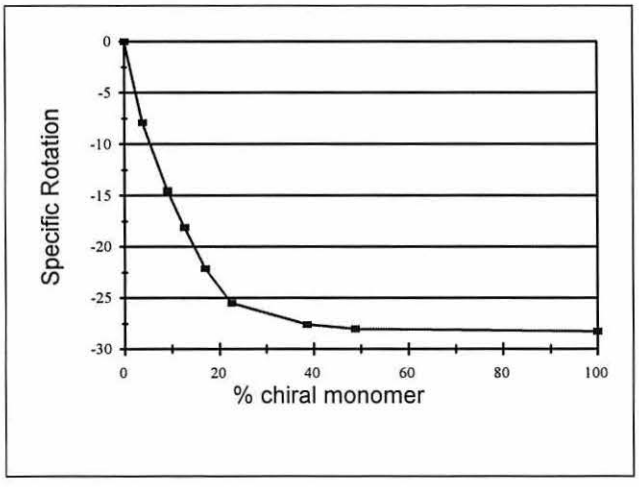
R = H, poly((**36**)-*co*-MMA),
R = Me, poly((**37**)-*co*-MMA)

Scheme 37. Reagents: (i) F_3CCO_2H, CH_2Cl_2.

Simultaneous removal of the Boc and ^{t}Bu protecting groups was achieved through acidolysis of the fully protected polymers by treatment with an excess of trifluoroacetic acid to furnish the poly(peptides) poly**(36)** and poly**(37)** **(Scheme 37)**. Cleavage of the protecting groups was shown by ^{1}H nmr, ^{13}C nmr and IR spectroscopy. This was evidenced by the loss of the Boc and ^{t}Bu groups and the appearance of the acid groups and $^{+}NH_3$ groups. The deprotected polymers were found only to be soluble in polar solvents such as DMF, DMSO and DMSO : acetonitrile mixtures.

2.16 Polarimetry on the deprotected polymer series, poly(36) and poly(37)

The polymers derived from the chiral monomer **(34)** gave the deprotected polymers in excellent yields, *ca.* 80 % and were found to be fully soluble in an acetonitrile : DMSO solvent mixture (1:1). The specific rotation of each of the polymers was recorded **(Table 7)**. When these values were plotted against the percentage incorporation of monomer **(34)** in the polymer, a curved plot was obtained with all the values negative **(Graph 11)**.



Graph 11. Specific rotation *vs* % incorporation of chiral monomer (**34**).

The specific rotation values were found to decrease rapidly between 0 % and 20 % chiral monomer incorporation. The greatest decrease in specific rotation value was observed between 0 % and 10 %. There was only a slight decrease in the specific rotation values between 20 % and 100 % chiral monomer incorporation.

Monomer **(34)** added(%)	Monomer **(34)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^6	M_w/M_n[d]	$[\alpha]_D^{28}$[e]
100	100	5.2	5.0	953	-28.3
60.0	48.8	41.5	6.0	145	-28.0
38.0	38.6	-	-	-	-27.6
25.0	22.6	-	-	-	-25.5
20.8	16.9	120	13.6	114	-22.1
20.0	12.6	62.2	9.2	147	-18.1
7.1	9.1	58.6	4.7	81	-14.5
3.6	3.9	81.4	9.3	114	-7.9
0[f]	0	11.8	29.3	2.5	0

Table 7. Physical data for the deprotected polymers derived from monomer (**34**).

a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations of the precursor polymer. b. Determined by GPC using DMF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the deprotected polymer series poly(**(36)**-*co*-MMA) at 301 K $CHCl_3$ and at 0.5 g / 100 ml. f. Homopolymer of MMA.

For the deprotected polymers derived from monomer **(35)** **(Table 8)**, when the specific rotation values were plotted against the percentage incorporation of chiral monomer **(35)**, a curved plot was again obtained **(Graph 12)**.

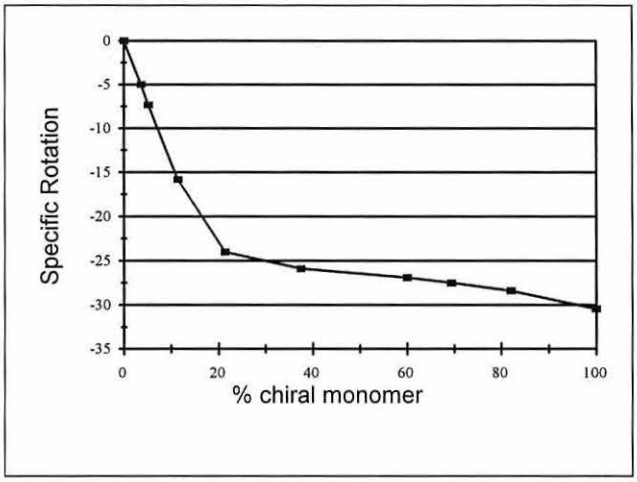
All the specific rotation values were found to be negative and decrease

rapidly as the percentage incorporation of chiral monomer **(35)** was increased from 0 % to 20 %. The greatest rate of decrease of specific rotation values occurred between 0 % and 10 % chiral monomer incorporation. Subsequently, the specific rotation values decreased linearly from 20 % to 100 % chiral monomer incorporation. Again, the origin of these non-linear effects of specific rotation is believed to be due to asymmetric induction from the (*S*)-serine chiral centre (see **Introduction 1.11 Optical Activity**).

Monomer **(35)** added(%)	Monomer **(35)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^6	M_w/M_n[d]	$[\alpha]^{28}_D$[e]
100	100	-	-	-	-30.4
85.0	82.0	23.3	6.4	274	-28.4
70.0	69.4	37.0	9.1	248	-27.5
69.7	60.0	41.5	6.0	145	-26.9
43.5	37.5	25.2	4.0	160	-25.9
13.5	21.4	-	-	-	-24.0
13.3	11.3	86.9	4.6	53	-15.8
7.1	5.2	45.2	1.9	41	-7.3
4.3	3.6	41.1	0.9	21	-5.0
0[f]	0	11.8	29.3	2.5	0

Table 8. Physical data for the deprotected polymers derived from monomer (**35**).

a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations of the precursor polymers. b. Determined by GPC using DMF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the deprotected polymer series poly((**37**)-*co*-MMA) at 301 K $CHCl_3$ and at 0.5 g / 100 ml. f. Homopolymer of MMA.



Graph 12. Specific rotation *vs* % incorporation of chiral monomer (**35**).

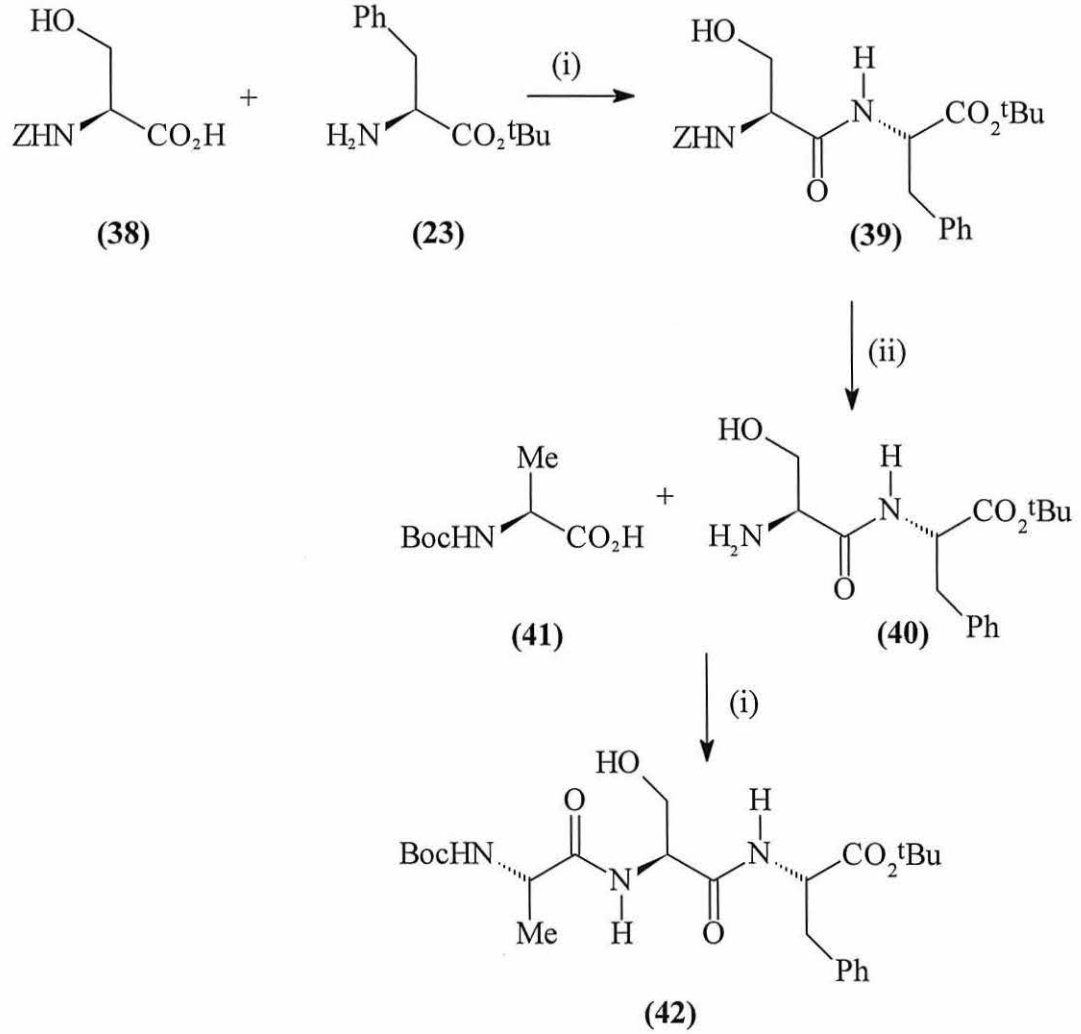
2.17 GPC data for the polymers derived from monomers (34) and (35)

The polymers derived from monomers **(34)** and **(35)** showed broad PDs from 3.0 to 21.6. Again, there was a large difference between the observed M_w and M_n values of the protected and deprotected polymers. The deprotected polymers M_w were *ca.* 1000 times greater than the protected polymers. Again, the protected and deprotected polymers with a low percentage incorporation of chiral monomer had very similar M_w and M_n values suggesting abnormal elution of the polymeric material from the column. A GPC-viscosity study was performed and the results are almost identical to those obtained from the study performed on the polymers derived from monomer **(25)**. The actual M_w values of the polymers with a high percentage incorporation of chiral monomer was 3 times greater than the observed values with polystyrene as the calibrant. For the polymers with a low percentage incorporation of

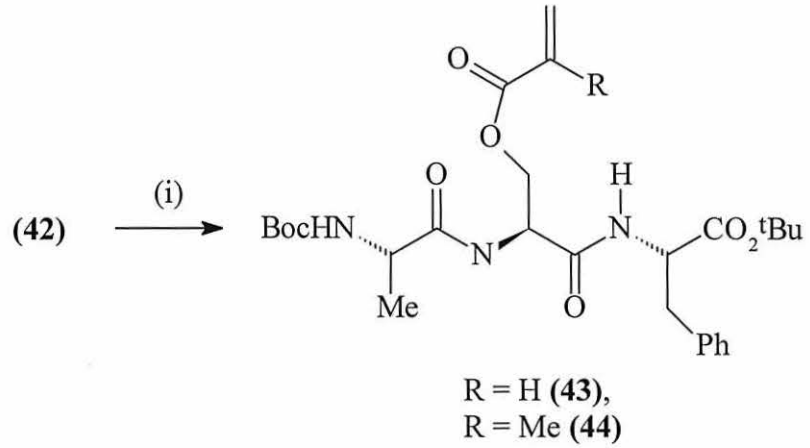
chiral monomer the actual M_w values were found to be *ca.* 2 times greater than the observed values. The intrinsic viscosity experiments again showed all the polymers to have a linear plot (log(intrinsic viscosity) *vs* log(M)). This GPC-viscosity study supports abnormal elution in the deprotected polymers.

2.18 Synthesis of acid labile tripeptide monomer, N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu

Coupling of *N*-Z-(*S*)-Ser **(38)** to compound **(23)** with DCC and HOBt led to the isolation of the dipeptide **(39)** in a yield of 90 %. Exposure to hydrogen, in the presence of a catalytic amount of Pd / carbon in methanol, yielded the free amine **(40)** in a yield of 93 %.[128] Coupling of the free dipeptide **(40)** to *N*-Boc-(*S*)-Ala **(41)** with DCC and HOBt furnished the tripeptide **(42)** in a yield of 88 % **(Scheme 38)**. This was subsequently acrylated and methacrylated to arrive at the polymerisable monomers **(43)** and **(44)** in yields of 75 % and 91 % respectively **(Scheme 39)**.



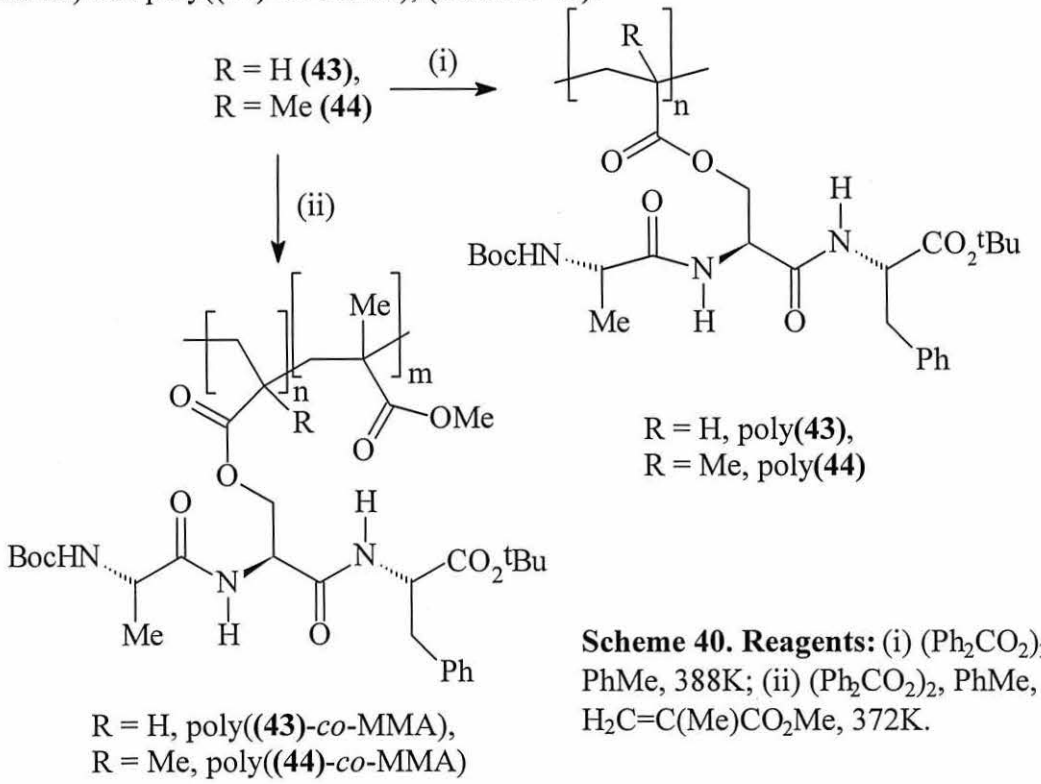
Scheme 38. Reagents: (i) DCC, HOBt, DMF; (ii) Pd, H_2, C, MeOH.



Scheme 39. Reagents: (i) $RC(=CH_2)COCl$, Et_3N, EtOAc.

2.19 Polymerisation of tripeptide monomers (43) and (44)

Polymerisation of the tripeptide monomers **(43)** and **(44)** was conducted at a concentration of *ca.* 1.3M in toluene, initiated by benzoyl peroxide to provide the homopolymers: poly(peptides) poly**(43)** and poly**(44)**. The tripeptide monomers were subsequently copolymerised with MMA at a concentration between 1M and 7M in toluene, initiated by benzoyl peroxide to provide the copolymers: poly(**(43)**-*co*-MMA) and poly(**(44)**-*co*-MMA), **(Scheme 40)**.



Scheme 40. Reagents: (i) $(Ph_2CO_2)_2$, PhMe, 388K; (ii) $(Ph_2CO_2)_2$, PhMe, $H_2C=C(Me)CO_2Me$, 372K.

All of the crude polymers were purified by dissolving them in a small amount of chloroform and precipitating them into an excess of light petroleum to provide the polymeric material as white solids.

Copolymerising the chiral monomers **(43)** and **(44)** with different percentages of MMA resulted in the synthesis of two series of copolymers. All of these polymers were found to rotate plane polarised light and the specific rotation values are recorded in **Table 9** (poly(**(43)**-*co*-MMA)) and **Table 10** (poly(**(44)**-*co*-MMA)).

Monomer **(43)** added(%)	Monomer **(43)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]_D^{26}$[e]
100	100	8.2	20.4	2.5	28.7
75.0	96.0	8.1	20.8	2.6	26.8
55.0	75.0	9.8	25.0	2.5	15.5
33.0	52.0	29.5	554	18.8	5.5
24.0	32.0	13.9	39.4	2.8	3.3
20.0	30.0	19.5	69.5	3.6	3.1
10.0	12.4	24.1	432	17.9	1.5
4.8	5.0	16.4	47.7	2.9	0.6
2.0	3.5	17.4	49.4	2.8	0.5
0[f]	0	11.8	28.3	2.5	0

Table 9. Physical data for polymers derived from monomer (**43**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations. b. Determined by GPC using DMF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly(**(43)**-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

Monomer **(44)** added(%)	Monomer **(44)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]_D^{26}$[e]
100	100	1.2	1.3	1.2	22.1
75.0	82.0	1.0	1.1	1.1	18.5
66.7	77.0	1.0	1.3	1.3	17.9
50.0	62.0	1.1	1.3	1.2	15.8
33.3	35.0	1.6	3.4	2.1	11.5
16.7	20.0	2.5	8.0	3.1	7.1
9.1	5.0	5.2	14.4	2.8	0.8
4.8	4.5	1.9	8.7	4.7	0.6
0[f]	0	11.8	28.3	2.5	0

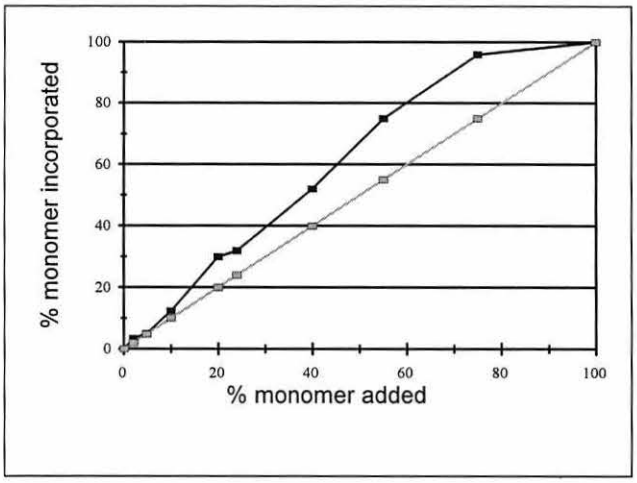
Table 10. Physical data for polymers derived from monomer (**44**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations. b. Determined by GPC using DMF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly((**44**)-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

2.20 Reactivity of the monomers (43) and (44)

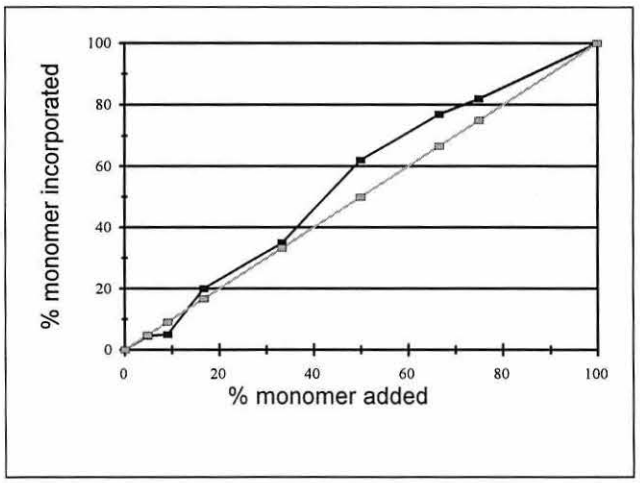
The reactivity of the two monomers could be expressed by plotting the ratio of monomer **(43)** or **(44)** added to the reaction, against the percentage incorporation of monomer **(43)** or **(44)** into the polymer series, poly((**43**)-*co*-MMA) or poly((**44**)-*co*-MMA), determined by ^{1}H nmr **(Graphs 13** and **14**, respectively). For monomer **(43),** these results showed there was preference between the reacting species, *i.e.* monomer **(43)** and MMA. The experimentally derived points were found

to lie to the left of the line expected for ideal, 1:1 copolymerisation. This revealed that the chiral monomer **(43)**, derived from an acrylate was more polymerisable than the more sterically hindered and disubstituted MMA.



Graph 13. Reactivity of the chiral monomer (**43**) (% conversion between 59-100 %).

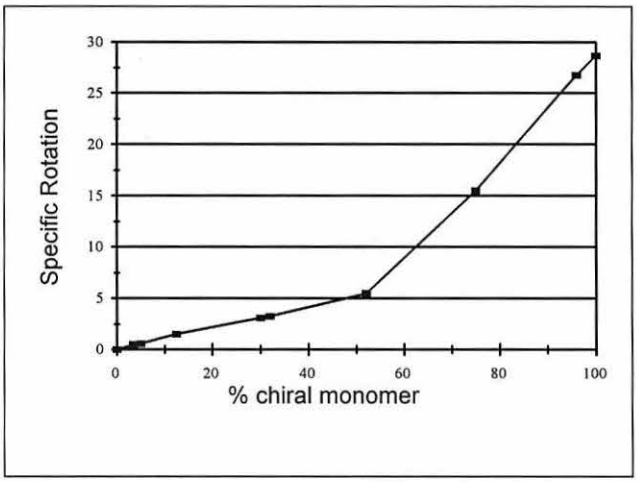
The series of polymers derived from the monomer **(44)** showed that there was no preference between the reacting species **(Graph 14)**. The experimentally derived points were found to lie approximately, within experimental error, on the line expected for ideal copolymerisation.



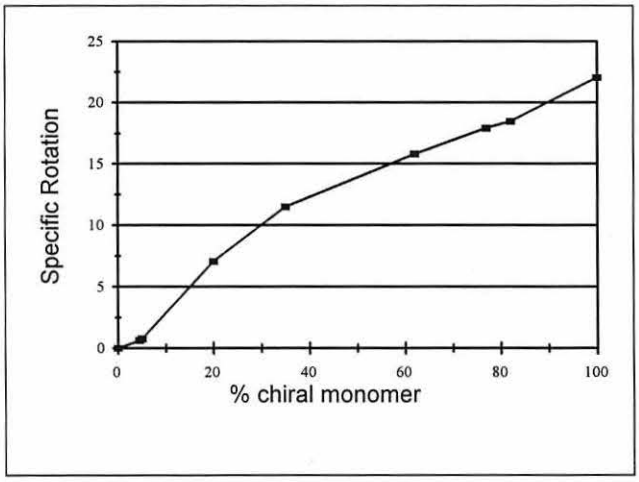
Graph 14. Reactivity of the chiral monomer (**44**) (% conversion between 27-99 %).

2.21 Polarimetry studies on the polymer series, poly(43) and poly(44)

When the specific rotation was plotted against the percentage of chiral monomer **(43)** present in the polymer, a non-linear plot was obtained for all the polymers of monomer **(43)** **(Graph 15)**. All the values observed were positive with the specific rotation values rising rapidly in a linear manner between 50 % and 100 % chiral monomer incorporation. Between 0 % and 50 % chiral monomer incorporation there was only a slight increase in the value of specific rotation.



Graph 15. Specific rotation *vs* % incorporation of chiral monomer (**43**).



Graph 16. Specific rotation *vs* % incorporation of chiral monomer (**44**).

When the specific rotations of the polymers were plotted against the

percentage of chiral monomer **(44)** incorporated into the polymer, a slightly curved plot was obtained **(Graph 16).** The specific rotation values were found to be positive and increase rapidly from 5 % to 35 %. Subsequently the specific rotation values were found to increase in a linear manner from 35 % to 100 % chiral monomer incorporation.

2.22 Increasing molecular weights of the polymers, poly(44)-co-MMA

The molecular weights of the polymers derived from monomer **(44)** showed that the polymers mainly consisted of low molecular weight material, *e.g.* 100 % monomer incorporation M_w 1,300 **(Table 10)**. This equates to a polymer incorporating *ca.* three monomer units. Hence, studies aimed at optimising the homopolymerisation reaction to increase the molecular weight of the polymers were undertaken. This was achieved by polymerising the monomer **(44)** at high concentration in DMF. The polymerisation reaction was carried out at different concentrations to study the effect of concentration upon the observed molecular weights.

Monomer	Conc.(M)[a]	M_n[b] $x10^3$	M_w[c] $x10^3$	M_w/M_n[d]	$[\alpha]_D^{26}$[e]
(44)	1.3	2.1	11.3	5.4	27.5
(44)	3.0	3.7	42.5	11.6	39.5
(44)	5.0	4.3	86.4	19.9	39.7

Table 11. Physical data for homopolymers derived from monomer (**44**).

a. Concentration of reaction mixture in a solution of DMF. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected homopolymers poly**(44)** at 299 K in $CHCl_3$ and at 1.0 g / 100 ml.

The results showed that reaction in DMF increased polymer molecular weights and that as the concentration was increased the observed molecular weights increased noticeably **(Table 11)**. Subsequently monomer **(44)** was copolymerised with MMA in DMF to provide the copolymer series, poly(**(45)**-*co*-MMA) **(Table 12)**. For all the copolymers, derived from monomer **(44)** polymerised in DMF, the M_w values had increased noticeably, although no noticeable effect was seen upon the PD values.

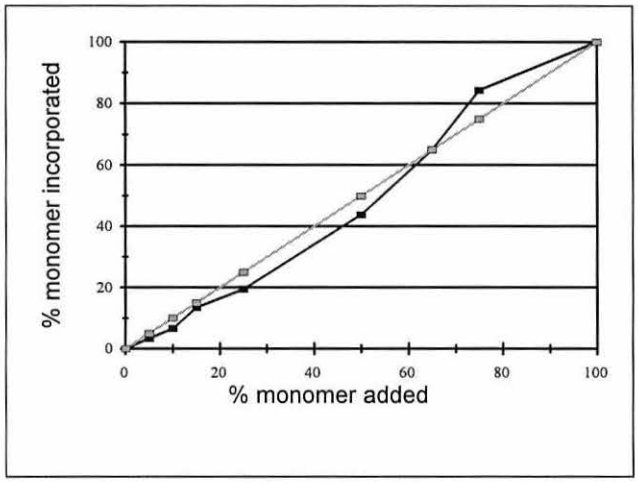
Monomer **(44)** added(%)	Monomer **(44)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[c]	$[\alpha]_D^{26}$[e]
100	100	4.4	86.4	19.9	39.5
75	84.4	13.6	71.0	5.2	23.1
65	65.0	2.0	25.3	12.4	16.1
50	43.9	12.9	57.9	4.5	11.4
25	19.4	9.7	24.7	2.6	5.0
15	13.5	4.0	25.3	6.2	3.3
10	6.7	10.6	35.7	3.4	0.7
5	3.4	10.8	30.0	2.8	-1.0
0[f]	0	11.8	28.3	2.5	0

Table 12. Physical data for polymers derived from monomer (**44**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly(**(44)**-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

2.23 Reactivity of monomer (44) in DMF

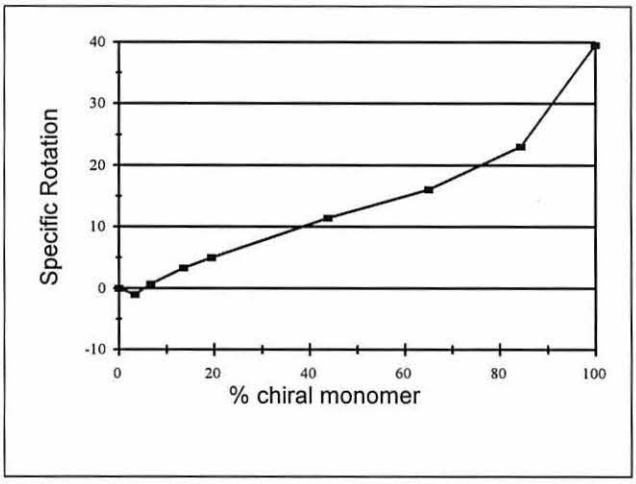
The reactivity the monomer **(44)** could be expressed by plotting the ratio of monomer **(44)** added to the reaction, against the ratio of monomer **(44)** present in the copolymers derived from monomer **(44)**, determined by ^{1}H nmr **(Graph 17)**. For monomer **(44),** these results showed there was no preference between the reacting species, *i.e.* monomer **(44)** and MMA. The experimentally derived points were found to fit the line for ideal copolymerisation derived from the equation y = x within the margins of experimental error.



Graph 17. Reactivity of the chiral monomer (**44**) (% conversion between 50-99 %).

2.24 Polarimetry on the polymers derived from monomer (44) in DMF

For the polymers derived from the polymerisation reaction between MMA and monomer **(44)** in DMF **(Table 12)**, when the specific rotation values were plotted against the percentage incorporation of chiral monomer **(44)**, an almost linear plot was obtained **(Graph 18)**. All values recorded were positive, except for the copolymer incorporating 4.5 % chiral monomer, with all the copolymer samples providing a linear plot. The homopolymer however, deviated from this line, with a specific rotation of +39.5.

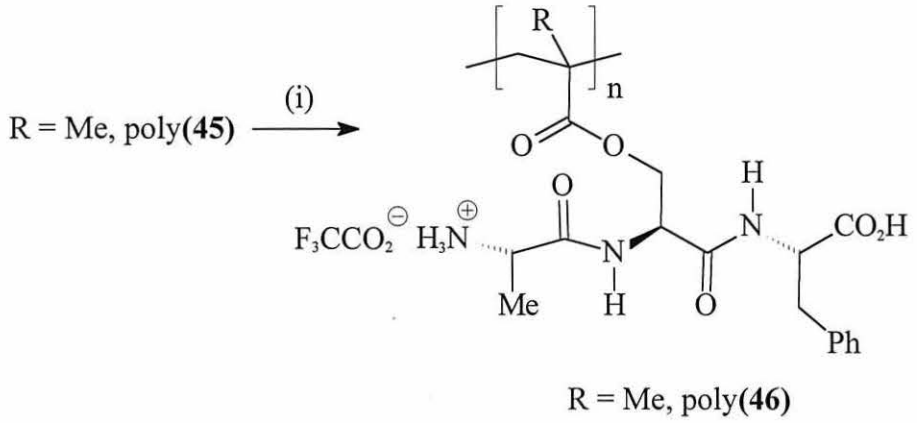


Graph 18. Specific rotation *vs* % incorporation of chiral monomer (**44**).

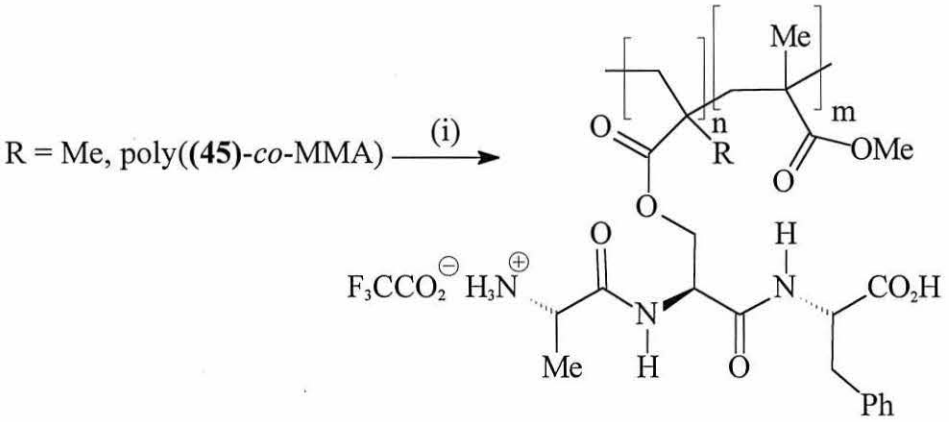
2.25 Removal of the protecting groups from the poly(45) in DMF series

Simultaneous removal of the Boc and ^{t}Bu protecting groups was achieved through acidolysis of the fully protected polymers with an excess of trifluoroacetic acid to furnish the poly(peptides) poly(**46**) and poly((**46**)-*co*-MMA) **(Scheme 41)**.

Cleavage of the protecting groups was shown by ^{1}H nmr, ^{13}C nmr and IR spectroscopy. This was evidenced by the loss of the Boc and ^{t}Bu groups and the appearance of acid groups and $^{+}NH_3$ groups. Unlike the parent polymers, these deprotected polymers were only soluble in polar solvents such as DMF, DMSO and DMSO : acetonitrile mixtures.



R = Me, poly(**46**)

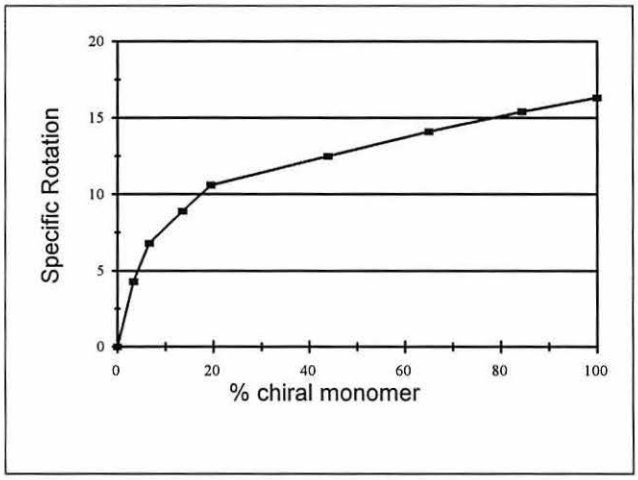


R = Me, poly((**46**)-*co*-MMA)

Scheme 41. Reagents: (i) F_3CCO_2H, CH_2Cl_2.

2.26 Polarimetry on the deprotected polymer series, poly(46)

The polymers derived from the polymerisation of chiral monomer **(44)** in DMF gave the deprotected polymers in excellent yields *ca.* 80 % and were found to be fully soluble in an acetonitrile : DMSO solvent mixture (1:1). The specific rotations of each of the polymers was recorded **(Table 13)**. When these values were plotted against the percentage incorporation of monomer **(44)** present in the precursor polymer, a curved plot was obtained with all the values positive **(Graph 19)**.



Graph 19. Specific rotation *vs* % incorporation of chiral monomer (**44**).

Monomer **(44)** added(%)	Monomer **(44)** incorporated(%)[a]	$[\alpha]_D^{26}$ [b]	$[\alpha]_D^{28}$ [c]
100	100	39.5	16.3
75.0	84.4	23.1	15.4
65.0	65.0	16.1	14.1
50.0	43.9	11.4	12.5
25.0	19.4	5.0	10.6
15.0	13.5	3.3	8.9
10.0	6.7	0.7	6.8
5.0	3.4	-1.0	4.3
0[d]	0	0	0

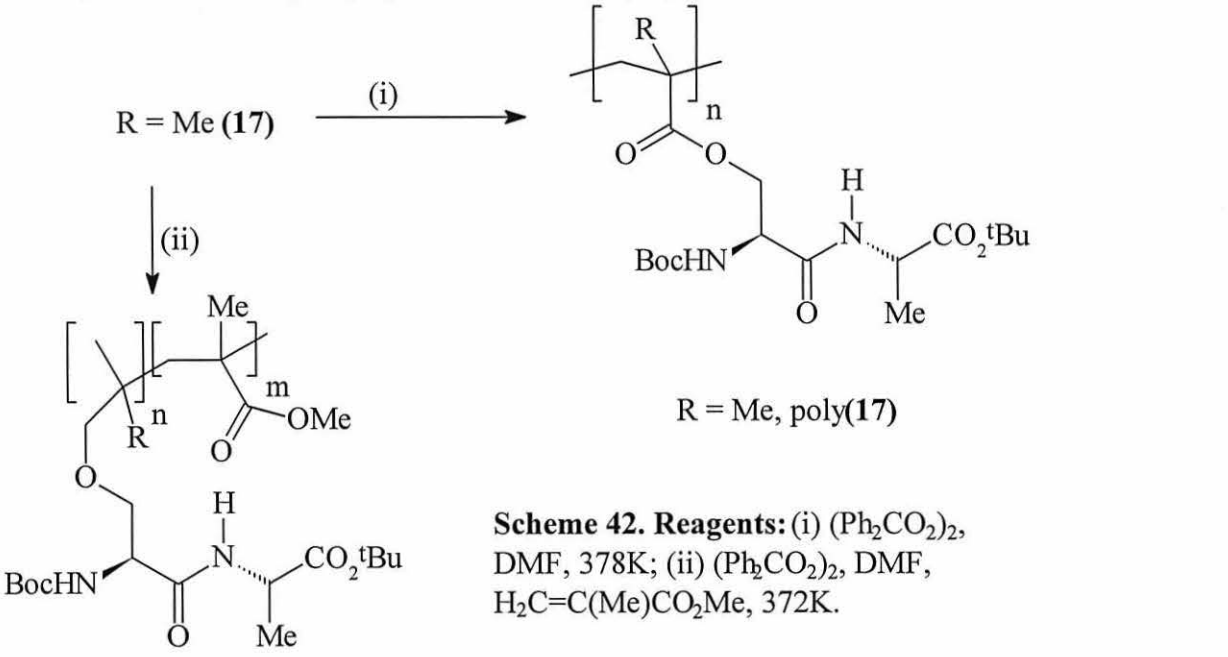
Table 13. Physical data for the deprotected polymers derived from monomer (**44**).

a. Determined by ^{1}H nmr measurements from comparison of the aromatic and methyl ester integrations of the precursor polymers. b. Specific rotation of the protected polymer series poly((**45**)-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. c. Specific rotation of the deprotected polymer series poly((**46**)-

co-MMA) at 301 K in DMSO : AcCN mixture (1:1) and at 0.5 g / 100 ml. d. Homopolymer of MMA.

The specific rotation values were found to increase rapidly as the percentage incorporation of chiral monomer **(44)** was increased from 0 % to 20 %. The greatest rate of increase in specific rotation values was found between 0 % and 10 % chiral monomer incorporation. The specific rotation values subsequently increased in a linear manner from 20 % to 100 % chiral monomer incorporation. Again, the origin of these non-linear effects of specific rotation is believed to be due to asymmetric induction from the (*S*)-serine chiral centre (see **Introduction 1.11 Optical Activity**).

2.27 Polymerisation of dipeptide monomer (17) in DMF



Scheme 42. Reagents: (i) $(Ph_2CO_2)_2$, DMF, 378K; (ii) $(Ph_2CO_2)_2$, DMF, $H_2C{=}C(Me)CO_2Me$, 372K.

Due to the success of increasing the molecular weights of the polymers derived from monomer **(44)** through changing the reaction solvent from toluene to DMF. It was proposed to attempt the polymerisation of monomer **(17)** in DMF. Polymerisation of the monomer was conducted at a concentration of 3M in DMF, initiated by benzoyl peroxide to provide the homopolymer, poly**(17)**. The dipeptide

monomer was subsequently copolymerised with MMA at a concentration of 3M in DMF, initiated by benzoyl peroxide to provide the copolymer, poly((**17**)-*co*-MMA) **(Scheme 42)**.

Copolymerisation of the chiral monomer **(17)** with different percentages of MMA resulted in the synthesis of a series of copolymers. All of these polymers were found to rotate plane polarised light and the specific rotation values of the polymers are recorded in **Table 14**.

Monomer **(17)** added(%)	Monomer **(17)** incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]_D^{26}$[e]
100	100	6.6	38.6	5.8	-1.6
90.0	89.4	11.2	165	14.8	0.5
75.0	68.4	10.3	134	13.0	4.4
60.0	62.2	13.2	199	15.0	5.4
55.0	46.1	5.8	35.6	6.1	6.1
50.0	41.5	8.0	201	25.0	6.1
40.0	34.2	4.7	22.0	4.7	6.0
25.0	15.1	7.9	36.0	4.6	5.3
10.0	6.9	10.4	35.4	3.4	4.2
5.0	3.4	7.4	22.3	3.0	2.2
0[f]	0	11.8	28.3	2.5	0

Table 14. Physical data for polymers derived from monomer (**17**).

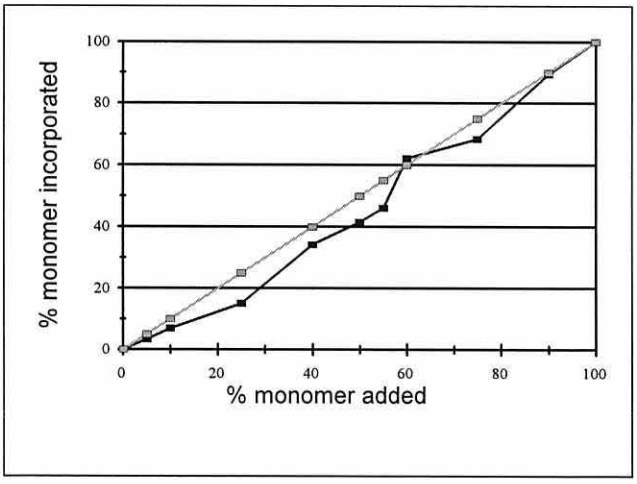
a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly((**17**)-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

2.28 GPC data for monomer (17)

There appear to be two distinct sizes of polymeric material: the polymers with a high percentage incorporation of chiral monomer, with high observed M_w values *ca.* 200,000 and the polymers with a low percentage incorporation of chiral monomer, with observed M_w values *ca.* 35,000. The homopolymer deviated from this trend with an M_w value of 38,600. These differences are probably due to steric effects of the copolymers, the copolymers containing high percentages of chiral monomer being hindered from entering the packing of the column.

2.29 Reactivity of the monomer (17)

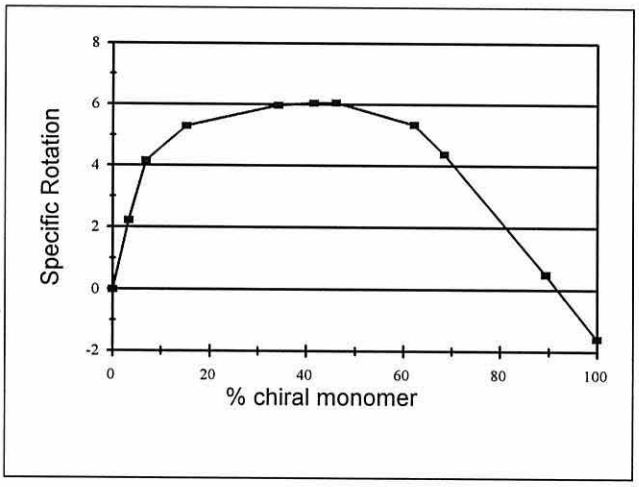
When the ratio of chiral monomer **(17)** added to the reaction was plotted against the ratio of monomer **(17)** incorporated into the polymers **(Graph 20)**, the results showed that there was a preference between the reacting species. The experimentally derived points lay slightly to the right of those expected for ideal copolymerisation. Since the polymerisable groups in the monomer **(17)** and MMA are the same, this difference in reactivity is probably due to the lower volume occupied by MMA but may just be caused by experimental error.



Graph 20. Reactivity of the chiral monomer (**17**) (% conversion between 55-88 %).

2.30 Polarimetry studies on the polymer series, poly(17)-co-MMA

The proportion of MMA present in each polymer was determined by comparison of the α and β protons and methyl ester resonances in the ^{1}H nmr. When the specific rotation was plotted against the percentage of chiral monomer **(17)** present in the polymer, a non-linear plot was obtained for the polymers of monomer **(17)** **(Graph 21)**. All values were found to be positive except for the homopolymer, which had a specific rotation of -1.6.

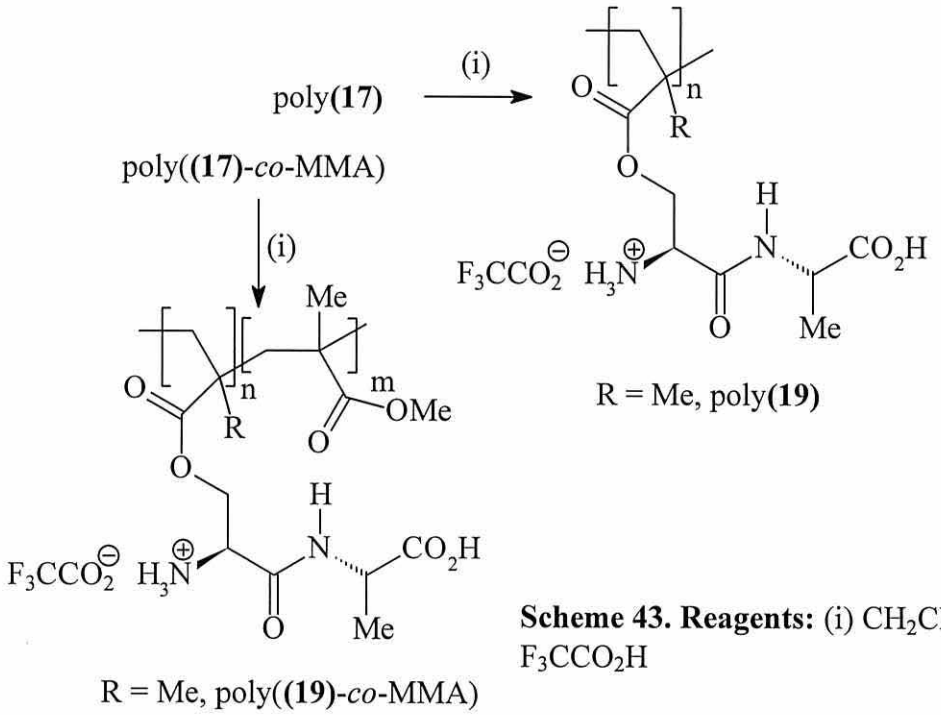


Graph 21. Specific rotation *vs* % incorporation of chiral monomer (**17**).

The specific rotations were found to increase rapidly as the percentage incorporation of chiral monomer **(17)** was increased from 0 % to 20 %. The greatest rate of increase in specific rotation values was found between 0 % and 10 % chiral monomer incorporation. The specific rotation values then peaked at *ca.* 40 % monomer incorporation before decreasing rapidly from 45 % to 100 % chiral monomer incorporation. The origin of this non-linear behaviour is likely to be the result of asymmetric induction from the (*S*)-serine chiral centre into the polymer backbone and conformational effects in the polymer chain (see **Introduction 1.11 Optical Activity**).

2.31 Removal of the protecting groups from poly(17)

Cleavage of the protecting groups from polymers derived from monomer **(17)** was achieved through acidolysis of the fully protected polymers by treatment with an excess of trifluoroacetic acid to furnish the poly(peptides), poly**(19)** and poly(**(19)**-*co*-MMA) **(Scheme 43)**.

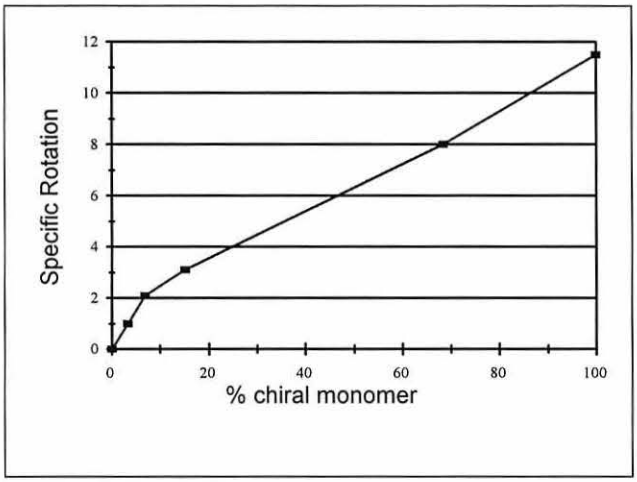


Scheme 43. Reagents: (i) CH_2Cl_2, F_3CCO_2H

Cleavage of the protecting groups was shown by ^1H nmr, ^{13}C nmr and IR spectroscopy. This was evidenced by the loss of the Boc and ^tBu groups and the appearance of acid and $^+NH_3$ groups. Unlike the parent polymers, these deprotected polymers were only soluble in polar solvents such as DMSO, DMF, H_2O and DMSO : AcCN mixtures. The homopolymer, poly**(17)** and the copolymers with a high percentage incorporation of chiral monomer were found to be fully soluble in water.

2.32 Polarimetry on the deprotected polymer series, poly(19)-co-MMA

The polymers derived from the chiral monomer **(17)** gave the deprotected polymers in excellent yields *ca.* 90 % and were found to be fully soluble in an acetonitrile : DMSO solvent mixture (1:1). The specific rotation of each of the polymers was recorded **(Table 15)**. When these values were plotted against the percentage incorporation of monomer **(17)** present, a non-linear plot was obtained **(Graph 22)**.



Graph 22. Specific rotation *vs* % incorporation of chiral monomer (**17**).

The specific rotation values were found to increase rapidly as the percentage of chiral monomer incorporated was increased from 0 % to 10 %. Subsequently, from 10 % to100 % chiral monomer incorporation the specific rotation values were found to increase linearly with percentage chiral monomer incorporation. Although the copolymers incorporating 62.2 % and 89.4 % were found to be fully soluble in the solvent system, unfortunately the sample solutions were too dense for specific rotation values to be obtained. Again, the origin of the non-linear behaviour is due to asymmetric induction into the polymer backbone from the (*S*)-serine chiral centre (see **Introduction 1.11 Optical Activity)**

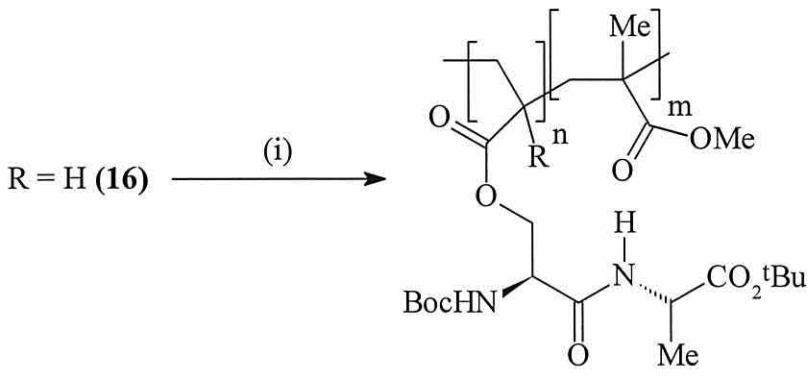
Monomer (17) added(%)	Monomer (17) incorporated(%)[a]	$[\alpha]_D^{26}$ [b]	$[\alpha]_D^{28}$ [c]
100	100	-1.6	11.5
90.0	89.4	0.5	-[d]
75.0	68.4	4.4	8.0
60.0	62.2	5.4	-[d]
25.0	15.1	5.3	3.1
10.0	6.9	4.2	2.1
5.0	3.4	2.2	1.0
0[e]	0	0	0

Table 15. Physical data for the polymers derived from monomer (**17**).

a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations of the precursor polymers. b. Specific rotation of the protected polymer series poly((**17**)-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. c. Specific rotation of the deprotected polymer series poly((**19**)-*co*-MMA) at 301 K in DMSO : AcCN mixture (1:1) and at 0.5 g / 100 ml. d. These polymers were too dense to obtain specific rotation readings. e. Homopolymer of MMA.

2.33 Polymerisation studies on monomer (16)

Due to the success achieved polymerising monomer **(17)** in DMF, it was proposed to attempt the copolymerisation of monomer **(16)** with MMA in DMF to form a series of copolymers **(Scheme 44)**. All of these polymers were found to rotate plane polarised light and their respective specific rotation values are recorded in **Table 16**.



R = H, poly((**16**)-*co*-MMA)

Scheme 44. Reagents: (i) $(Ph_2CO_2)_2$, DMF, $H_2C{=}C(Me)CO_2Me$, 372K .

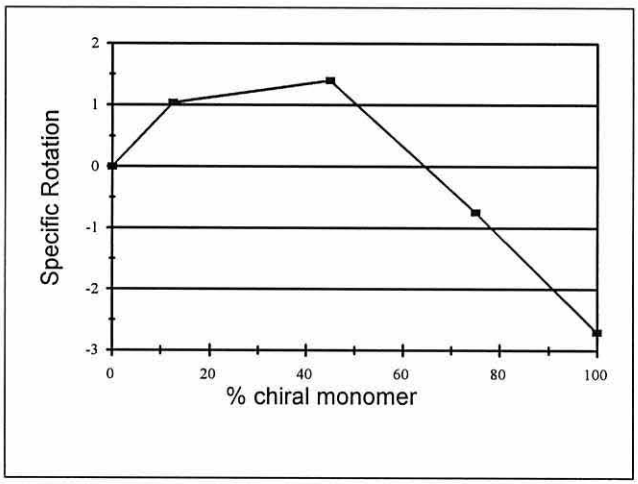
Monomer (**16**) added(%)	Monomer (**16**) incorporated(%)[a]	M_n[b] x10^3	M_w[c] x10^3	M_w/M_n[d]	$[\alpha]_D^{26}$[e]
100	100	71.4	989	13.9	-2.7
75.0	75.0	4.4	16.9	3.8	-0.7
50.0	45.0	5.7	29.2	5.1	1.4
25.0	12.5	5.6	25.4	4.5	1.0
0[f]	0	11.8	28.3	2.5	0

Table 16. Physical data for the polymers derived from monomer (**16**).

a. Determined by ^{1}H nmr measurements from comparison of the α and β protons and methyl ester integrations. b. Determined by GPC using THF as eluent and calibrated with poly(styrene). c. Weight average molecular weight, determined by GPC, as in b. d. M_w/M_n refers to the polydispersity value of the polymer, determined by GPC. e. Specific rotation of the protected polymer series poly((**16**)-*co*-MMA) at 299 K in $CHCl_3$ and at 1.0 g / 100 ml. f. Homopolymer of MMA.

2.34 Polarimetry studies on the polymer series, poly(16)

When the specific rotation values were plotted against the percentage of chiral monomer **(16)** incorporated into the polymer, a non-linear plot was observed **(Graph 23)**.



Graph 23. Specific rotation *vs* % incorporation of chiral monomer (**16**).

Initially the specific rotation values were positive and increased from 0 % to 40 % chiral monomer incorporation. Subsequently, the values were found to decrease in a linear manner from 40 % to 100 %. The sign of specific rotation becoming negative at *ca.* 65 % chiral monomer incorporation.

More copolymers need to be synthesised in this series to obtain a more realistic relationship between the percentage of chiral monomer incorporated into the polymer and the specific rotation values. However, it has been proven that monomer **(16)** and monomer **(17)** are appreciably more soluble in DMF than in toluene. This allowed the polymerisation reactions to be conducted in more concentrated solutions, to give polymeric material which was subsequently soluble in a chloroform solution.

2.35 Conclusions for dipeptides

It has been shown that a range of polymers derived from amino acids can be prepared with both acid and amine containing labile protecting groups. Homopolymers were successfully prepared from the serine derived dipeptide monomers **(16)**, **(17)**, **(25)**, **(26)**, **(34)** and **(35)** and found to form moderate molecular weight polymers, M_w *ca.* 40,000. Copolymerisation occurred readily with methyl methacrylate to give polymers with molecular weights in the region of *ca.* 100,000 and *ca.* 40,000 for the acrylate and methacrylate derived polymers respectively. The polymers were studied by polarimetry, before and after removal of the protecting groups. All the polymers displayed non-linear plots between the percentage of chiral monomer incorporated and the observed specific rotation. Both the protected and deprotected derived chiral monomers **(25)** and **(26)** displayed positive specific rotations. Whereas, the protected and deprotected polymers derived from the chiral monomers **(34)** and **(35)** displayed negative specific rotations. The cause for these non-linear effects of specific rotation with the percentage incorporation of chiral monomer is believed to be through asymmetric induction from the (*S*)-serine residue. In the case of the protected polymers derived from chiral monomer **(17)**, a change from negative to positive specific rotation was observed. This effect may be due to conformational effects, as this optical behaviour was not repeated in the polarimetric studies following removal of the protecting groups, where all the recorded values of specific rotation were positive. Similarly, for the protected polymers derived from the chiral monomer **(16)**, a change from negative to positive specific rotation was observed. Again, this may be due to conformational effects, although the deprotection of these polymers is required to confirm this assumption.

Homopolymerisation of the chiral monomers **(16)** and **(17)** allowed the synthesis of two water soluble polymers derived from a serine containing dipeptide. Furthermore, copolymers containing a high percentage of chiral monomer **(17)** were water soluble.

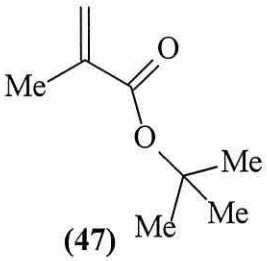
2.36 Conclusions for tripeptides

A range of polymers derived from three amino acids can be prepared with both acid and amine containing labile protecting groups. Homopolymers were successfully prepared from the chiral monomers **(43)** and **(44)** and found to form low molecular weight polymers, monomer **(43)** *ca.* 20,000 and monomer **(44)** *ca.* 1,300. Copolymerisation occurred readily with methyl methacrylate to yield moderate molecular weight polymers, monomer**(43)** M_w *ca.* 40,000 and monomer **(44)** M_w *ca.* 4,000. For the chiral monomer **(44)** the polymerisation conditions were optimised, through the use of DMF as solvent, leading to the preparation of homopolymer with molecular weight of *ca.* 86,000 and copolymers with molecular weights *ca.* 40,000. Analysis of the polymers by polarimetry revealed non-linear effects. Both the protected and deprotected polymers derived from the chiral monomers **(43)** and **(44)** were found to display positive values of specific rotation. Asymmetric induction from the serine residue is believed to be the cause for these non-linear effects of specific rotation with percentage incorporation of chiral monomer.

2.37 Scope for further work

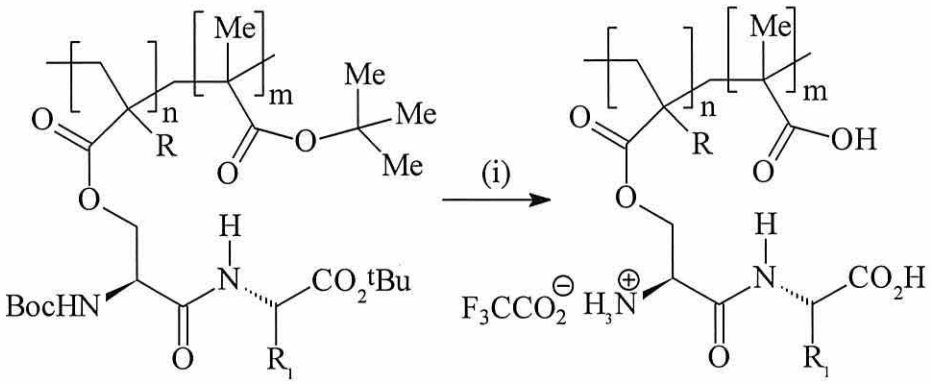
Cyclic voltammetry studies could be undertaken on the water soluble polymers derived from the chiral monomers **(16)** and **(17)**. This would allow an investigation of whether the same abnormal behaviour is observed as that previously reported for poly(serine).[60]

Copolymerisation of the chiral monomers with the achiral monomer *tert*-butyl methacrylate **(47)** **(Figure 5)** could be investigated. This should lead to a new series of copolymers derived from serine containing dipeptides. Furthermore, acidolysis of the copolymeric material should result in the cleavage of the *tert*-butyl ester enabling the synthesis of water soluble copolymers **(Scheme 45)**.



(47)

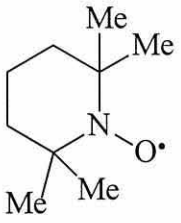
Figure 5.



R = H, Me
R_1 = amino acid side chain

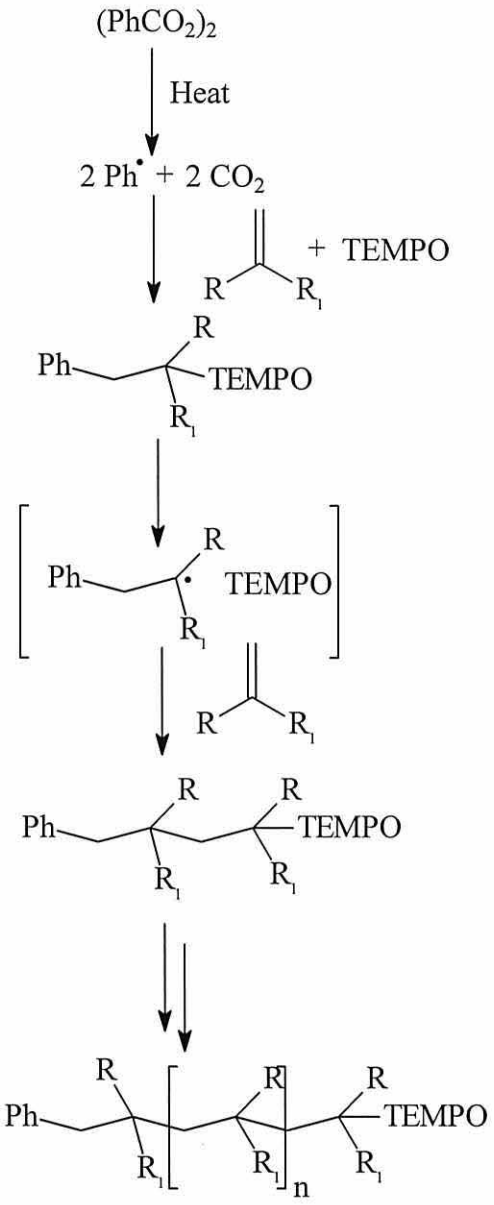
Scheme 45. (i) F_3CCO_2H, CH_2Cl_2.

Recent investigations have led to the synthesis of narrow polydispersity resins through a free-radical polymerisation.[129,130] These results are obtained by the addition of a nitroxide stable free radical to the polymerisation mixture. The nitroxide stable free radical TEMPO **(48)** **(Figure 6)** controls the addition of monomers to the growing polymer chain by reversibly terminating the growing polymer chain **(Scheme 46)**.



(48)

Figure 6.



Scheme 46. Polymerisation in presence of benzoyl peroxide and TEMPO.

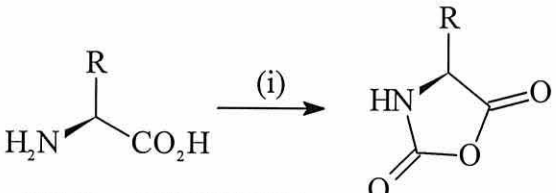
The addition of TEMPO to the polymerisation mixture of dipeptide and tripeptide monomers should enable the synthesis of novel poly(peptides) with extremely narrow polydispersities through a free-radical polymerisation. This is an important commercial aspect because free-radical polymerisation processes are easy to perform, economically viable and can be readily performed in bulk, or suspension

unlike living polymerisation systems, such as anionic,[4,5] cationic,[4,5] and group transfer polymerisation where the need for high purity monomers and solvents, reactive initiators and anhydrous conditions have limited the industrial applications of these materials.

3 Results and discussion

3.1 Monomer synthesis

The *N*-carboxyanhydrides were prepared by reaction of the desired amino acid with a solution of phosgene in toluene at 60 °C.[79,118] The reaction proceeded swiftly and provided the respective (*S*)-amino acid *N*-carboxyanhydrides in excellent yields *ca.* 80 % **(Scheme 47)**.

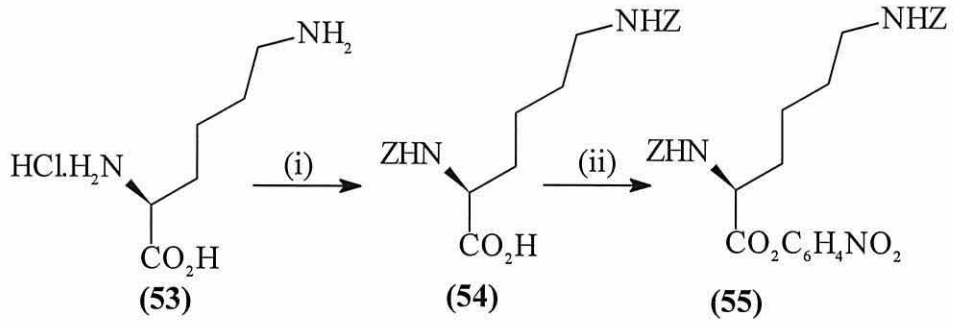


(49) R = $CH_2CH(CH_3)_2$, **(50)** R = $CH_2CH(CH_3)_2$,
(10) R = Me, **(51)** R = Me,
(20) R = CH_2Ph **(52)** R = CH_2Ph

Scheme 47. (i) $COCl_2$ in toluene, THF, 333K.

3.2 Preparation of lysine derivative (55)

Protection of (*S*)-lysine.HCl **(53)** with ZONSu in a water / acetone solvent mixture provided *N*-Z, *N*'-Z-(*S*)-lysine **(54)** in a yield of 80 %. Reaction of the protected amino acid **(54)** with DCC and *p*-nitrophenol in CH_2Cl_2 provided the desired lysine derivative **(55)** in a yield of 60 % **(Scheme 48)**.



(53) **(54)** **(55)**

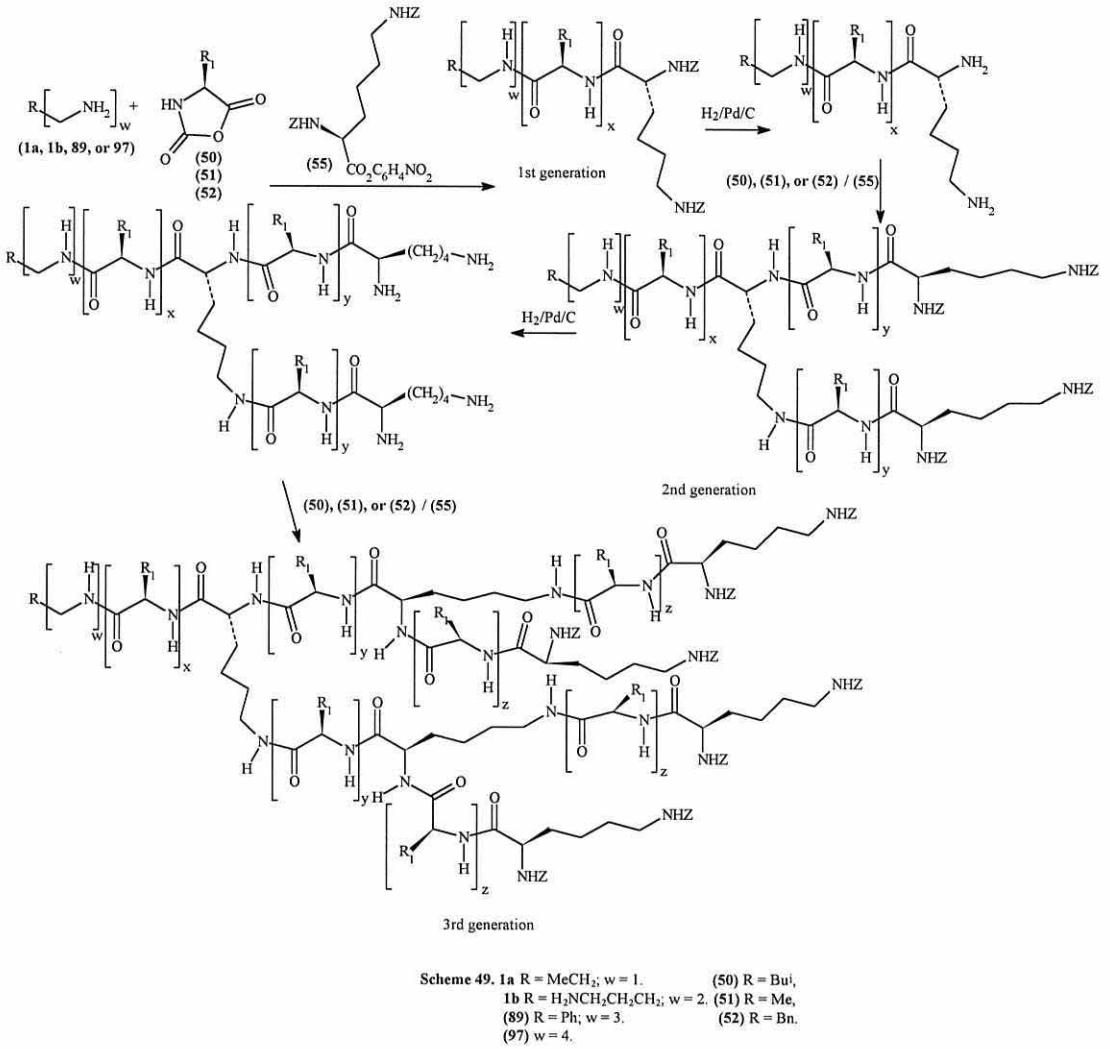
Scheme 48. (i) K_2CO_3, ZONSu, H_2O, Me_2CO;
(ii) *p*-$O_2C_6H_4OH$, DCC, CH_2Cl_2.

3.3 Solubility studies

Initial polymerisation studies were conducted in CH_2Cl_2 with a monomer : initiator ratio of 50 : 1 and a reaction period of 72 hours. Unfortunately, polymeric material precipitated out of the reaction solution after 24 hours and the reaction products were found to be insoluble in all common organic solvents except trifluoroacetic acid. Further investigations changed the solvent to DMF with a monomer : initiator ratio of 50 : 1. Again, the reaction products were found to be insoluble in all common organic solvents except trifluoroacetic acid. These insolubility problems were overcome by conducting the polymerisations in DMF and keeping the polymer chain relatively short (monomer : initiator ratio of 8 : 1), although even polymers prepared in this way were soluble only in polar aprotic solvents, which restricted the methods which could be used for their characterisation.

3.4 Propylamine initiated polymerisation of (S)-amino acid N-carboxyanhydrides

Initial studies were carried out using propylamine **(1a)** as a monofunctional initiator and the polymerisations were repeated to the third generation **(Scheme 49)**. The first generation polymer, poly**(56)** was obtained as a white solid by propylamine initiated polymerisation of (*S*)-leucine *N*-carboxyanhydride **(50)** with subsequent capping of the polymer with lysine derivative **(55)** in a yield of 58 %. Hydrogenation of the protected polymer, poly**(56)**, provided the deprotected polymeric material, poly**(57)** as a white solid in a yield of 94 %. Poly**(57)** was reacted further with (*S*)-alanine *N*-carboxyanhydride **(51)** and capped with lysine derivative **(55)** to provide the second generation polymeric material, poly**(58)** as a cream solid in a yield of 75 %. Again hydrogenation of the protected polymer, poly**(58)** provided access to the deprotected polymer, poly**(59)** as a white solid in a yield of 73 %. Subsequently, poly**(59)** was used to initiate the polymerisation of (*S*)-phenylalanine *N*-carboxyanhydride **(52)** and capped with lysine derivative **(55)** to provide the third generation polymeric material, poly**(60)** as a white solid in a yield of 77 %.



Scheme 49. **1a** R = $MeCH_2$; w = 1. **(50)** R = Bu^i,
1b R = $H_2NCH_2CH_2CH_2$; w = 2. **(51)** R = Me,
(89) R = Ph; w = 3. **(52)** R = Bn.
(97) w = 4.

The structures and molecular weights of the polymers are given in **Table 17**. In each case, the polymers were characterised by solution state ^{1}H NMR spectroscopy, solution or solid state ^{13}C NMR spectroscopy, IR spectroscopy and GPC. Typical GPC chromatograms are shown in **Figure 7**. It is apparent from **Figure 7** that the molecular weight of the polymer increases as each amino acid is added to the polymer and that the peak corresponding to the precursor polymer disappears at each stage.

The second series of propylamine initiated polymers again utilised (*S*)-leucine residues for the generation of the first generation material, poly**(61)** in a yield of 58 %. Hydrogenation and further reaction with (*S*)-phenylalanine *N*-carboxyanhydride **(52)** yielded the second generation material, poly**(63)** as a white solid in a combined yield of 66 %. Subsequent hydrogenation and reaction with (*S*)-alanine *N*-

carboxyanhydride **(51)** provided access to the third generation material, poly**(65)** in a combined yield of 57 %. Again, the structures and molecular weights of the polymers are given in **Table 17**.

Initiator	AA1[a]	AA2[a]	AA3[a]	M_n[b]	M_w[b]	PDI	M_n[c](calc.)	Yield(%)
1a	Leu(8)	-	-	1100	1230	1.1	1359	58
1a	Leu(8)	Ala(7)	-	3220	3720	1.2	2877	70
1a	Leu(8)	Ala(7)	Phe(4)	5240	7829	1.5	6277	56
1a	Leu(10)	-	-	2400	2800	1.1	1585	58
1a	Leu(10)	Phe(7)	-	5600	7400	1.3	2852	66
1a	Leu(10)	Phe(7)	Ala(5)	960	2020	2.1	5320	57
1a	Phe(10)	-	-	1800	2000	1.1	1925	71
1a	Phe(10)	Leu(8)	-	1700	2000	1.2	4257	61
1a	Phe(10)	Leu(8)	Ala(4)	2200	2200	1.0	6441	94

Table 17. Physical data for polymers derived initiator (**1a**).

a. The numbers in brackets correspond to the average number of amino acids incorporated into each branch of the polymer as determined by ^{1}H NMR spectroscopy. b. M_n and M_w values were obtained from GPC data calibrated with polystyrene standards. c. Calculated from the integration trace of the ^{1}H NMR spectrum.

The third series of polymers initiated by **(1a)** utilised (*S*)-phenylalanine *N*-carboxyanhydride **(52)** to provide the first generation material, poly**(66)** as a white solid in a yield of 71 %. Hydrogenation and further reaction with (*S*)-leucine *N*-carboxyanhydride **(50)** provided the second generation material, poly**(68)** in a combined yield of 61 %. Subsequent hydrogenation and further propagation with (*S*)-alanine *N*-carboxyanhydride **(51)** allowed access to the third generation material, poly**(70)** **(Scheme 49)**. Again, the structures and molecular weights of the polymers

are given in **Table 17**.

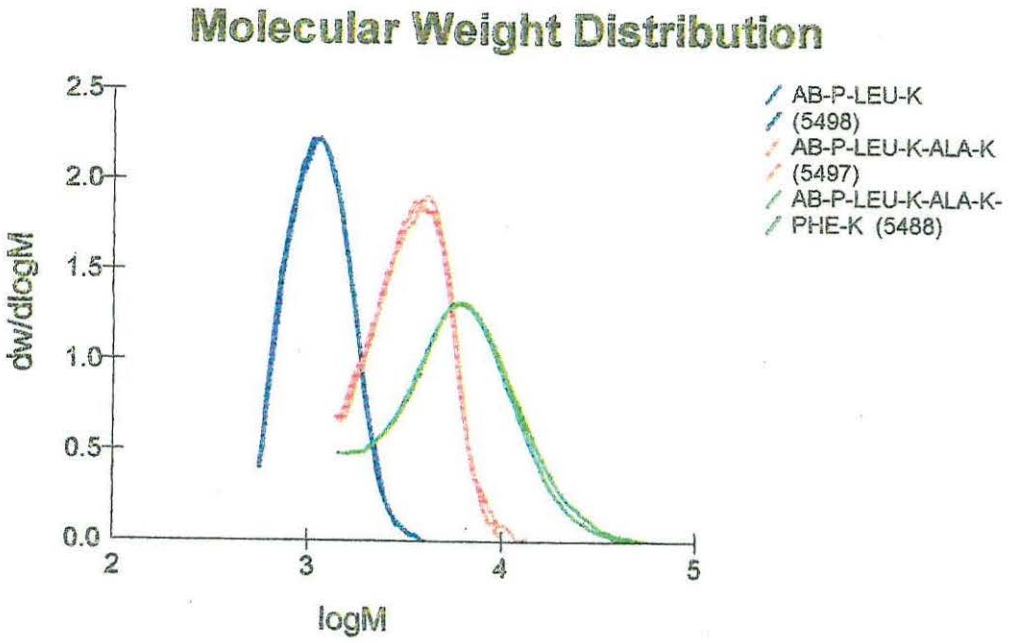


Figure 7.

3.5 1,4-Diaminobutane initiated polymerisation of (S)-amino acid N-carboxyanhydrides

Further studies were carried out using 1,4-diaminobutane **(1b)** as a multifunctional initiator for the polymerisation of (*S*)-amino acid *N*-carboxyanhydrides. Electrospray mass spectrometry confirmed that both amino functionalities were involved in initiating separate polymer chains.[131] The first generation polymer, poly**(71)** was obtained as a white solid by the 1,4-diaminobutane initiated polymerisation of (*S*)-leucine *N*-carboxyanhydride **(50)** with subsequent

capping of the polymer chains with lysine derivative **(55)** in a yield of 71 %. Hydrogenation of the protected polymer, poly**(71)**, provided the deprotected polymeric material, poly**(72)** as a white solid in a yield of 82 %. Poly**(72)** was reacted further with (*S*)-phenylalanine *N*-carboxyanhydride **(52)** and the polymer chains were capped with lysine derivative **(55)** to provide the second generation polymeric material, poly**(73)** as a white solid in a yield of 78 %. Again hydrogenation of the protected polymer, poly**(73)** provided access to the deprotected polymer, poly**(74)** as a white solid in a yield of 75 %. Subsequently, poly**(74)** was used to initiate the polymerisation of (*S*)-alanine *N*-carboxyanhydride **(51)** and the polymer chains were capped with lysine derivative **(55)** to provide the third generation polymeric material, poly**(75)** as a white solid in a yield of 76 % **(Scheme 49)**. The structures and molecular weights of the polymers are given in **Table 18**.

The second series of polymers initiated by **(1b)** utilised (*S*)-phenylalanine residues for the generation of the first generation material, poly**(76)** in a yield of 65 %. Hydrogenation and further reaction with (*S*)-leucine *N*-carboxyanhydride **(50)** yielded the second generation material, poly**(78)** as a white solid in a combined yield of 86 %. Subsequent hydrogenation and reaction with (*S*)-alanine *N*-carboxyanhydride **(51)** provided access to the third generation material, poly**(80)** in a combined yield of 75 %. Again, the structures and molecular weights of the polymers are given in **Table 18**. The third series of polymers initiated by **(1b)** utilised (*S*)-alanine residues for the generation of the first generation material, poly**(81)** in a yield of 96 %. Hydrogenation and further reaction with (*S*)-leucine *N*-carboxyanhydride **(50)** yielded the second generation material, poly**(83)** as a white solid in a combined yield of 54 %. Subsequent hydrogenation and reaction with (*S*)-phenylalanine *N*-carboxyanhydride **(52)** provided access to the third generation material, poly**(85)** in a combined yield of 66 %. Again, the structures and molecular weights of the polymers are given in **Table 18**.

Initiator	AA1[a]	AA2[a]	AA3[a]	M_n[b]	M_w[b]	PDI	M_n[c](calc.)	Yield(%)
1b	Leu(4)	-	-	2300	2640	1.2	1784	71
1b	Leu(4)	Phe(4)	-	3810	4890	1.3	5184	64
1b	Leu(4)	Phe(4)	Ala(4)	2430	4420	1.8	9280	57
1b	Phe(4)	-	-	2200	2680	1.2	2056	65
1b	Phe(4)	Leu(4)	-	3810	4890	1.3	4912	86
1b	Phe(4)	Leu(4)	Ala(4)	2430	4420	1.8	9280	75
1b	Ala(5)	-	-	2400	2900	1.2	1490	96
1b	Ala(5)	Leu(5)	-	2200	2700	1.2	4798	54
1b	Ala(5)	Leu(5)	Phe(4)	4300	7900	1.8	8422	66

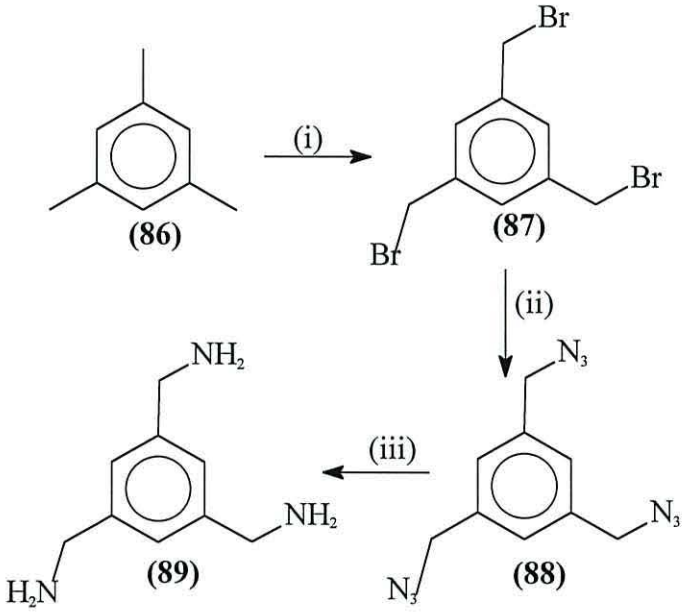
Table 18. Physical data for the polymers derived from initiator (**1b**).

a. The numbers in brackets correspond to the average number of amino acids incorporated into each branch of the polymer as determined by ^{1}H NMR spectroscopy. b. M_n and M_w values were obtained from GPC data calibrated with polystyrene standards. c. Calculated from the integration trace of the ^{1}H NMR spectrum.

As **Table 18** shows, the use of initiator **(1b)** bearing two primary amino groups provided the desired branched poly(amino acids) exactly as in the case of initator **(1a)**. However, an increasing discrepancy between the calculated and the experimental M_n values is apparent in these polymers. This is probably because GPC separation is based on molecular size rather than molecular weight and for branched polymers, the relationship between molecular weight and size is non-linear. Furthermore, the low molecular weights of alanine and leucine combined with the small number of residues being introduced meant that GPC was unable to detect the change in the size of the polymer.

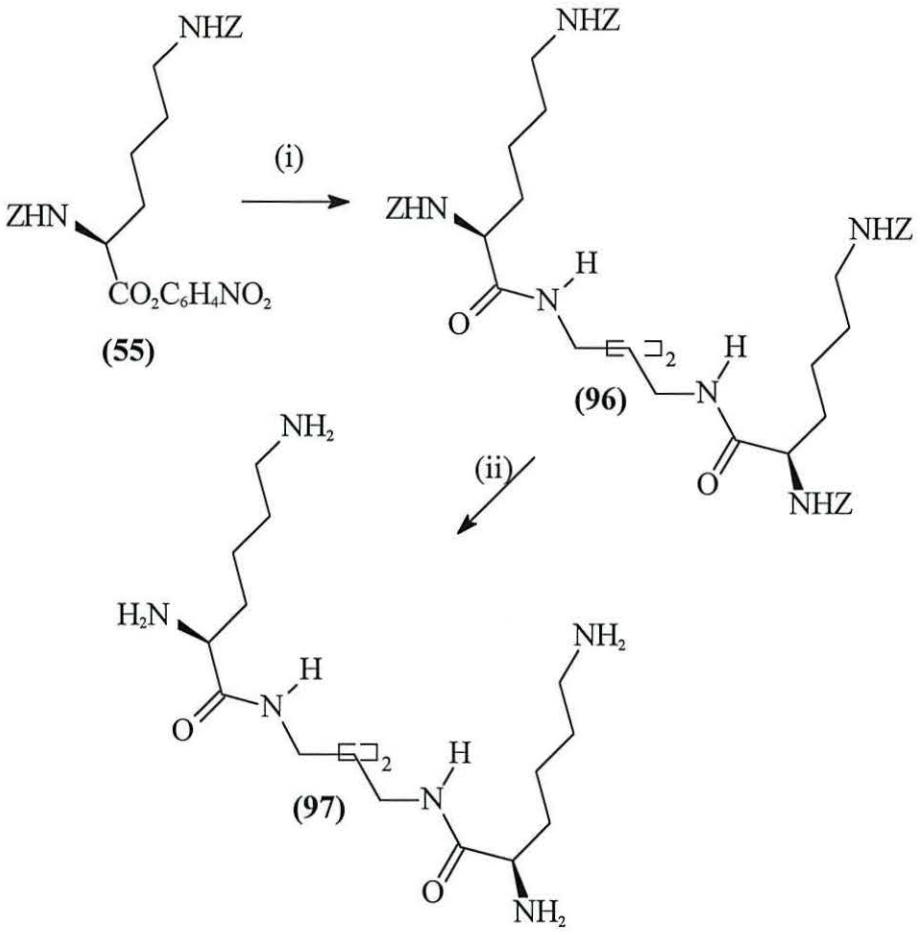
3.6 Synthesis of multifunctional initiators

Mesitylene **(86)** was first treated with AIBN and *N*-bromosuccinimide in benzene to furnish tribromomesitylene **(87)** in a yield of 75 %.[132] Subsequently the tribromide compound **(87)** was refluxed with sodium azide in acetone to provide the triazido derivative **(88)** in an excellent yield of 100 %. Reduction of triazide **(88)** proceeded quickly by reaction with $LiAlH_4$ to provide the multifunctional initiator **(89)** **(Scheme 50)** in a yield of 76 %.[133]



Scheme 50. (i) AIBN, NBS, C_6H_6; (ii) NaN_3, Me_2CO; (iii) $LiAlH_4$, THF.

Reaction of lysine derivative **(55)** with 1,4-diaminobutane provided compound **(96)** in a yield of 75 %. Hydrogenolysis of the benzyloxycarbonyl protecting groups allowed access to the initiator **(97)** with four free primary amino groups **(Scheme 51)**.



Scheme 51. (i) $C_4H_{12}N_2$, CH_2Cl_2; (ii) H_2, C, Pd, IMS.

3.7 Polymers prepared from multi-functionalised initiators (89) and (97)

Subsequent studies were carried out using triaminomesitylene **(89)** with three primary amino groups as a multifunctional initiator for the polymerisation of (*S*)-amino acid *N*-carboxyanhydrides and the polymers were grown to the second generation. The first generation polymer, poly**(90)** was obtained as a white solid through triaminomesitylene **(89)** initiated polymerisation of (*S*)-phenylalanine *N*-carboxyanhydride **(52)** with subsequent capping of the polymer chains with lysine derivative **(55)** in a yield of 79 %. Hydrogenation of the protected polymer, poly**(90)**, provided the deprotected polymeric material, poly**(91)** as a white solid in a yield of 92 %. Poly**(91)** was reacted further with (*S*)-leucine *N*-carboxyanhydride **(50)** and the

polymer chains were capped with lysine derivative **(55)** to provide the second generation polymeric material, poly**(92)** as a white solid in a yield of 64 %. **(Scheme 49)**. The structures and molecular weights of the polymers are given in **Table 19**. The second series of polymers initiated by **(89)** utilised (*S*)-leucine residues for the generation of the first generation material, poly**(93)** in a yield of 63 %. Hydrogenation and further reaction with (*S*)-phenylalanine *N*-carboxyanhydride **(52)** yielded the second generation material, poly**(95)** as a white solid in a combined yield of 81 %. Again, the structures and molecular weights of the polymers are given in **Table 19**.

Initiator	AA1[a]	AA2[a]	M_n[b]	M_w[b]	PDI	M_n[c](calc.)	Yield(%)
89	Phe(4)	-	2910	3740	1.3	3558	79
89	Phe(4)	Leu(4)	2800	3600	1.3	7842	64
89	Leu(4)	-	3500	4000	1.1	3048	63
89	Leu(4)	Phe(4)	4500	5100	1.1	8148	81

Table 19. Physical data for the polymers derived from initiator (**89**).

a. The numbers in brackets correspond to the average number of amino acids incorporated into each branch of the polymer as determined by ^{1}H NMR spectroscopy. b. M_n and M_w values were obtained from GPC data calibrated with polystyrene standards. c. Calculated from the integration trace of the ^{1}H NMR spectrum.

As **Table 19** shows, the use of initiator **(89)** bearing three primary amino groups provided the desired branched poly(amino acids) exactly as in the case of initiators **(1a)** and **(1b)**. The polymers were only taken to the second generation due to the highly branched nature of the polymers derived from initiator **(89)**. Again, an increasing discrepancy between the calculated and the experimental M_n values is apparent in these polymers. This is again probably due to the fact that GPC separation

is based on molecular size rather than molecular weight and for branched polymers; the relationship between molecular weight is non-linear. Evidence for the growth of polymeric material onto the first generation polymers is however clearly seen through examination of the ^{13}C nmr and the GPC traces **(Figure 8** and **Figure 9** respectively).

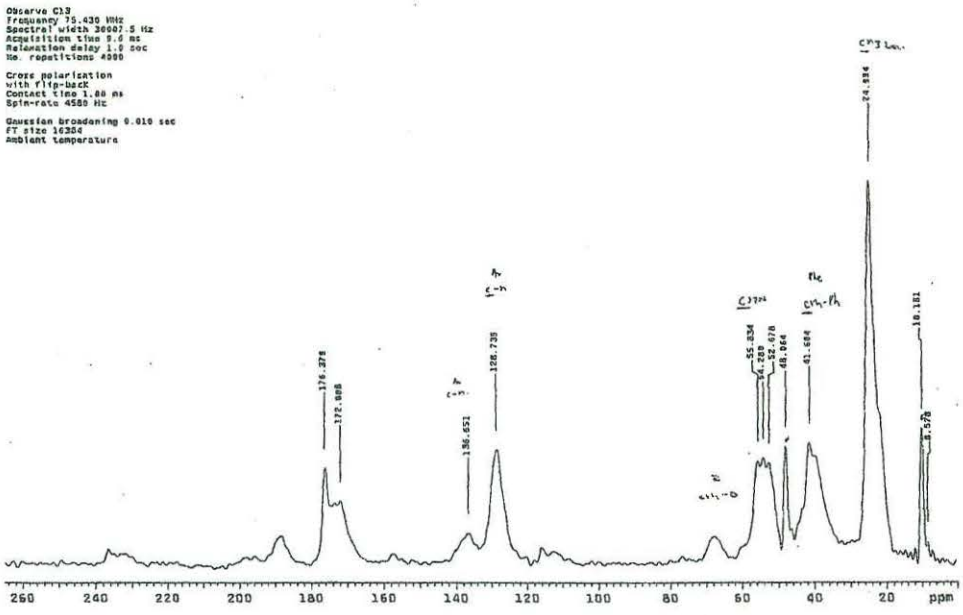


Figure 8.

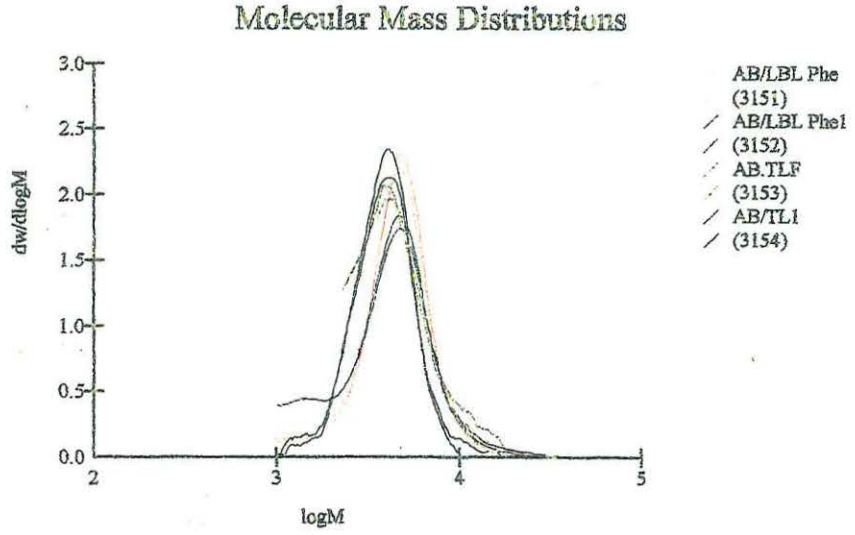


Figure 9.

As **Figure 8** shows, the peak at 41.6 ppm corresponding to the β-$\underline{C}H_2$ of the phenylalanine residues is clearly seen in the second generation material, poly**(95)**. This proves the presence of the phenylalanine residues. **Figure 9** shows, a single peak in the GPC trace for the second generation material, poly**(95)** (TLF). The absence of a peak corresponding to the first generation material, poly**(93)** (TL) provides evidence for the existence of a single polymeric species. Combining observations from the ^{13}C NMR and GPC has enabled the successful characterisation of these novel polymeric materials.

Further studies were carried out using the multifunctional initiator **(97)** with four primary amino groups for the polymerisation of (*S*)-amino acid *N*-carboxyanhydride. The first generation polymer, poly**(98)** was obtained as a white solid through 1,4 diaminobutane-1,4-di-(*S*)-lysine **(97)** initiated polymerisation of (*S*)-phenylalanine *N*-carboxyanhydride **(52)** with subsequent capping of the polymer chains with lysine derivative **(55)** in a yield of 80 %. Hydrogenation of the protected polymer, poly**(98)**, provided the deprotected polymeric material, poly**(99)** as a white solid in a yield of 90 %. Poly**(99)** was reacted further with (*S*)-leucine *N*-carboxyanhydride **(50)** and the polymer chains were capped with lysine derivative **(55)** to provide the second generation polymeric material, poly**(100)** as a white solid in a yield of 72 %. **(Scheme 49)**. The structures and molecular weights of the polymers are given in **Table 20**. The second series of polymers initiated by **(97)** utilised (*S*)-leucine residues for the generation of the first generation material, poly**(101)** in a yield of 60 %. Hydrogenation and further reaction with (*S*)-phenylalanine *N*-carboxyanhydride **(52)** yielded the second generation material, poly**(103)** as a white solid in a combined yield of 77 %. Again, the structures and molecular weights of the polymers are given in **Table 20**.

Initiator	AA1[a]	AA2[a]	M_n[b]	M_w[b]	PDI	M_n[c](calc.)	Yield(%)
97	Phe(4)	-	4530	5440	1.2	4280	80
97	Phe(4)	Leu(3)	4590	5920	1.3	9088	65
97	Leu(4)	-	3070	4100	1.3	3736	60
97	Leu(4)	Phe(3)	8270	33600	4.1	9360	77

Table 20. Physical data for the polymers derived from initiator **(97)**.

a. The numbers in brackets correspond to the average number of amino acids incorporated into each branch of the polymer as determined by ^{1}H NMR spectroscopy. b. M_n and M_w values were obtained from GPC data calibrated with polystyrene standards. c. Calculated from the integration trace of the ^{1}H NMR spectrum.

As **Table 20** shows, the use of initiator **(97)** bearing four primary amino groups provided the desired branched poly(amino acids) exactly as in the case of initiators **(1a)** and **(1b)**. The polymers were only taken to the second generation due to the highly branched nature of the polymers derived from initiator **(97)**. Again, an increasing discrepancy between the calculated and the experimental M_n values is apparent in these polymers, probably because GPC separation is based on molecular size rather than molecular weight. Again evidence for the growth of polymeric material onto the first generation polymers is clearly seen through examination of the ^{13}C NMR and the GPC traces **(Figure 10** and **Figure 11** respectively).

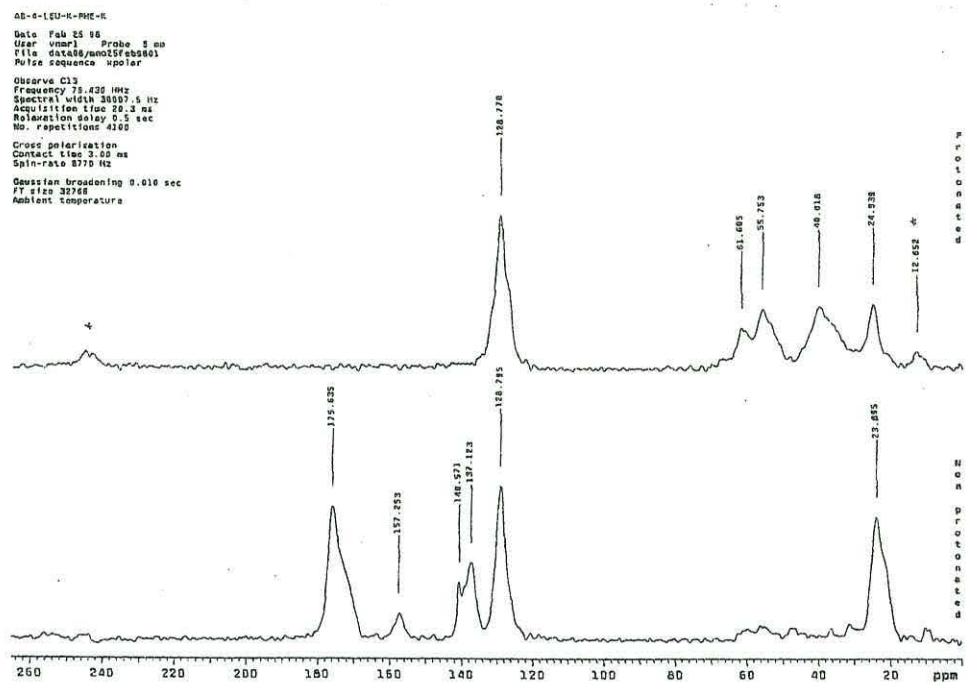


Figure 10.

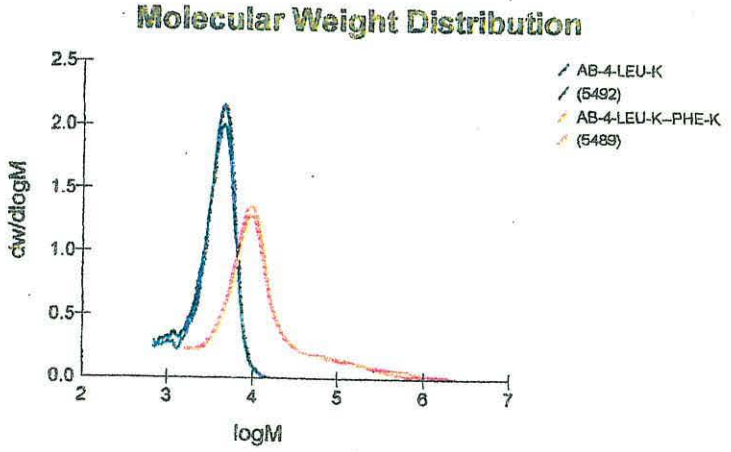


Figure 11.

As **Figure 10** shows, the peak at 40.0 ppm corresponding to the β-$\underline{C}H_2$ of the phenylalanine residues is clearly seen in the second generation material, poly**(103)**. This proves the presence of the phenylalanine residues. **Figure 11** shows, a single peak in the GPC trace for the second generation material, poly**(103)**. The absence of a peak corresponding to the first generation material, poly**(101)**, provides evidence for the existence of a single polymeric species. Again, combining observations from the ^{13}C NMR and GPC has enabled the successful characterisation of these novel polymeric materials.

3.8 Conclusions for poly(amino acids)

The synthesis of a new type of hybrid polymer was successfully achieved by combining the methodology from traditional type polymerisations with the precise branching and successive generation concepts found in dendrimer chemistry. The traditional type linear polymer part was achieved through the polycondensation reaction between a primary amine and an amino acid *N*-carboxyanhydride. The precise branching and successive generation concept found in dendrimer chemistry was achieved through termination of the polycondensation by the addition of *para*-nitrophenyl *N*-Z, *N*'-Z-(*S*)-lysine **(55)**. Subsequent hydrogenolysis of the benzyloxycarbonyl groups revealed two new primary amines, which were successfully used to initiate the polymerisation of further amino acid *N*-carboxyanhydride. Termination of the polycondensation through the addition of lysine derivative **(55)** provided access to the second generation material. Repetition of these steps allowed access to the higher generation materials.

This methodology has allowed the synthesis of a new type of hybrid polymer where the length of the polymer chains produced is inevitably polydisperse and the

degree of branching of the polymer is highly controlled. Furthermore, the methodology has enabled highly branched poly(amino acids) to be prepared through the initiation of Leuch's anhydrides by the poly-amine initiators **(89)** and **(97)** with three and four free primary amino groups respectively. All of the polymeric materials produced in this way are homochiral, biodegradable and have potential applications as asymmetric catalysts, biomimetic polymers and biocompatible polymers.

4 Overall conclusions

It has been shown that amino acids can be successfully used as starting materials for the preparation of novel polymers. As such they are versatile reagents which can readily undergo functional group interconversions to yield reactive monomers. In the work mentioned earlier, standard peptide chemistry coupled with acrylation or methacrylation led to the synthesis of reactive monomers which upon subsequent radical addition polymerisation provided novel poly(peptides) with both free acid and amino groups. The inherent chirality of the amino acids was unaffected. In a separate project, reaction of amino acids with phosgene led to the isolation of the respective *N*-carboxyanhydride. This monomer readily polymerises through a polycondensation scheme to provide poly(amino acids). Termination of the chain ends was successfully achieved by addition of lysine derivative **(55)** to provide a range of novel homochiral, highly branched poly(amides).

4.1 Scope for further work

Homopolymers of the poly(peptides) have potential as novel drug delivery systems. This novel drug delivery system could be achieved through the synthesis of a pentapeptide incorporating a polymerisable group on a (*S*)-serine residue and an active drug molecule attached to the free acid. Subsequent polymerisation will provide a large molecule incorporating an active drug molecule within each monomer unit.

It is known that low molecular weight proteins are able to move freely across cell membranes, usually through channels in the actual membrane. These low molecular weight proteins function as molecular chaperones, transporting active molecules to specific sites within the organism. The polymerisation of novel peptides

with an active molecule attached should provide an artificial low molecular weight protein and hence an artificial molecular chaperone. Furthermore, the polymer contains ester and amide functional groups, which can be cleaved enzymatically at certain pHs. Cleavage of these bonds will result in the release of the active molecule. Site specific delivery is achieved through tuning the pH at which the ester or amide bonds are digested to the pH environment found in the desired delivery site. Subsequently when the polymer reaches the desired delivery site the active molecule is released.

The advantage over conventional methods of delivery are: multiple copies of the active molecule are presented at the active site, it is less likely for a large molecule to be digested in transit compared to a small active molecule, the polymer itself acts as a molecular chaperone allowing site specific delivery and the by products of delivery are non immunogenic, and readily metabolised by the organism.

The observed values for the reactivity of the chiral monomers that were reported in chapter 2 are inaccurate. This is because all the experiments were performed in order to achieve high yields. This meant that the percentage conversion of the monomers was high, *ca.* 80 %. This is due to the reactivity of the monomers being related to the initiator concentration. At low percentage conversion of monomer the main growth limiting steps are the rate of initiation and the rate of propagation of the polymer, these two steps give the respective reactivity of a monomer. However, at high percentage incorporation of monomer the rate of termination reactions decrease and the rate of propagation increases due to the gel effect resulting in inaccurate reactivity values. The values given in chapter 2 give the respective reactivity ratios for the chiral monomers at high percentage conversions. To further investigate the reactivity of the monomers, a series of experiments need to be conducted keeping the

percentage conversion of monomer below 20 %. This will provide information on the true reactivity between the two monomers, *i.e.* chiral monomer and methyl methacrylate.

For branched polymers it is known that the relationship between molecular size and molecular weight is non-linear. However, the polymers reported in chapter 3 are not randomly branched but contain precise branching. Therefore a series of experiments are required to investigate the magnitude of change between the observed and calculated M_n values. This can be achieved by growing a polymer of similar size, *i.e.* same monomer : initiator ratio without the termination of the polymer chains by the lysine derivative **(55)**. Subsequent analysis of the terminated and unterminated polymers by GPC will provide two different elution times. The difference between these values will give an indication of the magnitude of change between the observed and calculated M_n values.

All the polymers in this work utilised hydrophobic amino acids so as to enable easy identification of the successsive generations through nmr. This was because all the amino acids used showed characteristic peaks in the nmr spectrum. The resulting polymers were found to be insoluble in most common organic solvents. Further studies could be undertaken to increase the solubility of the polymeric materials, this could be achieved by inserting generations of hydrophilic amino acids, such as (*S*)-glutamate, between generations of hydrophobic amino acids.

5 Experimental

5.1 General Methods

^{1}H NMR spectra were recorded at 250 MHz on a Brucker AM250 spectrometer fitted with a ^{1}H-^{13}C dual probe and were recorded at 293 K in $CDCl_3$ unless otherwise stated. Spectra were internally referenced to either TMS or to the residual solvent peak and peaks are reported in ppm downfield of TMS. Multiplicities are reported as singlet (s), doublet (d), triplet (t), quartet (q), some combination of these, broad (br), or multiplet (m). ^{13}C NMR spectra were recorded at 62.9MHz on the same spectrometer as the ^{1}H nmr spectra, at 293 K and in $CDCl_3$, unless otherwise stated. Spectra were referenced to the solvent peak and are reported in ppm downfield of TMS. Peak assignments were made by DEPT editing of the spectra. Solid state ^{13}C NMR spectra were recorded at 300MHz, using the EPSRC service at Durham University.

Infra red spectra were recorded on a Perkin Elmer 1600 series FTIR spectrometer, only characteristic absorptions are recorded and peaks are reported as strong (s), moderate (m), weak (w), or broad (br). Mass spectra were recorded using the FAB technique (Cs^+ ion bombardment at 25kV) on a VG Autospec spectrometer, or by electron ionisation (EI) on either a VG model 12-253 quadrupole spectrometer or a VG Quattro II triple quadrupole spectrometer. Only significant fragment ions are reported and only molecular ions are assigned. High resolution mass measurements were made on a VG ZAB-E spectrometer. Optical rotations were recorded on an Optical Activity Ltd. Polar 2001 polarimeter, at a concentration of 1.0 g / 100 ml in $CHCl_3$, unless otherwise stated. Elemental analyses were performed within the Chemistry department on a Carlo Erba Model 1106 or Model 1108 analyser.

5.2 Experimental for chapter II

N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu ***(24)***.

To a solution of *N*-Boc-(*S*)-serine **(14)** (7.05g, 34.4 mmoles, 1.3eq.) in glass distilled DMF (75 ml) was added DCC (5.45g, 26.4 mmoles, 1.0eq.), HOBt (5.7g, 42.3 mmoles, 1.6eq.) and (*S*)-Phe-O^{t}Bu **(23)** (5.85g, 26.4 mmoles, 1.0eq.). The mixture was stirred at room temperature for 14 hours after which the solvent was removed *in vacuo* and ethyl acetate (60 ml) was added to the brown oil residue. Filtration through celite removed a white solid (DCHU) and the filtrate was washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (2x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a yellow oil. Residual DMF was removed as an azeotrope with CH_2Cl_2 (2x 25 ml) to provide the title compound as a yellow solid. Yield 10.6g (98 %); m.p. 47 °C; $[\alpha]^{25}_D$ -2.2 (c = 0.8, $CHCl_3$); υ_{max} ($CHCl_3$) 3299 (br), 2977 (m), 1718 (s), 1654 (s), 1527 (m), 1368 (s) and 1159 cm^{-1} (s); δ_H 1.39 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.41 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 3.01 (1H, dd *J* 6.3, 14.0Hz, 1x β-C$\underline{H}_2$Ph), 3.08 (1H, dd *J* 6.2, 14.0Hz, 1x β-C$\underline{H}_2$Ph), 3.62 (2H, brm, 1x β-C$\underline{H}_2$ + 1x α-C$\underline{H}$), 3.92 (1H, brd *J* 8.3Hz, 1x β-C$\underline{H}_2$), 4.15 (1H, brs, O$\underline{H}$), 4.70 (1H, q *J* 6.4Hz, Phe-α-C$\underline{H}$), 5.50 (1H, brd *J* 5.3Hz, Boc-N$\underline{H}$), 7.12 (1H, brd, *J* 7.6Hz, N$\underline{H}$CO), 7.15-7.30 (5H, m, ArC$\underline{H}$); δ_C 27.9 (1x C($\underline{C}$H$_3$)$_3$), 28.2 (1x C($\underline{C}$H$_3$)$_3$), 37.8 ($\underline{C}$H$_2$Ph), 54.0 (Ser-α-$\underline{C}$H), 55.4 (Phe-α-$\underline{C}$H), 62.8 (Ser-β-$\underline{C}$H$_2$), 80.2 (1x $\underline{C}$(CH$_3$)$_3$), 82.5 (1x $\underline{C}$(CH$_3$)$_3$), 126.9 (1x Ar$\underline{C}$H), 128.4 (1x Ar$\underline{C}$H), 129.4 (1x Ar$\underline{C}$H), 136.1 (Ar *ipso*$\underline{C}$), 155.8 (Boc $\underline{C}$O), 170.4 (1x $\underline{C}$ON), 170.9 (1x $\underline{C}$O$_2$); m/z (CI) 409 (MH^+); Found 409.2343 ($C_{21}H_{33}N_2O_6$ requires 409.2338).

O-Acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu ***(25)***.

To a solution of *N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu **(24)** (0.5g, 1.2 mmoles, 1.0eq.) in ethyl acetate (25 ml), cooled with ice was added triethylamine (0.5 ml, 3.7 mmoles, 3.0eq.). After stirring for 10 minutes, acryloyl chloride (0.15 ml, 1.9 mmoles, 1.5eq.) was added dropwise *via* a syringe. Subsequently the solution was allowed to warm to room temperature and stirred for a further 15 hours. The reaction mixture was filtered through celite to remove a white solid (triethylamine hydrochloride). The filtrate was washed with sat. Na_2CO_3 (2x 25 ml). Subsequently the aqueous layer was back extracted with ethyl acetate (2x 15 ml). The combined organic layers were then washed with sat. Na_2CO_3 (4x 25 ml), water (2x 20 ml), 2M HCl (3x 25 ml) and water (3x 25 ml). The organic layer was dried ($MgSO_4$) and the solvent removed *in vacuo* to leave a yellow coloured foaming oil. Flash chromatography, eluting with ethyl acetate-light petroleum (1.5:8.5) afforded the title compound as a white solid. Yield 0.5g (90 %); m.p. 72 $^{\circ}$C; $[\alpha]^{25}_{D}$ +49.3; Found C, 61.8; H, 7.8; N, 6.1. $C_{24}H_{34}N_2O_7$.25 % H_2O requires C, 61.7; H, 7.5; N, 6.0 %; υ_{max} ($CHCl_3$) 3418 (br), 2979 (s), 1729 (s), 1661 (s), 1522 (s), 1456 (m), 1408 (m), 1392 (m), 1368 (s), 1253 (m) and 1160 cm^{-1} (s); δ_H 1.35 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.37 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 3.05 (2H, d *J* 5.9Hz, C$\underline{H}_2$Ph), 4.28-4.40 (3H, brm, 1x α-C$\underline{H}$ + β-C$\underline{H}_2$), 4.66 (1H, q *J* 6.1Hz, Phe-α-C$\underline{H}$), 5.24 (1H, brd *J* 4.6Hz, Boc N$\underline{H}$), 5.79 (1H, d *J* 10.4Hz, 1x =C$\underline{H}_2$), 6.03 (1H, dd *J* 10.4, 17.2Hz, =C$\underline{H}$), 6.35 (1H, d *J* 17.2Hz, 1x =C$\underline{H}_2$), 6.72 (1H, d *J* 7.2Hz, N$\underline{H}$CO), 7.08-7.12 (2H, m, 2x ArC$\underline{H}$), 7.18-7.23 (3H, m, 3x ArC$\underline{H}$); δ_C 27.9 (1x C($\underline{C}$H$_3$)$_3$), 28.2 (1x C($\underline{C}$H$_3$)$_3$), 38.0 ($\underline{C}$H$_2$Ph), 53.6 (1x α-$\underline{C}$H), 53.8 (1x α-$\underline{C}$H), 64.2 (Ser-β-$\underline{C}$H$_2$), 80.6 (1x $\underline{C}$(CH$_3$)$_3$), 82.5 (1x $\underline{C}$(CH$_3$)$_3$), 127.0 (1x Ar$\underline{C}$H), 127.6 (=$\underline{C}$H), 128.4 (1x Ar$\underline{C}$H), 129.5 (1x Ar$\underline{C}$H), 131.8 (=$\underline{C}$H$_2$), 136.0 (Ar *ipso*$\underline{C}$), 155.2 (Boc $\underline{C}$O), 165.7 (NH$\underline{C}$O), 168.5 (1x $\underline{C}$O$_2$), 170.0 (1x $\underline{C}$O$_2$); m/z (CI) 463 (MH^+); Found 463.24444 ($C_{24}H_{35}N_2O_7$ requires 463.24443).

O-Methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu ***(26)***.

To a solution of *N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu **(24)** (3.8g, 9.4 mmoles, 1.0eq.) in ethyl acetate (75 ml), cooled with ice was added triethylamine (3.9 ml, 28.1 mmoles, 3.0eq.). After stirring at 0 °C for 5 minutes, methacryloyl chloride (1.4 ml, 14.1 mmoles, 1.5eq.) was added dropwise *via* a syringe. Subsequently the solution was allowed to warm to room temperature then stirred for a further 17 hours. The reaction mixture was filtered to remove a white solid (triethylamine hydrochloride) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). Subsequently the aqueous layer was back extracted with ethyl acetate (2x 15 ml). The combined organic layers were then washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (3x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$) and the solvent removed *in vacuo* to leave a colourless oil. This was recrystallised from light petroleum (20 ml) to provide the title compound as a white solid. Yield 3.8g (85 %); m.p. 56 °C; $[\alpha]^{25}_D$ +39.3; Found C, 62.7; H, 7.8; N, 5.8. $C_{25}H_{36}N_2O_7$ requires C, 63.0; H, 7.6; N, 5.9 %; υ_{max} ($CHCl_3$) 3407 (br), 2979 (s), 1724 (s), 1656 (s), 1523 (s), 1456 (m), 1392 (m), 1368 (s), 1322 (m), 1296 (m), 1250 (m) and 1158 cm^{-1} (s); δ_H 1.38 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.45 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.91 (3H, s, =CC$\underline{H}_3$), 3.09 (2H, d *J* 6.2Hz, C$\underline{H}_2$Ph), 4.33 (1H, brm *J* 5.8, 1x β-C$\underline{H}_2$O), 4.42 (2H, brm, Ser-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.72 (1H, q *J* 6.1Hz, Phe-α-C$\underline{H}$), 5.30 (1H, brs, Boc-N$\underline{H}$), 5.57 (1H, s, 1x =C$\underline{H}_2$), 6.07 (1H, s, 1x =C$\underline{H}_2$), 6.65 (1H, brd *J* 7.4Hz, N$\underline{H}$CO), 7.13-7.28 (5H, m, ArC$\underline{H}$); δ_C 18.2 (=C$\underline{C}$H$_3$), 27.9 (1x C($\underline{C}$H$_3$)$_3$), 28.2 (1x C($\underline{C}$H$_3$)$_3$), 38.1 ($\underline{C}$H$_2$Ph), 53.8 (2x α-$\underline{C}$H), 64.3 ($\underline{C}$H$_2$O), 82.5 (2x $\underline{C}$(CH$_3$)$_3$), 126.5 (=$\underline{C}$H$_2$), 127.0 (1x Ar$\underline{C}$H), 128.4 (1x Ar$\underline{C}$H), 129.5 (1x Ar$\underline{C}$H), 135.9 (Ar *ipso*$\underline{C}$ + =$\underline{C}$CH$_3$), 156.4 (N$\underline{C}$O$_2$), 168.6 (2x $\underline{C}$O$_2$); m/z (CI) 477 (MH^+); Found 477.2601 ($C_{25}H_{37}N_2O_7$ requires 477.2601).

Homopolymerisations, Method A

The amino acid monomer **(25)** or **(26)** was suspended in toluene to form a 1.0M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling at 273 K and then heated to reflux at 388 K

under a nitrogen atmosphere. Heating was continued for 4 hours, after which time the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 100 ml). The precipitated white solid was collected by filtration and dried *in vacuo* for 5 hours.

Copolymerisations, Method B

The amino acid derived monomer **(25)** or **(26)** was suspended in freshly distilled methyl methacrylate and toluene to form a 1.0M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling to 273 K and then heated to reflux at 372 K under a nitrogen atmosphere. Heating was either continued for 3 hours, or until the polymer had gelled out of solution, after which time the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 150 ml). The precipitated white solid was collected by filtration and dried *in vacuo* at 298 K for 5 hours.

Removal of the polymer protecting groups, Method C

The polymer was dissolved in CH_2Cl_2 (2 ml) and trifluoroacetic acid (2 ml) was added. The solution was stirred at room temperature for 17 hours. This was added slowly, with stirring to diethyl ether (40 ml). The precipitated white solid was collected by filtration and subsequently washed with diethyl ether (100 ml) and dried *in vacuo* at 298 K for 12 hours.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method A)** of monomer **(25)** (300mg, 0.7 mmoles) and benzoyl peroxide (1.6mg, 0.01eq.) in sodium dried toluene (0.65 ml). Yield 175mg (58 %); $[\alpha]^{26}_D$ +37.1 (c = 0.8, $CHCl_3$); υ_{max} ($CHCl_3$) 3358 (br), 2978 (s), 2932 (s), 1730 (s), 1655 (s), 1525 (s), 1455 (m), 1392 (m), 1368 (s), 1251 (s) and 1160 cm^{-1} (s); δ_H 1.2-1.8 (21H, brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$), 3.0-3.2 (2H, brs, C$\underline{H}_2$Ph), 4.1-4.4 (3H, brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (1H, brs, Phe-α-C$\underline{H}$), 7.1-7.4 (6H,

brm, ArC<u>H</u> + CON<u>H</u>); δ_C 27.9 (C(<u>C</u>H_3)$_3$), 28.3 (C(<u>C</u>H_3)$_3$), 38.2 (<u>C</u>H_2Ph), 53.5 (α-<u>C</u>H), 53.8 (α-<u>C</u>H), 64.5 (<u>C</u>H_2O), 79.9 (<u>C</u>(CH$_3$)$_3$), 81.7 (<u>C</u>(CH$_3$)$_3$), 126.8 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 128.9 (Ar<u>C</u>H), 136.3 (Ar *ipso*<u>C</u>), 155.7 (N<u>C</u>O_2), 169.1 (<u>C</u>ONH), 170.0 (<u>C</u>O_2); GPC (THF) M_n 4,780, M_w 47,350, M_w/M_n 9.9.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 8.4:1.6.

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.4g, 0.9 mmoles, 3.0eq.), methyl methacrylate (0.03 ml, 0.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (1.0 ml, 1.2M). Yield 0.38g (86 %); $[\alpha]^{28}_D$ +30.1; υ_{max} ($CHCl_3$) 3332 (br), 2978 (s), 2934 (s), 1731 (s), 1656 (s), 1525 (s), 1455 (m), 1393 (m), 1368 (s), 1309 (m), 1251 (s), 1159 (s) and 1054 cm^{-1} (w); δ_H 1.1-1.9 (brm, C<u>H</u>$_2$ + C<u>H</u> + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 2.7-3.1 (brs, C<u>H</u>$_2$Ph), 3.3-3.5 (brs, CO_2C<u>H</u>$_3$), 3.8-4.3 (brm, α-C<u>H</u>+β-C<u>H</u>$_2$O), 4.45-4.65 (brs, Ser-α-C<u>H</u>), 6.7-7.1 (brm, ArC<u>H</u>+N<u>H</u>CO); δ_C 27.9 (C(<u>C</u>H_3)$_3$), 28.3 (C(<u>C</u>H_3)$_3$), 38.2 (<u>C</u>H_2Ph), 51.8 (O<u>C</u>H_3), 53.8 (α-<u>C</u>H), 64.5 (<u>C</u>H_2O), 79.8 (<u>C</u>(CH$_3$)$_3$), 81.9 (<u>C</u>(CH$_3$)$_3$), 126.8 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 128.9 (Ar<u>C</u>H), 129.5 (Ar<u>C</u>H), 129.8 (Ar<u>C</u>H), 136.3 (Ar *ipso*<u>C</u>), 155.7 (Boc-NH<u>C</u>O), 169.1 (<u>C</u>ONH), 170.0 (<u>C</u>O_2); GPC (THF) M_n 9,500, M_w 38,050, M_w/M_n 4.0.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 8.4:1.6

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 8.4:1.6 **(Method C)** (190mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 8.4:1.6 as a white solid. Yield 152mg (84 %); $[\alpha]^{28}_D$ +24.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3434 (brs), 2946 (s), 1727 (s), 1686 (s), 1638 (m), 1546 (w), 1499 (w), 1438 (w), 1204 (s) and 1139 cm^{-1} (s); δ_H (DMSO-d_6) 0.9-1.5 (brm, C<u>H</u>$_2$+C<u>H</u>+C<u>H</u>$_3$), 2.8-2.9 (brd, 1x C<u>H</u>$_2$Ph), 3.0-3.1 (brd, 1x C<u>H</u>$_2$Ph), 3.4-3.7 (brs, CO_2C<u>H</u>$_3$), 3.9-4.3 (brs, 1x β-C<u>H</u>$_2$O), 4.4-4.8 (brs, α-C<u>H</u>+β-C<u>H</u>$_2$O), 7.0-7.3 (brm, ArC<u>H</u> + N<u>H</u>CO), 8.2-8.5 (brs, N<u>H</u>$_3$), 8.6-9.0 (brs, CO_2<u>H</u>); δ_C (DMSO-d_6) 22.2 (<u>C</u>H_2), 38.6 (<u>C</u>H_2Ph), 51.8 (CO_2<u>C</u>H_3), 54.1 (2x α-<u>C</u>H), 64.2 (<u>C</u>H_2O), 117.1 (q *J* 296Hz, <u>C</u>F_3CO_2), 126.8 (Ar<u>C</u>H), 128.4 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 137.0 (Ar *ipso*<u>C</u>), 158.5 (q *J* 32Hz,

$CF_3\underline{C}O_2$), 167.5 (<u>C</u>ONH), 172.1 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$); GPC (DMF) M_n 11,700,000, M_w 16,000,000, M_w/M_n 1.5.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 5.4:4.6.

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.3g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.09 ml, 0.8 mmoles, 1.3eq.) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (1 ml, 1.4M). Yield 0.2g (62 %); $[\alpha]^{23}_D$ +20.7 (c = 0.7, $CHCl_3$); υ_{max} 3342 (br), 2978 (s), 1730 (s), 1670 (s), 1522 (s), 1455 (m), 1392 (m), 1368 (s), 1250 (s), 1159 (s), 1057 (w) and 1030 cm^{-1} (w); δ_H 1.1-1.8 (brm, $C\underline{H}_3$ + $C\underline{H}$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_2$), 2.9-3.2 (brs, $C\underline{H}_2Ph$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.1-4.6 (brm, α-$C\underline{H}$+β-$C\underline{H}_2O$), 4.6-4.8 (brs, Ser-α-$C\underline{H}$), 7.1-7.4 (brm, Ar$C\underline{H}$+N$\underline{H}$CO); GPC (THF) M_n 4,780, M_w 47,350, M_w/M_n 9.9.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 5.4:4.6.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 5.4:4.6 **(Method C)** (120mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 5.4:4.6 as a white solid. Yield 90mg (76 %); $[\alpha]^{25}_D$ +20.7 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3486 (brs), 2946 (s), 1727 (s), 1682 (s), 1441 (m), 1246 (s), 1201 (s) and 1148 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.0 (brm, $C\underline{H}_2$+$C\underline{H}$+$C\underline{H}_3$), 2.7-2.85 (brd, 1x $C\underline{H}_2Ph$), 2.9-3.1 (brd, 1x $C\underline{H}_2Ph$), 3.3-3.6 (brs, $CO_2C\underline{H}_3$), 3.9-4.2 (brm, α-$C\underline{H}$+β-$C\underline{H}_2O$), 4.4-4.5 (brs, Phe-α-$C\underline{H}$), 6.9-7.2 (brm, Ar$C\underline{H}$ + N$\underline{H}$CO), 8.0-8.4 (brs, $N\underline{H}_3$), 8.5-8.8 (brs, $\underline{C}O_2H$).

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 5.2:4.8

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.3g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.15 ml, 1.4 mmoles, 2.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (1 ml, 1.4M). Yield 0.3g (61 %); $[\alpha]^{23}_D$ +20.4 (c = 0.7, $CHCl_3$); υ_{max} 3342 (br), 2978 (s), 1730 (s), 1670 (s), 1522 (s), 1455 (m), 1392 (m), 1368 (s), 1250 (s), 1159 (s), 1057 (w) and 1030 cm^{-1} (w); δ_H 1.1-

1.8 (brm, C$\underline{H}_3$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_2$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, CO$_2$C$\underline{H}_3$), 4.1-4.6 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.65-4.8 (brs, Ser-α-C$\underline{H}$), 7.1-7.40 (brm, ArC$\underline{H}$+N$\underline{H}$CO); GPC (THF) M_n 5,320, M_w 66,400, M_w/M_n 12.5.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 7.5:2.5

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.3g, 0.7 mmoles, 2.5eq.), methyl methacrylate (0.03 ml, 0.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (1.0 ml). Yield 0.25g (76 %); $[\alpha]^{23}_D$ +26.9 (c = 0.5, $CHCl_3$); υ_{max} 3417 (s), 2977 (s), 1728 (s), 1664 (s), 1512 (m), 1452 (m), 1368 (s), 1247 (s) and 1157 cm^{-1} (s); δ_H 1.2-1.8 (brm, C$\underline{H}_3$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_2$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.5-3.7 (brs, CO$_2$C$\underline{H}_3$), 4.1-4.4 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.5-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); GPC (THF) M_n 3,490, M_w 33,450, M_w/M_n 9.6.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 7.5:2.5

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 7.5:2.5 **(Method C)** (137mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 7.5:2.5 as a white solid Yield 90mg (67 %); $[\alpha]^{25}_D$ +22.6 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3434 (br), 2954 (s), 1726 (s), 1686 (s), 1546 (w), 1500 (w), 1437 (w), 1203 (s) and 1139 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.0 (brm, C$\underline{H}_2$+C$\underline{H}$+C$\underline{H}_3$), 2.7-2.85 (brd, 1x C$\underline{H}_2$Ph), 2.9-3.1 (brd, 1x C$\underline{H}_2$Ph), 3.3-3.6 (brs, CO$_2$C$\underline{H}_3$), 3.9-4.2 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.4-4.6 (brs, Phe-α-C$\underline{H}$), 6.9-7.2 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.0-8.5 (brs, N$\underline{H}_3$), 8.6-8.9 (brs, $\underline{C}O_2H$); δ_C (DMSO-d_6) 36.0 ($\underline{C}H_2$Ph), 51.8 (O$\underline{C}H_3$), 53.6 (Ser-α-$\underline{C}$H), 54.2 (Phe-α-$\underline{C}$H), 64.2 ($\underline{C}H_2$O), 126.8 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.4 (Ar *ipso*$\underline{C}$), 165.0 ($\underline{C}$ONH), 171.3 ($\underline{C}O_2$); GPC (DMF) M_n 5,370,000, M_w 13,100,000, M_w/M_n 2.7.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 3.4:6.6.

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.3g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.28 ml, 2.6 mmoles, 3.8eq.) and benzoyl peroxide (8mg, 0.01eq.) in sodium dried toluene (0.7 ml, 3.3M). Yield 0.4g (59 %); $[\alpha]^{23}_{D}$ +15.5 (c = 0.9, $CHCl_3$); υ_{max} 3355 (m), 2981 (m), 2930 (m), 1731 (s), 1667 (m), 1498 (m), 1453 (m), 1392 (m), 1368 (m), 1243(m) and 1154 cm^{-1} (s); δ_H 0.75-2.0 (brm, C$\underline{H}_3$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_2$), 2.95-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.1-4.5 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.5 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 38.2 (C$\underline{H}_2$Ph), 51.8 (OC$\underline{H}_3$), 53.8 (1x α-C$\underline{H}$), 54.4 (1x α-C$\underline{H}$), 64.5 (C$\underline{H}_2$O), 79.8 (C(CH$_3$)$_3$), 81.9 (C(CH$_3$)$_3$), 126.8 (ArC$\underline{H}$), 128.3 (ArC$\underline{H}$), 128.9 (ArC$\underline{H}$), 129.5 (ArC$\underline{H}$), 129.8 (ArC$\underline{H}$), 136.3 (Ar *ipso*C), 155.7 (Boc-NHCO), 169.1 (CONH), 170.0 ($\underline{C}O_2$); GPC (THF) M_n 20,250, M_w 447,000, M_w/M_n 22.1.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 3.4:6.6.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 3.4:6.6 **(Method C)** (170mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 3.4:6.6 as a white solid. Yield 130mg (77 %); $[\alpha]^{25}_{D}$ +18.9 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3486 (br), 2946 (s), 1727 (s), 1686 (s), 1546 (w), 1500 (w), 1441 (m), 1246 (m), 1201 (s) and 1148 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.2 (brm, C$\underline{H}_2$+C$\underline{H}$+C$\underline{H}_3$), 2.8-3.0 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 3.9-4.3 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.4-4.6 (brs, Phe-α-C$\underline{H}$), 7.1-7.4 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.7-8.9 ($CO_2\underline{H}$+N$\underline{H}_3$); δ_C (DMSO-d_6) 18.7 (C$\underline{H}_3$), 36.0 (C$\underline{H}_2$Ph), 52.0 (OC$\underline{H}_3$), 54.3 (α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 131.9 (ArC$\underline{H}$), 133.5 (ArC$\underline{H}$), 134.5 (ArC$\underline{H}$), 139.4 (Ar *ipso*C), 165.0 (CONH), 171.3 ($\underline{C}O_2$); GPC (DMF) M_n 2,485,000, M_w 12,700,000, M_w/M_n 5.4.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 2.7:7.3.

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.3g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.45 ml, 4.2 mmoles, 6.4eq.) and benzoyl peroxide (12mg, 0.01eq.) in sodium dried toluene (1.0 ml, 3.3M). Yield 0.5g (62 %); $[\alpha]^{23}_{D}$ +13.9 (c = 0.5, $CHCl_3$); υ_{max} 3356 (br), 2982 (m), 2950 (m), 1730 (s), 1667 (m), 1498 (m), 1452 (m), 1368 (m), 1243(s) and 1154 cm^{-1} (s); δ_H 0.7-1.3 (brm, C$\underline{H}$ + C$\underline{H}_2$), 1.3-1.4 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.4-1.5 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.7-2.3 (brs, C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.1-4.5 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.5 (C$\underline{H}_3$), 18.7 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 38.3 (C$\underline{H}_2$Ph), 51.8 (OC$\underline{H}_3$), 53.8 (2x α-C$\underline{H}$), 64.5 (C$\underline{H}_2$O), 79.8 (C(CH$_3$)$_3$), 82.2 (C(CH$_3$)$_3$), 126.9 (ArC$\underline{H}$), 128.3 (ArC$\underline{H}$), 129.5 (ArC$\underline{H}$), 136.3 (Ar *ipso*C), 156.2 (NC$\underline{O}_2$), 169.1 (C$\underline{O}$NH), 170.0 (C$\underline{O}_2$); GPC (THF) M_n 20,550, M_w 552,000, M_w/M_n 26.9.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 2.7:7.3.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 2.7:7.3 **(Method C)** (160mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 2.7:7.3 as a white solid. Yield 150mg (94 %); $[\alpha]^{25}_{D}$ +17.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3486 (br), 2946 (s), 1727 (s), 1441 (m), 1246 (m), 1201 (s) and 1148 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.2 (brm, C$\underline{H}_2$+C$\underline{H}$+C$\underline{H}_3$), 2.8-2.9 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 3.9-4.3 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.4-4.6 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.2-8.5 (brs, N$\underline{H}_3$ + $CO_2\underline{H}$); δ_C (DMSO-d_6) 21.5 (C$\underline{H}$), 23.5 (C$\underline{H}_3$), 41.9 (C$\underline{H}_2$Ph), 49.1 (C$\underline{C}$H$_3$), 49.4 (C$\underline{C}$H$_3$), 56.9 (OC$\underline{H}_3$), 59.1 (2x α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 131.8 (ArC$\underline{H}$), 133.5 (ArC$\underline{H}$), 134.5 (ArC$\underline{H}$), 142.2 (Ar *ipso*C), 177.1 (C$\underline{O}$NH), 181.4 (C$\underline{O}_2$), 182.3 (C$\underline{O}_2$); GPC (DMF) M_n 3,810,000, M_w 18,000,000, M_w/M_n 4.7.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1.4:8.6

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.2g, 0.4 mmoles, 1.0eq.), methyl methacrylate (0.4 ml, 4.0 mmoles, 10.0eq.) and benzoyl peroxide (15mg, 0.01eq.) in sodium dried toluene (1.0 ml, 3.8M). Yield 0.5g (63 %); $[\alpha]^{23}_{D}$ +10.0 (c = 0.6, $CHCl_3$); υ_{max} 3414 (br), 3019 (s), 2950 (m), 1729 (s), 1667 (m), 1486 (m), 1450 (m), 1368 (m), 1242 (s), 1217 (s), 1193 (s) and 1153 cm^{-1} (s); δ_H 0.7-1.3 (brm, C$\underline{H}$ + C$\underline{H}_2$), 1.3-1.4 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.4-1.6 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.7-2.2 (brs, C$\underline{H}_3$), 3.0-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.1-4.5 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.4 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.2 (C(C$\underline{H}_3$)$_3$), 38.3 (C$\underline{H}_2$Ph), 44.5 (C$\underline{C}$H$_3$), 44.9 (C$\underline{C}$H$_3$), 51.8 (O$\underline{C}$H$_3$), 53.8 (2x α-C$\underline{H}$), 64.5 (C$\underline{H}_2$O), 79.8 (C$\underline{(}$CH$_3$)$_3$), 82.2 (C$\underline{(}$CH$_3$)$_3$), 126.9 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.5 (Ar$\underline{C}$H), 136.3 (Ar *ipso*$\underline{C}$), 156.2 (N$\underline{C}O_2$), 169.1 ($\underline{C}$ONH), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 19,000, M_w 404,000, M_w/M_n 21.3.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 1.4:8.6.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 1.4:8.6 **(Method C)** (230mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 1.4:8.6 as a white solid. Yield 215mg (94 %); $[\alpha]^{25}_{D}$ +11.0 (c = 1.0, DMSO : AcCN 1:1); υ_{max} (KBr) 3589 (br), 3030 (m), 2990 (s), 1731 (s), 1682 (s), 1482 (s), 1450 (s), 1389 (m), 1324 (m), 1273 (s), 1243 (s), 1196 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.2 (brm, C$\underline{H}_2$+C$\underline{H}$+C$\underline{H}_3$), 2.8-2.9 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 3.9-4.3 (brs, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.4-4.6 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.1-8.4 (brs, N$\underline{H}_3$), 8.7-8.9 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 (C$\underline{H}_2$), 18.6 (C$\underline{H}_3$), 36.1 (C$\underline{H}_2$Ph), 44.1 (C$\underline{C}$H$_3$), 44.5 (C$\underline{C}$H$_3$), 51.7 (α-C$\underline{H}$), 52.0 (O$\underline{C}$H$_3$), 54.3 (α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 126.8 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 139.4 (Ar *ipso*$\underline{C}$), 165.0 ($\underline{C}$ONH), 176.5 ($\underline{C}O_2$), 177.4 ($\underline{C}O_2$); GPC (DMF) M_n 1,830,000, M_w 10,550,000, M_w/M_n 5.8.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.6:9.4

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.3g, 0.6 mmoles, 1.0eq.), methyl methacrylate (1.39 ml, 13.0 mmoles, 20.0eq.) and benzoyl peroxide (30mg, 0.01eq.) in sodium dried toluene (0.5 ml, 6.8M). Yield 1.2g (76 %); $[\alpha]^{23}_{D}$ +5.8 ($CHCl_3$); υ_{max} 3417 (br), 2997 (s), 2950 (s), 1731 (s), 1667 (m), 1485 (m), 1450 (s), 1389 (m), 1368 (m), 1274 (s), 1242 (s), 1193 (s) and 1151 cm^{-1} (s); δ_H 0.7-1.3 (brm, C$\underline{H}$ + C$\underline{H}_2$), 1.3-1.4 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.4-1.5 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.7-2.2 (brs, C$\underline{H}_3$), 3.0-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.1-4.5 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.4 ($\underline{C}H_3$), 18.7 ($\underline{C}H_3$), 27.8 (C($\underline{C}H_3$)$_3$), 28.2 (C($\underline{C}H_3$)$_3$), 38.3 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 51.8 (O$\underline{C}H_3$), 52.6 (α-$\underline{C}$H), 54.4 (α-$\underline{C}$H), 64.5 ($\underline{C}H_2$O), 79.8 (C($\underline{C}H_3$)$_3$), 82.1 (C($\underline{C}H_3$)$_3$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.5 (Ar$\underline{C}$H), 136.3 (Ar *ipso*$\underline{C}$), 156.2 (N$\underline{C}O_2$), 169.1 ($\underline{C}$ONH), 176.9 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 30,000, M_w 285,500, M_w/M_n 9.5.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 0.6:9.4.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 0.6:9.4 **(Method C)** (500mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 0.6:9.4 as a white solid. Yield 480mg (96 %); $[\alpha]^{25}_{D}$ +6.2 (c = 1.0, DMSO : AcCN 1:1); υ_{max} (KBr) 3589 (br), 2990 (s), 2981 (s), 1731 (s), 1449 (s), 1272 (s), 1243 (s), 1190 (s) and 1143 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.2 (brm, C$\underline{H}_2$+C$\underline{H}$+C$\underline{H}_3$), 2.8-2.9 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 3.9-4.3 (brs, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.4-4.6 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.2-8.5 (brs, N$\underline{H}_3$), 8.7-8.8 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.2 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 36.0 ($\underline{C}H_2$Ph), 44.0 ($\underline{C}CH_3$), 44.4 ($\underline{C}CH_3$), 51.8 (O$\underline{C}H_3$), 54.3 (α-$\underline{C}$H), 64.2 ($\underline{C}H_2$O), 126.5 (Ar$\underline{C}$H), 127.8 (Ar$\underline{C}$H), 128.9 (Ar$\underline{C}$H), 139.4 (Ar *ipso*$\underline{C}$), 165.0 ($\underline{C}$ONH), 176.3 ($\underline{C}O_2$), 177.2 ($\underline{C}O_2$); GPC (DMF) M_n 1,620,000, M_w 9,080,000, M_w/M_n 5.6.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.3:9.7

This polymer was obtained by the polymerisation **(Method B)** of monomer **(25)** (0.15g, 0.3 mmoles, 1.0eq.), methyl methacrylate (1.4 ml, 13.0 mmoles, 40.0eq.) and benzoyl peroxide (32mg, 0.01eq.) in sodium dried toluene (0.5 ml, 7.0M). Yield 1.3g (82 %); $[\alpha]^{23}_{D}$ +3.8 ($CHCl_3$); υ_{max} 3427 (br), 2997 (m), 2950 (s), 1731 (s), 1485 (m), 1449 (m), 1388 (m), 1368 (m), 1274 (m), 1242 (s), 1193 (s) and 1151 cm^{-1} (s); δ_H 0.7-0.8 (brs, C$\underline{H}_2$), 0.9-1.1 (brs, C$\underline{H}$), 1.3-1.4 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.4-1.5 (brs, 1x C(C$\underline{H}_3$)$_3$), 1.7-2.1 (brs, C$\underline{H}_3$), 3.0-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, CO$_2$C$\underline{H}_3$), 4.1-4.5 (brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.5 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 38.4 (C$\underline{H}_2$Ph), 44.5 (C$\underline{C}$H$_3$), 44.9 (C$\underline{C}$H$_3$), 51.8 (OC$\underline{H}_3$), 53.8 (α-C$\underline{H}$), 54.4 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 80.2 (C$\underline{(}$CH$_3$)$_3$), 82.2 (C$\underline{(}$CH$_3$)$_3$), 126.9 (ArC$\underline{H}$), 128.3 (ArC$\underline{H}$), 129.5 (ArC$\underline{H}$), 136.3 (Ar *ipso*C), 155.5 (NC$\underline{O}_2$), 169.1 (C$\underline{O}$NH), 170.0 (C$\underline{O}_2$), 176.9 (C$\underline{O}_2$), 177.8 (C$\underline{O}_2$); GPC (THF) M_n 21,800, M_w 100,450, M_w/M_n 4.6.

Poly(O-acryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 0.3:9.7.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 0.3:9.7 **(Method C)** (503mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 0.3:9.7 as a white solid. Yield 437mg (87 %); $[\alpha]^{25}_{D}$ +3.6 (c = 1.0, DMSO : AcCN 1:1); υ_{max} (KBr) 3589 (br), 3001 (m), 2952 (s), 1724 (s), 1560 (m), 1458 (s), 1389 (m), 1273 (s), 1241 (s), 1196 (s) and 1152 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-1.9 (brm, C$\underline{H}_2$+C$\underline{H}$+C$\underline{H}_3$), 2.8-2.9 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.8 (brs, CO$_2$C$\underline{H}_3$), 3.9-4.3 (brs, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.4-4.6 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO); δ_C (DMSO-d_6) 16.4 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 36.1 (C$\underline{H}_2$Ph), 44.5 (C$\underline{C}$H$_3$), 44.8 (C$\underline{C}$H$_3$), 51.8 (OC$\underline{H}_3$), 52.7 (α-C$\underline{H}$), 54.4 (α-C$\underline{H}$), 65.8 (C$\underline{H}_2$O), 126.8 (ArC$\underline{H}$), 128.5 (ArC$\underline{H}$), 129.4 (ArC$\underline{H}$), 165.0 (C$\underline{O}$NH), 177.0 (C$\underline{O}_2$), 177.8 (C$\underline{O}_2$); GPC (DMF) M_n 338,500, M_w 3,765,000, M_w/M_n 11.1.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu) 1.7M.

This polymer was obtained by the polymerisation **(Method A)** of monomer **(26)** (248mg, 0.5 mmoles) and benzoyl peroxide (1.3mg, 0.01eq.) in sodium dried toluene (0.3 ml, 1.7M). Yield 158mg (64 %); $[\alpha]^{26}_{D}$ +33.9 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3331 (br), 3013 (s), 2966 (s), 1725 (s), 1672 (s), 1514 (s), 1495 (m), 1390 (m), 1361 (s), 1214 (s) and 1155 cm^{-1} (s); δ_H 1.1-1.6 (23H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 3.0-3.2 (2H, brd, C$\underline{H}_2$Ph), 4.1-4.5 (3H, brm, α-C$\underline{H}$+β-C$\underline{H}_2$O), 4.6-4.8 (1H, brs, Phe-α-C$\underline{H}$), 5.2-5.3 (1H, brs, N$\underline{H}$CO$_2$), 7.1-7.4 (6H, brm, ArC$\underline{H}$ + CON$\underline{H}$); δ_C 18.2 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.2 (C(C$\underline{H}_3$)$_3$), 38.1 (C$\underline{H}_2$Ph), 53.5 (α-C$\underline{H}$), 53.8 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 79.9 (C(CH$_3$)$_3$), 82.5 (C(CH$_3$)$_3$), 127.0 (ArCH), 128.4 (ArCH), 129.6 (ArCH), 136.4 (Ar *ipso*C), 156.7 (NCO$_2$), 169.1 (CONH), 170.1 (CO$_2$); GPC (THF) M_n 995, M_w 3,645, M_w/M_n 3.7.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu) 3.6M.

This polymer was obtained by the polymerisation **(Method A)** of monomer **(26)** (0.85g, 1.8 mmoles) and benzoyl peroxide (1.8mg, 0.01eq.) in sodium dried toluene (0.5 ml, 3.6M). Yield 643mg (76 %); $[\alpha]^{26}_{D}$ +33.7 (c = 1.2, $CHCl_3$); GPC (THF) M_n 3,625, M_w 12,750, M_w/M_n 3.5. υ_{max}, δ_H and δ_C data same as for the previous experiment.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate)

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu) **(Method C)** (324mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate) as a white solid. Yield 301mg (97 %); $[\alpha]^{28}_{D}$ +19.2 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3434 (br), 3077 (br), 1700 (br), 1571 (s), 1456 (s) and 1194 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.2 (6H, brm, C$\underline{H}_2$+C$\underline{H}_3$), 2.8-2.9 (1H, brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (1H, brd, 1x C$\underline{H}_2$Ph), 3.9-4.3 (3H, brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.7 (1H, brs, Phe-α-C$\underline{H}$), 7.0-7.4 (6H, brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.2-8.6 (3H, brs, N$\underline{H}_3$), 8.7-9.1 (1H, brs, CO$_2$$\underline{H}$); δ_C (DMSO-d_6) 18.8 (C$\underline{H}_3$),

36.6 ($\underline{C}H_2Ph$), 44.2 ($\underline{C}CH_3$), 51.3 ($CO_2\underline{C}H_3$), 54.1 (2x α-$\underline{C}H$), 64.2 ($\underline{C}H_2O$), 116.1 (q *J* 296Hz, $\underline{C}F_3CO_2$), 126.7 (Ar$\underline{C}H$), 128.3 (Ar$\underline{C}H$), 129.4 (Ar$\underline{C}H$), 136.9 (Ar *ipso*$\underline{C}$), 158.7 (q *J* 32Hz, $CF_3\underline{C}O_2$), 165.6 ($\underline{C}ONH$), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu) 4M DMF.

This polymer was obtained by the polymerisation **(Method A)** of monomer **(26)** (320mg, 0.7 mmoles) and benzoyl peroxide (2.0mg, 0.01eq.) in anhydrous DMF (0.2 ml, 4.0M). Yield 227mg (71 %); $[\alpha]^{26}_D$ +26.4 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3413 (br), 3331 (br), 3013 (s), 2966 (s), 2931 (m), 1726 (s), 1673 (s), 1514 (s), 1496 (m), 1450 (m), 1390 (s), 1361 (s), 1214 (s) and 1155 cm^{-1} (s); δ_H 0.8-1.6 (23H, brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$), 2.9-3.2 (2H, brs, $C\underline{H}_2Ph$), 4.0-4.6 (3H, brm, α-$C\underline{H}$+β-$C\underline{H}_2O$), 4.6-4.8 (1H, brs, Phe-α-$C\underline{H}$), 7.0-7.3 (6H, brm, Ar$C\underline{H}$ + CON$\underline{H}$); δ_C 20.3 ($\underline{C}H_3$), 27.9 ($C(\underline{C}H_3)_3$), 28.4 ($C(\underline{C}H_3)_3$), 38.2 ($\underline{C}H_2Ph$), 45.0 ($\underline{C}CH_3$), 53.8 (α-$\underline{C}H$), 54.1 (α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 80.0 ($\underline{C}(CH_3)_3$), 82.0 ($\underline{C}(CH_3)_3$), 126.9 (Ar$\underline{C}H$), 128.3 (Ar$\underline{C}H$), 129.6 (Ar$\underline{C}H$), 136.3 (Ar *ipso*$\underline{C}$), 156.3 ($N\underline{C}O_2$), 169.9 ($\underline{C}ONH$), 170.1 ($\underline{C}O_2$), 176.6 ($\underline{C}O_2$); GPC (THF) M_n 6,220, M_w 20,850, M_w/M_n 3.4.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 7.3:2.7

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.4g, 0.9 mmoles, 1.6eq.), methyl methacrylate (0.06 ml, 0.6 mmoles, 1.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in sodium dried toluene (1.0 ml, 0.9M). Yield 0.3g (63 %); $[\alpha]^{31}_D$ +24.0 (c = 0.6, $CHCl_3$); υ_{max} 3346 (br), 3017 (s), 2997 (m), 1725 (s), 1508 (s), 1368 (s), 1218 (s) and 1156 cm^{-1} (s); δ_H 0.5-1.8 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$), 2.8-2.9 (brs, $C\underline{H}_2Ph$), 3.2-3.4 (brs, $CO_2C\underline{H}_3$), 3.8-4.1 (brm, α-$C\underline{H}$+β-$C\underline{H}_2O$), 4.4-4.6 (brs, Phe-α-$C\underline{H}$), 6.8-7.1 (brm, Ar$C\underline{H}$+N$\underline{H}$CO); δ_C 18.7 ($\underline{C}H_3$), 27.9 ($C(\underline{C}H_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 38.3 ($\underline{C}H_2Ph$), 44.8 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 51.8 ($O\underline{C}H_3$), 53.8 (α-$\underline{C}H$), 54.2 (α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 80.1 ($\underline{C}(CH_3)_3$), 82.1 ($\underline{C}(CH_3)_3$), 126.9 (Ar$\underline{C}H$), 128.3 (Ar$\underline{C}H$), 129.5 (Ar$\underline{C}H$), 136.2 (Ar *ipso*$\underline{C}$), 155.6 ($N\underline{C}O_2$), 168.9 ($\underline{C}ONH$), 170.1 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$); GPC (THF) M_n 8,225, M_w 39,400, M_w/M_n 4.8.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 7.3:2.7

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 7.3:2.7 **(Method C)** (90mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 7.3:2.7 as a white solid. Yield 54mg (61 %); $[\alpha]^{28}_{D}$ +23.7 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3454 (br), 3216 (br), 3078 (br), 2954 (s), 1730 (s), 1682 (s), 1542 (m), 1454 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.1 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 2.8-3.0 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.6 (brs, CO$_2$C$\underline{H}_3$), 3.9-4.3 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.6 (brs, α-C$\underline{H}$), 6.9-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.1-8.6 (brs, N$\underline{H}_3$), 8.7-9.0 (brs, CO$_2\underline{H}$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 2:3

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (1.0g, 2.0 mmoles, 1.0eq.), methyl methacrylate (0.55 ml, 5.2 mmoles, 2.5eq.) and benzoyl peroxide (19mg, 0.01eq.) in sodium dried toluene (1.0 ml, 4.7M). Yield 1.1g (69 %); $[\alpha]^{30}_{D}$ +21.5 (c = 0.6, CHCl$_3$); υ_{max} 3344 (br), 2980 (s), 2950 (s), 1731 (s), 1677 (s), 1508 (s), 1497 (s), 1455 (s), 1392 (s), 1368 (s), 1247 (s) and 1156 cm^{-1} (s); δ_H 0.7-2.1 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.9-3.1 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, CO$_2$C$\underline{H}_3$), 4.0-4.2 (brs, β-C$\underline{H}_2$O), 4.3-4.5 (brs, α-C$\underline{H}$), 4.6-4.7 (brs, Phe-α-C$\underline{H}$), 6.9-7.4 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.8 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 19.4 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 38.2 (C$\underline{H}_2$Ph), 44.6 (C$\underline{C}$H$_3$), 44.9 (C$\underline{C}$H$_3$), 51.8 (OC$\underline{H}_3$), 53.8 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 80.2 (C(CH$_3$)$_3$), 82.2 (C(CH$_3$)$_3$), 126.9 (ArCH), 128.3 (ArCH), 129.5 (ArCH), 136.2 (Ar *ipso*C), 155.6 (NCO$_2$), 168.8 (CONH), 170.0 (CO$_2$), 176.8 (CO$_2$), 177.8 (CO$_2$); GPC (THF) M_n 9,045, M_w 73,100, M_w/M_n 8.1.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 2:3.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 2:3 **(Method C)** (0.5g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 2:3 as a white solid. Yield 504mg (99 %); $[\alpha]^{28}_{D}$ +27.3 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 2.8-3.1 (brs, C$\underline{H}_2$Ph), 3.3-3.7 (brs, CO$_2$C$\underline{H}_3$), 4.0-4.3 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.7 (brs, α-C$\underline{H}$), 7.1-7.5 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.4-8.7 (brs, N$\underline{H}_3$), 8.8-9.2 (brs, CO$_2\underline{H}$); δ_C (DMSO-d_6) 16.3 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 36.7 (C$\underline{H}_2$Ph), 43.9 (C$\underline{C}$H$_3$), 44.4 (C$\underline{C}$H$_3$), 51.8 (CO$_2$C$\underline{H}_3$), 53.8 (1x α-C$\underline{H}$), 54.1 (1x α-C$\underline{H}$), 64.4 (C$\underline{H}_2$O), 116.2 (q *J* 296Hz, C$\underline{F}_3$CO$_2$), 126.8 (ArC$\underline{H}$), 128.4 (ArC$\underline{H}$), 129.5 (ArC$\underline{H}$), 136.9 (Ar *ipso*C), 158.6 (q *J* 32Hz, CF$_3$C$\underline{O}_2$), 165.8 (C$\underline{O}$NH), 171.8 (C$\underline{O}_2$), 176.6 (C$\underline{O}_2$), 177.4 (C$\underline{O}_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 5.6:4.4

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.5g, 1.0 mmoles, 1.0eq.), methyl methacrylate (0.14 ml, 1.3 mmoles, 1.3eq.) and benzoyl peroxide (6mg, 0.01eq.) in sodium dried toluene (1.0 ml, 2.0M). Yield 0.4g (60 %); $[\alpha]^{31}_{D}$ +23.6 (c = 0.6, CHCl$_3$); υ_{max} 3345 (br), 2980 (s), 1729 (s), 1677 (s), 1508 (s), 1457 (m), 1392 (m), 1368 (m), 1247 (s) and 1156 cm^{-1} (s); δ_H 0.7-2.1 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.9-3.1 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, CO$_2$C$\underline{H}_3$), 3.9-4.2 (brs, β-C$\underline{H}_2$O), 4.3-4.5 (brs, α-C$\underline{H}$), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.8 (C$\underline{H}_2$), 18.8 (C$\underline{H}_3$), 19.0 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 38.3 (C$\underline{H}_2$Ph), 44.6 (C$\underline{C}$H$_3$), 51.8 (OC$\underline{H}_3$), 53.9 (2x α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 80.2 (C$\underline{(}$CH$_3$)$_3$), 82.1 (C$\underline{(}$CH$_3$)$_3$), 126.9 (ArC$\underline{H}$), 128.3 (ArC$\underline{H}$), 129.5 (ArC$\underline{H}$), 136.2 (Ar *ipso*C), 155.5 (NC$\underline{O}_2$), 168.9 (C$\underline{O}$NH), 170.0 (C$\underline{O}_2$), 176.8 (C$\underline{O}_2$), 177.8 (C$\underline{O}_2$); GPC (THF) M_n 9,060, M_w 32,950, M_w/M_n 3.6.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 5.6:4.4.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 5.6:4.4 **(Method C)** (127mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 5.6:4.4 as a white solid. Yield 110mg (87 %); $[\alpha]^{28}_{D}$ +26.6 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3454 (br), 3216 (br), 3078 (br), 2954 (s), 1730 (s), 1682 (s), 1542 (m), 1454 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.4-2.1 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 2.7-2.9 (brd, 1x C$\underline{H}_2$Ph), 2.95-3.1 (brd, 1x C$\underline{H}_2$Ph), 3.3-3.5 (brs, $CO_2C\underline{H}_3$), 3.7-4.3 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.3-4.6 (brs, α-C$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.2-8.6 (brs, N$\underline{H}_3$), 8.7-9.0 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 18.7 ($\underline{C}H_3$), 38.5 ($\underline{C}H_2$Ph), 44.2 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 51.8 ($CO_2\underline{C}H_3$), 53.7 (α-$\underline{C}$H), 54.0 (α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.9 (Ar *ipso*$\underline{C}$), 165.6 ($\underline{C}$ONH), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1.5:8.5

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.15g, 0.3 mmoles, 1.0eq.), methyl methacrylate (0.34 ml, 3.2 mmoles, 10.0eq.) and benzoyl peroxide (15mg, 0.01eq.) in sodium dried toluene (0.8 ml, 1.9M). Yield 0.4g (80 %); $[\alpha]^{31}_{D}$ +13.5 (c = 0.6, $CHCl_3$); υ_{max} 3344 (br), 2980 (s), 1730 (s), 1677 (s), 1508 (m), 1491 (m), 1455 (m), 1392 (m), 1368 (m), 1246 (s) and 1155 cm^{-1} (s); δ_H 0.7-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.2 (brs, β-C$\underline{H}_2$O), 4.3-4.5 (brs, α-C$\underline{H}$), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 6.9-7.4 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.3 ($\underline{C}H_2$), 18.6 ($\underline{C}H_3$), 19.4 ($\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.2 (C($\underline{C}H_3$)$_3$), 38.4 ($\underline{C}H_2$Ph), 41.3 ($\underline{C}CH_3$), 44.5 ($\underline{C}CH_3$), 51.7 ($O\underline{C}H_3$), 53.7 (α-$\underline{C}$H), 54.4 (α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 80.4 ($\underline{C}(CH_3)_3$), 82.3 ($\underline{C}(CH_3)_3$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.5 (Ar$\underline{C}$H), 136.1 (Ar *ipso*$\underline{C}$), 155.5 ($N\underline{C}O_2$), 168.9 ($\underline{C}$ONH), 170.0 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 9,800, M_w 33,650, M_w/M_n 3.4.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 1.5:8.5.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 1.5:8.5 **(Method C)** (107mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 1.5:8.5 as a white solid. Yield 102mg (96 %); $[\alpha]^{28}_{D}$ +19.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3452 (br), 3310 (br), 3214 (br), 3048 (br), 2998 (s), 2953 (s), 1730 (s), 1702 (brs), 1543 (s), 1490 (s), 1483 (s), 1438 (s), 1364 (s), 1268 (s), 1232 (s), 1202 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.8-2.2 (brm, C$\underline{H}_2$+C$\underline{H}_3$), 2.7-2.8 (brd, 1x C$\underline{H}_2$Ph), 2.9-3.0 (brd, 1x C$\underline{H}_2$Ph), 3.1-3.7 (brs, $CO_2C\underline{H}_3$), 3.8-4.3 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.3-4.5 (brs, Phe-α-C$\underline{H}$), 6.9-7.2 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.2-8.5 (brs, N$\underline{H}_3$), 8.6-8.9 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 18.8 ($\underline{C}H_3$), 36.6 ($\underline{C}H_2$Ph), 44.2 ($\underline{C}CH_3$), 51.9 ($CO_2\underline{C}H_3$), 54.1 (2x α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 126.7 (Ar$\underline{C}$H), 128.5 (Ar$\underline{C}$H), 129.6 (Ar$\underline{C}$H), 137.0 (Ar *ipso*$\underline{C}$), 165.6 ($\underline{C}$ONH), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1:9

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.3g, 0.6 mmoles, 1.0eq.), methyl methacrylate (0.7 ml, 7.6 mmoles, 12.0eq.) and benzoyl peroxide (17mg, 0.01eq.) in sodium dried toluene (0.4 ml, 7.0M). Yield 0.83g (82 %); $[\alpha]^{31}_{D}$ +10.6 (c = 0.6, $CHCl_3$); υ_{max} 3344 (br), 2981 (m), 2950 (m), 1734 (s), 1677 (m), 1508 (w), 1490 (m), 1455 (m), 1392 (m), 1368 (m), 1246 (m) and 1155 cm^{-1} (s); δ_H 0.7-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.2 (brs, β-C$\underline{H}_2$O), 4.3-4.5 (brs, α-C$\underline{H}$), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 6.9-7.4 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.4 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.2 (C($\underline{C}H_3$)$_3$), 38.4 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 51.8 ($O\underline{C}H_3$), 53.8 (α-$\underline{C}$H), 54.5 (α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 80.4 ($\underline{C}(CH_3)_3$), 82.2 ($\underline{C}(CH_3)_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.5 (Ar$\underline{C}$H), 136.2 (Ar *ipso*$\underline{C}$), 155.6 ($N\underline{C}O_2$), 168.9 ($\underline{C}$ONH), 170.0 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$); GPC (THF) M_n 10,105, M_w 47,150, M_w/M_n 4.7.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1:13

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.3g, 0.6 mmoles, 1.0eq.), methyl methacrylate (1.35 ml, 12.6 mmoles, 20.0eq.) and benzoyl peroxide (32mg, 0.01eq.) in sodium dried toluene (0.3 ml, 7.8M). Yield 1.1g (66 %); $[\alpha]^{31}_{D}$ +8.0 (c = 0.6, $CHCl_3$); υ_{max} 3345 (br), 2994 (m), 2950 (m), 1730 (s), 1677 (m), 1508 (w), 1486 (m), 1450 (m), 1392 (w), 1368 (w), 1273 (m), 1243 (m), 1192 (s) and 1152 cm^{-1} (s); δ_H 0.7-1.6 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$), 1.7-2.1 (brs, C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.2 (brs, β-C$\underline{H}_2$O), 4.3-4.5 (brs, α-C$\underline{H}$), 4.6-4.8 (brs, Phe-α-C$\underline{H}$), 7.1-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 16.4 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.2 (C($\underline{C}H_3$)$_3$), 38.3 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 51.7 (O$\underline{C}H_3$), 53.4 (α-$\underline{C}$H), 54.4 (α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 82.1 ($\underline{C}(CH_3)_3$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.5 (Ar$\underline{C}$H), 136.2 (Ar *ipso*$\underline{C}$), 155.6 (N$\underline{C}O_2$), 168.9 ($\underline{C}$ONH), 170.0 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 8,735, M_w 33,950, M_w/M_n 3.9.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 1:13.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 1:13 **(Method C)** (0.4g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 1:13 as a white solid. Yield 304mg (78 %); $[\alpha]^{28}_{D}$ +9.5 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3549 (br), 3226 (br), 2998 (s), 2954 (s), 1732 (s), 1622 (w), 1524 (w), 1484 (s), 1451 (s), 1389 (m), 1370 (m), 1268 (s), 1244 (s), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-1.2 (brm, C$\underline{H}_2$), 1.3-1.4 (brs, C$\underline{H}_2$), 1.6-2.4 (brs, C$\underline{H}_3$), 2.8-3.1 (brs, C$\underline{H}_2$Ph), 3.3-4.0 (brs, $CO_2C\underline{H}_3$), 4.1-4.4 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.7 (brs, Phe-α-C$\underline{H}$), 7.1-7.4 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.4-8.7 (brs, N$\underline{H}_3$), 8.8-9.0 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.3 ($\underline{C}H_2$), 18.5 ($\underline{C}H_3$), 38.6 ($\underline{C}H_2$Ph), 43.9 ($\underline{C}CH_3$), 44.3 ($\underline{C}CH_3$), 51.8 ($CO_2\underline{C}H_3$), 53.7 (2x α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 126.8 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.6 (Ar *ipso*$\underline{C}$), 165.6 ($\underline{C}$ONH), 172.0 ($\underline{C}O_2$), 176.3 ($\underline{C}O_2$), 177.2 ($\underline{C}O_2$), 177.4 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 9.5:0.5

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.8g, 1.7 mmoles, 9.0eq.), methyl methacrylate (0.02 ml, 0.2 mmoles, 1.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in sodium dried toluene (0.75 ml, 2.5M). Yield 0.7g (83 %); $[\alpha]^{31}_{D}$ +25.2 ($CHCl_3$); υ_{max} 3343 (br), 2979 (s), 2950 (s), 1730 (s), 1677 (s), 1522 (s), 1456 (m), 1392 (m), 1368 (s), 1249 (s) and 1158 cm^{-1} (s); δ_H 0.7-1.9 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.7-3.0 (brs, C$\underline{H}_2$Ph), 3.2-3.4 (brs, $CO_2C\underline{H}_3$), 3.7-4.3 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.7 (brs, Phe-α-C$\underline{H}$), 6.8-7.3 (brm, ArC$\underline{H}$+N$\underline{H}$CO); δ_C 18.7 (C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.4 (C(C$\underline{H}_3$)$_3$), 38.1 (C$\underline{H}_2$Ph), 44.9 (C$\underline{C}$H$_3$), 51.7 (OC$\underline{H}_3$), 53.9 (α-C$\underline{H}$), 54.0 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 80.2 (C(CH$_3$)$_3$), 82.1 (C(CH$_3$)$_3$), 127.0 (ArC$\underline{H}$), 128.4 (ArC$\underline{H}$), 129.6 (ArC$\underline{H}$), 136.3 (Ar *ipso*C), 156.4 (N$\underline{C}O_2$), 169.1 (C$\underline{O}$NH), 170.2 ($\underline{C}O_2$), 177.1 ($\underline{C}O_2$); GPC (THF) M_n 6,780, M_w 40,550, M_w/M_n 6.0.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 9.5:0.5.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 9.5:0.5 **(Method C)** (220mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 9.5:0.5 as a white solid. Yield 0.2g (93 %); $[\alpha]^{28}_{D}$ +19.9 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3452 (br), 3214 (br), 3082 (br), 2929 (s), 1732 (s), 1678 (s), 1549 (m), 1451 (m), 1202 (s) and 1140 cm^{-1} (s); δ_H (DMSO-d_6) 0.4-1.9 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 2.8-2.9 (brd, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 4.0-5.2 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 6.9-7.4 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.1-8.7 (brs, N$\underline{H}_3$), 8.8-9.0 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 18.5 (C$\underline{H}_3$), 38.6 (C$\underline{H}_2$Ph), 44.2 (C$\underline{C}$H$_3$), 51.8 ($CO_2C\underline{H}_3$), 53.7 (1x α-C$\underline{H}$), 54.0 (1x α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 126.8 (ArC$\underline{H}$), 128.3 (ArC$\underline{H}$), 129.4 (ArC$\underline{H}$), 136.9 (Ar *ipso*C), 165.6 (C$\underline{O}$NH), 172.0 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 8.4:1.6

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.3g, 0.7 mmoles, 8.0eq.), methyl methacrylate (0.02 ml, 0.2 mmoles, 2.0eq.) and

benzoyl peroxide (2mg, 0.01eq.) in sodium dried toluene (0.3 ml, 3M). Yield 0.25g (74 %); $[\alpha]^{31}_{D}$ +24.6 (c = 0.8, $CHCl_3$); υ_{max} 3344 (br), 2978 (s), 1730 (s), 1677 (s), 1520 (s), 1455 (m), 1392 (m), 1368 (s), 1250 (s) and 1156 cm^{-1} (s); δ_H 0.7-1.9 (brm, C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 2.7-3.0 (brs, C<u>H</u>$_2$Ph), 3.2-3.4 (brs, $CO_2C\underline{H}_3$), 3.8-4.4 (brm, α-C<u>H</u> + β-C<u>H</u>$_2$O), 4.4-4.7 (brs, Phe-α-C<u>H</u>), 6.9-7.3 (brm, ArC<u>H</u>+N<u>H</u>CO); δ_C 18.7 (<u>C</u>H$_3$), 27.9 (C(<u>C</u>H$_3$)$_3$), 28.3 (C(<u>C</u>H$_3$)$_3$), 38.1 (<u>C</u>H$_2$Ph), 44.9 (<u>C</u>CH$_3$), 51.7 (O<u>C</u>H$_3$), 53.9 (α-<u>C</u>H), 54.0 (α-<u>C</u>H), 64.2 (<u>C</u>H$_2$O), 80.2 (<u>C</u>(CH$_3$)$_3$), 82.1 (<u>C</u>(CH$_3$)$_3$), 126.9 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.6 (Ar<u>C</u>H), 136.2 (Ar *ipso*<u>C</u>), 156.4 (N<u>C</u>O$_2$), 169.1 (<u>C</u>ONH), 170.2 (<u>C</u>O$_2$), 177.1 (<u>C</u>O$_2$); GPC (THF) M_n 7,030, M_w 38,150, M_w/M_n 5.4.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 3:7.

This polymer was obtained by the polymerisation **(Method B)** of monomer **(26)** (0.15g, 0.3 mmoles, 1.0eq.), methyl methacrylate (0.17 ml, 1.6 mmoles, 5.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in sodium dried toluene (0.6 ml, 3M). Yield 0.2g (55 %); $[\alpha]^{28}_{D}$ +19.4 (c = 0.8, $CHCl_3$); υ_{max} 3414 (br), 3345 (br), 3019 (s), 2983 (s), 1728 (s), 1677 (s), 1514 (s), 1456 (s), 1393 (m), 1369 (s), 1215 (s) and 1155 cm^{-1} (s); δ_H 0.7-1.1 (brm, C<u>H</u>$_2$), 1.2-1.3 (brs, 1x C(C<u>H</u>$_3$)$_3$), 1.3-1.4 (brs, 1x C(C<u>H</u>$_3$)$_3$), 1.6-2.5 (brm, C<u>H</u>$_2$ + C<u>H</u>$_3$), 2.9-3.1 (brs, C<u>H</u>$_2$Ph), 3.3-3.6 (brs, $CO_2C\underline{H}_3$), 3.9-4.2 (brs, β-C<u>H</u>$_2$O), 4.2-4.4 (brs, α-C<u>H</u>), 4.6-4.7 (brs, Phe-α-C<u>H</u>), 6.9-7.3 (brm, ArC<u>H</u>+N<u>H</u>CO); δ_C 16.5 (<u>C</u>H$_2$), 18.7 (<u>C</u>H$_3$), 27.9 (C(<u>C</u>H$_3$)$_3$), 28.2 (C(<u>C</u>H$_3$)$_3$), 38.3 (<u>C</u>H$_2$Ph), 44.5 (<u>C</u>CH$_3$), 44.9 (<u>C</u>CH$_3$), 51.8 (O<u>C</u>H$_3$), 53.9 (α-<u>C</u>H), 54.4 (α-<u>C</u>H), 64.3 (<u>C</u>H$_2$O), 80.4 (<u>C</u>(CH$_3$)$_3$), 82.3 (<u>C</u>(CH$_3$)$_3$), 127.0 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.5 (Ar<u>C</u>H), 136.2 (Ar *ipso*<u>C</u>), 156.4 (N<u>C</u>O$_2$), 169.1 (<u>C</u>ONH), 170.0 (<u>C</u>O$_2$), 177.0 (<u>C</u>O$_2$) 177.8 (<u>C</u>O$_2$), 178.0 (<u>C</u>O$_2$); GPC (THF) M_n 8,735, M_w 33,950, M_w/M_n 3.9.

Poly(O-methacryloyl-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 3:7.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 3:7 **(Method C)** (170mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 3:7 as a white solid. Yield 164mg (97 %); $[\alpha]^{28}_{D}$ +26.4 (c = 0.5, DMSO :

AcCN 1:1); υ_{max} (KBr) 3452 (br), 3310 (br), 3214 (br), 3048 (br), 2998 (s), 2953 (s), 1730 (s), 1702 (brs), 1543 (s), 1490 (s), 1483 (s), 1438 (s), 1364 (s), 1268 (s), 1232 (s), 1202 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.8-2.2 (brm, C$\underline{H}_2$+C$\underline{H}_3$), 3.1-3.2 (brd, 1x C$\underline{H}_2$Ph), 3.3-3.4 (brd, 1x C$\underline{H}_2$Ph), 3.5-3.7 (brs, $CO_2C\underline{H}_3$), 3.8-4.5 (brm, α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.7-4.8 (brs, Phe-α-C$\underline{H}$), 7.3-7.5 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.5-8.8 (brs, N$\underline{H}_3$), 8.9-9.1 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 18.8 ($\underline{C}H_3$), 37.6 ($\underline{C}H_2$Ph), 44.2 ($\underline{C}CH_3$), 51.8 ($CO_2\underline{C}H_3$), 54.1 (2x α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 126.8 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.6 (Ar$\underline{C}$H), 136.9 (Ar *ipso*$\underline{C}$), 165.6 ($\underline{C}$ONH), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$).

N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu ***(33)***.

To a solution of *N*-Boc-(*S*)-serine **(14)** (4.6g, 22.4 mmoles, 1.3eq.) in glass distilled DMF (50 ml) was added DCC (3.6g, 17.2 mmoles, 1.0eq.), HOBt (3.7g, 27.5 mmoles, 1.6eq.) and (*S*)-Pro-O^{t}Bu **(32)** (2.9g, 17.2 mmoles, 1.0eq.). The mixture was stirred at room temperature for 48 hours after which the solvent was removed *in vacuo* and ethyl acetate (100 ml) was added to the yellow oil residue. Filtration through celite removed a white solid (DCHU) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). The aqueous layer was back extracted with ethyl acetate (2x 15 ml) and the combined organic layers were subsequently washed with sat. Na_2CO_3 (3x 25 ml), water (3x 25 ml), 2M HCl (2x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to provide the title compound as a yellow foaming oil. Yield 5.4g (87 %); R_f ethyl acetate : light petrol (1.5:8.5) 0.43 (PMA); $[\alpha]^{28}_D$ -4.6 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3386 (br), 2977 (s), 1719 (s), 1639 (s), 1500 (m), 1450 (s), 1367 (s), 1251 (s), 1158 (s) and 1060 cm^{-1} (w); δ_H 1.42 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.45 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.90-2.10 (3H, brm, Pro-γ-C$\underline{H}_2$ + O$\underline{H}$), 2.20-2.40 (2H, brm, Pro-β-C$\underline{H}_2$), 3.60-3.80 (2H, brm, Pro-NC$\underline{H}_2$), 3.90 (1H, dd *J* 4.6, 11.3Hz, 1x β-C$\underline{H}_2$O), 4.06 (1H, dd *J* 12.0, 17.6Hz, Pro-α-C$\underline{H}$), 4.47 (1H, dd *J* 4.5, 4.6Hz, 1x β-C$\underline{H}_2$O), 4.60 (1H, brs, Ser-α-C$\underline{H}$), 5.53 (1H, brd *J* 8.3, Boc-N$\underline{H}$); δ_C 24.8 (Pro-γ-$\underline{C}H_2$), 27.9 (1x C($\underline{C}H_3$)$_3$), 28.3 (1x C($\underline{C}H_3$)$_3$), 29.0 (Pro-β-$\underline{C}H_2$), 47.1 (N$\underline{C}H_2$), 51.4 (Pro-α-$\underline{C}$H), 59.8 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 79.8 ($\underline{C}$(CH$_3$)$_3$), 81.4 ($\underline{C}$(CH$_3$)$_3$),

155.3 (N<u>C</u>O$_2$), 167.5 (<u>C</u>O$_2$), 170.6 (N<u>C</u>O); m/z (CI) 359 (MH^+); Found 359.2182 ($C_{17}H_{31}N_2O_6$ requires 359.2182).

O-Acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu ***(34)***.

To a solution of *N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu **(33)** (3.0g, 8.4 mmoles, 1.0eq.) in ethyl acetate (40 ml) was added triethylamine (3.5 ml, 25.1 mmoles, 3.0eq.). The solution was cooled to 0 °C and acryloyl chloride (1.0 ml, 12.6 mmoles, 1.5eq.) was added dropwise *via* a syringe. Subsequently the solution was warmed to room temperature and stirred for a further 20 hours. Filtration through celite removed a white solid (triethylamine hydrochloride). The filtrate was subsequently washed with sat. Na_2CO_3 (2x 25 ml) and the aqueous layer back extracted with ethyl acetate (2x 15 ml). The combined organic layers were washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (3x 25 ml) and water (2x 25 ml). Subsequently the organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to afford a yellow foaming oil. Flash chromatography, eluting with ethyl acetate : light petroleum (3:7) afforded the title compound as a colourless foaming oil. Yield 3.1g (89 %); R_f Ethyl acetate : light petrol (3 : 7) 0.43 (PMA); $[\alpha]^{28}_D$ -21.4 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3404 (br), 3344 (br), 2977 (s), 2933 (s), 1729 (s), 1649 (s), 1502 (m), 1439 (s), 1408 (s), 1392 (m), 1368 (s), 1252 (s), 1162 (s) and 1065 cm^{-1} (m); δ_H 1.31 (9H, s, 1x C(C<u>H</u>$_3$)$_3$), 1.33 (9H, s, 1x C(C<u>H</u>$_3$)$_3$), 1.80-2.10 (4H, brm, Pro-β-C<u>H</u>$_2$ + γ-C<u>H</u>$_2$), 3.50-3.70 (2H, brm, Pro-NC<u>H</u>$_2$), 4.02 (1H, dd *J* 8.1, 11.2Hz, 1x β-C<u>H</u>$_2$O), 4.31 (1H, dd *J* 4.1, 4.4Hz, Pro-α-C<u>H</u>), 4.40 (1H, dd *J* 4.3, 11.2Hz, 1x β-C<u>H</u>$_2$O), 4.71 (1H, ddd *J* 4.2, 8.5, 8.2Hz, Ser-α-C<u>H</u>), 5.48 (1H, brd *J* 8.6, Boc-N<u>H</u>), 5.75 (1H, d *J* 10.3Hz, 1x =C<u>H</u>$_2$), 6.01 (1H, dd *J* 10.4, 17.3Hz, =C<u>H</u>), 6.34 (1H, d *J* 17.2Hz, 1x =C<u>H</u>$_2$); δ_C 24.8 (Pro-γ-<u>C</u>H$_2$), 27.9 (1x C(<u>C</u>H$_3$)$_3$), 28.3 (1x C(<u>C</u>H$_3$)$_3$), 29.0 (Pro-β-<u>C</u>H$_2$), 47.1 (N<u>C</u>H$_2$), 51.4 (Pro-α-<u>C</u>H), 59.8 (Ser-α-<u>C</u>H), 64.2 (<u>C</u>H$_2$O), 79.8 (<u>C</u>(CH$_3$)$_3$), 81.4 (<u>C</u>(CH$_3$)$_3$), 128.0 (=<u>C</u>H$_2$), 131.4 (=<u>C</u>H), 155.3 (N<u>C</u>O$_2$), 165.9 (=CH<u>C</u>O$_2$), 167.5 (<u>C</u>O$_2$), 170.6 (N<u>C</u>O); m/z (CI) 413 (MH^+); Found 413.2288 ($C_{20}H_{33}N_2O_7$ requires 413.2288).

O-Methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu ***(35)***.

To a solution of *N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu **(33)** (9.0g, 25.1 mmoles, 1.0eq.) in ethyl acetate (75 ml), cooled with ice was added triethylamine (10.5 ml, 75.4 mmoles, 3.0eq.). After stirring at 0 °C for 5 minutes, methacryloyl chloride (3.7 ml, 37.7 mmoles, 1.5eq.) was added dropwise *via* a syringe. Subsequently the solution was allowed to warm to room temperature then stirred for a further 22 hours. The reaction mixture was filtered to remove a white solid (triethylamine hydrochloride) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). Subsequently the aqueous layer was back extracted with ethyl acetate (2x 15 ml). The combined organic layers were then washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (3x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$) and the solvent removed *in vacuo* to leave a yellow foaming oil. Flash chromatography, eluting with ethyl acetate : light petroleum (2:8) afforded the title compound as a colourless foaming oil. Yield 8.86g (81 %); R_f Ethyl acetate : light petroleum (2:8) 0.41; $[\alpha]^{25}_D$ -28.4; Found C, 59.4; H, 7.9; N, 6.2. $C_{21}H_{34}N_2O_7$ requires C, 59.1; H, 8.0; N, 6.6 %; υ_{max} ($CHCl_3$) 3426 (br), 2977 (s), 1736 (s), 1648 (s), 1508 (m), 1448 (s), 1392 (m), 1368 (s), 1249 (s), 1155 (s) and 1056 cm^{-1} (w); δ_H 1.40 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.42 (9H, s, 1x C(C$\underline{H}_3$)$_3$), 1.93 (3H, s, =CC$\underline{H}_3$), 2.00-2.30 (4H, brm, Pro-β-C$\underline{H}_2$ + γ-C$\underline{H}_2$), 3.60-3.80 (2H, brm, Pro-NC$\underline{H}_2$), 4.06 (1H, dd *J* 8.0, 11.3Hz, 1x β-C$\underline{H}_2$O), 4.40 (1H, dd *J* 4.2, 4.25Hz, Pro-α-C$\underline{H}$), 4.56 (1H, dd *J* 4.0, 11.5Hz, 1x β-C$\underline{H}_2$O), 4.82 (1H, dd *J* 4.3, 8.25Hz, Ser-α-C$\underline{H}$), 5.47 (1H, brd *J* 10.1Hz, Boc-N$\underline{H}$), 5.57 (1H, s, 1x =C$\underline{H}_2$), 6.14 (1H, s, 1x =C$\underline{H}_2$); δ_C 18.2 (=C$\underline{C}$H$_3$), 24.8 (Pro-γ-$\underline{C}$H$_2$), 27.9 (1x C($\underline{C}$H$_3$)$_3$), 28.2 (1x C($\underline{C}$H$_3$)$_3$), 28.9 (Pro-β-$\underline{C}$H$_2$), 47.1 (N$\underline{C}$H$_2$), 51.4 (Pro-α-$\underline{C}$H), 59.8 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}$H$_2$O), 79.7 ($\underline{C}$(CH$_3$)$_3$), 81.3 ($\underline{C}$(CH$_3$)$_3$), 126.2 (=$\underline{C}$H$_2$), 135.8 (=$\underline{C}$CH$_3$), 155.2 (N$\underline{C}$O$_2$), 167.2 ($\underline{C}$O$_2$), 167.4 ($\underline{C}$O$_2$), 170.5 (N$\underline{C}$O); m/z (CI) 427 (MH^+); Found 427.2444 ($C_{21}H_{35}N_2O_7$ requires 427.2444).

Homopolymerisations, Method D

The amino acid monomer **(34)** or **(35)** was suspended in toluene to form a 2.2M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling at 273 K and then heated to reflux at 388 K under a nitrogen atmosphere. Heating was continued for 4 hours, after which time the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 100 ml). The precipitated white solid was collected by filtration and dried *in vacuo* for 5 hours.

Copolymerisations, Method E

The amino acid derived monomer **(34)** or **(35)** was suspended in freshly distilled methyl methacrylate and toluene to form a 1.5M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling to 273 K and then heated to reflux at 372 K under a nitrogen atmosphere. Heating was either continued for 3 hours, or until the polymer had gelled out of solution, after which time the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 150 ml). The precipitated white solid was collected by filtration and dried *in vacuo* at 298 K for 5 hours.

Removal of the polymer protecting groups, Method F

The polymer was dissolved in CH_2Cl_2 (2 ml) and trifluoroacetic acid (2 ml) was added. The solution was stirred at room temperature for 17 hours. This was added slowly, with stirring to diethyl ether (40 ml). The precipitated white solid was collected by filtration and subsequently washed with diethyl ether (100 ml) and dried *in vacuo* at 298 K for 12 hours.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method D)** of monomer **(34)** (300mg, 0.7 mmoles) and benzoyl peroxide (3.0mg, 0.01eq.) in sodium dried toluene (0.33 ml). Yield 281mg (94 %); $[\alpha]^{26}_{D}$ -38.2 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3426 (br), 2977 (s), 2931 (m), 1736 (s), 1648 (s), 1508 (m), 1448 (m), 1392 (m), 1367 (s), 1249 (m), 1155 (s) and 1056 cm^{-1} (w); δ_H 1.1-1.5 (21H, brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$), 1.7-2.2 (4H, brm, β + γ-C$\underline{H}_2$), 3.7-3.9 (2H, brs, NC$\underline{H}_2$), 3.9-4.0 (1H, brs, Pro-α-C$\underline{H}$), 4.3-4.4 (2H, brs, β-C$\underline{H}_2$O), 4.5-4.9 (2H, brm, Ser-α-C$\underline{H}$ + Boc-N$\underline{H}$); δ_C 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 47.1 (N$\underline{C}H_2$), 51.4 (Pro-α-$\underline{C}$H), 59.8 (Ser-α-$\underline{C}$H), 64.3 ($\underline{C}H_2$O), 79.2 ($\underline{C}$(CH$_3$)$_3$), 81.2 ($\underline{C}$(CH$_3$)$_3$), 156.3 (N$\underline{C}O_2$), 169.9 (N$\underline{C}$O), 170.1 ($\underline{C}O_2$); GPC (THF) M_n 4,160, M_w 12,550, M_w/M_n 3.0.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate).

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu) **(Method F)** (190mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate) as a white solid. Yield 0.15g (85 %); $[\alpha]^{28}_{D}$ -28.3 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3452 (br), 2997 (s), 2952 (s), 1735 (s), 1719 (s), 1701 (s), 1685 (s), 1676 (s), 1654 (s), 1560 (m), 1508 (m), 1458 (m), 1214 (s) and 1108 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (3H, brm, C$\underline{H}_2$ + C$\underline{H}$), 1.5-2.4 (4H, brm, Pro-β + γ-C$\underline{H}_2$), 3.5-3.9 (2H, brm, NC$\underline{H}_2$), 4.1-4.7 (4H, brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.2 (1H, brs, N$\underline{H}_3$), 8.4-8.8 (3H, brs, CO$_2\underline{H}$); GPC (DMF) M_n 5,200, M_w 4,955,000, M_w/M_n 953.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 1:1.3.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.4g, 1.0 mmoles, 1.0eq.), methyl methacrylate (0.14 ml, 1.3 mmoles, 1.3eq.) and benzoyl peroxide (6.0mg, 0.01eq.) in sodium dried toluene (0.33 ml, 1.5M). Yield 0.38g (71 %). $[\alpha]^{26}_{D}$ -32.0 (c = 0.9, $CHCl_3$); υ_{max} ($CHCl_3$) 3427 (br), 2977 (s), 2931 (m), 1736 (s), 1648 (s), 1501 (m), 1448 (m), 1392 (m), 1367 (s), 1249 (m), 1219 (m),

1155 (s) and 1056 cm^{-1} (w); δ_H 1.2-1.7 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.8-2.5 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.7 (brm, NC$\underline{H}_2$), 3.7-3.9 ($CO_2C\underline{H}_3$), 4.3-4.5 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.9 (brm, Ser-α-C$\underline{H}$ + Boc-N$\underline{H}$); δ_C 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 29.1 (β-$\underline{C}H_2$), 47.0 (N$\underline{C}H_2$), 51.3 (Pro-α-$\underline{C}H$), 51.8 ($CO_2\underline{C}H_3$), 59.8 (Ser-α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 79.4 ($\underline{C}(CH_3)_3$), 80.8 ($\underline{C}(CH_3)_3$), 155.4 (N$\underline{C}O_2$), 167.6 (N$\underline{C}O$), 170.1 ($\underline{C}O_2$); GPC (THF) M_n 5,280, M_w 40,150, M_w/M_n 7.6.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 3.9:6.1.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.4g, 1.0 mmoles, 3.8eq.), methyl methacrylate (0.08 ml, 0.8 mmoles, 6.2eq.) and benzoyl peroxide (9mg, 0.01eq.) in sodium dried toluene (0.3 ml, 5.7M). Yield 0.3g (75 %); $[\alpha]^{26}_D$ -30.5 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3458 (br), 3356 (br), 2984 (s), 2950 (m), 1732 (s), 1654 (s), 1484 (m), 1449 (m), 1392 (m), 1368 (m), 1275 (m), 1243 (s), 1219 (s), 1152 (s) and 1062 cm^{-1} (w); δ_H 0.9-1.7 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.8-2.2 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.7-3.9 (brs, NC$\underline{H}_2$), 4.0-4.5 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.9 (brm, Ser-α-C$\underline{H}$ + Boc-N$\underline{H}$); δ_C 24.8 (γ-$\underline{C}H_2$), 28.0 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.1 (β-$\underline{C}H_2$), 47.0 (N$\underline{C}H_2$), 51.4 (Pro-α-$\underline{C}H$), 51.8 ($CO_2\underline{C}H_3$), 59.8 (Ser-α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 79.7 ($\underline{C}(CH_3)_3$), 80.8 ($\underline{C}(CH_3)_3$), 155.6 (N$\underline{C}O_2$), 167.5 (N$\underline{C}O$), 170.0 ($\underline{C}O_2$); GPC (THF) M_n 7,800, M_w 32,700, M_w/M_n 4.2.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 3.9:6.1.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 3.9:6.1 **(Method F)** (145mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 3.9:6.1 as a white solid. Yield 97mg (68 %); $[\alpha]^{28}_D$ -27.6 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3529 (br), 2958 (s), 2953 (s), 1732 (s), 1670 (s), 1457 (s), 1388 (m), 1280 (m), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + C$\underline{H}$), 1.6-2.4 (Pro-β + γ-C$\underline{H}_2$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.6 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 7.8-8.3 (brs, N$\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$).

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 4.9:5.1.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.7g, 1.7 mmoles, 1.5eq.), methyl methacrylate (0.13 ml, 1.1 mmoles, 1.0eq.) and benzoyl peroxide (16mg, 0.01eq.) in sodium dried toluene (0.5 ml, 4.4M). Yield 0.6g (74 %); $[\alpha]^{26}_{D}$ -33.1 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3427 (br), 3356 (br), 2978 (s), 2950 (m), 1736 (s), 1649 (s), 1508 (m), 1448 (s), 1392 (m), 1368 (s), 1248 (s), 1219 (s), 1157 (s) and 1056 cm^{-1} (w); δ_H 0.9-1.6 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.8-2.6 (brm, β + γ-C$\underline{H}_2$), 3.3-3.5 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brs, NC$\underline{H}_2$), 4.2-4.4 (brs, β-C$\underline{H}_2$O), 4.4-4.8 (brm, Ser-α-C$\underline{H}$ + Pro-α-C$\underline{H}$), 5.4-6.0 (brs, Boc-N$\underline{H}$); δ_C 14.3 (C$\underline{H}$), 19.4 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.8 (C(C$\underline{H}_3$)$_3$), 28.4 (C(C$\underline{H}_3$)$_3$), 29.4 (β-C$\underline{H}_2$), 41.3 (C$\underline{C}$H$_3$), 46.9 (N$\underline{C}$H$_2$), 51.8 ($CO_2C\underline{H}_3$ + Pro-α-C$\underline{H}$), 59.8 (Ser-α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 79.5 (C(CH$_3$)$_3$), 81.1 (C(CH$_3$)$_3$), 155.4 (N$\underline{C}O_2$), 167.5 (N$\underline{C}$O), 170.6 ($\underline{C}O_2$), 174.5 ($\underline{C}O_2$); GPC (THF) M_n 10,900, M_w 149,000, M_w/M_n 13.7.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 4.9:5.1.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 4.9:5.1 **(Method F)** (195mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 4.9:5.1 as a white solid. Yield 155mg (96 %); $[\alpha]^{28}_{D}$ -28.0 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3529 (br), 2958 (s), 2953 (s), 1732 (s), 1670 (s), 1457 (s), 1388 (m), 1280 (m), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 1.6-2.4 (Pro-β + γ C$\underline{H}_2$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.6 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.3 (brs, N$\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.6 (C$\underline{H}_2$), 18.9 (C$\underline{H}_3$), 24.7 (γ-C$\underline{H}_2$), 29.0 (β-C$\underline{H}_2$), 40.5 (C$\underline{C}$H$_3$), 44.0 (C$\underline{C}$H$_3$), 47.4 (N$\underline{C}$H$_2$), 51.8 ($CO_2C\underline{H}_3$), 54.7 (Pro-α-C$\underline{H}$), 58.4 (Ser-α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 165.6 (N$\underline{C}$O), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$); GPC (DMF) M_n 41,450, M_w 5,995,000, M_w/M_n 145.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 1.7:8.3.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.7g, 1.6 mmoles, 1.0eq.), methyl methacrylate (0.5 ml, 4.3 mmoles, 3.8eq.) and

benzoyl peroxide (16mg, 0.01eq.) in sodium dried toluene (0.5 ml, 5.8M). Yield 0.8g (76 %); $[\alpha]^{26}_{D}$ -19.9 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3417 (br), 3367 (br), 2981 (s), 2951 (m), 1732 (s), 1651 (s), 1508 (m), 1480 (m), 1448 (s), 1392 (m), 1368 (s), 1286 (m), 1243 (s), 1219 (s), 1194 (m), 1154 (s) and 1061 cm^{-1} (w); δ_H 0.7-1.5 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.7-2.5 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.7-4.0 (brs, NC$\underline{H}_2$), 4.1-4.4 (brs, β-C$\underline{H}_2$O), 4.4-4.8 (brm, Ser-α-C$\underline{H}$ + Pro-α-C$\underline{H}$), 5.4-5.7 (brs, Boc-N$\underline{H}$); δ_C 16.4 ($\underline{C}$H), 17.7 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 28.8 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 54.3 (Pro-α-$\underline{C}$H), 59.7 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 79.6 ($\underline{C}(CH_3)_3$), 80.9 ($\underline{C}(CH_3)_3$), 155.3 (N$\underline{C}O_2$), 167.3 (N$\underline{C}$O), 170.6 ($\underline{C}O_2$), 176.3 ($\underline{C}O_2$); GPC (THF) M_n 10,250, M_w 221,500, M_w/M_n 21.6.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 1.7:8.3.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 1.7:8.3 **(Method F)** (440mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 1.7:8.3 as a white solid. Yield 360mg (92 %); $[\alpha]^{28}_{D}$ -22.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3568 (br), 2956 (s), 2930 (s), 1735 (s), 1654 (s), 1560 (m), 1542 (m), 1508 (m), 1458 (s), 1388 (m), 1274 (m), 1202 (s) and 1143 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.2 (brm, C$\underline{H}_2$ + C$\underline{H}$), 1.4-2.3 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.3-3.6 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 3.8-4.5 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 7.9-8.7 (brm, N$\underline{H}_3$ + $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.5 ($\underline{C}H_2$), 18.8 ($\underline{C}H_3$), 24.7 (γ-$\underline{C}H_2$), 28.7 (β-$\underline{C}H_2$), 44.2 ($\underline{C}CH_3$), 44.5 ($\underline{C}CH_3$), 46.8 (N$\underline{C}H_2$), 51.9 ($CO_2\underline{C}H_3$), 54.0 (Pro-α-$\underline{C}$H), 59.0 (Ser-α-$\underline{C}$H), 64.3 ($\underline{C}H_2O$), 156.4 (N$\underline{C}$O), 172.4 ($\underline{C}O_2$), 176.4 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$); GPC (DMF) M_n 119,500, M_w 13,600,000, M_w/M_n 114.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 1.3:8.7.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.6g, 1.6 mmoles, 1.0eq.), methyl methacrylate (0.74 ml, 6.2 mmoles, 4.0eq.) and benzoyl peroxide (19mg, 0.01eq.) in sodium dried toluene (0.3 ml, 7.4M). Yield 0.9g

(73 %); $[\alpha]^{26}_{D}$ -17.1 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3427 (br), 2983 (m), 2950 (m), 1732 (s), 1654 (m), 1508 (m), 1449 (m), 1391 (m), 1368 (m), 1286 (m), 1243 (s), 1194 (m), 1152 (s) and 1054 cm^{-1} (w); δ_H 0.5-1.5 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.6-2.4 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brs, NC$\underline{H}_2$), 4.0-4.3 (brs, β-C$\underline{H}_2$O), 4.4-4.8 (brm, Ser-α-C$\underline{H}$ + Pro-α-C$\underline{H}$), 5.4-5.7 (brs, Boc-N$\underline{H}$); δ_C 16.4 (C$\underline{H}$), 18.7 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 28.8 (β-C$\underline{H}_2$), 44.5 (C$\underline{C}H_3$), 44.8 (C$\underline{C}H_3$), 47.0 (NC$\underline{H}_2$), 51.7 ($CO_2C\underline{H}_3$), 54.2 (Pro-α-C$\underline{H}$), 59.7 (Ser-α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 79.6 (C$\underline{(CH_3)_3}$), 80.9 (C$\underline{(CH_3)_3}$), 155.3 (N$\underline{C}O_2$), 167.3 (N$\underline{C}$O), 170.6 ($\underline{C}O_2$), 177.1 ($\underline{C}O_2$), 178.1 ($\underline{C}O_2$); GPC (THF) M_n 10,900, M_w 209,000, M_w/M_n 19.2.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 1.3:8.7.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 1.3:8.7 **(Method F)** (0.5g) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 1.3:8.7 as a white solid. Yield 0.4g (87 %); $[\alpha]^{28}_{D}$ -18.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3529 (br), 2958 (s), 2953 (s), 1732 (s), 1670 (s), 1457 (s), 1388 (m), 1280 (m), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + C$\underline{H}$), 1.6-2.2 (Pro-β + γ-C$\underline{H}_2$), 3.2-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 3.9-4.5 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.2 (brm, N$\underline{H}_3$), 8.3-8.5 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 18.0 ($\underline{C}$H), 18.7 ($\underline{C}H_3$), 22.1 (γ-$\underline{C}H_2$), 28.9 (β-$\underline{C}H_2$), 44.0 ($\underline{C}CH_3$), 44.4 ($\underline{C}CH_3$), 44.9 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 54.1 (Pro-α-$\underline{C}$H), 58.6 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2$O), 165.6 (N$\underline{C}$O), 172.0 ($\underline{C}O_2$), 176.3 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$); GPC (DMF) M_n 62,150, M_w 9,160,000, M_w/M_n 147.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 1:10.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.5g, 1.2 mmoles, 1.0eq.), methyl methacrylate (1.9 ml, 16.0 mmoles, 13eq.) and benzoyl peroxide (43mg, 0.01eq.) in sodium dried toluene (0.3 ml, 7.7M). Yield 1.8g (78 %); $[\alpha]^{26}_{D}$ -14.9 (c = 0.8, $CHCl_3$); υ_{max} ($CHCl_3$) 3427 (br), 3000 (s), 2950 (s), 1731 (s), 1654 (m), 1485 (m), 1449 (s), 1390 (m), 1368 (m), 1274 (s), 1243 (s), 1193 (s),

1151 (s). and 1063 cm^{-1} (w); δ_H 0.6-1.5 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.7-2.3 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brs, NC$\underline{H}_2$), 4.1-4.3 (brs, β-C$\underline{H}_2$O), 4.4-4.7 (brm, Ser-α-C$\underline{H}$ + Pro-α-C$\underline{H}$), 5.3-5.6 (brs, Boc-N$\underline{H}$); δ_C 16.4 (C$\underline{H}$), 18.7 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 28.8 (β-C$\underline{H}_2$), 44.5 (C$\underline{C}$H$_3$), 44.8 (C$\underline{C}$H$_3$), 47.0 (NC$\underline{H}_2$), 51.7 ($CO_2C\underline{H}_3$), 52.7 (C$\underline{H}_2$), 54.3 (Pro-α-C$\underline{H}$), 59.7 (Ser-α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 79.7 (C$\underline{C}$(CH$_3$)$_3$), 81.1 (C$\underline{C}$(CH$_3$)$_3$), 155.5 (NC$\underline{O}_2$), 167.6 (NC$\underline{O}$), 170.6 (C$\underline{O}_2$), 176.8 (C$\underline{O}_2$), 177.7 (C$\underline{O}_2$), 178.0 (C$\underline{O}_2$); GPC (THF) M_n 17,650, M_w 128,500, M_w/M_n 7.3.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 1:10.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 1:10 **(Method F)** (0.7g) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 1:10 as a white solid. Yield 0.6g (89 %); $[\alpha]^{28}_D$ -14.5 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3568 (br), 2956 (s), 1734 (s), 1672 (m), 1488 (m), 1458 (s), 1388 (m), 1274 (m), 1238 (m), 1190 (s) and 1152 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$ + C$\underline{H}$), 1.4-2.3 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.3-3.9 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.4 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.4 (brs, N$\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.1 (C$\underline{H}_2$), 18.5 (C$\underline{H}_3$), 24.7 (γ-C$\underline{H}_2$), 29.0 (β-C$\underline{H}_2$), 43.9 (C$\underline{C}$H$_3$), 44.3 (C$\underline{C}$H$_3$), 47.4 (NC$\underline{H}_2$), 51.8 ($CO_2C\underline{H}_3$), 54.7 (Pro-α-C$\underline{H}$), 58.5 (Ser-α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 172.4 (C$\underline{O}_2$), 176.2 (C$\underline{O}_2$), 177.2 (C$\underline{O}_2$); GPC (DMF) M_n 58,550, M_w 4,745,000, M_w/M_n 81.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 0.4:9.6.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.1g, 0.2 mmoles, 1.0eq.), methyl methacrylate (0.7 ml, 6.4 mmoles, 27eq.) and benzoyl peroxide (16mg, 0.01eq.) in sodium dried toluene (0.3 ml, 6.6M). Yield 0.65g (88 %); $[\alpha]^{26}_D$ -7.3 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3427 (br), 3000 (s), 2951 (s), 1731 (s), 1654 (m), 1485 (m), 1450 (s), 1390 (m), 1368 (m), 1274 (s), 1243 (s), 1193 (s), 1151 (s) and 1063 cm^{-1} (w); δ_H 0.7-1.1 (brm, C$\underline{H}_3$), 1.3-1.4 (brs, C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$), 1.7-2.1 (brm, C$\underline{H}_2$ + (Pro-β + γ-C$\underline{H}_2$)), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brs, NC$\underline{H}_2$), 4.1-

4.3 (brs, β-C$\underline{H}_2$O), 4.4-4.7 (brm, Ser-α-C$\underline{H}$ + Pro-α-C$\underline{H}$), 5.3-5.6 (brs, Boc-N$\underline{H}$); δ_C 16.4 (C$\underline{H}$), 18.7 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 29.0 (β-C$\underline{H}_2$), 44.5 (C$\underline{C}$H$_3$), 44.8 (C$\underline{C}$H$_3$), 47.0 (N$\underline{C}$H$_2$), 51.8 (CO$_2$C$\underline{H}_3$), 52.7 (C$\underline{H}_2$), 54.4 (Pro-α-C$\underline{H}$), 59.7 (Ser-α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 79.7 (C$\underline{C}$(CH$_3$)$_3$), 81.1 (C$\underline{C}$(CH$_3$)$_3$), 155.5 (N$\underline{C}$O$_2$), 167.6 (N$\underline{C}$O), 170.6 (C$\underline{O}_2$), 176.9 (C$\underline{O}_2$), 177.8 (C$\underline{O}_2$), 178.0 (C$\underline{O}_2$); GPC (THF) M_n 8,855, M_w 33,850, M_w/M_n 3.8.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 0.4:9.6.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 0.4:9.6 **(Method F)** (0.3g) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 0.4:9.6 as a white solid. Yield 0.2g (67 %); $[\alpha]^{28}_D$ -7.9 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3545 (br), 2999 (s), 2955 (s), 1734 (s), 1670 (s), 1476 (m), 1451 (s), 1366 (m), 1276 (m), 1190 (s) and 1152 cm^{-1} (s); δ_H (DMSO-d$_6$) 0.4-1.1 (brm, C$\underline{H}_2$ + C$\underline{H}$), 1.2-2.2 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.1-3.7 (brm, CO$_2$C$\underline{H}_3$ + NC$\underline{H}_2$), 3.9-4.7 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 7.8-8.2 (brm, N$\underline{H}_3$), 8.2-8.6 (brs, CO$_2$$\underline{H}$); δ_C (DMSO-d$_6$) 16.4 (C$\underline{H}_2$), 18.5 (C$\underline{H}_3$), 22.1 (γ-C$\underline{H}_2$), 28.2 (β-C$\underline{H}_2$), 44.0 (C$\underline{C}H_3$), 44.4 (C$\underline{C}H_3$), 45.4 (N$\underline{C}H_2$), 51.8 (CO$_2C\underline{H}_3$), 54.1 (α-C$\underline{H}$), 58.6 (α-C$\underline{H}$), 64.1 (C$\underline{H}_2$O), 156.2 (N$\underline{C}$O), 176.3 (C$\underline{O}_2$), 177.3 (C$\underline{O}_2$); GPC (DMF) M_n 81,400, M_w 9,255,000, M_w/M_n 114.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 2.3:7.7.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.5g, 1.2 mmoles, 2.5eq.), methyl methacrylate (0.45 ml, 3.6 mmoles, 7.5eq.) and benzoyl peroxide (23mg, 0.01eq.) in sodium dried toluene (0.3 ml, 7.6M). Yield 0.8g (84 %); $[\alpha]^{26}_D$ -23.1 (c = 0.6, CHCl$_3$); υ_{max} (CHCl$_3$) 3458 (br), 3356 (br), 2984 (s), 2950 (m), 1732 (s), 1654 (s), 1484 (m), 1449 (m), 1392 (m), 1368 (m), 1275 (m), 1243 (s), 1219 (s), 1152 (s) and 1062 cm^{-1} (w); δ_H 0.7-1.6 (brm, C$\underline{H}_2$ + C$\underline{H}$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.7-2.2 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, CO$_2$C$\underline{H}_3$), 3.6-3.8 (brs, NC$\underline{H}_2$), 4.0-4.4 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.5-4.8 (brm, Ser-α-C$\underline{H}$), 5.4-5.6 (brs, Boc-N$\underline{H}$); δ_C 16.4 (C$\underline{H}$), 18.7 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.8 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 29.0 (β-C$\underline{H}_2$), 44.5 (C$\underline{C}$H$_3$),

44.8 ($\underline{C}CH_3$), 47.0 ($N\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 52.7 ($\underline{C}H_2$), 54.4 (Pro-α-$\underline{C}H$), 59.8 (Ser-α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 79.7 ($\underline{C}(CH_3)_3$), 80.2 ($\underline{C}(CH_3)_3$), 155.5 ($N\underline{C}O_2$), 167.4 ($N\underline{C}O$), 170.5 ($\underline{C}O_2$), 176.3 ($\underline{C}O_2$), 178.9 ($\underline{C}O_2$); GPC (THF) M_n 13,700, M_w 135,500, M_w/M_n 9.9.

Poly(O-acryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 2.3:7.7.

Deprotection of poly(*O*-acryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 2.3:7.7 **(Method F)** (205mg) gave poly(*O*-acryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 2.3:7.7 as a white solid. Yield 155mg (96 %); $[\alpha]^{28}_D$ -25.5 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3529 (br), 2958 (s), 2953 (s), 1732 (s), 1670 (s), 1457 (s), 1388 (m), 1280 (m), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, $C\underline{H}_2$ + $C\underline{H}_3$), 1.6-2.4 (Pro-β + γ $C\underline{H}_2$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + $NC\underline{H}_2$), 4.1-4.6 (brm, 2x α-$C\underline{H}$ + β-$C\underline{H}_2O$), 8.0-8.3 (brs, $N\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$).

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 6.5:3.5.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.2g, 0.4 mmoles, 6.5eq.), methyl methacrylate (0.03 ml, 0.2 mmoles, 3.5eq.) and benzoyl peroxide (2mg, 0.01eq.) in sodium dried toluene (0.2 ml, 3.0M). Yield 120mg (66 %); $[\alpha]^{26}_D$ -35.2 (c = 0.8, $CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 3348 (br), 2979 (s), 1732 (s), 1651 (s), 1504 (s), 1446 (s), 1392 (m), 1368 (s), 1247 (s), 1157 (s) and 1053 cm^{-1} (m); δ_H 0.6-1.4 (brm, $C\underline{H}_2$ + $C\underline{H}$ + $C\underline{H}_3$), 1.4-1.5 (brs, 2x $C(C\underline{H}_3)_3$), 1.7-1.8 (brs, $C\underline{H}_2$ + $C\underline{H}$), 1.9-2.5 (brm, Pro-β + γ-$C\underline{H}_2$), 3.4-3.5 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brs, $NC\underline{H}_2$), 4.3-4.4 (brs, β-$C\underline{H}_2O$), 4.5-4.8 (brm, Ser-α-$C\underline{H}$ + Pro-α-$C\underline{H}$), 5.4-5.8 (brs, Boc-N$\underline{H}$).

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 8.5:1.5.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(34)** (0.3g, 0.7 mmoles, 8.5eq.), methyl methacrylate (0.02 ml, 0.1 mmoles, 1.5eq.) and benzoyl peroxide (4mg, 0.01eq.) in sodium dried toluene (0.3 ml, 3.0M). Yield 185mg (63 %); $[\alpha]^{26}_D$ -37.5 (c = 0.8, $CHCl_3$); υ_{max} ($CHCl_3$) 3432 (br), 3019 (s), 2982

(s), 1732 (s), 1650 (s), 1503(m), 1436 (s), 1393 (m), 1368 (s), 1215 (s), 1156 (s) and 1057 cm^{-1} (w); δ_H 0.7-1.3 (brm, C$\underline{H}_2$ + C$\underline{H}$ + C$\underline{H}_3$), 1.3-1.5 (brs, 2x C(C$\underline{H}_3$)$_3$), 1.7-2.5 (brm, C$\underline{H}_2$ + C$\underline{H}$ + (Pro-β + γ-C$\underline{H}_2$)), 3.4-3.5 (brs, $CO_2C\underline{H}_3$), 3.6-4.0 (brs, NC$\underline{H}_2$), 4.3-4.4 (brs, β-C$\underline{H}_2$O), 4.5-4.8 (brm, Ser-α-C$\underline{H}$ + Pro-α-C$\underline{H}$), 5.4-5.8 (brs, Boc-N$\underline{H}$); GPC (THF) M_n 6,680, M_w 17,000, M_w/M_n 2.5.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method D)** of monomer **(35)** (0.4g, 0.9 mmoles) and benzoyl peroxide (3.0mg, 0.01eq.) in sodium dried toluene (0.33 ml, 2.7M). Yield 0.3g (67 %); $[\alpha]^{26}_D$ -44.2 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3422 (br), 2978 (s), 1728 (s), 1650 (s), 1443 (m), 1367 (m), 1249 (m) and 1154 cm^{-1} (s); δ_H 1.0-1.6 (23H, brm, C$\underline{H}_2$ + C$\underline{H}_3$ + 2x C(C$\underline{H}_3$)$_3$), 1.8-2.3 (4H, brm, Pro-β + γ- C$\underline{H}_2$), 3.4-3.8 (2H, brs, NC$\underline{H}_2$), 4.2-4.4 (2H, brs, β-C$\underline{H}_2$O), 4.5-4.9 (3H, brm, Pro-α-C$\underline{H}$ + Ser-α-C$\underline{H}$ + Boc-N$\underline{H}$); δ_C 18.7 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 29.0 (β-C$\underline{H}_2$), 44.5 (C$\underline{C}H_3$), 47.1 (NC$\underline{H}_2$), 51.4 (Pro-α-C$\underline{H}$), 59.8 (Ser-α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 79.3 (C(CH$_3$)$_3$), 81.0 (C(CH$_3$)$_3$), 156.3 (NC$\underline{O}_2$), 169.9 (NC$\underline{O}$), 170.8 ($\underline{C}O_2$); GPC (THF) M_n 2,225, M_w 12,100, M_w/M_n 5.4.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate).

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu) **(Method F)** (185mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate) as a white solid. Yield 0.15g (83 %); $[\alpha]^{28}_D$ -30.4 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3452 (br), 2997 (s), 2952 (s), 1735 (s), 1719 (s), 1701 (s), 1685 (s), 1676 (s), 1654 (s), 1560 (m), 1508 (m), 1458 (m), 1214 (s) and 1108 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (5H, brm, C$\underline{H}_2$ + C$\underline{H}_3$), 1.4-2.4 (4H, brm, Pro-β + γ-C$\underline{H}_2$), 3.3-3.7 (2H, brm, NC$\underline{H}_2$), 4.0-4.5 (4H, brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.2 (1H, brs, N$\underline{H}_3$), 8.4-8.8 (3H, brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 (C$\underline{H}_2$), 18.6 (C$\underline{H}_3$), 24.7 (γ-C$\underline{H}_2$), 28.6 (β-C$\underline{H}_2$), 44.8 (C$\underline{C}H_3$), 46.8 (NC$\underline{H}_2$), 54.1 (α-C$\underline{H}$), 58.8 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 156.2 (NC$\underline{O}$), 173.2 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 3.8:6.2.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.35g, 0.8 mmoles, 1.0eq.), methyl methacrylate (0.11 ml, 1.1 mmoles, 1.3eq.) and benzoyl peroxide (5mg, 0.01eq.) in sodium dried toluene (0.3 ml, 4.6M). Yield 0.3g (63 %); $[\alpha]^{26}_{D}$ -33.3 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 3339 (br), 2979 (s), 2950 (m), 1732 (s), 1651 (s), 1502 (s), 1444 (s), 1392 (m), 1368 (s), 1275 (m), 1246 (s), 1154 (s) and 1059 cm^{-1} (w); δ_H 0.7-1.5 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.7-2.3 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.5 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brs, NC$\underline{H}_2$), 4.2-4.4 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.8 (brm, Ser-α-C$\underline{H}$), 5.4-5.6 (brs, Boc-N$\underline{H}$); δ_C 16.4 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 28.0 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}H$), 59.8 (Ser-α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 79.8 ($\underline{C}(CH_3)_3$), 81.2 ($\underline{C}(CH_3)_3$), 155.5 (N$\underline{C}O_2$), 167.4 (N$\underline{C}O$), 170.5 ($\underline{C}O_2$), 176.2 ($\underline{C}O_2$); GPC (THF) M_n 5,760, M_w 22,150, M_w/M_n 3.8.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 3.8:6.2.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 3.8:6.2 **(Method F)** (230mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 3.8:6.2 as a white solid. Yield 210mg (86 %); $[\alpha]^{28}_{D}$ -25.9 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3529 (br), 2958 (s), 2953 (s), 1732 (s), 1670 (s), 1457 (s), 1388 (m), 1280 (m), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 1.6-2.4 (Pro-β + γ-C$\underline{H}_2$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.6 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.3 (brs, N$\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.6 ($\underline{C}H_2$), 18.9 ($\underline{C}H_3$), 24.7 (γ-$\underline{C}H_2$), 29.0 (β-$\underline{C}H_2$), 40.5 ($\underline{C}CH_3$), 44.0 ($\underline{C}CH_3$), 47.4 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.7 (Pro-α-$\underline{C}H$), 58.4 (Ser-α-$\underline{C}H$), 64.2 ($\underline{C}H_2O$), 165.6 (N$\underline{C}O$), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$); GPC (DMF) M_n 25,200, M_w 3,995,000, M_w/M_n 160.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 1.1:8.9.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.9g, 2.2 mmoles, 1.0eq.), methyl methacrylate (1.5 ml, 14.1 mmoles, 6.5eq.) and benzoyl peroxide (41mg, 0.01eq.) in sodium dried toluene (0.5 ml, 8.2M). Yield 1.8g (78 %); $[\alpha]^{26}_{D}$ -16.1 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 3019 (s), 2952 (m), 1728 (s), 1655 (s), 1513 (s), 1478 (s), 1434 (s), 1368 (m), 1215 (s), 1153 (s) and 1056 cm^{-1} (w); δ_H 0.5-1.4 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.5-2.1 (brm, Pro-β + γ-C$\underline{H}_2$), 3.3-3.4 (brs, $CO_2C\underline{H}_3$), 3.5-3.7 (brm, NC$\underline{H}_2$), 4.0-4.3 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.5 (brs, Ser-α-C$\underline{H}$), 5.1-5.4 (brs, Boc-N$\underline{H}$); δ_C 16.5 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.8 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}$H), 54.4 ($\underline{C}H_2$), 59.8 (Ser-α-$\underline{C}$H), 64.3 ($\underline{C}H_2O$), 79.8 ($\underline{C}(CH_3)_3$), 81.3 ($\underline{C}(CH_3)_3$), 155.6 (N$\underline{C}O_2$), 167.6 (N$\underline{C}$O), 170.5 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$); GPC (THF) M_n 6,430, M_w 77,200, M_w/M_n 12.0.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 1.1:8.9.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 1.1:8.9 **(Method F)** (0.75g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 1.1:8.9 as a white solid. Yield 0.7g (89 %); $[\alpha]^{28}_{D}$ -15.8 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3545 (br), 2999 (s), 2955 (s), 1734 (s), 1670 (s), 1476 (m), 1451 (s), 1366 (m), 1276 (m), 1190 (s) and 1152 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$), 1.4-2.4 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.0-4.5 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.2-8.4 (brs, N$\underline{H}_3$), 8.4-8.8 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 18.6 ($\underline{C}H_3$), 24.7 (γ-$\underline{C}H_2$), 28.6 (β-$\underline{C}H_2$), 44.8 ($\underline{C}CH_3$), 45.2 ($\underline{C}CH_3$), 46.8 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.1 (α-$\underline{C}$H), 58.8 (α-$\underline{C}$H), 64.3 ($\underline{C}H_2O$), 156.2 (N$\underline{C}$O), 172.4 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$), 178.1 ($\underline{C}O_2$); GPC (DMF) M_n 86,900, M_w 4,580,000, M_w/M_n 53.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 4.6:5.4.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.7g, 1.6 mmoles, 1.5eq.), methyl methacrylate (0.1 ml, 1.1 mmoles, 1.0eq.) and benzoyl peroxide (16mg, 0.01eq.) in sodium dried toluene (0.5 ml, 4.5M). Yield 0.6g (74 %); $[\alpha]^{26}_{D}$ -34.6 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3429 (br), 3381 (br), 2979 (s), 1735 (s), 1655 (s), 1482 (m), 1439 (s), 1392 (m), 1368 (s), 1246 (s), 1153 (s) and 1059 cm^{-1} (w); δ_H 0.5-1.4 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.5-2.1 (brm, β + γ-C$\underline{H}_2$), 3.3-3.4 (brs, $CO_2C\underline{H}_3$), 3.4-3.8 (brm, NC$\underline{H}_2$), 4.0-4.3 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.5 (brs, Ser-α-C$\underline{H}$), 5.2-5.4 (brs, Boc-N$\underline{H}$); δ_C 16.8 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}$H), 54.4 ($\underline{C}H_2$), 59.8 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 79.7 ($\underline{C}$(CH$_3$)$_3$), 81.3 ($\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}O_2$), 167.4 (N$\underline{C}$O), 170.5 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$); GPC (THF) M_n 9,785, M_w 44,000, M_w/M_n 4.5.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 3.1:6.9.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.65g, 1.5 mmoles, 1.0eq.), methyl methacrylate (0.4 ml, 4.0 mmoles, 2.6eq.) and benzoyl peroxide (14mg, 0.01eq.) in sodium dried toluene (0.5 ml, 5.9M). Yield 0.8g (77 %); $[\alpha]^{26}_{D}$ -30.5 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3429 (br), 3019 (s), 2979 (m), 1729 (s), 1649 (s), 1512 (s), 1477 (s), 1434 (s), 1393 (m), 1368 (m), 1217 (s), 1154 (s) and 1056 cm^{-1} (w); δ_H 0.5-1.4 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.5-2.1 (brm, Pro-β + γ-C$\underline{H}_2$), 3.2-3.4 (brs, $CO_2C\underline{H}_3$), 3.4-3.8 (brm, NC$\underline{H}_2$), 4.0-4.3 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.4-4.5 (brs, Ser-α-C$\underline{H}$), 5.2-5.4 (brs, Boc-N$\underline{H}$); δ_C 16.8 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.8 (Pro-α-$\underline{C}$H), 54.4 ($\underline{C}H_2$), 59.8 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 79.7 ($\underline{C}$(CH$_3$)$_3$), 81.3 ($\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}O_2$), 167.4 (N$\underline{C}$O), 170.5 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$); GPC (THF) M_n 9,015, M_w 33,500, M_w/M_n 3.7.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 2.1:7.9.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.5g, 1.2 mmoles, 1.0eq.), methyl methacrylate (0.8 ml, 7.7 mmoles, 6.4eq.) and benzoyl peroxide (22mg, 0.01eq.) in sodium dried toluene (0.5 ml, 6.8M). Yield 0.9g (62 %); $[\alpha]^{26}_{D}$ -25.0 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 2981 (s), 1732 (s), 1655 (s), 1483 (s), 1448 (s), 1392 (m), 1368 (s), 1245 (s), 1153 (s) and 1062 cm^{-1} (w); δ_H 0.7-1.5 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 1.6-2.3 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.5 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brm, NC$\underline{H}_2$), 4.1-4.5 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.5-4.8 (brs, Ser-α-C$\underline{H}$), 5.3-5.6 (brs, Boc-N$\underline{H}$); δ_C 16.4 ($\underline{C}H_2$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 46.9 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.6 (Pro-α-$\underline{C}$H), 54.3 ($\underline{C}H_2$), 59.7 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 79.6 ($\underline{C}(CH_3)_3$), 81.3 ($\underline{C}(CH_3)_3$), 155.2 (N$\underline{C}O_2$), 167.6 (N$\underline{C}$O), 170.5 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$); GPC (THF) M_n 11,700, M_w 131,500, M_w/M_n 11.2.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 2.1:7.9.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 2.1:7.9 **(Method F)** (235mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 2.1:7.9 as a white solid. Yield 207mg (87 %); $[\alpha]^{28}_{D}$ -24.0 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3568 (br), 2956 (s), 2930 (s), 1735 (2s), 1654 (s), 1560 (m), 1542 (m), 1508 (m), 1458 (s), 1388 (m), 1274 (m), 1202 (s) and 1143 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$), 1.4-2.4 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.0-4.5 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 7.9-8.3 (brs, N$\underline{H}_3$), 8.4-8.8 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 18.5 ($\underline{C}H_3$), 24.7 (γ-$\underline{C}H_2$), 29.0 (β-$\underline{C}H_2$), 44.1 ($\underline{C}CH_3$), 44.5 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.7 (Pro-α-$\underline{C}$H), 58.5 (Ser-α-$\underline{C}$H), 64.3 ($\underline{C}H_2O$), 156.2 (N$\underline{C}$O), 172.4 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 0.5:9.5.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.4g, 0.9 mmoles, 1.0eq.), methyl methacrylate (1.3 ml, 12.3 mmoles, 13.0eq.) and benzoyl peroxide (33mg, 0.01eq.) in sodium dried toluene (0.3 ml, 8.3M). Yield 1.1g (65 %); $[\alpha]^{26}_{D}$ -9.0 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 3020 (s), 2951 (s), 1728 (s), 1650 (s), 1485 (s), 1448 (s), 1435 (s), 1392 (m), 1368 (s), 1274 (s), 1216 (s), 1194 (s), 1153 (s) and 1063 cm^{-1} (w); δ_H 0.7-1.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 1.3-1.4 (brs, 2x C(C$\underline{H}_3$)$_3$), 1.7-2.2 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-3.9 (brm, NC$\underline{H}_2$), 4.2-4.5 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.7 (brs, Ser-α-C$\underline{H}$), 5.4-5.5 (brs, Boc-N$\underline{H}$); δ_C 16.4 ($\underline{C}H_3$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 46.9 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}H$), 54.4 ($\underline{C}H_2$), 59.7 (Ser-α-$\underline{C}H$), 64.2 ($\underline{C}H_2O$), 79.6 ($\underline{C}(CH_3)_3$), 81.3 ($\underline{C}(CH_3)_3$), 155.6 ($N\underline{C}O_2$), 167.7 ($N\underline{C}O$), 170.5 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 9,090, M_w 46,100, M_w/M_n 5.1.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 0.5:9.5.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 0.5:9.5 **(Method F)** (0.5g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 0.5:9.5 as a white solid. Yield 0.5g (98 %); $[\alpha]^{28}_{D}$ -7.3 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3568 (br), 2956 (s), 1734 (s), 1672 (m), 1488 (m), 1458 (s), 1388 (m), 1274 (m), 1238 (m), 1190 (s) and 1152 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$), 1.4-2.4 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.3-3.9 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.6 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 7.8-8.4 (brs, N$\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 18.5 ($\underline{C}H_3$), 24.7 (γ-$\underline{C}H_2$), 29.0 (β-$\underline{C}H_2$), 44.1 ($\underline{C}CH_3$), 44.4 ($\underline{C}CH_3$), 47.4 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.7 (Pro-α-$\underline{C}H$), 58.5 (Ser-α-$\underline{C}H$), 64.3 ($\underline{C}H_2O$), 172.4 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$), 177.5 ($\underline{C}O_2$); GPC (DMF) M_n 45,150, M_w 1,865,000, M_w/M_n 41.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 0.4:9.6.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.2g, 0.5 mmoles, 1.0eq.), methyl methacrylate (1.2 ml, 11.5 mmoles, 23.0eq.) and benzoyl peroxide (31mg, 0.01eq.) in sodium dried toluene (0.3 ml, 8.0M). Yield 1.2g (85 %); $[\alpha]^{26}_{D}$ -5.6 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3437 (br), 2996 (s), 2950 (s), 1731 (s), 1657 (m), 1485 (s), 1449 (s), 1435 (s), 1389 (m), 1367 (s), 1273 (s), 1243 (s), 1193 (s), 1151 (s) and 1064 cm^{-1} (w); δ_H 0.7-1.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 1.3-1.4 (brs, 2x C(C$\underline{H}_3$)$_3$), 1.7-2.2 (brm, (Pro-β + γ-C$\underline{H}_2$) + C$\underline{H}_3$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-3.8 (brm, NC$\underline{H}_2$), 4.2-4.5 (brs, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.7 (brs, Ser-α-C$\underline{H}$), 5.4-5.6 (brs, Boc-N$\underline{H}$); δ_C 16.4 (C$\underline{H}_2$), 18.7 (C$\underline{H}_3$), 24.8 (γ-C$\underline{H}_2$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.3 (C(C$\underline{H}_3$)$_3$), 29.0 (β-C$\underline{H}_2$), 44.5 (C$\underline{C}$H$_3$), 44.8 (C$\underline{C}$H$_3$), 47.0 (N$\underline{C}$H$_2$), 51.7 ($CO_2\underline{C}H_3$), 52.6 (Pro-α-C$\underline{H}$), 54.3 (C$\underline{H}_2$), 59.7 (Ser-α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 79.7 (C$\underline{C}$(CH$_3$)$_3$), 81.3 (C$\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}O_2$), 167.7 (N$\underline{C}$O), 170.5 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 12,100, M_w 45,400, M_w/M_n 3.8.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 0.4:9.6.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 0.4:9.6 **(Method F)** (470mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 0.4:9.6 as a white solid. Yield 385mg (82 %); $[\alpha]^{28}_{D}$ -5.0 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3569 (br), 2998 (s), 2953 (s), 1735 (s), 1676 (m), 1484 (s), 1450 (s), 1389 (m), 1280 (s), 1245 (s), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-2.4 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + (Pro-β + γ-C$\underline{H}_2$)), 3.3-4.6 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$ + 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.3 (brs, N$\underline{H}_3$), 8.3-8.7 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.6 (C$\underline{H}_2$), 18.9 (C$\underline{H}_3$), 24.7 (γ-C$\underline{H}_2$), 29.0 (β-C$\underline{H}_2$), 40.3 (C$\underline{C}$H$_3$), 44.3 (C$\underline{C}$H$_3$), 47.4 (N$\underline{C}$H$_2$), 51.9 ($CO_2\underline{C}H_3$), 54.2 (2x α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 165.6 (N$\underline{C}$O), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$); GPC (DMF) M_n 41,100, M_w 860,000, M_w/M_n 21.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 3:2.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.7g, 1.6 mmoles, 2.3eq.), methyl methacrylate (0.8 ml, 0.7 mmoles, 1.0eq.) and benzoyl peroxide (21mg, 0.01eq.) in sodium dried toluene (0.5 ml, 4.0M). Yield 0.65g (84 %); $[\alpha]^{26}_{D}$ -36.6 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 3339 (br), 2979 (s), 1731 (s), 1651 (s), 1501 (s), 1446 (s), 1392 (m), 1368 (s), 1274 (s), 1248 (s), 1155 (s) and 1058 cm^{-1} (m); δ_H 0.7-1.6 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + 2x C(C$\underline{H}_3$)$_3$), 1.7-2.3 (brm, Pro-β + γ-C$\underline{H}_2$), 3.5-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-4.0 (brm, NC$\underline{H}_2$), 4.2-4.5 (brm, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.8 (brs, Ser-α-C$\underline{H}$), 5.4-5.6 (brs, Boc-N$\underline{H}$); δ_C 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}$H), 59.8 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 79.6 ($\underline{C}(CH_3)_3$), 81.2 ($\underline{C}(CH_3)_3$), 155.6 (N$\underline{C}O_2$), 167.7 (N$\underline{C}$O), 170.6 ($\underline{C}O_2$); GPC (THF) M_n 7,340, M_w 34,750, M_w/M_n 4.7.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 3:2.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 3:2 **(Method F)** (230mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 3:2 as a white solid. Yield 220mg (96 %); $[\alpha]^{28}_{D}$ -26.9 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3529 (br), 2958 (s), 2953 (s), 1732 (s), 1670 (s), 1457 (s), 1388 (m), 1280 (m), 1195 (s) and 1150 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-1.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$), 1.6-2.4 (Pro-β + γ-C$\underline{H}_2$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.6 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.3 (brs, N$\underline{H}_3$), 8.4-8.7 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.6 ($\underline{C}H_2$), 18.9 ($\underline{C}H_3$), 24.7 (γ-$\underline{C}H_2$), 29.0 (β-$\underline{C}H_2$), 40.5 ($\underline{C}CH_3$), 44.0 ($\underline{C}CH_3$), 47.4 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.7 (Pro-α-$\underline{C}$H), 58.4 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 165.6 (N$\underline{C}$O), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$); GPC (DMF) M_n 41,450, M_w 5,995,000, M_w/M_n 145.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 8.5:1.5.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.6g, 1.4 mmoles, 8.5eq.), methyl methacrylate (0.03 ml, 0.2 mmoles, 1.5eq.) and benzoyl peroxide (4mg, 0.01eq.) in sodium dried toluene (0.5 ml, 3.2M). Yield 0.52g (82 %); $[\alpha]^{26}_{D}$ -40.1 ($CHCl_3$); υ_{max} ($CHCl_3$) 3430 (br), 3339 (br), 2978 (s), 1734 (s), 1650 (s), 1501 (m), 1441 (s), 1392 (m), 1368 (s), 1274 (m), 1248 (s), 1154 (s) and 1056 cm^{-1} (m); δ_H 0.7-1.6 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + 2x C(C$\underline{H}_3$)$_3$), 1.7-2.3 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-4.1 (brs, NC$\underline{H}_2$), 4.1-4.6 (brm, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.9 (brs, Ser-α-C$\underline{H}$), 5.4-5.9 (brs, Boc-N$\underline{H}$); δ_C 19.8 ($\underline{C}H_3$), 24.9 (γ-$\underline{C}H_2$), 28.0 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}$H), 59.8 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 79.6 ($\underline{C}$(CH$_3$)$_3$), 81.2 ($\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}O_2$), 167.8 (N$\underline{C}$O), 170.7 ($\underline{C}O_2$); GPC (THF) M_n 6,510, M_w 35,750, M_w/M_n 5.5.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 8.5:1.5.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 8.5:1.5 **(Method F)** (160mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 8.5:1.5 as a white solid. Yield 142mg (91 %); $[\alpha]^{28}_{D}$ -28.4 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3442 (br), 3000 (m), 2952 (m), 1744 (s), 1671 (s), 1654 (s), 1458 (s), 1366 (m), 1202 (s) and 1134 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-1.5 (brm, C$\underline{H}_2$+C$\underline{H}_3$), 1.6-2.4 (brm, Pro-β + γ-C$\underline{H}_2$), 3.3-3.9 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.8 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.4 (brs, N$\underline{H}_3$), 8.4-8.9 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 18.8 ($\underline{C}H_3$), 29.0 (β-$\underline{C}H_2$), 44.3 ($\underline{C}CH_3$), 47.4 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.1 (2x α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 165.6 (N$\underline{C}$O), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$); GPC (DMF) M_n 23,300, M_w 6,385,000, M_w/M_n 274.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Pro-O^{t}Bu-co-MMA) 7:3.

This polymer was obtained by the polymerisation **(Method E)** of monomer **(35)** (0.6g, 1.45 mmoles, 7.0eq.), methyl methacrylate (0.08 ml, 0.6 mmoles, 3.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in sodium dried toluene (0.5 ml, 3.6M). Yield 0.5g (77 %); $[\alpha]^{26}_{D}$ -38.3 ($CHCl_3$); υ_{max} ($CHCl_3$) 3428 (br), 3019 (s), 2978 (m), 1729 (s), 1649 (s), 1512 (s), 1477 (s), 1433 (s), 1392 (m), 1368 (s), 1217 (s), 1155 (s) and 1054 cm^{-1} (w); δ_H 0.7-1.6 (brm, C$\underline{H}_3$ + C$\underline{H}_3$ + 2x C(C$\underline{H}_3$)$_3$), 1.7-2.3 (brm, Pro-β + γ-C$\underline{H}_2$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.6-4.1 (brs, NC$\underline{H}_2$), 4.2-4.6 (brm, Pro-α-C$\underline{H}$ + β-C$\underline{H}_2$O), 4.6-4.9 (brs, Ser-α-C$\underline{H}$), 5.4-5.9 (brs, Boc-N$\underline{H}$); δ_C 16.5 ($\underline{C}H_3$), 18.7 ($\underline{C}H_3$), 24.8 (γ-$\underline{C}H_2$), 27.9 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 29.0 (β-$\underline{C}H_2$), 44.5 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 47.0 (N$\underline{C}H_2$), 51.7 ($CO_2\underline{C}H_3$), 52.7 (Pro-α-$\underline{C}$H), 59.8 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 79.5 ($\underline{C}$(CH$_3$)$_3$), 81.2 ($\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}O_2$), 167.6 (N$\underline{C}$O), 170.6 ($\underline{C}O_2$); GPC (THF) M_n 9,235, M_w 49,450, M_w/M_n 5.4.

Poly(O-methacryloyl-(S)-Ser-(S)-Pro trifluoroacetate-co-MMA) 7:3.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Pro-O^{t}Bu-*co*-MMA) 7:3 **(Method F)** (250mg) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Pro trifluoroacetate-*co*-MMA) 7:3 as a white solid. Yield 220mg (88 %); $[\alpha]^{28}_{D}$ -27.5 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3452 (br), 3143 (br), 2959 (m), 1732 (s), 1670 (s), 1458 (s), 1368 (m), 1186 (s) and 1140 cm^{-1} (s); δ_H (DMSO-d_6) 0.6-1.4 (brm, C$\underline{H}_3$+C$\underline{H}_3$), 1.6-2.4 (brm, Pro-β + γ-C$\underline{H}_2$), 3.3-3.8 (brm, $CO_2C\underline{H}_3$ + NC$\underline{H}_2$), 4.1-4.6 (brm, 2x α-C$\underline{H}$ + β-C$\underline{H}_2$O), 8.0-8.4 (brs, N$\underline{H}_3$), 8.4-8.9 (brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_3$), 18.8 ($\underline{C}H_3$), 29.0 (β-$\underline{C}H_2$), 44.3 ($\underline{C}CH_3$), 47.4 (N$\underline{C}H_2$), 51.8 ($CO_2\underline{C}H_3$), 54.1 (2x α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 165.6 (N$\underline{C}$O), 172.0 ($\underline{C}O_2$), 176.0 ($\underline{C}O_2$); GPC (DMF) M_n 36,950, M_w 9,150,000, M_w/M_n 248.

N-Z-(S)-Ser-(S)-Phe-O^{t}Bu ***(39)***.

To a solution of *N*-Z-(*S*)-serine **(38)** (7.6g, 31.8 mmoles, 1.1eq.) in glass distilled DMF (80 ml) was added DCC (6.0g, 28.9 mmoles, 1.0eq.), HOBt (6.2g, 46.3 mmoles, 1.6eq.) and (*S*)-Phe-O^{t}Bu **(23)** (6.4g, 28.9 mmoles, 1.0eq.). The mixture was stirred at room temperature for 13.5 hours after which the solvent was removed *in vacuo* and ethyl acetate (100 ml) was added to the yellow oil residue. Filtration through celite removed a white solid (DCHU) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). The aqueous layer was back extracted with ethyl acetate (2x 15 ml) and the combined organic layers were subsequently washed with sat. Na_2CO_3 (3x 25 ml), water (3x 25 ml), 2M HCl (2x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to provide the title compound as a white crystalline solid. Yield 12.7g (90 %); m.p. 59 °C; $[\alpha]^{28}_D$ -2.7 (c = 0.6, $CHCl_3$); R_f ethyl acetate : light petrol (1 : 1) 0.44 (PMA); Found C, 64.5; H, 6.8; N, 6.5. $C_{24}H_{30}N_2O_6.0.33\ H_2O$ requires C, 64.5; H, 6.5; N, 6.3 %; υ_{max} ($CHCl_3$) 3326 (br), 2978 (s), 1725 (s), 1664 (s), 1528 (m), 1500 (m), 1454 (s), 1369 (m), 1254 (s), 1155 (s) and 1060 cm^{-1} (w); δ_H 1.40 (9H, s, C(C$\underline{H}_3$)$_3$), 3.01 (1H, dd *J* 6.8, 14.2Hz, 1x β-C$\underline{H}_2$Ph), 3.11 (1H, dd *J* 6.5, 14.4Hz, 1x β-C$\underline{H}_2$Ph), 3.59-3.65 (2H, m, O$\underline{H}$ + 1x β-C$\underline{H}_2$O), 3.96 (1H, brd *J* 7.8Hz, Ser-α-C$\underline{H}$), 4.27 (1H, brm, 1x β-C$\underline{H}_2$O), 4.73 (1H, q *J* 6.4Hz, Phe-α-C$\underline{H}$), 5.08 (2H, s, PhC$\underline{H}_2$O), 5.97 (1H, brd *J* 7.5Hz, Z-N$\underline{H}$), 7.14-7.33 (11H, m, ArC$\underline{H}$ + N$\underline{H}$CO); δ_C 27.9 (C(C$\underline{H}_3$)$_3$), 37.7 (Phe-β-C$\underline{H}_2$), 54.0 (Phe-α-C$\underline{H}$), 55.7 (Ser-α-C$\underline{H}$), 62.8 (C$\underline{H}_2$O), 67.1 (PhC$\underline{H}_2$O), 82.5 (C(CH$_3$)$_3$), 127.0 (ArC$\underline{H}$), 127.5 (ArC$\underline{H}$), 128.0 (ArC$\underline{H}$), 128.4 (ArC$\underline{H}$), 128.6 (ArC$\underline{H}$), 129.4 (ArC$\underline{H}$), 136.0 (Ar *ipso* C), 156.4 (NC$\underline{O}_2$), 170.5 (C$\underline{O}_2$), 170.7 (NHC$\underline{O}$); m/z (CI) 443 (MH^+); Found 443.2186 ($C_{24}H_{31}N_2O_6$ requires 443.2182).

(S)-Ser-(S)-Phe-O^{t}Bu ***(40)***.

To a solution of N-Z-(S)-Ser-(S)-Phe-O^{t}Bu **(39)** (12.7g, 28.7 mmoles, 1.0eq.) in MeOH (100 ml) was added 10 % Pd / C (0.3g). The resulting suspension was exposed

to hydrogen at atmospheric pressure and stirred for 15 hours. Subsequently the suspension was filtered through celite to remove a black solid (Pd / C), dried ($MgSO_4$) and the solvent removed *in vacuo* to afford the title compound as a white solid. Yield 8.2g (93 %); m.p. 27 °C; $[\alpha]^{28}_D$ -5.1 (c = 0.6, $CHCl_3$); R_f ethyl acetate : light petrol (1 : 1) 0.07 (PMA); υ_{max} ($CHCl_3$) 3345 (br), 3015 (s), 2978 (s), 1727 (s), 1656 (s), 1528 (m), 1454 (s), 1369 (s), 1216 (s) and 1055 cm^{-1} (s); δ_H 1.41 (9H, s, C(C<u>H</u>$_3$)$_3$), 2.87 (1H, brs, O<u>H</u>), 3.02 (1H, dd *J* 6.7, 13.8Hz, 1x β-C<u>H</u>$_2$Ph), 3.12 (1H, dd *J* 6.2, 13.8Hz, 1x β-C<u>H</u>$_2$Ph), 3.42 (1H, t *J* 5.1Hz, Ser-α-C<u>H</u>), 3.61 (1H, dd *J* 5.1, 10.9Hz, 1x β-C<u>H</u>$_2$O), 3.71 (1H, dd *J* 5.4, 10.9Hz, 1x β-C<u>H</u>$_2$O), 4.72 (1H, q *J* 6.5Hz, Phe-α-C<u>H</u>), 7.15-7.31 (5H, m, ArC<u>H</u>), 7.81 (1H, d *J* 8.3Hz, N<u>H</u>CO); δ_C 27.9 (C(<u>C</u>H$_3$)$_3$), 38.1 (Phe-β-<u>C</u>H$_2$), 53.4 (Phe-α-<u>C</u>H), 56.2 (Ser-α-<u>C</u>H), 64.9 (<u>C</u>H$_2$O), 82.4 (<u>C</u>(CH$_3$)$_3$), 126.9 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.5 (Ar<u>C</u>H), 136.2 (Ar *ipso* <u>C</u>), 170.6 (<u>C</u>O$_2$), 173.3 (NH<u>C</u>O).

N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu ***(42)***.

To a solution of *N*-Boc-(*S*)-alanine **(41)** (5.5g, 29.1 mmoles, 1.1eq.) in glass distilled DMF (80 ml) was added DCC (5.5g, 26.5 mmoles, 1.0eq.), HOBt (4.6g, 34.4 mmoles, 1.3eq.) and (*S*)-Ser-(*S*)-Phe-O^{t}Bu **(40)** (8.2g, 26.5 mmoles, 1.0eq.). The mixture was stirred at room temperature for 18 hours after which the solvent was removed *in vacuo* and ethyl acetate (70 ml) was added to the yellow oil residue. Filtration through celite removed a white solid (DCHU) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). The aqueous layer was back extracted with ethyl acetate (2x 15 ml) and the combined organic layers were subsequently washed with sat. Na_2CO_3 (3x 25 ml), water (3x 25 ml), 2M HCl (2x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a cream solid. Column chromatography eluting with ethyl acetate : light petrol (3 : 2) afforded the title compound as a white solid. Yield 11.1g (88 %); m.p. 74 °C; R_f ethyl acetate : light petrol (3 : 2) 0.3 (PMA); $[\alpha]^{26}_D$ -30.0 (c = 0.6, $CHCl_3$); Found C, 59.7; H, 7.5; N, 8.7. $C_{24}H_{37}N_3O_7$ requires C, 60.1; H, 7.8; N, 8.8 %; υ_{max} ($CHCl_3$) 3305 (br), 2979 (s), 2932 (s), 1652 (brs), 1522 (brs), 1455 (m), 1392 (m), 1368 (m), 1250 (brs), 1161 (brs)

and 1067 cm^{-1} (m); δ_H 1.32 (3H, d *J* 7.1Hz, C<u>H</u>$_3$), 1.41 (9H, s, C(C<u>H</u>$_3$)$_3$), 1.44 (9H, s, C(C<u>H</u>$_3$)$_3$), 3.05 (1H, dd *J* 6.5, 14.0Hz, 1x β-C<u>H</u>$_2$Ph), 3.13 (1H, dd *J* 6.2, 14.0Hz, 1x β-C<u>H</u>$_2$Ph), 3.60-3.80 (2H, brm, O<u>H</u> + 1x β-C<u>H</u>$_2$O), 4.00 (1H, brm, 1x β-C<u>H</u>$_2$O), 4.20 (1H, p *J* 7.1Hz, Ala-α-C<u>H</u>), 4.50 (1H, t *J* 6.1Hz, Ser-α-C<u>H</u>), 4.70 (1H, q *J* 6.5Hz, Phe-α-C<u>H</u>), 5.30 (1H, d *J* 7.2Hz, Boc-N<u>H</u>), 7.10-7.30 (7H, m, ArC<u>H</u> + (2x N<u>H</u>CO)); δ_C 18.6 (<u>C</u>H$_3$), 27.8 (C(<u>C</u>H$_3$)$_3$), 28.3 (C(<u>C</u>H$_3$)$_3$), 37.8 (Phe-β-<u>C</u>H$_2$), 51.8 (Ala-α-<u>C</u>H), 54.1 (Phe-α-<u>C</u>H), 54.5 (Ser-α-<u>C</u>H), 62.7 (<u>C</u>H$_2$O), 79.7 (<u>C</u>(CH$_3$)$_3$), 82.2 (<u>C</u>(CH$_3$)$_3$), 126.7 (Ar<u>C</u>H), 128.2 (Ar<u>C</u>H), 129.2 (Ar<u>C</u>H), 136.0 (Ar *ipso* <u>C</u>), 155.4 (N<u>C</u>O$_2$), 170.0 (NH<u>C</u>O), 170.2 (NH<u>C</u>O), 170.7 (<u>C</u>O$_2$); m/z (CI) 480 (MH^+); Found 480.2706 ($C_{24}H_{38}N_3O_7$ requires 480.2710).

O-Acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu ***(43)***.

Triethylamine (2.6 ml, 18.8 mmoles, 3.0eq.) was added to a solution of *N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu **(42)** (3.0g, 6.3 mmoles, 1.0eq.) in ethyl acetate (50 ml). Subsequently the solution was cooled to 0 °C and acryloyl chloride (0.6 ml, 7.8 mmoles, 1.3eq.) was added dropwise *via* a syringe to the stirring mixture. The mixture was warmed to room temperature and stirred for a further 18 hours after which the solvent was removed *in vacuo*. Filtration through celite removed a white solid (triethylamine hydrochloride) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). The aqueous layer was back extracted with ethyl acetate (2x 15 ml) and the combined organic layers were subsequently washed with sat. Na_2CO_3 (3x 25 ml), water (3x 25 ml), 2M HCl (2x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to provide the title compound as a white solid. Yield 2.5g (75 %); m.p. 68 °C; R_f ethyl acetate : light petrol (2 : 3) 0.3 (PMA); $[\alpha]^{28}_D$ +6.2 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3416 (br), 2978 (s), 1720 (s), 1648 (s), 1522 (m), 1451 (m), 1367 (m), 1250 (m) and 1060 cm^{-1} (s); δ_H 1.31 (3H, d *J* 6.9Hz, C<u>H</u>$_3$), 1.37 (9H, s, C(C<u>H</u>$_3$)$_3$), 1.42 (9H, s, C(C<u>H</u>$_3$)$_3$), 3.07 (2H, d *J* 6.1Hz, β-C<u>H</u>$_2$Ph), 3.70-4.00 (1H, brm, Ala-α-C<u>H</u>), 4.29 (1H, dd *J* 5.3, 11.3Hz, 1x β-C<u>H</u>$_2$O), 4.46 (1H, dd *J* 5.3, 11.3Hz, 1x β-C<u>H</u>$_2$O), 4.71 (1H, q *J* 6.4Hz, Phe-α-C<u>H</u>), 4.79 (1H, q

J 5.3Hz, Ser-α-C<u>H</u>), 5.20 (1H, d *J* 7.2Hz, Boc-N<u>H</u>), 5.82 (1H, d *J* 10.4Hz, =C<u>H</u>$_2$), 6.10 (1H, dd *J* 10.4, 17.2Hz, =C<u>H</u>), 6.40 (1H, d *J* 17.2Hz, =C<u>H</u>$_2$), 7.10-7.30 (7H, m, ArC<u>H</u> + (2x N<u>H</u>CO)); δ_C 18.5 (<u>C</u>H$_3$), 27.9 (C(<u>C</u>H$_3$)$_3$), 28.3 (C(<u>C</u>H$_3$)$_3$), 38.0 (Phe-β-<u>C</u>H$_2$), 52.0 (Ala-α-<u>C</u>H), 54.0 (Phe-α-<u>C</u>H), 54.3 (Ser-α-<u>C</u>H), 63.8 (<u>C</u>H$_2$O), 80.1 (<u>C</u>(CH$_3$)$_3$), 82.3 (<u>C</u>(CH$_3$)$_3$), 126.9 (Ar<u>C</u>H), 127.6 (=<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 131.7 (=<u>C</u>H$_2$), 136.1 (Ar *ipso* <u>C</u>), 155.5 (N<u>C</u>O$_2$), 170.0 (NH<u>C</u>O), 170.2 (NH<u>C</u>O), 173.0 (<u>C</u>O$_2$), 173.4 (<u>C</u>O$_2$).

O-Methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu ***(44)***.

Triethylamine (1.6 ml, 11.8 mmoles, 3.0eq.) was added to a solution of *N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu **(42)** (1.9g, 3.9 mmoles, 1.0eq.) in ethyl acetate (50 ml). Subsequently the solution was cooled to 0 °C and methacryloyl chloride (0.5 ml, 5.1 mmoles, 1.3eq.) was added dropwise *via* a syringe to the stirring mixture. The mixture was warmed to room temperature and stirred for a further 18 hours after which the solvent was removed *in vacuo*. Filtration through celite removed a white solid (triethylamine hydrochloride) and the filtrate was washed with sat. Na_2CO_3 (2x 25 ml). The aqueous layer was back extracted with ethyl acetate (2x 15 ml) and the combined organic layers were subsequently washed with sat. Na_2CO_3 (3x 25 ml), water (3x 25 ml), 2M HCl (2x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to provide a white solid. This was subsequently recrystallised from light petrol (25 ml) to provide the title compound. Yield 2.0g (91 %); m.p. 64 °C; $[\alpha]^{26}_D$ +10.0 (c = 0.6, $CHCl_3$); Found C, 60.8; H, 7.7; N, 7.6. $C_{28}H_{41}N_3O_8$.33 % EtOAc requires C, 61.0; H, 7.6; N, 7.3 %; υ_{max} ($CHCl_3$) 3393 (br), 2979 (s), 2932 (s), 1725 (s), 1647 (s), 1515 (m), 1454 (m), 1392 (m), 1368 (m), 1322 (m), 1294 (m), 1250 (m), 1161 (s) and 1060 cm^{-1} (m); δ_H 1.27 (3H, d *J* 7.1Hz, C<u>H</u>$_3$), 1.33 (9H, s, C(C<u>H</u>$_3$)$_3$), 1.39 (9H, s, C(C<u>H</u>$_3$)$_3$), 2.00 (3H, s, =CC<u>H</u>$_3$), 3.03 (2H, d *J* 6.2Hz, β-C<u>H</u>$_2$Ph), 4.20 (1H, p *J* 6.6Hz, Ala-α-C<u>H</u>), 4.27 (1H, dd *J* 5.4, 11.3Hz, 1x β-C<u>H</u>$_2$O), 4.37 (1H, dd *J* 5.5, 11.3Hz, 1x β-C<u>H</u>$_2$O), 4.71 (1H, q *J* 6.3Hz, Phe-α-C<u>H</u>), 4.80 (1H, q *J* 5.5Hz, Ser-α-C<u>H</u>), 5.14 (1H, d *J* 7.1Hz, Boc-N<u>H</u>), 5.57 (1H, s, =C<u>H</u>$_2$),

6.07 (1H, s, =C$\underline{H}_2$), 6.96 (1H, brd *J* 7.2Hz, N$\underline{H}$CO), 7.09 (1H, brd *J* 7.0Hz, N$\underline{H}$CO), 7.15-7.30 (5H, m, ArC$\underline{H}$); δ_C 17.9 (=C$\underline{C}H_3$), 18.2 ($\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 38.0 (Phe-β-$\underline{C}H_2$), 50.3 (Ala-α-$\underline{C}$H), 52.2 (Phe-α-$\underline{C}$H), 53.9 (Ser-α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 80.3 ($\underline{C}$(CH$_3$)$_3$), 82.4 ($\underline{C}$(CH$_3$)$_3$), 126.6 (=$\underline{C}H_2$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 135.5 (Ar *ipso* $\underline{C}$), 136.0 (=$\underline{C}CH_3$), 155.6 (N$\underline{C}O_2$), 168.1 (NH$\underline{C}$O), 169.9 (NH$\underline{C}$O), 172.9 ($\underline{C}O_2$); m/z (CI) 548 (MH^+); Found 548.2960 ($C_{28}H_{42}N_3O_8$ requires 548.2970).

Homopolymerisations, Method G

The amino acid monomer **(43)** or **(44)** was suspended in toluene to form a 1.3M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling at 273 K and then heated to reflux at 383 K under a nitrogen atmosphere. Heating was continued for 2 hours, after which time the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 150 ml). The precipitated white solid was collected by filtration and dried *in vacuo* for 5 hours.

Copolymerisations, Method H

The amino acid derived monomer **(43)** or **(44)** was suspended in freshly distilled methyl methacrylate and toluene to form a 3.0M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling to 273 K and then heated to reflux at 368 K under a nitrogen atmosphere. Heating was either continued for 3 hours, or until the polymer had gelled out of solution, after which time the crude polymer was dissolved in chloroform (*ca.* 10 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 150 ml). The precipitated white solid was collected by filtration and dried *in vacuo* at 298 K for 5 hours.

Removal of the polymer protecting groups, Method I

The polymer was dissolved in CH_2Cl_2 (2 ml) and trifluoroacetic acid (2 ml) was added. The solution was stirred at room temperature for 17 hours. This was added slowly, with stirring, to diethyl ether (40 ml). The precipitated white solid was collected by filtration and subsequently washed with diethyl ether (100 ml) and dried *in vacuo* at 298 K for 12 hours.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method G)** of monomer **(43)** (0.7g, 1.3 mmoles) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (1.0 ml). Yield 0.4g (59 %); $[\alpha]^{26}_D$ +28.7 (c = 0.6, $CHCl_3$); υ_{max} (KBr) 3307 (br), 2980 (s), 2935 (m), 1738 (s), 1648 (s), 1522 (s), 1455 (m), 1369 (s), 1252 (s), 1168 (s) and 1068 cm^{-1} (m); δ_H 0.9-1.6 (24H, brm, C$\underline{H}$ + C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.8-3.2 (2H, brs, C$\underline{H}_2$Ph), 3.4-3.5 (1H, brd, 1x β-C$\underline{H}_2$O), 3.8-3.9 (1H, brd, 1x β-C$\underline{H}_2$O), 4.0-4.2 (1H, brs, Ala-α-C$\underline{H}$), 4.3-4.4 (1H, brs, Ser-α-C$\underline{H}$), 4.5-4.6 (1H, brq, Phe-α-C$\underline{H}$), 5.1-5.2 (1H, brd, Boc-N$\underline{H}$), 6.8-7.2 (7H, brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 18.2 (Ala-$\underline{C}H_3$), 20.3 ($\underline{C}H_2$), 27.8 (C($\underline{C}H_3$)$_3$), 28.2 (C($\underline{C}H_3$)$_3$), 37.7 ($\underline{C}H_2$Ph), 50.2 (Ala-α-$\underline{C}$H), 54.0 (Phe-α-$\underline{C}$H), 54.2 (Ser-α-$\underline{C}$H), 62.6 ($\underline{C}H_2$O), 80.2 ($\underline{C}$(CH$_3$)$_3$), 82.5 ($\underline{C}$(CH$_3$)$_3$), 126.9 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.3 (Ar$\underline{C}$H), 136.0 (Ar *ipso*$\underline{C}$), 155.5 (N$\underline{C}O_2$), 170.1 ($\underline{C}$ONH), 170.3 ($\underline{C}$ONH), 173.2 ($\underline{C}O_2$); GPC (DMF) M_n 8,235, M_w 20,350, M_w/M_n 2.5.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 5.2:4.8.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.3g, 0.6 mmoles, 2.0eq.), methyl methacrylate (0.19 ml, 1.8 mmoles, 3.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (0.5 ml, 3.5M). Yield 0.3g (63 %); $[\alpha]^{26}_D$ +5.5 (c = 0.9, $CHCl_3$); υ_{max} (KBr) 3371 (br), 2979 (s), 2935 (m), 1734 (s), 1675 (m), 1522 (s), 1450 (s), 1368 (s), 1263 (s), 1158 (s) and 1065 cm^{-1} (w); δ_H 0.7-2.4 (brm, C$\underline{H}$ + C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.3-3.8 (brs, 1x β-C$\underline{H}_2$O + CO$_2$C$\underline{H}_3$), 3.9-4.4 (brm, 1x β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$ + Ser-α-C$\underline{H}$), 4.5-4.8 (brs,

Phe-α-C<u>H</u>), 5.0-5.1 (brs, Boc-N<u>H</u>), 6.8-7.5 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 16.3 (<u>C</u>H_2), 18.6 (<u>C</u>H_3), 18.7 (Ala-<u>C</u>H_3), 27.9 (C(<u>C</u>H_3)$_3$), 28.4 (C(<u>C</u>H_3)$_3$), 38.2 (<u>C</u>H_2Ph), 44.5 (<u>C</u>CH_3), 44.9 (<u>C</u>H), 50.4 (Ala-α-<u>C</u>H), 51.7 (CO_2<u>C</u>H_3), 54.1 (α-<u>C</u>H), 63.4 (<u>C</u>H_2O), 80.4 (<u>C</u>(CH$_3$)$_3$), 82.6 (<u>C</u>(CH$_3$)$_3$), 126.8 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 136.1 (Ar *ipso*<u>C</u>), 155.7 (N<u>C</u>O_2), 165.7 (<u>C</u>ONH), 168.6 (<u>C</u>ONH), 170.2 (<u>C</u>O_2), 173.2 (<u>C</u>O_2), 176.4 (<u>C</u>O_2); GPC (DMF) M_n 29,500, M_w 553,500, M_w/M_n 18.8.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.5:9.5.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.4g, 0.8 mmoles, 1.0eq.), methyl methacylate (1.6 ml, 15.0 mmoles, 20.0eq.) and benzoyl peroxide (20mg, 0.01eq.) in sodium dried toluene (0.5 ml, 6.1M). Yield 1.4g (70 %); $[\alpha]^{26}_D$ +0.6 (c = 0.5, $CHCl_3$); υ_{max} (KBr) 3383 (br), 2979 (s), 2951 (s), 1730 (s), 1675 (m), 1522 (m), 1450 (m), 1375 (m), 1368 (m), 1263 (s), 1188 (s), 1151 (s) and 1063 cm^{-1} (w); δ_H 0.5-2.2 (brm, C<u>H</u> + C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 2.8-2.9 (brs, C<u>H</u>$_2$Ph), 3.1-3.5 (brs, 1x β-C<u>H</u>$_2$O + CO_2C<u>H</u>$_3$), 3.6-3.7 (brs, 1x β-C<u>H</u>$_2$O), 4.3-4.6 (brm, Ala-α-C<u>H</u> + Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 6.8-7.1 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 16.4 (<u>C</u>H_2), 18.6 (Ala-<u>C</u>H_3), 18.7 (<u>C</u>H_3), 27.8 (C(<u>C</u>H_3)$_3$), 28.3 (C(<u>C</u>H_3)$_3$), 38.2 (<u>C</u>H_2Ph), 44.5 (<u>C</u>CH_3), 44.8 (<u>C</u>H), 51.7 (CO_2<u>C</u>H_3), 52.1 (α-<u>C</u>H), 54.1 (α-<u>C</u>H), 64.0 (<u>C</u>H_2O), 80.2 (<u>C</u>(CH$_3$)$_3$), 82.5 (<u>C</u>(CH$_3$)$_3$), 126.8 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 136.1 (Ar *ipso*<u>C</u>), 155.7 (N<u>C</u>O_2), 168.6 (<u>C</u>ONH), 170.2 (<u>C</u>O_2), 176.9 (<u>C</u>O_2), 177.8 (<u>C</u>O_2), 178.1 (<u>C</u>O_2); GPC (DMF) M_n 16,350, M_w 47,650, M_w/M_n 2.9.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 9.6:0.4.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.6g, 1.1 mmoles, 3.0eq.), methyl methacrylate (40μl, 0.4 mmoles, 1.0eq.) and benzoyl peroxide (4mg, 0.01eq.) in sodium dried toluene (0.9 ml, 1.6M). Yield 0.6g (94 %); $[\alpha]^{26}_D$ +26.8 ($CHCl_3$); υ_{max} (KBr) 3327 (br), 2979 (s), 2933 (s), 1775 (s), 1654 (s), 1522 (s), 1458 (m), 1368 (m), 1275 (m), 1240 (m), 1160 (s), 1096 (s) and 976 cm^{-1} (s); δ_H 0.7-2.0 (brm, C<u>H</u> + C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 2.7-3.0 (brs, C<u>H</u>$_2$Ph), 3.2-3.5

(brs, 1x β-C$\underline{H}_2$O + $CO_2C\underline{H}_3$), 3.8-4.4 (brm, 1x β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.4-4.7 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 5.0-5.1 (brs, Boc-N$\underline{H}$), 6.8-7.2 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 16.4 ($\underline{C}H_2$), 18.9 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3)_3$), 28.4 (C($\underline{C}H_3)_3$), 38.2 ($\underline{C}H_2$Ph), 44.3 ($\underline{C}CH_3$), 44.6 ($\underline{C}H$), 50.3 (Ala-α-$\underline{C}H$), 51.7 ($CO_2\underline{C}H_3$), 52.0 (α-$\underline{C}H$), 54.0 (α-$\underline{C}H$), 64.2 ($\underline{C}H_2O$), 79.4 (C($\underline{C}H_3)_3$), 82.1 (C($\underline{C}H_3)_3$), 126.8 (Ar$\underline{C}H$), 128.3 (Ar$\underline{C}H$), 129.5 (Ar$\underline{C}H$), 136.3 (Ar *ipso*$\underline{C}$), 155.4 (N$\underline{C}O_2$), 168.7 ($\underline{C}ONH$), 170.1 ($\underline{C}O_2$), 173.5 ($\underline{C}O_2$); GPC (DMF) M_n 8,100, M_w 20,750, M_w/M_n 2.6.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 7.5:2.5.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.5g, 1.0 mmoles, 5.5eq.), methyl methacrylate (90μl, 0.9 mmoles, 4.5eq.) and benzoyl peroxide (4mg, 0.01eq.) in sodium dried toluene (0.8 ml, 2.1M). Yield 0.4g (65 %); $[\alpha]^{26}_D$ +15.5 (c = 0.6, $CHCl_3$); υ_{max} (KBr) 3325 (br), 2975 (s), 1735 (s), 1663 (s), 1523 (s), 1463 (m), 1368 (m), 1256 (s), 1163 (s), 1088 (w) and 1038 cm^{-1} (w); δ_H 0.7-1.6 (brm, C$\underline{H}$ + $C\underline{H}_2$ + 2x C($C\underline{H}_3)_3$ + $C\underline{H}_3$), 2.9-3.1 (brs, $C\underline{H}_2$Ph), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 4.0-4.3 (brm, β-C$\underline{H}_2$O), 4.3-4.5 (brm, Ala-α-C$\underline{H}$), 4.5-4.7 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.9-5.1 (brs, Boc-N$\underline{H}$), 6.9-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 17.9 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.7 (C($\underline{C}H_3)_3$), 28.2 (C($\underline{C}H_3)_3$), 37.7 ($\underline{C}H_2$Ph), 43.9 ($\underline{C}CH_3$), 44.2 ($\underline{C}H$), 50.1 (Ala-α-$\underline{C}H$), 51.9 ($CO_2\underline{C}H_3$), 53.9 (α-$\underline{C}H$), 63.6 ($\underline{C}H_2O$), 79.6 (C($\underline{C}H_3)_3$), 82.2 (C($\underline{C}H_3)_3$), 126.8 (Ar$\underline{C}H$), 128.3 (Ar$\underline{C}H$), 129.3 (Ar$\underline{C}H$), 136.1 (Ar *ipso*$\underline{C}$), 155.4 (N$\underline{C}O_2$), 167.7 ($\underline{C}ONH$), 168.2 ($\underline{C}ONH$), 170.1 ($\underline{C}O_2$), 173.5 ($\underline{C}O_2$); GPC (DMF) M_n 9,815, M_w 24,950, M_w/M_n 2.5.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 3.2:6.8.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.4g, 0.8 mmoles, 1.0eq.), methyl methacrylate (0.3 ml, 3.1 mmoles, 4.0eq.) and benzoyl peroxide (9mg, 0.01eq.) in sodium dried toluene (0.7 ml, 3.9M). Yield 0.4g (61 %); $[\alpha]^{26}_D$ +3.3 (c = 0.6, $CHCl_3$); υ_{max} (KBr) 3371 (br), 2979 (s), 1734 (s), 1663 (s), 1508 (s), 1450 (m), 1388 (m), 1368 (s), 1250 (s), 1161 (s), 1075 (w) and 1025 cm^{-1}

(w); δ_H 0.7-1.6 (brm, C<u>H</u> + C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 2.9-3.1 (brd, C<u>H</u>$_2$Ph), 3.4-3.7 (brs, CO$_2$C<u>H</u>$_3$), 4.0-4.5 (brm, β-C<u>H</u>$_2$O + Ala-α-C<u>H</u>), 4.6-4.8 (brm, Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 4.9-5.1 (brs, Boc-N<u>H</u>), 6.8-7.3 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 18.1 (Ala-<u>C</u>H$_3$ + <u>C</u>H$_3$), 27.8 (C(<u>C</u>H$_3$)$_3$), 28.8 (C(<u>C</u>H$_3$)$_3$), 37.9 (<u>C</u>H$_2$Ph), 44.3 (<u>C</u>CH$_3$), 44.6 (<u>C</u>H), 50.4 (Ala-α-<u>C</u>H), 52.1 (CO$_2$<u>C</u>H$_3$), 53.8 (α-<u>C</u>H), 63.8 (<u>C</u>H$_2$O), 79.7 (<u>C</u>(CH$_3$)$_3$), 82.4 (<u>C</u>(CH$_3$)$_3$), 126.9 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.3 (Ar<u>C</u>H), 136.0 (Ar *ipso*<u>C</u>), 155.6 (N<u>C</u>O$_2$), 168.0 (<u>C</u>ONH), 169.9 (<u>C</u>O$_2$), 172.8 (<u>C</u>O$_2$); GPC (DMF) M_n 13,900, M_w 39,350, M_w/M_n 2.8.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1.2:8.8.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.3g, 0.5 mmoles, 1.0eq.), methyl methacrylate (0.5 ml, 4.3 mmoles, 9.0eq.) and benzoyl peroxide (11mg, 0.01eq.) in sodium dried toluene (0.7 ml, 3.9M). Yield 0.5g (79 %); $[\alpha]^{26}_D$ +1.5 ($CHCl_3$); υ_{max} (KBr) 3371 (br), 2979 (s), 2944 (s), 1733 (s), 1677 (s), 1511 (s), 1452 (s), 1386 (m), 1362 (s), 1243 (s), 1148 (s), 1065 (w) and 989 cm^{-1} (w); δ_H 0.8-2.1 (brm, C<u>H</u> + C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 3.0-3.1 (brd, C<u>H</u>$_2$Ph), 3.4-3.7 (brs, CO$_2$C<u>H</u>$_3$), 4.0-4.4 (brm, β-C<u>H</u>$_2$O + Ala-α-C<u>H</u>), 4.6-4.8 (brm, Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 5.0-5.1 (brs, Boc-N<u>H</u>), 6.9-7.3 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 16.4 (<u>C</u>H$_2$), 18.7 (Ala-<u>C</u>H$_3$ + <u>C</u>H$_3$), 27.8 (C(<u>C</u>H$_3$)$_3$), 28.3 (C(<u>C</u>H$_3$)$_3$), 37.8 (<u>C</u>H$_2$Ph), 44.4 (<u>C</u>CH$_3$), 44.8 (<u>C</u>H), 50.4 (Ala-α-<u>C</u>H), 51.7 (CO$_2$<u>C</u>H$_3$), 52.8 (α-<u>C</u>H), 54.0 (α-<u>C</u>H), 63.8 (<u>C</u>H$_2$O), 79.8 (<u>C</u>(CH$_3$)$_3$), 82.3 (<u>C</u>(CH$_3$)$_3$), 126.9 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 136.0 (Ar *ipso*<u>C</u>), 156.3 (N<u>C</u>O$_2$), 168.0 (<u>C</u>ONH), 169.9 (<u>C</u>O$_2$), 172.8 (<u>C</u>O$_2$), 176.9 (<u>C</u>O$_2$), 177.7 (<u>C</u>O$_2$); GPC (DMF) M_n 24,100, M_w 431,500, M_w/M_n 17.9.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.3:9.7.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (52mg, 10μmoles, 1.0eq.), methyl methacrylate (0.5 ml, 4.8 mmoles, 49eq.) and benzoyl peroxide (12mg, 0.01eq.) in sodium dried toluene (0.2 ml, 6.9M). Yield 0.4g (78 %); $[\alpha]^{26}_D$ +0.5 ($CHCl_3$); υ_{max} (KBr) 3383 (br), 2979 (s), 2951 (s), 1730 (s), 1675

(m), 1522 (m), 1450 (m), 1375 (m), 1368 (m), 1263 (s), 1188 (s), 1151 (s) and 1063 cm^{-1} (w); δ_H 0.8-2.3 (brm, C<u>H</u> + C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 3.0-3.1 (brd, C<u>H</u>$_2$Ph), 3.4-3.9 (brs, $CO_2C\underline{H}_3$), 4.0-4.5 (brm, β-C<u>H</u>$_2$O + Ala-α-C<u>H</u>), 4.6-4.8 (brm, Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 5.0-5.1 (brs, Boc-N<u>H</u>), 6.9-7.3 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 16.4 (<u>C</u>H$_2$), 18.7 (Ala-<u>C</u>H$_3$ + <u>C</u>H$_3$), 27.9 (C(<u>C</u>H$_3$)$_3$), 28.4 (C(<u>C</u>H$_3$)$_3$), 37.9 (<u>C</u>H$_2$Ph), 44.5 (<u>C</u>CH$_3$), 44.9 (<u>C</u>H), 50.6 (Ala-α-<u>C</u>H), 51.8 ($CO_2\underline{C}H_3$), 52.9 (α-<u>C</u>H), 54.3 (α-<u>C</u>H), 64.0 (<u>C</u>H$_2$O), 79.8 (<u>C</u>(CH$_3$)$_3$), 82.2 (<u>C</u>(CH$_3$)$_3$), 127.0 (Ar<u>C</u>H), 128.4 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 136.1 (Ar *ipso*<u>C</u>), 156.4 (N<u>C</u>O$_2$), 168.1 (<u>C</u>ONH), 176.9 (<u>C</u>O$_2$), 177.8 (<u>C</u>O$_2$), 178.1 (<u>C</u>O$_2$); GPC (DMF) M_n 17,400, M_w 49,350, M_w/M_n 2.8.

Poly(O-acryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 3:7.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(43)** (0.3g, 0.6 mmoles, 2.0eq.), methyl methacrylate (0.2 ml, 2.3 mmoles, 8.0eq.) and benzoyl peroxide (7mg, 0.01eq.) in sodium dried toluene (0.2 ml, 1.3M). Yield 0.4g (66 %); $[\alpha]^{26}_D$ +3.1 (c = 0.5, $CHCl_3$); υ_{max} (KBr) 3366 (br), 2981 (s), 1735 (s), 1675 (m), 1508 (s), 1458 (m), 1369 (m), 1249 (s), 1160 (s) and 1063 cm^{-1} (w); δ_H 0.8-2.2 (brm, C<u>H</u> + C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$), 2.9-3.2 (brs, C<u>H</u>$_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.5 (brm, β-C<u>H</u>$_2$O + Ala-α-C<u>H</u>), 4.6-4.8 (brm, Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 5.0-5.1 (brs, Boc-N<u>H</u>), 6.9-7.4 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 16.4 (<u>C</u>H$_2$), 18.7 (Ala-<u>C</u>H$_3$ + <u>C</u>H$_3$), 27.9 (C(<u>C</u>H$_3$)$_3$), 28.4 (C(<u>C</u>H$_3$)$_3$), 37.9 (<u>C</u>H$_2$Ph), 44.5 (<u>C</u>CH$_3$), 44.9 (<u>C</u>H), 50.8 (Ala-α-<u>C</u>H), 51.8 ($CO_2\underline{C}H_3$), 52.9 (α-<u>C</u>H), 54.3 (α-<u>C</u>H), 64.0 (<u>C</u>H$_2$O), 79.9 (<u>C</u>(CH$_3$)$_3$), 82.2 (<u>C</u>(CH$_3$)$_3$), 126.9 (Ar<u>C</u>H), 128.3 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 136.1 (Ar *ipso*<u>C</u>), 156.4 (N<u>C</u>O$_2$), 168.1 (<u>C</u>ONH), 176.9 (<u>C</u>O$_2$), 177.7 (<u>C</u>O$_2$); GPC (DMF) M_n 19,500, M_w 69,500, M_w/M_n 3.6.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method G)** of monomer **(44)** (0.5g, 0.9 mmoles, 1.0eq.) and benzoyl peroxide (4mg, 0.01eq.) in sodium dried toluene (0.8 ml, 1.1M). Yield 0.4g (88 %); $[\alpha]^{26}_{D}$ +22.1 ($CHCl_3$); υ_{max} ($CHCl_3$) 3299 (br), 2978 (s), 1726 (s), 1655 (s), 1512 (s), 1452 (m), 1368 (m), 1249 (s), 1159 (s) and 1062 cm^{-1} (w); δ_H 1.0-1.7 (26H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.1 (2H, brd, C$\underline{H}_2$Ph), 4.0-4.6 (3H, brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.7-4.9 (2H, brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 5.0-5.1 (1H, brs, Boc-N$\underline{H}$), 6.9-7.5 (7H, brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 18.2 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 38.0 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 50.3 (Ala-α-$\underline{C}$H), 52.9 (Phe-α-$\underline{C}$H), 54.0 (Ser-α-$\underline{C}$H), 63.8 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 82.5 ($\underline{C}(CH_3)_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.1 (Ar *ipso*$\underline{C}$), 155.6 (N$\underline{C}O_2$), 168.1 ($\underline{C}$ONH), 170.0 ($\underline{C}O_2$), 173.3 ($\underline{C}O_2$); GPC (DMF) M_n 1,150, M_w 1,345, M_w/M_n 1.2. GPC (THF) M_n 6,945, M_w 23,600, M_w/M_n 3.4.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 6.2:3.8.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.5g, 0.9 mmoles, 1.0eq.), methyl methacrylate (0.1 ml, 0.9 mmoles, 1.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in sodium dried toluene (1.0 ml, 1.6M). Yield 0.4g (76 %); $[\alpha]^{26}_{D}$ +15.8 (c = 0.6, $CHCl_3$); υ_{max} ($CHCl_3$) 3300 (br), 2979 (s), 1728 (s), 1655 (s), 1512 (s), 1452 (m), 1368 (s), 1249 (s), 1158 (s) and 1063 cm^{-1} (w); δ_H 0.5-2.0 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.8-3.0 (brd, C$\underline{H}_2$Ph), 3.3-3.5 (brs, $CO_2C\underline{H}_3$), 3.9-4.3 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.4-4.7 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.8-4.9 (brs, Boc-N$\underline{H}$), 6.7-7.2 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 18.2 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 38.0 ($\underline{C}H_2$Ph), 44.6 ($\underline{C}CH_3$), 50.4 (Ala-α-$\underline{C}$H), 51.7 ($CO_2\underline{C}H_3$), 52.8 (α-$\underline{C}$H), 53.9 (α-$\underline{C}$H), 63.9 ($\underline{C}H_2O$), 79.8 ($\underline{C}(CH_3)_3$), 82.3 ($\underline{C}(CH_3)_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.0 (Ar *ipso*$\underline{C}$), 156.4 (N$\underline{C}O_2$), 168.2 ($\underline{C}$ONH), 170.0 ($\underline{C}O_2$), 173.1 ($\underline{C}O_2$); GPC (DMF) M_n 1,070, M_w 1,300, M_w/M_n 1.2. GPC (THF) M_n 15,100, M_w 212,000, M_w/M_n 14.0.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.5:9.5.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.4g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.8 ml, 7.3 mmoles, 10.0eq.) and benzoyl peroxide (19mg, 0.01eq.) in sodium dried toluene (1.0 ml, 4.4M). Yield 0.9g (80 %); $[\alpha]^{26}_{D}$ +0.8 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3356 (br), 2994 (s), 2950 (s), 1731 (s), 1655 (m), 1486 (m), 1450 (m), 1368 (m), 1244 (s), 1192 (s), 1152 (s) and 1063 cm^{-1} (w); δ_H 0.7-2.1 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.1 (brs, C$\underline{H}_2$Ph), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 4.0-4.4 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.5-4.7 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 16.4 ($\underline{C}H_2$), 18.7 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.8 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 38.2 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 50.5 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 52.6 (α-$\underline{C}$H), 54.3 (α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 79.9 (C($\underline{C}H_3$)$_3$), 82.4 (C($\underline{C}H_3$)$_3$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.0 (Ar *ipso*$\underline{C}$), 156.3 ($N\underline{C}O_2$), 168.4 ($\underline{C}$ONH), 170.0 ($\underline{C}O_2$), 173.2 ($\underline{C}O_2$), 177.0 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.1 ($\underline{C}O_2$); GPC (DMF) M_n 5,195, M_w 14,400, M_w/M_n 2.8. GPC (THF) M_n 8,430, M_w 18,200, M_w/M_n 2.2.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.45:9.55.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.3g, 0.5 mmoles, 1.0eq.), methyl methacrylate (1.0 ml, 9.1 mmoles, 20.0eq.) and benzoyl peroxide (23mg, 0.01eq.) in sodium dried toluene (0.7 ml, 5.6M). Yield 0.3g (29 %); $[\alpha]^{26}_{D}$ +0.6 ($CHCl_3$); υ_{max} ($CHCl_3$) 3344 (br), 2982 (s), 2950 (s), 1730 (s), 1654 (m), 1512 (m), 1451 (m), 1368 (m), 1245 (s), 1153 (s) and 1063 cm^{-1} (w); δ_H 0.7-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.0-3.2 (brd, C$\underline{H}_2$Ph), 3.5-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.5 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.6-4.8 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.9-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 16.4 ($\underline{C}H_2$), 18.2 (Ala-$\underline{C}H_3$), 18.7 ($\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 38.0 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.9 ($\underline{C}CH_3$), 50.3 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 52.3 (α-$\underline{C}$H), 53.9 (α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 79.9 (C($\underline{C}H_3$)$_3$), 82.4 (C($\underline{C}H_3$)$_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.0 (Ar *ipso*$\underline{C}$), 156.4

(N<u>C</u>O$_2$), 168.0 (<u>C</u>ONH), 170.0 (<u>C</u>O$_2$), 172.8 (<u>C</u>O$_2$), 176.9 (<u>C</u>O$_2$), 177.8 (<u>C</u>O$_2$); GPC (DMF) M_n 1,845, M_w 8,700, M_w/M_n 4.7. GPC (THF) M_n 4,545, M_w 12,100, M_w/M_n 2.6.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1:4.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.4g, 0.8 mmoles, 1.0eq.), methyl methacrylate (0.4 ml, 3.8 mmoles, 5.0eq.) and benzoyl peroxide (11mg, 0.01eq.) in sodium dried toluene (1.0 ml, 3.3M). Yield 0.7g (83 %); $[\alpha]^{26}_D$ +7.1 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3347 (br), 3019 (s), 2951 (s), 1728 (s), 1654 (m), 1514 (m), 1435 (m), 1369 (m), 1218 (s), 1155 (s) and 1067 cm^{-1} (w); δ_H 0.7-2.2 (brm, C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$ + Ala-C<u>H</u>$_3$), 2.9-3.1 (brs, C<u>H</u>$_2$Ph), 3.4-3.7 (brs, CO$_2$C<u>H</u>$_3$), 4.0-4.4 (brm, β-C<u>H</u>$_2$O + Ala-α-C<u>H</u>), 4.5-4.7 (brm, Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 7.0-7.4 (brm, ArC<u>H</u> + (2x CON<u>H</u>)); δ_C 16.4 (<u>C</u>H$_2$), 18.2 (Ala-<u>C</u>H$_3$), 18.7 (<u>C</u>H$_3$), 27.9 (C(<u>C</u>H$_3$)$_3$), 28.3 (C(<u>C</u>H$_3$)$_3$), 38.0 (<u>C</u>H$_2$Ph), 44.5 (<u>C</u>CH$_3$), 44.8 (<u>C</u>CH$_3$), 50.3 (Ala-α-<u>C</u>H), 51.8 (CO$_2$<u>C</u>H$_3$), 52.3 (α-<u>C</u>H), 53.9 (α-<u>C</u>H), 64.0 (<u>C</u>H$_2$O), 79.9 (<u>C</u>(CH$_3$)$_3$), 82.4 (<u>C</u>(CH$_3$)$_3$), 127.0 (Ar<u>C</u>H), 128.4 (Ar<u>C</u>H), 129.4 (Ar<u>C</u>H), 136.0 (Ar *ipso*<u>C</u>), 156.4 (N<u>C</u>O$_2$), 168.0 (<u>C</u>ONH), 170.0 (<u>C</u>O$_2$), 172.8 (<u>C</u>O$_2$), 176.9 (<u>C</u>O$_2$), 177.8 (<u>C</u>O$_2$); GPC (DMF) M_n 2,550, M_w 7,990, M_w/M_n 3.1. GPC (THF) M_n 12,900, M_w 198,000, M_w/M_n 15.3.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 8.2:1.8.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.6g, 1.1 mmoles, 3.0eq.), methyl methacrylate (40µl, 0.4 mmoles, 1.0eq.) and benzoyl peroxide (4mg, 0.01eq.) in sodium dried toluene (1.0 ml, 1.5M). Yield 0.5g (76 %); $[\alpha]^{26}_D$ +18.5 ($CHCl_3$); υ_{max} ($CHCl_3$) 3300 (br), 2979 (s), 2951 (m), 1728 (s), 1655 (s), 1514 (m), 1454 (m), 1392 (m), 1368 (m), 1249 (s), 1160 (s) and 1025 cm^{-1} (w); δ_H 0.7-1.9 (brm, C<u>H</u>$_2$ + 2x C(C<u>H</u>$_3$)$_3$ + C<u>H</u>$_3$ + Ala-C<u>H</u>$_3$), 2.8-3.0 (brd, C<u>H</u>$_2$Ph), 3.3-3.5 (brs, CO$_2$C<u>H</u>$_3$), 3.9-4.2 (brm, 1x β-C<u>H</u>$_2$O + Ala-α-C<u>H</u>), 4.2-4.4 (brm, 1x β-C<u>H</u>$_2$O), 4.4-4.7 (brm, Ser-α-C<u>H</u> + Phe-α-C<u>H</u>), 5.0-5.1 (brs, Boc-N<u>H</u>), 6.7-7.2 (brm, ArC<u>H</u> +

(2x CONH)); δ_C 18.2 (Ala-CH$_3$ + CH$_3$), 27.9 (C(CH$_3$)$_3$), 28.3 (C(CH$_3$)$_3$), 38.0 (CH$_2$Ph), 44.5 (CCH$_3$), 44.9 (CCH$_3$), 50.2 (Ala-α-CH), 51.8 (CO$_2$CH$_3$), 52.2 (α-CH), 53.9 (α-CH), 64.0 (CH$_2$O), 80.3 (C(CH$_3$)$_3$), 82.4 (C(CH$_3$)$_3$), 127.0 (ArCH), 128.4 (ArCH), 129.4 (ArCH), 136.0 (Ar *ipso*C), 155.6 (NCO$_2$), 168.1 (CONH), 169.9 (CO$_2$), 172.9 (CO$_2$), 173.3 (CO$_2$); GPC (DMF) M_n 1,020, M_w 1,080, M_w/M_n 1.1. GPC (THF) M_n 26,650, M_w 987,500, M_w/M_n 37.1.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 3.5:6.5.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.5g, 0.9 mmoles, 1.0eq.), methyl methacrylate (0.2 ml, 1.9 mmoles, 2.0eq.) and benzoyl peroxide (7mg, 0.01eq.) in sodium dried toluene (1.0 ml, 2.3M). Yield 0.5g (73 %); $[\alpha]^{26}_D$ +11.5 (c = 0.6, CHCl$_3$); υ_{max} (CHCl$_3$) 3334 (br), 2980 (s), 2951 (m), 1727 (s), 1655 (s), 1512 (m), 1454 (m), 1368 (m), 1247 (m), 1157 (s) and 1055 cm^{-1} (w); δ_H 0.8-2.0 (brm, CH$_2$ + 2x C(CH$_3$)$_3$ + CH$_3$ + Ala-CH$_3$), 2.9-3.2 (brd, CH$_2$Ph), 3.4-3.6 (brs, CO$_2$CH$_3$), 4.1-4.3 (brm, 1x β-CH$_2$O + Ala-α-CH), 4.4-4.5 (brm, 1x β-CH$_2$O), 4.6-4.8 (brm, Ser-α-CH + Phe-α-CH), 4.9-5.1 (brs, Boc-NH), 6.9-7.4 (brm, ArCH + (2x CONH)); δ_C 18.1 (Ala-CH$_3$ + CH$_3$), 27.8 (C(CH$_3$)$_3$), 28.3 (C(CH$_3$)$_3$), 37.8 (CH$_2$Ph), 44.4 (CCH$_3$), 44.6 (CCH$_3$), 50.4 (Ala-α-CH), 51.8 (CO$_2$CH$_3$), 53.9 (α-CH), 64.0 (CH$_2$O), 79.9 (C(CH$_3$)$_3$), 82.5 (C(CH$_3$)$_3$), 126.9 (ArCH), 128.3 (ArCH), 129.3 (ArCH), 136.0 (Ar *ipso*C), 155.3 (NCO$_2$), 168.0 (CONH), 170.0 (CO$_2$), 173.1 (CO$_2$), 177.7 (CO$_2$); GPC (DMF) M_n 1,630, M_w 3,430, M_w/M_n 2.1. GPC (THF) M_n 15,600, M_w 1,670,000, M_w/M_n 107.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 7.7:2.3.

This polymer was obtained by the polymerisation **(Method H)** of monomer **(44)** (0.5g, 0.9 mmoles, 2.0eq.), methyl methacrylate (50μl, 0.5 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in sodium dried toluene (1.0 ml, 1.3M). Yield 0.4g (86 %); $[\alpha]^{26}_D$ +17.9 (c = 0.8, CHCl$_3$); υ_{max} (CHCl$_3$) 3300 (br), 2979 (s), 2951 (m), 1728 (s), 1655 (s), 1513 (s), 1454 (m), 1392 (m), 1368 (s), 1250 (s), 1161 (s) and

1068 cm^{-1} (w); δ_H 0.7-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.5 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.6-4.8 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.9-5.1 (brs, Boc-N$\underline{H}$), 6.9-7.4 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 18.0 ($\underline{C}H_2$), 18.2 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 37.9 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 50.3 (Ala-α-$\underline{C}$H), 51.9 ($CO_2\underline{C}H_3$), 52.9 (α-$\underline{C}$H), 54.0 (α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 79.9 (C($\underline{C}H_3$)$_3$), 82.4 (C($\underline{C}H_3$)$_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.1 (Ar *ipso*$\underline{C}$), 155.6 (N$\underline{C}O_2$), 168.0 ($\underline{C}$ONH), 169.9 ($\underline{C}O_2$), 173.1 ($\underline{C}O_2$); GPC (DMF) M_n 1,015, M_w 1,285, M_w/M_n 1.3. GPC (THF) M_n 13,000, M_w 52,950, M_w/M_n 4.1.

Homopolymerisations, Method J

The amino acid monomer **(44)** was suspended in anhydrous DMF to form a solution of 1.3, 3 or 5M and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling at 273 K and then heated to reflux at 383 K under a nitrogen atmosphere. Heating was continued for 4 hours, after which time the DMF was distilled off and the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring, to an excess of light petroleum (*ca.* 150 ml). The precipitated white solid was collected by filtration, reprecipitated from light petroleum (25 ml), filtered and dried *in vacuo* for 5 hours.

Copolymerisations, Method K

The amino acid derived monomer **(44)** was suspended in freshly distilled methyl methacrylate and anhydrous DMF to form a 3.0M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling to 273 K and then heated to reflux at 368 K under a nitrogen atmosphere. Heating was either continued for 3 hours, or until the polymer had gelled out of solution. After this time, the DMF was distilled off and the crude polymer was dissolved in chloroform (*ca.* 10 ml). This was added slowly, with stirring, to an excess of light petroleum (*ca.* 125 ml). The precipitated white solid was collected by

filtration and dried *in vacuo* at 298 K for 5 hours.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu)1.3M.

This polymer was obtained by the polymerisation **(Method J)** of monomer **(44)** (0.7g, 1.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (1.0 ml, 1.3M). Yield 0.5g (63 %); $[\alpha]^{26}_{D}$ +27.5 (c = 1.0, $CHCl_3$); Found C, 59.8; H, 7.5; N, 7.6. $C_{28}H_{41}N_3O_8$.0.17 $CHCl_3$ requires C, 59.6; H, 7.3; N, 7.4 %; υ_{max} ($CHCl_3$) 3299 (br), 2978 (s), 2933 (s), 1729 (s), 1657 (s), 1522 (s), 1454 (m), 1391 (m), 1368 (s), 1250 (s), 1160 (s) and 1064 cm^{-1} (w); δ_H 0.8-1.7 (26H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.7-3.0 (2H, brm, C$\underline{H}_2$Ph), 3.9-4.3 (3H, brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.4-4.7 (2H, brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.9-5.0 (1H, brs, Boc-N$\underline{H}$), 6.8-7.2 (7H, brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); GPC (THF) M_n 2,100, M_w 11,250, M_w/M_n 5.4.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu)3M.

This polymer was obtained by the polymerisation **(Method J)** of monomer **(44)** (0.7g, 1.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (0.4 ml, 3M). Yield 0.6g (80 %); $[\alpha]^{26}_{D}$ +39.5 (c = 1.0, $CHCl_3$); Found C, 60.3; H, 7.5; N, 7.6. $C_{28}H_{41}N_3O_8$.0.1 $CHCl_3$ requires C, 60.3; H, 7.4; N, 7.5 %; υ_{max} ($CHCl_3$) 3298 (br), 2979 (s), 2934 (s), 1730 (s), 1659 (s), 1520 (s), 1455 (m), 1392 (m), 1368 (s), 1250 (s), 1161 (s) and 1069 cm^{-1} (w); δ_H 0.8-1.9 (26H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.8-3.1 (2H, brm, C$\underline{H}_2$Ph), 3.8-4.3 (3H, brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.5-4.7 (2H, brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.9-5.0 (1H, brs, Boc-N$\underline{H}$), 6.6-7.3 (7H, brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); GPC (THF) M_n 3,660, M_w 42,450, M_w/M_n 11.6.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate).

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu) **(Method I)** (230mg) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate) as a white solid. Yield 180mg (78 %); $[\alpha]^{28}_{D}$ +16.3 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3588 (br), 3097 (br), 2954 (s), 1726 (s), 1671 (s), 1545 (m), 1458 (m), 1202 (s)

and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.2 (8H, brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.6-2.8 (1H, brdd, 1x C$\underline{H}_2$Ph), 2.8-3.0 (1H, brdd, 1x C$\underline{H}_2$Ph), 3.3-4.7 (5H, brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.6-7.5 (7H, brm, ArC$\underline{H}$ + 2x N$\underline{H}$CO), 7.8-8.2 (3H, brm, $^{+}$N$\underline{H}_3$), 8.3-8.7 (1H, brs, $CO_2\underline{H}$); δ_C (DMSO-d_6) 17.2 (C$\underline{H}_3$), 36.7 (C$\underline{H}_2$Ph), 43.9 (C$\underline{C}$H$_3$), 44.4 (C$\underline{C}$H$_3$), 48.0 (Ala-α-C$\underline{H}$), 53.8 (α-C$\underline{H}$), 54.1 (α-C$\underline{H}$), 64.4 (C$\underline{H}_2$O), 126.5 (Ar$\underline{C}$H), 128.2 (Ar$\underline{C}$H), 129.2 (Ar$\underline{C}$H), 137.2 (Ar *ipso*$\underline{C}$), 169.5 ($\underline{C}$ONH), 172.6 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu)5M.

This polymer was obtained by the polymerisation **(Method J)** of monomer **(44)** (0.7g, 1.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (260µl, 5M). Yield 0.5g (76 %); $[\alpha]^{26}_D$ +39.7 (c = 1.0, $CHCl_3$); Found C, 60.4; H, 7.5; N, 7.6. $C_{28}H_{41}N_3O_8$.0.1 $CHCl_3$ requires C, 60.3; H, 7.4; N, 7.5 %; υ_{max} ($CHCl_3$) 3299 (br), 2979 (s), 2934 (s), 1729 (s), 1658 (s), 1522 (s), 1454 (m), 1392 (m), 1368 (s), 1250 (s), 1160 (s) and 1069 cm^{-1} (w); δ_H 0.7-2.5 (26H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.7-3.2 (2H, brm, C$\underline{H}_2$Ph), 3.7-4.3 (3H, brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.4-4.7 (2H, brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.8-5.0 (1H, brs, Boc-N$\underline{H}$), 6.6-7.3 (7H, brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); GPC (THF) M_n 4,350, M_w 86,350, M_w/M_n 19.9.

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 4.4:5.6.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.5g, 0.8 mmoles, 1.0eq.), methyl methacrylate (90µl, 0.8 mmoles, 1.0eq.) and benzoyl peroxide (4mg, 0.01eq.) in anhydrous DMF (0.2 ml, 5M). Yield 0.5g (91 %); $[\alpha]^{26}_D$ +11.4 ($CHCl_3$); υ_{max} (KBr) 3325 (br), 2980 (s), 2936 (s), 1734 (s), 1663 (s), 1517 (s), 1456 (s), 1393 (m), 1368 (s), 1249 (s), 1159 (s) and 1068 cm^{-1} (m); δ_H 0.5-2.5 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.2 (brm, C$\underline{H}_2$Ph), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.5 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.6-4.9 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 5.0-5.1 (brd, Boc-N$\underline{H}$), 6.9-7.4 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C (solid state) 17.6 ($\underline{C}H_2$), 18.2 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 28.4 (2x C($\underline{C}H_3$)$_3$), 38.0 (C$\underline{H}_2$Ph), 44.8 (2x $\underline{C}$CH$_3$), 50.2

(Ala-α-CH), 51.8 (CO_2CH_3), 52.2 (α-CH), 53.9 (α-CH), 64.0 (CH_2O), 80.4 (2x $C(CH_3)_3$), 128.6 (ArCH), 137.0 (Ar *ipso*C), 155.1 (NCO_2), 169.6 (CONH), 172.9 (CO_2), 176.3 (CO_2); GPC (THF) M_n 12,900, M_w 57,850, M_w/M_n 4.5.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 4.4:5.6.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 4.4:5.6 **(Method I)** (0.23g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 4.4:5.6 as a white solid. Yield 0.2g (84 %); $[\alpha]^{28}_D$ +12.5 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.4-2.1 (brm, CH_2 + CH_3 + Ala-CH_3), 2.6-2.8 (brm, 1x CH_2Ph), 2.8-3.0 (brm, 1x CH_2Ph), 3.5-3.7 (brs, CO_2CH_3), 4.0-4.7 (brm, Ala-α-CH + β-CH_2O + Ser-α-CH + Phe-α-CH), 6.9-7.2 (brm, ArCH + NHCO), 7.8-8.0 (brs, $^+NH_3$), 8.5-8.6 (brm, CO_2H); δ_C (DMSO-d_6) 17.2 (CH_3), 36.8 (CH_2Ph), 43.9 (CCH_3), 44.3 (CCH_3), 49.0 (Ala-α-CH), 51.8 (CO_2CH_3), 53.6 (α-CH), 55.3 (α-CH), 126.5 (ArCH), 128.2 (ArCH), 129.3 (ArCH), 137.4 (Ar *ipso*C), 169.4 (CONH), 172.6 (CO_2), 176.5 (CO_2).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1.9:8.1.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.4g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.2 ml, 2.2 mmoles, 3.0eq.) and benzoyl peroxide (7mg, 0.01eq.) in anhydrous DMF (0.3 ml, 5M). Yield 0.5g (87 %); $[\alpha]^{26}_D$ +5.0 ($CHCl_3$); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H 0.7-2.2 (brm, CH_2 + 2x $C(CH_3)_3$ + CH_3 + Ala-CH_3), 2.9-3.2 (brm, CH_2Ph), 3.4-3.8 (brs, CO_2CH_3), 4.0-4.5 (brm, β-CH_2O + Ala-α-CH), 4.6-4.8 (brm, Ser-α-CH + Phe-α-CH), 7.0-7.4 (brm, ArCH + (2x CONH)); δ_C 16.5 (CH_2), 18.2 (Ala-CH_3 + CH_3), 27.9 ($C(CH_3)_3$), 28.4 ($C(CH_3)_3$), 38.0 (CH_2Ph), 44.5 (CCH_3), 44.9 (CCH_3), 50.4 (Ala-α-CH), 51.8 (CO_2CH_3), 54.1 (α-CH), 64.1 (CH_2O), 79.8

($\underline{C}(CH_3)_3$), 80.4 ($\underline{C}(CH_3)_3$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.5 (Ar$\underline{C}$H), 137.0 (Ar *ipso*$\underline{C}$), 156.2 (N$\underline{C}O_2$), 169.6 ($\underline{C}$ONH), 172.9 ($\underline{C}O_2$), 178.1 ($\underline{C}O_2$); GPC (THF) M_n 9,650, M_w 24,650, M_w/M_n 2.6.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 1.9:8.1.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 1.9:8.1 **(Method I)** (0.2g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 1.9:8.1 as a white solid. Yield 0.19g (95 %); $[\alpha]^{28}_D$ +10.6 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3370 (br), 2993 (s), 1732 (s), 1541 (s), 1458 (m), 1203 (m), 1151 (s) and 1004 cm^{-1} (w); δ_H (DMSO-d_6) 0.6-2.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.7-2.9 (brm, 1x C$\underline{H}_2$Ph), 2.9-3.1 (brm, 1x C$\underline{H}_2$Ph), 3.3-3.6 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.9-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 7.8-8.1 (brs, $^+N\underline{H}_3$), 8.2-8.7 (brm, $CO_2\underline{H}$); δ_C (DMSO-d_6) 17.2 ($\underline{C}H_3$), 36.7 ($\underline{C}H_2$Ph), 44.0 ($\underline{C}CH_3$), 44.2 ($\underline{C}CH_3$), 48.1 (Ala-α-$\underline{C}$H), 51.9 ($CO_2\underline{C}H_3$), 53.6 (α-$\underline{C}$H), 55.4 (α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 126.5 (Ar$\underline{C}$H), 128.2 (Ar$\underline{C}$H), 129.2 (Ar$\underline{C}$H), 137.3 (Ar *ipso*$\underline{C}$), 169.5 ($\underline{C}$ONH), 172.6 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.7:9.3.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.3g, 0.6 mmoles, 1.0eq.), methyl methacrylate (0.5 ml, 5.0 mmoles, 9.0eq.) and benzoyl peroxide (13mg, 0.01eq.) in anhydrous DMF (0.5 ml, 5.5M). Yield 0.6g (74 %); $[\alpha]^{26}_D$ +0.7 ($CHCl_3$); υ_{max} (KBr) 3630 (br), 3358 (br), 2982 (s), 2952 (s), 1734 (s), 1662 (m), 1489 (s), 1451 (s), 1390 (m), 1368 (s), 1246 (s), 1152 (s) and 1065 cm^{-1} (w); δ_H 0.7-2.2 (brm, C$\underline{H}_2$ + 2x C($\underline{C}H_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.2 (brs, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.4 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.6-4.8 (brs, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 16.4 ($\underline{C}H_2$), 18.7 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.8 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 38.2 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 51.8 ($CO_2\underline{C}H_3$), 54.3 (α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 79.9 ($\underline{C}(CH_3)_3$), 82.3 ($\underline{C}(CH_3)_3$), 126.9 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.4 (Ar *ipso*$\underline{C}$), 156.3 (N$\underline{C}O_2$), 169.6 ($\underline{C}$ONH), 173.2

($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.1 ($\underline{C}O_2$); GPC (THF) M_n 10,550, M_w 35,650, M_w/M_n 3.4.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 0.7:9.3.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 0.7:9.3 **(Method I)** (0.3g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 0.7:9.3 as a white solid. Yield 0.2g (71 %); $[\alpha]^{28}_D$ +6.8 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3003 (s), 2954 (s), 1734 (s), 1560 (m), 1458 (m), 1400 (m), 1377 (m), 1288 (m), 1201 (s) and 1147 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.1 (brm, $C\underline{H}_2$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 2.8-3.0 (brm, 1x $C\underline{H}_2Ph$), 3.0-3.2 (brm, 1x $C\underline{H}_2Ph$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, Ala-α-$C\underline{H}$ + β-$C\underline{H}_2O$ + Ser-α-$C\underline{H}$ + Phe-α-$C\underline{H}$), 7.0-7.3 (brm, Ar$C\underline{H}$ + N$\underline{H}$CO), 7.8-8.0 (brs, $^+N\underline{H}_3$), 8.1-8.6 (brm, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.4 ($\underline{C}H_2$), 17.1 ($\underline{C}H_3$), 18.5 ($\underline{C}H_3$), 36.7 ($\underline{C}H_2Ph$), 44.0 ($\underline{C}CH_3$), 44.3 ($\underline{C}CH_3$), 48.4 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 53.5 (α-$\underline{C}$H), 126.6 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.3 (Ar$\underline{C}$H), 137.4 (Ar *ipso*$\underline{C}$), 169.5 ($\underline{C}$ONH), 172.5 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 0.3:9.7.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.2g, 0.4 mmoles, 1.0eq.), methyl methacrylate (0.7 ml, 6.9 mmoles, 19.0eq.) and benzoyl peroxide (18mg, 0.01eq.) in anhydrous DMF (1.5 ml, 5M). Yield 0.8g (94 %); $[\alpha]^{26}_D$ -1.0 ($CHCl_3$); υ_{max} (KBr) 3568 (br), 3368 (br), 2996 (s), 2952 (s), 1732 (s), 1659 (m), 1487 (s), 1450 (s), 1389 (m), 1368 (s), 1272 (s), 1244 (s), 1194 (s), 1150 (s) and 1064 cm^{-1} (w); δ_H 0.7-2.0 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 2.9-3.1 (brs, $C\underline{H}_2Ph$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.4 (brm, β-$C\underline{H}_2O$ + Ala-α-$C\underline{H}$), 4.5-4.7 (brs, Ser-α-$C\underline{H}$ + Phe-α-$C\underline{H}$), 7.0-7.3 (brm, Ar$C\underline{H}$ + (2x CON$\underline{H}$)); δ_C 16.4 ($\underline{C}H_2$), 18.7 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.8 ($C(\underline{C}H_3)_3$), 28.4 ($C(\underline{C}H_3)_3$), 38.2 ($\underline{C}H_2Ph$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 51.8 ($CO_2\underline{C}H_3$), 52.6 (α-$\underline{C}$H), 54.4 (α-$\underline{C}$H), 64.1 ($\underline{C}H_2O$), 79.9 ($\underline{C}(CH_3)_3$), 82.3 ($\underline{C}(CH_3)_3$), 126.8 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.4 (Ar *ipso*$\underline{C}$), 156.3

($N\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.0 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 10,750, M_w 29,950, M_w/M_n 2.8.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 0.3:9.7.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 0.3:9.7 **(Method I)** (0.3g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 0.3:9.7 as a white solid. Yield 0.26g (86 %); $[\alpha]^{28}_D$ +4.3 (c = 0.7, DMSO : AcCN 1:1); δ_H (DMSO-d_6) 0.6-2.2 (brm, $C\underline{H}_2$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 2.8-3.0 (brm, 1x $C\underline{H}_2Ph$), 3.0-3.2 (brm, 1x $C\underline{H}_2Ph$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.1-4.7 (brm, Ala-α-C$\underline{H}$ + β-$C\underline{H}_2O$ + Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.0-8.2 (brs, $^+N\underline{H}_3$), 8.5-8.8 (brm, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.3 ($\underline{C}H_2$), 18.5 ($\underline{C}H_3$), 36.7 ($\underline{C}H_2Ph$), 44.0 ($\underline{C}CH_3$), 44.4 ($\underline{C}CH_3$), 48.2 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 53.5 (α-$\underline{C}$H), 126.5 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.3 (Ar$\underline{C}$H), 137.4 (Ar *ipso*$\underline{C}$), 169.5 ($\underline{C}$ONH), 172.6 ($\underline{C}O_2$), 176.4 ($\underline{C}O_2$), 177.5 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 8.4:1.6.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.4g, 0.8 mmoles, 3.0eq.), methyl methacrylate (30μl, 0.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (0.2 ml, 5M). Yield 0.4g (88 %); $[\alpha]^{26}_D$ +23.1 ($CHCl_3$); υ_{max} (KBr) 3568 (br), 3316 (br), 2980 (s), 2935 (s), 1732 (s), 1654 (s), 1522 (s), 1456 (s), 1393 (s), 1368 (s), 1250 (s), 1158 (s) and 1068 cm^{-1} (m); δ_H 1.0-1.9 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 2.7-3.0 (brs, $C\underline{H}_2Ph$), 3.2-3.5 (brs, $CO_2C\underline{H}_3$), 3.7-3.8 (brm, 1x β-$C\underline{H}_2O$), 3.9-4.4 (brm, 1x β-$C\underline{H}_2O$ + Ala-α-C$\underline{H}$), 4.4-4.7 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 5.0-5.2 (brs, Boc-N$\underline{H}$), 6.7-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 18.3 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 ($C(\underline{C}H_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 37.7 ($\underline{C}H_2Ph$), 44.5 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 50.2 (Ala-α-$\underline{C}$H), 52.0 ($CO_2\underline{C}H_3$ + α-$\underline{C}$H), 54.2 (α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 82.5 ($\underline{C}(CH_3)_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.3 (Ar$\underline{C}$H), 136.1 (Ar *ipso*$\underline{C}$), 156.6 ($N\underline{C}O_2$), 168.1 ($\underline{C}$ONH), 170.1 ($\underline{C}O_2$), 170.4 ($\underline{C}O_2$), 173.3 ($\underline{C}O_2$); GPC (THF) M_n 13,550, M_w 70,950, M_w/M_n 5.2.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 8.4:1.6.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 8.4:1.6 **(Method I)** (0.15g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 8.4:1.6 as a white solid. Yield 0.13g (86 %); $[\alpha]^{28}_{D}$ +15.4 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.4-2.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.7-2.9 (brm, 1x C$\underline{H}_2$Ph), 2.9-3.1 (brm, 1x C$\underline{H}_2$Ph), 3.3-3.6 (brs, $CO_2C\underline{H}_3$), 3.7-4.7 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.9-7.4 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 7.8-8.3 (brm, $^{+}N\underline{H}_3$), 8.4-8.8 (brm, $CO_2\underline{H}$); δ_C (DMSO-d_6) 17.3 ($\underline{C}H_3$), 36.7 ($\underline{C}H_2$Ph), 43.9 ($\underline{C}CH_3$), 44.4 ($\underline{C}CH_3$), 48.2 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 53.6 (α-$\underline{C}$H), 55.3 (α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 126.6 (Ar$\underline{C}$H), 128.3 (Ar$\underline{C}$H), 129.3 (Ar$\underline{C}$H), 137.4 (Ar *ipso*$\underline{C}$), 169.6 ($\underline{C}$ONH), 172.6 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 6.5:3.5.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.6g, 1.1 mmoles, 3.0eq.), methyl methacrylate (80μl, 0.7 mmoles, 2.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in anhydrous DMF (0.5 ml, 3M). Yield 0.55g (81 %); $[\alpha]^{26}_{D}$ +16.1 (c = 0.7, $CHCl_3$); υ_{max} (KBr) 3325 (br), 2980 (s), 2936 (s), 1734 (s), 1663 (s), 1517 (s), 1456 (s), 1393 (m), 1368 (s), 1249 (s), 1159 (s) and 1068 cm^{-1} (m); δ_H 0.7-1.9 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.2 (brm, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.5 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.6-4.9 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 5.2-5.4 (brs, Boc-N$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 18.3 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 37.8 ($\underline{C}H_2$Ph), 44.5 ($\underline{C}CH_3$), 50.2 (Ala-α-$\underline{C}$H), 51.9 ($CO_2\underline{C}H_3$ + α-$\underline{C}$H), 54.0 (α-$\underline{C}$H), 62.6 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 82.5 ($\underline{C}(CH_3)_3$), 127.0 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 136.1 (Ar *ipso*$\underline{C}$), 156.4 (N$\underline{C}O_2$), 168.1 ($\underline{C}$ONH), 170.1 ($\underline{C}O_2$), 170.4 ($\underline{C}O_2$), 173.4 ($\underline{C}O_2$); GPC (THF) M_n 2,035, M_w 25,250, M_w/M_n 12.4.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 6.5:3.5.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 6.5:3.5 **(Method I)** (0.18g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 6.5:3.5 as a white solid. Yield 0.14g (79 %); $[\alpha]^{28}_{D}$ +14.1 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3369 (br), 2982 (s), 1729 (s), 1668 (s), 1541 (s), 1456 (m), 1205 (s), 1159 (s) and 1004 cm^{-1} (w); δ_H (DMSO-d_6) 0.4-2.1 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.6-2.8 (brm, 1x C$\underline{H}_2$Ph), 2.8-3.1 (brm, 1x C$\underline{H}_2$Ph), 3.6-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.9-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 7.6-8.2 (brm, $^{+}N\underline{H}_3$), 8.3-8.8 (brm, $CO_2\underline{H}$); δ_C (DMSO-d_6) 17.0 (C$\underline{H}_3$ + C$\underline{H}_2$), 36.7 (C$\underline{H}_2$Ph), 43.9 (C$\underline{C}H_3$), 44.2 (C$\underline{C}H_3$), 48.1 (Ala-α-C$\underline{H}$), 51.6 ($CO_2C\underline{H}_3$), 53.5 (α-C$\underline{H}$), 55.4 (α-C$\underline{H}$), 64.4 (C$\underline{H}_2$O), 126.5 (ArC$\underline{H}$), 128.2 (ArC$\underline{H}$), 129.2 (ArC$\underline{H}$), 137.3 (Ar *ipso*C), 169.5 (C$\underline{O}$NH), 172.5 ($C\underline{O}_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu-co-MMA) 1.4:8.6.

This polymer was obtained by the polymerisation **(Method K)** of monomer **(44)** (0.3g, 0.6 mmoles, 1.5eq.), methyl methacrylate (0.3 ml, 3.2 mmoles, 8.5eq.) and benzoyl peroxide (9mg, 0.01eq.) in anhydrous DMF (0.9 ml, 3M). Yield 0.5g (79 %); $[\alpha]^{26}_{D}$ +3.3 (c = 0.7, $CHCl_3$); υ_{max} (KBr) 3630 (br), 3358 (br), 2982 (s), 2952 (s), 1734 (s), 1662 (m), 1489 (s), 1451 (s), 1390 (m), 1368 (s), 1246 (s), 1152 (s) and 1065 cm^{-1} (w); δ_H 0.7-1.9 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.9-3.2 (brm, C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.4 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.6-4.9 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 5.2-5.4 (brs, Boc-N$\underline{H}$), 6.9-7.3 (brm, ArC$\underline{H}$ + (2x CON$\underline{H}$)); δ_C 16.4 (C$\underline{H}_2$), 18.7 (Ala-C$\underline{H}_3$ + C$\underline{H}_3$), 27.8 (C(C$\underline{H}_3$)$_3$), 28.4 (C(C$\underline{H}_3$)$_3$), 38.2 (C$\underline{H}_2$Ph), 44.5 (C$\underline{C}H_3$), 44.8 (C$\underline{C}H_3$), 50.4 (Ala-α-C$\underline{H}$), 51.8 ($CO_2C\underline{H}_3$ + α-C$\underline{H}$), 54.2 (α-C$\underline{H}$), 63.4 (C$\underline{H}_2$O), 79.8 (C(CH$_3$)$_3$), 82.1 (C(CH$_3$)$_3$), 127.0 (ArC$\underline{H}$), 128.3 (ArC$\underline{H}$), 129.4 (ArC$\underline{H}$), 136.1 (Ar *ipso*C), 156.4 (N$\underline{C}O_2$), 168.3 (C$\underline{O}$NH), 170.4 ($C\underline{O}_2$), 173.4 ($C\underline{O}_2$), 176.9 ($C\underline{O}_2$), 177.8 ($C\underline{O}_2$), 178.0 ($C\underline{O}_2$); GPC (THF) M_n 4,025, M_w 25,250, M_w/M_n 6.2.

Poly(O-methacryloyl-(S)-Ala-(S)-Ser-(S)-Phe trifluoroacetate-co-MMA) 1.4:8.6.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe-O^{t}Bu-*co*-MMA) 1.4:8.6 **(Method I)** (0.25g) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate-*co*-MMA) 1.4:8.6 as a white solid. Yield 0.2g (80 %); $[\alpha]^{28}_{D}$ +8.9 (c = 0.7, DMSO : AcCN 1:1); υ_{max} (KBr) 3370 (br), 2993 (s), 1732 (s), 1541 (s), 1458 (m), 1203 (m), 1151 (s) and 1004 cm^{-1} (w); δ_H (DMSO-d_6) 0.5-2.2 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 2.8-3.0 (brm, 1x C$\underline{H}_2$Ph), 3.0-3.2 (brm, 1x C$\underline{H}_2$Ph), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 7.0-7.3 (brm, ArC$\underline{H}$ + N$\underline{H}$CO), 8.0-8.2 (brs, $^+N\underline{H}_3$), 8.5-8.8 (brm, $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.3 ($\underline{C}H_2$), 17.1 ($\underline{C}H_3$), 18.5 ($\underline{C}H_3$), 36.7 ($\underline{C}H_2$Ph), 43.9 ($\underline{C}CH_3$), 44.3 ($\underline{C}CH_3$), 48.3 (Ala-α-$\underline{C}$H), 51.9 ($CO_2\underline{C}H_3$), 53.6 (α-$\underline{C}$H), 55.3 (α-$\underline{C}$H), 126.6 (Ar$\underline{C}$H), 128.2 (Ar$\underline{C}$H), 129.2 (Ar$\underline{C}$H), 137.4 (Ar *ipso*$\underline{C}$), 169.5 ($\underline{C}$ONH), 172.6 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$), 177.6 ($\underline{C}O_2$).

Control Experiment

Poly(O-methacryloyl-N-Boc-(S)-Ala-(S)-Ser-(S)-Phe-O^{t}Bu)3M.

A solution of monomer **(44)** (0.2g, 0.3 mmoles, 1.0eq.), in anhydrous DMF (0.1 ml, 3M) was heated at 373K for 2 hours. Subsequently the DMF was removed by distillation. The residual solid was taken up into a solution of $CHCl_3$ (4 ml) and precipitated into light petroleum (125 ml), providing a fine white solid which was collected by filtration and dried *in vacuo* for 5 hours. The petroleum was removed *in vacuo* to provide a white solid. Both solids contained no evidence of polymeric material. Yield 0.1g (75 %); TLC (PMA) ethyl acetate : light petrol (1:1): 0.53 (Starting material), 0.53 (Product); δ_H 1.27 (3H, d *J* 7.1Hz, C$\underline{H}_3$), 1.33 (9H, s, C(C$\underline{H}_3$)$_3$), 1.39 (9H, s, C(C$\underline{H}_3$)$_3$), 2.00 (3H, s, =CC$\underline{H}_3$), 3.03 (2H, d *J* 6.2Hz, β-C$\underline{H}_2$Ph), 4.20 (1H, t *J* 6.6Hz, Ala-α-C$\underline{H}$), 4.27 (1H, dd *J* 5.4, 11.3Hz, 1x β-C$\underline{H}_2$O), 4.37 (1H, dd *J* 5.5, 11.3Hz, 1x β-C$\underline{H}_2$O), 4.71 (1H, q *J* 6.3Hz, Phe-α-C$\underline{H}$), 4.80 (1H, q *J* 5.5Hz, Ser-α-C$\underline{H}$), 5.14 (1H, d *J* 7.1Hz, Boc-N$\underline{H}$), 5.57 (1H, s, =C$\underline{H}_2$), 6.07 (1H, s, =C$\underline{H}_2$), 6.96 (1H, brd *J* 7.2Hz, N$\underline{H}$CO), 7.09 (1H, brd *J* 7.0Hz, N$\underline{H}$CO), 7.15-7.30 (5H, m, ArC$\underline{H}$).

N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu ***(15)***.

To a solution of *N*-Boc-(*S*)-serine **(14)** (7.9g, 38.5 mmoles, 1.2eq.) in glass distilled DMF (60 ml) under an argon atmosphere was added DCC (6.6g, 32.0 mmoles, 1.0eq.), HOBt (5.6g, 41.7 mmoles, 1.3eq.) and (*S*)-Ala-O^{t}Bu **(13)** (4.6g, 32.0 mmoles, 1.0eq.). The mixture was stirred for 60 hours after which the solvent was removed *in vacuo* and ethyl acetate (50 ml) was added to the brown oil. Filtration through celite removed a white solid (DCHU) and the filtrate was washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (3x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a light brown oil. This was purified by column chromatography eluting with ethyl acetate : light petroleum (1 : 1) to afford the title compound as a white solid. Yield 8.2g (77 %). δ_H 1.35 (3H, d *J* 7.1Hz, C$\underline{H}_3$), 1.41 (9H, s, C(C$\underline{H}_3$)$_3$), 1.44 (9H, s, C(C$\underline{H}_3$)$_3$), 3.5 (1H, brm, 1x β-C$\underline{H}_2$O), 3.63 (1H, brs, O$\underline{H}$), 3.82 (1H, brm, 1x β-C$\underline{H}_2$O), 4.05 (1H, brs, Ala-α-C$\underline{H}$), 4.27 (1H, quintet *J* 6.1Hz, Ser-α-C$\underline{H}$), 5.54 (1H, d *J* 7.5Hz, Boc-N$\underline{H}$), 7.07 (1H, brd *J* 6.6Hz, CON$\underline{H}$).

O-Acryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu ***(16)***.

To a solution of *N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu **(15)** (3.4g, 10.2 mmoles, 1.0eq.) in ethyl acetate (50 ml) cooled with ice was added triethylamine (4.3 ml, 30.5 mmoles, 3.0eq.), then acryloyl chloride (1.2 ml, 14.3 mmoles, 1.4eq.) was added dropwise with a syringe over a period of 5 minutes. The reaction mixture was stirred with ice for 1 hour and then at room temperature for a further 48 hours. This was subsequently filtered to remove a white solid (triethylamine hydrochloride) and the filtrate was washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (3x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a white solid. This was recrystallised from light petroleum (40 ml) to afford the title compound as a white solid. Yield 2.6g (66 %). δ_H 1.38 (3H, d *J* 7.1Hz, C$\underline{H}_3$), 1.44 (9H, s, C(C$\underline{H}_3$)$_3$), 1.48 (9H, s, C(C$\underline{H}_3$)$_3$), 4.3-4.5 (4H, brm, β-C$\underline{H}_2$O + Ala-α-

C<u>H</u> + Ser-α-C<u>H</u>), 5.42 (1H, brd *J* 7.1Hz, Boc-N<u>H</u>), 5.87 (1H, d *J* 10.4Hz, 1x =C<u>H</u>$_2$), 6.12 (1H, dd *J* 10.4, 17.3Hz, =C<u>H</u>), 6.45 (1H, d *J* 17.3Hz, 1x =C<u>H</u>$_2$), 6.83 (1H, brd *J* 7.7Hz, CON<u>H</u>).

O-Methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu ***(17)***.

To a solution of *N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu **(15)** (3.3g, 10.1 mmoles, 1.0eq.) in ethyl acetate (50 ml) cooled with ice was added triethylamine (4.2 ml, 30.2 mmoles, 3.0eq.), then methacryloyl chloride (1.5 ml, 15.1 mmoles, 1.5eq.) was added dropwise with a syringe over a period of 5 minutes. The reaction mixture was stirred with ice for 1 hour and then at room temperature for a further 18 hours. This was subsequently filtered to remove a white precipitate (triethylamine hydrochloride) and the filtrate was washed with sat. Na_2CO_3 (4x 25 ml), water (2x 25 ml), 2M HCl (3x 25 ml) and water (2x 25 ml). The organic layer was dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to leave a white solid. This was recrystallised from light petroleum (40 ml) to afford the title compound as a white solid. Yield 3.9g (96 %). δ_H 1.35 (3H, d *J* 7.1Hz, C<u>H</u>$_3$), 1.41 (9H, s, C(C<u>H</u>$_3$)$_3$), 1.44 (9H, s, C(C<u>H</u>$_3$)$_3$), 2.19 (3H, s, =CC<u>H</u>$_3$), 4.3-4.5 (4H, brm, β-C<u>H</u>$_2$O + Ala-α-C<u>H</u> + Ser-α-C<u>H</u>), 5.46 (1H, d *J* 7.3Hz, Boc-N<u>H</u>), 5.58 (1H, s, 1x =C<u>H</u>$_2$), 6.10 (1H, s, 1x =C<u>H</u>$_2$), 6.86 (1H, brd *J* 7.1Hz, CON<u>H</u>).

Homopolymerisations, Method L

The amino acid monomer **(16)** or **(17)** was suspended in anhydrous DMF to form a 4M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling at 273 K and then heated to reflux at 383K under a nitrogen atmosphere. Heating was continued for 4 hours, after which time the DMF was distilled off and the crude polymer was dissolved in chloroform (*ca.* 5 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 150 ml). The precipitated white solid was collected by filtration and dried *in vacuo* for 5 hours.

Copolymerisations, Method M

The amino acid derived monomer **(16)** or **(17)** was suspended in freshly distilled methyl methacrylate and anhydrous DMF to form a 3.0M solution and benzoyl peroxide (1mol %) was added. The mixture was degassed with nitrogen for 15 minutes with cooling to 273 K and then heated to reflux at 368 K under a nitrogen atmosphere. Heating was either continued for 3 hours, or until the polymer had gelled out of solution, after which time the DMF was distilled off and the crude polymer was dissolved in chloroform (*ca.* 10 ml). This was added slowly, with stirring to an excess of light petroleum (*ca.* 125 ml). The precipitated white solid was collected by filtration and dried *in vacuo* at 298 K for 5 hours.

Removal of the polymer protecting groups, Method N

The polymer was dissolved in CH_2Cl_2 (2 ml) and trifluoroacetic acid (2 ml) was added. The solution was stirred at room temperature for 17 hours. This was added slowly, with stirring to diethyl ether (40 ml). The precipitated white solid was collected by filtration and subsequently washed with diethyl ether (100 ml) and dried *in vacuo* at 298 K for 36 hours.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method L)** of monomer **(17)** (0.4g, 1.0 mmoles, 1.0eq.) and benzoyl peroxide (2mg, 0.01eq.) in anhydrous DMF (0.25 ml, 4M). Yield 0.3g (82 %); $[\alpha]^{26}_D$ -1.6 ($CHCl_3$); υ_{max} ($CHCl_3$) 3326 (br), 2978 (s), 1734 (s), 1664 (s), 1523 (s), 1453 (m), 1368 (s), 1249 (s), 1158 (s) and 1055 cm^{-1} (w); δ_H 0.6-1.9 (26H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 4.0-4.6 (4H, brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$ + Ser-α-C$\underline{H}$); δ_C 16.4 (C$\underline{H}_2$), 18.6 (Ala-C$\underline{H}_3$ + C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.4 (C(C$\underline{H}_3$)$_3$), 44.5 (C$\underline{C}$H$_3$), 44.8 (C$\underline{C}$H$_3$), 48.8 (Ala-α-C$\underline{H}$), 54.3 (Ser-α-C$\underline{H}$), 64.6 (C$\underline{H}_2$O), 80.1 (C$\underline{C}$(CH$_3$)$_3$), 82.5 (C$\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}$O$_2$), 168.1 (C$\underline{O}$NH), 171.5 (C$\underline{O}_2$); GPC (THF) M_n 6,640, M_w 38,600, M_w/M_n 5.8.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate).

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu) **(Method N)** (70mg) gave poly(*O*-methacryloyl-(*S*)-Ala-(*S*)-Ser-(*S*)-Phe trifluoroacetate) as a white solid. Yield 60mg (89 %); $[\alpha]^{28}_{D}$ +11.5 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (D_2O) 0.4-0.8 (2H, brm, C$\underline{H}_2$), 1.1-1.3 (3H, brm, Ala-C$\underline{H}_3$), 1.5-1.9 (3H, brm, C$\underline{H}_3$), 3.9-4.4 (4H, brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 1.5:8.5.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.3g, 0.8 mmoles, 1.0eq.), methyl methacrylate (0.2 ml, 2.3 mmoles, 3.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (0.8 ml, 4M). Yield 0.5g (95 %); $[\alpha]^{26}_{D}$ +5.3 ($CHCl_3$); υ_{max} ($CHCl_3$) 3342 (br), 2982 (s), 2950 (s), 1733 (s), 1672 (s), 1487 (s), 1452 (s), 1391 (s), 1368 (s), 1244 (s), 1151 (s) and 1060 cm^{-1} (m); δ_H 0.6-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.3-3.5 (brs, $CO_2C\underline{H}_3$), 3.8-4.1 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.1-4.4 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.8-6.9 (brs, CON$\underline{H}$); δ_C 16.5 (C$\underline{H}_2$), 18.6 (Ala-C$\underline{H}_3$ + C$\underline{H}_3$), 27.9 (C(C$\underline{H}_3$)$_3$), 28.2 (C(C$\underline{H}_3$)$_3$), 44.5 (C$\underline{C}$H$_3$), 44.8 (C$\underline{C}$H$_3$), 48.8 (Ala-α-C$\underline{H}$), 51.7 ($CO_2C\underline{H}_3$), 54.3 (Ser-α-C$\underline{H}$), 64.2 (C$\underline{H}_2$O), 80.0 (C$\underline{C}$(CH$_3$)$_3$), 81.8 (C$\underline{C}$(CH$_3$)$_3$), 156.4 (N$\underline{C}O_2$), 168.4 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$), 176.8 ($\underline{C}O_2$), 177.7 ($\underline{C}O_2$), 178.1 ($\underline{C}O_2$); GPC (THF) M_n 7,875, M_w 35,950, M_w/M_n 4.6.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate-co-MMA) 1.5:8.5.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu-*co*-MMA) 1.5:8.5 **(Method N)** (0.2g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Ala trifluoroacetate-*co*-MMA) 1.5:8.5 as a white solid. Yield 0.2g (91 %); $[\alpha]^{28}_{D}$ +3.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.4-3.6 (brs,

$CO_2C\underline{H}_3$), 4.0-4.6 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$), 8.0-8.6 (brm, $^{+}N\underline{H}_3$ + N$\underline{H}$CO + $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.5 ($\underline{C}H_2$), 18.6 ($\underline{C}H_3$ + Ala-$\underline{C}H_3$), 44.0 ($\underline{C}CH_3$), 44.3 ($\underline{C}CH_3$), 49.9 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 53.6 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 115.8 (q *J* 296Hz, $F_3\underline{C}CO_2$), 158.6 (q *J* 32Hz, $F_3C\underline{C}O_2$), 165.4 ($\underline{C}$ONH), 173.3 ($\underline{C}O_2$), 176.4 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 0.7:9.3.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.3g, 0.7 mmoles, 1.0eq.), methyl methacrylate (0.7 ml, 6.4 mmoles, 9.0eq.) and benzoyl peroxide (17mg, 0.01eq.) in anhydrous DMF (1.0 ml, 7M). Yield 0.7g (80 %); $[\alpha]^{26}_D$ +4.2 ($CHCl_3$); υ_{max} ($CHCl_3$) 3630 (br), 3362 (br), 2994 (s), 2950 (s), 1731 (s), 1680 (s), 1486 (s), 1450 (s), 1390 (m), 1368 (s), 1274 (s), 1243 (s), 1192 (s), 1151 (s) and 1062 cm^{-1} (m); δ_H 0.7-2.3 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.3 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.4-4.5 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.9-7.0 (brs, CON$\underline{H}$); δ_C 16.4 ($\underline{C}H_2$), 17.0 ($\underline{C}H_2$), 18.6 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.2 (C($\underline{C}H_3$)$_3$), 44.4 ($\underline{C}CH_3$), 44.7 ($\underline{C}CH_3$), 48.7 (Ala-α-$\underline{C}$H), 51.6 ($CO_2\underline{C}H_3$), 54.3 (Ser-α-$\underline{C}$H), 64.6 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 81.9 ($\underline{C}(CH_3)_3$), 155.3 ($N\underline{C}O_2$), 168.3 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$), 176.8 ($\underline{C}O_2$), 177.6 ($\underline{C}O_2$), 177.9 ($\underline{C}O_2$); GPC (THF) M_n 10,400, M_w 35,350, M_w/M_n 3.4.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate-co-MMA) 0.7:9.3.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu-*co*-MMA) 0.7:9.3 **(Method N)** (0.3g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Ala trifluoroacetate-*co*-MMA) 0.7:9.3 as a white solid. Yield 0.3g (94 %); $[\alpha]^{28}_D$ +2.1 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.3-3.7 (brs, $CO_2C\underline{H}_3$), 3.8-4.4 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$), 8.0-8.6 (brm, $^{+}N\underline{H}_3$ + N$\underline{H}$CO + $CO_2\underline{H}$); δ_C (DMSO-d_6) 16.3 ($\underline{C}H_2$), 17.7 (Ala-$\underline{C}H_3$), 18.5 ($\underline{C}H_3$), 44.0 ($\underline{C}CH_3$),

44.3 ($\underline{C}CH_3$), 49.9 (Ala-α-$\underline{C}H$), 51.8 ($CO_2\underline{C}H_3$), 53.8 (Ser-α-$\underline{C}H$), 64.2 ($\underline{C}H_2O$), 115.6 (q *J* 296Hz, $F_3\underline{C}CO_2$), 158.5 (q *J* 32Hz, $F_3C\underline{C}O_2$), 165.4 ($\underline{C}ONH$), 173.3 ($\underline{C}O_2$), 176.3 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$), 177.5 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 0.3:9.7.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.1g, 0.2 mmoles, 1.0eq.), methyl methacrylate (0.5 ml, 4.7 mmoles, 19.0eq.) and benzoyl peroxide (12mg, 0.01eq.) in anhydrous DMF (1.0 ml, 5M). Yield 0.5g (90 %); $[\alpha]^{26}_D$ +2.2 ($CHCl_3$); υ_{max} ($CHCl_3$) 3364 (br), 2997 (s), 2950 (s), 1734 (s), 1662 (m), 1485 (s), 1450 (s), 1397 (m), 1368 (m), 1274 (s), 1243 (s), 1193 (s), 1150 (s) and 1063 cm^{-1} (w); δ_H 0.7-2.3 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 3.5-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.3 (brm, β-$C\underline{H}_2O$ + Ala-α-$C\underline{H}$), 4.4-4.5 (brm, Ser-α-$C\underline{H}$ + Phe-α-$C\underline{H}$), 6.9-7.0 (brs, $CON\underline{H}$); δ_C 16.5 ($\underline{C}H_2$), 18.7 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 ($C(\underline{C}H_3)_3$), 28.2 ($C(\underline{C}H_3)_3$), 44.4 ($\underline{C}CH_3$), 44.8 ($\underline{C}CH_3$), 48.8 (Ala-α-$\underline{C}H$), 51.8 ($CO_2\underline{C}H_3$), 54.4 (Ser-α-$\underline{C}H$), 64.4 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 82.1 ($\underline{C}(CH_3)_3$), 155.5 ($N\underline{C}O_2$), 168.3 ($\underline{C}ONH$), 171.6 ($\underline{C}O_2$), 176.9 ($\underline{C}O_2$), 177.8 ($\underline{C}O_2$), 178.0 ($\underline{C}O_2$); GPC (THF) M_n 7,375, M_w 22,250, M_w/M_n 3.0.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate-co-MMA) 0.3:9.7.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu-*co*-MMA) 0.3:9.7 **(Method N)** (0.2g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Ala trifluoroacetate-*co*-MMA) 0.3:9.7 as a white solid. Yield 0.2g (94 %); $[\alpha]^{28}_D$ +1.0 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3333 (br), 2959 (s), 1735 (s), 1560 (m), 1498 (m), 1458 (m), 1282 (m), 1244 (m), 1150 (s) and 984 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.2 (brm, $C\underline{H}_2$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 3.4-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.4 (brm, Ala-α-$C\underline{H}$ + β-$C\underline{H}_2O$ + Ser-α-$C\underline{H}$), 8.3-8.6 (brm, $^+N\underline{H}_3$ + $N\underline{H}CO$); δ_C (DMSO-d_6) 16.3 ($\underline{C}H_2$), 18.6 ($\underline{C}H_3$), 44.0 ($\underline{C}CH_3$), 44.4 ($\underline{C}CH_3$), 51.8 ($CO_2\underline{C}H_3$), 53.7 (2x α-$\underline{C}H$), 115.8 (q *J* 296Hz, $F_3\underline{C}CO_2$), 158.6 (q *J* 32Hz, $F_3C\underline{C}O_2$), 176.3 ($\underline{C}O_2$), 177.3 ($\underline{C}O_2$), 177.5 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 6.8:3.2.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.4g, 1.0 mmoles, 3.0eq.), methyl methacrylate (40µl, 0.3 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (0.4 ml, 3M). Yield 0.4g (97 %); $[\alpha]^{26}_{D}$ +4.4 ($CHCl_3$); υ_{max} ($CHCl_3$) 3324 (br), 2980 (s), 2935 (s), 1732 (s), 1668 (s), 1518 (s), 1455 (s), 1392 (s), 1368 (s), 1249 (s), 1157 (s) and 1056 cm^{-1} (m); δ_H 0.7-2.4 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.5-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.3 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.4-4.7 (brm, Ser-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 6.9-7.0 (brs, CON$\underline{H}$); δ_C 18.2 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 28.0 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 44.9 ($\underline{C}CH_3$), 48.8 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 54.0 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 80.1 ($\underline{C}(CH_3)_3$), 81.7 ($\underline{C}(CH_3)_3$), 155.6 ($N\underline{C}O_2$), 168.4 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 10,250, M_w 134,000, M_w/M_n 13.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate-co-MMA) 6.8:3.2.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu-*co*-MMA) 6.8:3.2 **(Method N)** (0.1g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Ala trifluoroacetate-*co*-MMA) 6.8:3.2 as a white solid. Yield 0.1g (92 %); $[\alpha]^{28}_{D}$ +8.0 (c = 0.5, DMSO : AcCN 1:1); υ_{max} (KBr) 3343 (br), 3095 (br), 2954 (s), 1735 (s), 1676 (s), 1552 (m), 1525 (m), 1454 (m), 1188 (s) and 1018 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.1 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 3.9-4.8 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$), 8.1-8.9 (brm, $^{+}N\underline{H}_3$ + N$\underline{H}$CO); δ_C (DMSO-d_6) 16.3 ($\underline{C}H_2$), 17.3 (Ala-$\underline{C}H_3$), 18.3 ($\underline{C}H_3$), 44.0 ($\underline{C}CH_3$), 44.3 ($\underline{C}CH_3$), 49.7 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 53.8 (Ser-α-$\underline{C}$H), 64.2 ($\underline{C}H_2O$), 115.8 (q *J* 296Hz, $F_3\underline{C}CO_2$), 158.5 (q *J* 32Hz, $F_3C\underline{C}O_2$), 165.4 ($\underline{C}$ONH), 173.3 ($\underline{C}O_2$), 176.3 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 8.9:1.1.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.8g, 2.0 mmoles, 9.0eq.), methyl methacrylate (20µl, 0.2 mmoles, 1.0eq.) and benzoyl peroxide (5mg, 0.01eq.) in anhydrous DMF (0.7 ml, 3M). Yield 0.7g (85 %); $[\alpha]^{26}_{D}$ +0.5 ($CHCl_3$); υ_{max} ($CHCl_3$) 3324 (br), 2980 (s), 2935 (s), 1732 (s), 1668 (s), 1518 (s), 1455 (s), 1392 (s), 1368 (s), 1249 (s), 1157 (s) and 1056 cm^{-1} (m); δ_H 0.5-2.1 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 3.9-4.7 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$ + Ser-α-C$\underline{H}$), 6.9-7.0 (brs, CON$\underline{H}$); δ_C 18.3 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 28.0 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 44.9 ($\underline{C}CH_3$), 48.8 (Ala-α-$\underline{C}$H), 51.7 ($CO_2\underline{C}H_3$), 53.9 (Ser-α-$\underline{C}$H), 64.0 ($\underline{C}H_2O$), 80.1 ($\underline{C}(CH_3)_3$), 81.6 ($\underline{C}(CH_3)_3$), 155.6 ($N\underline{C}O_2$), 168.7 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 11,150, M_w 164,500, M_w/M_n 14.8.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate-co-MMA) 8.9:1.1.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu-*co*-MMA) 8.9:1.1 **(Method N)** (0.4g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Ala trifluoroacetate-*co*-MMA) 8.9:1.1 as a white solid. Yield 0.2g (65 %); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (D_2O) 0.5-2.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$); δ_C (DMSO-d_6) 17.3 ($\underline{C}H_3$), 19.9 ($\underline{C}H_3$), 44.0 ($\underline{C}CH_3$), 48.0 (Ala-α-$\underline{C}$H), 51.7 ($CO_2\underline{C}H_3$), 53.6 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 115.9 (q *J* 296Hz, $F_3\underline{C}CO_2$), 158.7 (q *J* 32Hz, $F_3C\underline{C}O_2$), 165.3 ($\underline{C}$ONH), 173.3 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 3.4:6.6.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.5g, 1.3 mmoles, 2.0eq.), methyl methacrylate (0.2 ml, 1.9 mmoles, 3.0eq.) and benzoyl peroxide (6mg, 0.01eq.) in anhydrous DMF (0.8 ml, 3M). Yield 0.5g (72 %); $[\alpha]^{26}_{D}$ +6.0 ($CHCl_3$); υ_{max} ($CHCl_3$) 3326 (br), 2980 (s), 2954 (s), 1734 (s), 1676 (s),

1522 (m), 1452 (m), 1390 (m), 1368 (s), 1246 (s), 1151 (s) and 1057 cm^{-1} (w); δ_H 0.7-2.1 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.3-3.5 (brs, $CO_2C\underline{H}_3$), 3.9-4.2 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$), 4.3-4.5 (brm, Ser-α-C$\underline{H}$), 6.9-7.0 (brs, CON$\underline{H}$); δ_C 18.6 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 28.0 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 44.5 ($\underline{C}CH_3$), 48.8 (Ala-α-$\underline{C}$H), 51.8 ($CO_2\underline{C}H_3$), 53.8 (Ser-α-$\underline{C}$H), 63.9 ($\underline{C}H_2O$), 80.2 ($\underline{C}$(CH$_3$)$_3$), 81.8 ($\underline{C}$(CH$_3$)$_3$), 155.6 ($N\underline{C}O_2$), 168.8 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$), 173.5 ($\underline{C}O_2$); GPC (THF) M_n 4,650, M_w 21,950, M_w/M_n 4.7.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 6.2:3.8.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.6g, 1.5 mmoles, 6.0eq.), methyl methacrylate (90μl, 0.8 mmoles, 4.0eq.) and benzoyl peroxide (6mg, 0.01eq.) in anhydrous DMF (0.7 ml, 3M). Yield 0.6g (84 %); $[\alpha]^{26}_D$ +5.4 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3324 (br), 2980 (s), 2935 (s), 1732 (s), 1668 (s), 1518 (s), 1455 (s), 1392 (m), 1368 (s), 1249 (s), 1157 (s) and 1056 cm^{-1} (w); δ_H 0.8-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.5-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.8 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$ + Ser-α-C$\underline{H}$); δ_C 18.4 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 (C($\underline{C}H_3$)$_3$), 28.4 (C($\underline{C}H_3$)$_3$), 44.9 ($\underline{C}CH_3$), 48.8 (Ala-α-$\underline{C}$H), 51.9 ($CO_2\underline{C}H_3$), 53.4 (Ser-α-$\underline{C}$H), 64.3 ($\underline{C}H_2O$), 80.2 ($\underline{C}$(CH$_3$)$_3$), 81.8 ($\underline{C}$(CH$_3$)$_3$), 155.5 ($N\underline{C}O_2$), 168.9 ($\underline{C}$ONH), 171.6 ($\underline{C}O_2$), 177.9 ($\underline{C}O_2$); GPC (THF) M_n 13,200, M_w 199,000, M_w/M_n 15.

Poly(O-methacryloyl-(S)-Ser-(S)-Ala trifluoroacetate-co-MMA) 6.2:3.8.

Deprotection of poly(*O*-methacryloyl-*N*-Boc-(*S*)-Ser-(*S*)-Ala-O^{t}Bu-*co*-MMA) 6.2:3.8 **(Method N)** (0.2g) gave poly(*O*-methacryloyl-(*S*)-Ser-(*S*)-Ala trifluoroacetate-*co*-MMA) 6.2:3.8 as a white solid. Yield 0.2g (69 %); υ_{max} (KBr) 3500 (br), 3333 (br), 3214 (br), 3048 (br), 3003 (s), 2954 (s), 1730 (s), 1702 (s), 1543 (m), 1498 (m), 1454 (m), 1389 (m), 1365 (m), 1201 (s) and 1144 cm^{-1} (s); δ_H (DMSO-d_6) 0.5-2.3 (brm, C$\underline{H}_2$ + C$\underline{H}_3$ + Ala-C$\underline{H}_3$), 3.4-3.6 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, Ala-α-C$\underline{H}$ + β-C$\underline{H}_2$O + Ser-α-C$\underline{H}$); δ_C (DMSO-d_6) 17.3 ($\underline{C}H_3$), 20.0 ($\underline{C}H_3$), 44.0 ($\underline{C}CH_3$), 48.1 (Ala-α-$\underline{C}$H), 51.7 ($CO_2\underline{C}H_3$), 53.6 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2O$), 115.9 (q *J* 296Hz, $F_3\underline{C}CO_2$), 158.7 (q *J*

32Hz, $F_3C\underline{C}O_2$), 165.3 (<u>C</u>ONH), 173.3 ($\underline{C}O_2$), 176.5 ($\underline{C}O_2$).

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 4.6:5.4.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.3g, 0.8 mmoles, 11.0eq.), methyl methacrylate (60µl, 0.6 mmoles, 9.0eq.) and benzoyl peroxide (14mg, 0.01eq.) in anhydrous DMF (0.7 ml, 2M). Yield 0.3g (80 %); $[\alpha]^{26}_D$ +6.1 (c = 0.7, $CHCl_3$); υ_{max} ($CHCl_3$) 3630 (br), 3358 (br), 2982 (s), 2952 (s), 1734 (s), 1662 (m), 1489 (s), 1451 (s), 1390 (m), 1368 (s), 1246 (s), 1152 (s) and 1065 cm^{-1} (w); δ_H 0.8-2.1 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 3.5-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, β-$C\underline{H}_2O$ + Ala-α-C<u>H</u> + Ser-α-C<u>H</u> + Phe-α-C<u>H</u>); δ_C 18.6 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 27.9 ($C(\underline{C}H_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 44.6 ($\underline{C}CH_3$), 48.8 (Ala-α-<u>C</u>H), 51.9 ($CO_2\underline{C}H_3$), 53.2 (Ser-α-<u>C</u>H), 54.2 ($\underline{C}H_2$), 64.6 ($\underline{C}H_2O$), 80.2 ($\underline{C}(CH_3)_3$), 81.8 ($\underline{C}(CH_3)_3$), 155.5 ($N\underline{C}O_2$), 168.9 (<u>C</u>ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 5,840, M_w 35,550, M_w/M_n 6.1.

Poly(O-methacryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 4.2:5.8 .

This polymer was obtained by the polymerisation **(Method M)** of monomer **(17)** (0.5g, 1.3 mmoles, 1.0eq.), methyl methacrylate (0.1 ml, 1.3 mmoles, 1.0eq.) and benzoyl peroxide (6mg, 0.01eq.) in anhydrous DMF (0.7 ml, 3M). Yield 0.5g (84 %); $[\alpha]^{26}_D$ +6.1 (c = 0.7, $CHCl_3$);υ_{max} ($CHCl_3$) 3402 (br), 3331 (br), 2982 (s), 2937 (m), 1730 (s), 1675 (s), 1516 (s), 1455 (s), 1393 (m), 1369 (s), 1215 (s), 1156 (s) and 1058 cm^{-1} (w); δ_H 0.8-2.2 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + Ala-$C\underline{H}_3$), 3.4-3.7 (brs, $CO_2C\underline{H}_3$), 4.0-4.4 (brm, β-$C\underline{H}_2O$ + Ala-α-C<u>H</u>), 4.4-4.7 (brm, Ser-α-C<u>H</u>); δ_C 18.7 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$), 28.0 ($C(\underline{C}H_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 44.6 ($\underline{C}CH_3$), 48.8 (Ala-α-<u>C</u>H), 51.9 ($CO_2\underline{C}H_3$), 53.2 (Ser-α-<u>C</u>H), 54.2 ($\underline{C}H_2$), 64.6 ($\underline{C}H_2O$), 80.3 ($\underline{C}(CH_3)_3$), 81.8 ($\underline{C}(CH_3)_3$), 155.6 ($N\underline{C}O_2$), 169.0 (<u>C</u>ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 7,990, M_w 201,000, M_w/M_n 25.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu).

This polymer was obtained by the polymerisation **(Method L)** of monomer **(16)** (0.9g, 2.3 mmoles, 1.0eq.) and benzoyl peroxide (10mg, 0.01eq.) in toluene (0.5 ml, 4.6M). Yield 0.6g (72 %); $[\alpha]^{26}_{D}$ -2.7 ($CHCl_3$); υ_{max} ($CHCl_3$) 3332 (br), 2979 (s), 2934 (s), 1731 (s), 1664 (s), 1524 (s), 1455 (m), 1392 (m), 1368 (s), 1250 (s), 1160 (s) and 1056 cm^{-1} (m); δ_H 1.0-1.6 (24H, brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}$ + Ala-C$\underline{H}_3$), 4.0-4.6 (4H, brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$ + Ser-α-C$\underline{H}$), 5.3-5.4 (1H, brs, Boc-N$\underline{H}$), 6.8-6.9 (1H, brd, N$\underline{H}$CO); δ_C 18.2 (Ala-$\underline{C}H_3$ + $\underline{C}$H), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 48.7 (Ala-α-$\underline{C}$H + $\underline{C}$CH), 53.6 (Ser-α-$\underline{C}$H), 64.3 ($\underline{C}H_2$O), 79.8 ($\underline{C}$(CH$_3$)$_3$), 81.3 ($\underline{C}$(CH$_3$)$_3$), 155.6 (N$\underline{C}$O$_2$), 168.4 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$); GPC (DMF) M_n 71,400, M_w 989,000, M_w/M_n 13.9.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 4.5:5.5.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(16)** (0.2g, 0.4 mmoles, 1.0eq.), methyl methacrylate (50µl, 0.4 mmoles, 1.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (0.3 ml, 3M). Yield 0.2g (84 %); $[\alpha]^{26}_{D}$ +1.4 ($CHCl_3$); υ_{max} ($CHCl_3$) 3346 (br), 2979 (s), 2952 (m), 1734 (s), 1670 (s), 1522 (s), 1453 (s), 1390 (m), 1368 (s), 1246 (s), 1157 (s) and 1056 cm^{-1} (w); δ_H 0.8-2.2 (brm, C$\underline{H}_2$ + 2x C(C$\underline{H}_3$)$_3$ + C$\underline{H}_3$ + C$\underline{H}$ + Ala-C$\underline{H}_3$), 3.5-3.7 (brs, CO$_2$C$\underline{H}_3$), 4.0-4.7 (brm, β-C$\underline{H}_2$O + Ala-α-C$\underline{H}$ + Ser-α-C$\underline{H}$); δ_C 18.3 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$ + $\underline{C}$H), 27.9 (C($\underline{C}H_3$)$_3$), 28.3 (C($\underline{C}H_3$)$_3$), 44.6 ($\underline{C}CH_3$), 48.8 (Ala-α-$\underline{C}$H), 51.9 (CO$_2\underline{C}H_3$), 53.2 (Ser-α-$\underline{C}$H), 64.4 ($\underline{C}H_2$O), 80.1 ($\underline{C}$(CH$_3$)$_3$), 81.6 ($\underline{C}$(CH$_3$)$_3$), 155.3 (N$\underline{C}$O$_2$), 169.0 ($\underline{C}$ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 5,740, M_w 29,200, M_w/M_n 5.1.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 1.3:8.7.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(16)** (0.1g, 0.3 mmoles, 1.0eq.), methyl methacrylate (90µl, 0.8 mmoles, 3.0eq.) and benzoyl peroxide (3mg, 0.01eq.) in anhydrous DMF (0.3 ml, 3M). Yield 0.1g (73 %);

$[\alpha]^{26}_{D}$ +1.0 ($CHCl_3$); υ_{max} ($CHCl_3$) 3350 (br), 3019 (s), 2951 (m), 1729 (s), 1675 (s), 1518 (s), 1450 (s), 1435 (m), 1393 (m), 1369 (s), 1218 (s), 1154 (s) and 1062 cm^{-1} (w); δ_H 0.6-2.5 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + C<u>H</u> + Ala-$C\underline{H}_3$), 3.4-3.9 (brs, $CO_2C\underline{H}_3$), 4.0-4.7 (brm, β-$C\underline{H}_2O$ + Ala-α-C<u>H</u> + Ser-α-C<u>H</u>), 7.0-7.2 (brm, N<u>H</u>CO); δ_C 18.3 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$ + <u>C</u>H), 27.9 ($C(\underline{C}H_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 44.6 ($\underline{C}CH_3$), 48.8 (Ala-α-<u>C</u>H), 51.9 ($CO_2\underline{C}H_3$), 53.2 (Ser-α-<u>C</u>H), 64.4 ($\underline{C}H_2O$), 80.1 ($\underline{C}(CH_3)_3$), 81.6 ($\underline{C}(CH_3)_3$), 155.3 ($N\underline{C}O_2$), 169.0 (<u>C</u>ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 5,610, M_w 25,400, M_w/M_n 4.5.

Poly(O-acryloyl-N-Boc-(S)-Ser-(S)-Ala-O^{t}Bu-co-MMA) 3:1.

This polymer was obtained by the polymerisation **(Method M)** of monomer **(16)** (0.4g, 1.1 mmoles, 3.0eq.), methyl methacrylate (40μl, 0.4 mmoles, 1.0eq.) and benzoyl peroxide (4mg, 0.01eq.) in anhydrous DMF (0.5 ml, 3M). Yield 0.3g (68 %); $[\alpha]^{26}_{D}$ -0.7 ($CHCl_3$); υ_{max} ($CHCl_3$) 3343 (br), 2979 (s), 2951 (m), 1734 (s), 1670 (s), 1523 (s), 1455 (s), 1368 (s), 1248 (s), 1159 (s) and 1056 cm^{-1} (w); δ_H 0.9-2.0 (brm, $C\underline{H}_2$ + 2x $C(C\underline{H}_3)_3$ + $C\underline{H}_3$ + C<u>H</u> + Ala-$C\underline{H}_3$), 3.5-3.8 (brs, $CO_2C\underline{H}_3$), 4.0-4.8 (brm, β-$C\underline{H}_2O$ + Ala-α-C<u>H</u> + Ser-α-C<u>H</u>); δ_C 18.3 (Ala-$\underline{C}H_3$ + $\underline{C}H_3$ + <u>C</u>H), 27.9 ($C(\underline{C}H_3)_3$), 28.3 ($C(\underline{C}H_3)_3$), 44.6 ($\underline{C}CH_3$), 48.8 (Ala-α-<u>C</u>H), 51.9 ($CO_2\underline{C}H_3$), 53.2 (Ser-α-<u>C</u>H), 64.4 ($\underline{C}H_2O$), 80.1 ($\underline{C}(CH_3)_3$), 81.6 ($\underline{C}(CH_3)_3$), 155.3 ($N\underline{C}O_2$), 169.0 (<u>C</u>ONH), 171.5 ($\underline{C}O_2$); GPC (THF) M_n 4,410, M_w 16,850, M_w/M_n 3.8.

5.3 Experimental for chapter 3

5.4 Synthesis of monomers

(*S*)-leucine *N*-carboxyanhydride **(50)**

To a suspension of (*S*)-leucine **(49)** (6.0g, 45.7 mmoles, 1.0eq.) in dry and distilled THF (50 ml) cooled to 273 K was added 20 % phosgene solution in toluene (25.2 ml, 50.2 mmoles, 1.1eq.). The reaction mixture was heated at 303 K for 3 hours. Subsequently the solution was degassed with dry N_2 for 15 minutes and filtered to remove a white solid (unreacted amino acid), dried ($MgSO_4$), filtered and the solvent

removed *in vacuo* to yield the title compound as a crystalline white solid. Yield 5.9g (82 %); υ_{max} 1852 (s) and 1782 (m); δ_H ($CDCl_3$) 0.85 (6H, 2x d *J* 7.7Hz, C<u>H</u>$_3$), 1.50-1.75 (3H, brm, C<u>H</u>$_2$, + C<u>H</u>), 4.20 (1H, quartet *J* 3.9Hz, α-C<u>H</u>), 6.92 (1H, brs, N<u>H</u>).

(*S*)-alanine *N*-carboxyanhydride **(51)**

To a suspension of (*S*)-alanine **(10)** (5.0g, 56.1 mmoles, 1.0eq.) in dry and distilled THF (35 ml) cooled to 273 K was added 20 % phosgene solution in toluene (31.0 ml, 61.7 mmoles, 1.1eq.). The reaction mixture was heated at 303 K for 3 hours. Subsequently the solution was degassed with dry N_2 for 15 minutes and filtered to remove a white solid (unreacted amino acid), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield the title compound as a white solid. Yield 4.7g (74 %); δ_H ($CDCl_3$) 1.59 (3H, d *J* 7.7Hz, C<u>H</u>$_3$), 4.43 (1H, quartet *J* 7.7Hz, α-C<u>H</u>), 6.60 (1H, brs, N<u>H</u>).

(*S*)-phenylalanine *N*-carboxyanhydride **(52)**

To a suspension of (*S*)-phenylalanine **(20)** (6.0g, 36.3 mmoles, 1.0eq.) in dry and distilled THF (50 ml) cooled to 273 K was added 20 % phosgene solution in toluene (20.0 ml, 50.2 mmoles, 1.1eq.). The reaction mixture was heated at 303 K for 3 hours. Subsequently the solution was degassed with dry N_2 for 15 minutes and filtered to remove a white solid (unreacted amino acid), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield the title compound as a white solid. Yield 6.3g (89 %); δ_H ($CDCl_3$) 3.00 (1H, dd *J* 7.7, 15.4Hz, 1x C<u>H</u>$_2$Ph), 3.30 (1H, dd *J* 7.7, 14.2Hz, 1x C<u>H</u>$_2$Ph), 4.55 (1H, m, α-C<u>H</u>), 6.23 (1H, brs, N<u>H</u>), 7.14-7.40 (5H, brm, ArC<u>H</u>).

N-Z, *N*'-Z-(*S*)-lysine **(54)**

To a solution of (*S*)-lysine.HCl **(53)** (9.1g, 49.6 mmoles, 1.0eq.) in an acetone / water solvent mixture (100 ml : 100 ml) was added K_2CO_3 (24.0g, 173.7 mmoles, 3.5eq.) and ZONSu (29.2g, 124.0 mmoles, 2.5eq.) and the solution was stirred at room temperature for 18 hours. Subsequently the reaction mixture was washed with ether

(2x 50 ml) and acidified to pH 3. The mixture was extracted with ethyl acetate (4x 50 ml), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to yield the title compound as a colourless oil. Yield 16.2g (80 %); δ_H ($CDCl_3$) 1.32-1.52 (4H, brm, C$\underline{H}_2$), 1.55-1.95 (2H, brm, C$\underline{H}_2$), 3.05-3.28 (2H, brs, *N*C$\underline{H}_2$), 4.07-4.2 (1H, brq, α-C$\underline{H}$), 4.39 (1H, brs, N$\underline{H}$), 4.97-5.18 (4H, brs, C$\underline{H}_2$O), 5.69 (1H, brd, N$\underline{H}$), 7.23-7.41 (10H, brm, ArC$\underline{H}$).

N-Z, *N*'-Z-(*S*)-lysine *p*-nitrophenyl ester **(55)**

To a solution of *N*-Z, *N*'-Z-(*S*)-lysine **(54)** (4.4g, 10.5 mmoles, 1.0eq.) in CH_2Cl_2 (50 ml) was added DCC (2.2g, 10.5 mmoles, 1.0eq.) and the solution was stirred rapidly for 5 minutes. Subsequently, *p*-nitrophenol (1.5g, 10.5 mmoles, 1.0eq.) was added and the solution was stirred at room temperature for 18 hours. Subsequently the reaction mixture was filtered to remove a white precipitate (DCHU). Then the reaction mixture was washed with Na_2CO_3 (8x 25 ml), water (2x 25 ml), 2M HCl (25 ml) and water (2x 15 ml), dried $MgSO_4$, filtered and the solvent removed *in vacuo* to provide the title compound as a colourless oil. Yield 3.4g (60 %); δ_H ($CDCl_3$) 1.40-2.05 (6H, brm, C$\underline{H}_2$), 3.05-3.24 (2H, brs, *N*C$\underline{H}_2$), 4.42-4.58 (1H, brq, α-C$\underline{H}$), 4.95 (1H, brs, N$\underline{H}$), 4.97-5.12 (4H, brs, C$\underline{H}_2$O), 5.69 (1H, brd, N$\underline{H}$), 7.10-7.34 (12H, brm, ArC$\underline{H}$ + *o*-ArC$\underline{H}$), 8.19 (2H, d *J* 11.6Hz, *m*-ArC$\underline{H}$).

5.5 Highly branched poly(amino acids) via ring opening polymerisation

Ist generation polymerisations, method O

To oven dried and nitrogen purged glassware was added monomer **(50**, **51**, or **52)**. Dry and distilled DMF (*ca.* 50 ml) was injected into the flask. Subsequently, a stock solution of the primary amine in dry and distilled DMF was prepared and 1 ml of this was injected into the reaction mixture. The reaction mixture was stirred under an argon atmosphere for 24 hours, after which time the reaction was terminated by the injection of a solution of lysine derivative **(55)** in dry and distilled DMF and the

reaction mixture was stirred for a further 15 hours. Subsequently the solvent was removed *in vacuo*, washed with ethyl acetate (1x 50 ml) and filtered. The residue was further washed with ethyl acetate (3x 50 ml) (to remove starting materials, by products and oligomers) to provide the polymeric material.

Hydrogenation of 1st and 2nd generation polymers, method P

To a solution of the first or second generation polymer in DMF was added Pd / C (*ca.* 300mg). The reaction mixture was exposed to hydrogen for 96 hours. Subsequently the reaction mixture was filtered through celite and the solvent removed *in vacuo* to provide the deprotected polymers.

2nd and 3rd generation polymers, method Q

To oven dried and nitrogen purged glassware was added first or second generation polymer. Dry and distilled DMF (*ca.* 70 ml) was injected into the flask. Subsequently, a concentrated solution of the monomer **(50**, **51**, or **52)** in dry and distilled DMF (*ca.* 5 ml) was injected into the reaction mixture. The reaction mixture was stirred under an argon atmosphere for 24 hours, after which time the reaction was terminated by the injection of a solution of lysine derivative **(55)** in dry and distilled DMF (*ca.* 10 ml) and the reaction mixture was stirred for a further 15 hours. Subsequently the solvent was removed *in vacuo*, washed with ethyl acetate (1x 50 ml) and filtered. The residue was further washed with ethyl acetate (3x 50 ml) (to remove starting materials, by products and oligomers) to provide the polymeric material.

*Poly(propylamine(((S)-Leu)$_s$-N-Z, N'-Z-(S)-Lys), poly(**56**).*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(50)** (2.0g, 12.7 mmoles, 8.0eq.), initiated by propylamine **(1a)** (0.1 ml, 1.6 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.3g, 2.4 mmoles, 1.5eq.) in dried and distilled DMF (40 ml). Yield 1.3g (58 %); υ_{max} (KBr) 3290 (br), 3055 (s), 2958 (s), 2870 (s), 1654 (s), 1544 (s), 1468 (m), 1400

(m), 1386 (m), 1334 (m), 1283 (s) and 1192 cm^{-1} (w); δ_H (DMSO-d_6) 0.8-1.0 (51H, brs, 16x Leu-C$\underline{H}_3$ + C$\underline{H}_3$), 1.2-1.8 (34H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 3x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.9-3.1 (2H, brs, *N*C$\underline{H}_2$), 3.7-3.9 (1H, brs, Lys-α-C$\underline{H}$), 4.1-4.5 (8H, brm, 8x Leu-α-C$\underline{H}$), 4.9-5.1 (4H, brs, 2x C$\underline{H}_2$O), 7.1-7.4 (10H, brm, ArC$\underline{H}$), 7.7-8.7 (9H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 21.7 (C$\underline{H}_3$), 22.3 (C$\underline{H}_3$), 24.1 (C$\underline{H}$), 40.9 (C$\underline{H}_2$), 50.8 (α-C$\underline{H}$), 51.1 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 127.8 (ArC$\underline{H}$), 128.5 (ArC$\underline{H}$), 128.9 (ArC$\underline{H}$), 136.3 (Ar *ipso*C), 168.6 (C$\underline{O}$NH), 170.0 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 1,100, M_w 1,230, M_w/M_n 1.1.

*Poly(propylamine(((S)-Leu)$_8$-(S)-Lys), poly**(57)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(56)** (0.6g, 0.5 mmoles, 1.0eq.) in dried and distilled DMF (40 ml). Yield 0.5g (94 %); δ_H (DMSO-d_6) 0.7-1.0 (51H, brs, 16x Leu-C$\underline{H}_3$ + C$\underline{H}_3$), 1.2-1.9 (34H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 3x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.9-3.1 (2H, brs, *N*C$\underline{H}_2$), 3.7-3.9 (1H, brs, Lys-α-C$\underline{H}$), 4.1-4.5 (8H, brm, 8x Leu-α-C$\underline{H}$), 7.2-8.4 (13H, brm, CON$\underline{H}$ + 2x N$\underline{H}_2$).

*Poly(propylamine(((S)-Leu)$_8$-(S)-Lys-((S)-Ala)$_{14}$-N-Z, N'-Z-(S)-Lys), poly**(58)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(51)** (0.6g, 4.9 mmoles, 14.0eq.), initiated by poly**(57)** (0.4g, 0.3 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.6g, 1.0 mmoles, 3.0eq.) in dried and distilled DMF (70 ml). Yield 0.7g (75 %); υ_{max} (KBr) 3283 (br), 2958 (s), 1654 (s), 1541 (s), 1456 (m), 1387 (m), 1340 (m) and 1253 cm^{-1} (m); δ_H (DMSO-d_6) 0.7-2.2 (139H, brm, 16x Leu-C$\underline{H}_3$, C$\underline{H}_3$, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 9x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$ + 14x Ala-C$\underline{H}_3$), 2.9-3.1 (6H, brs, *N*C$\underline{H}_2$), 3.6-3.9 (3H, brs, Lys-α-C$\underline{H}$), 4.0-4.5 (22H, brm, 8x Leu-α-C$\underline{H}$ + 14x Ala-α-C$\underline{H}$), 5.0-5.4 (8H, brs, 4x C$\underline{H}_2$O), 7.3-7.6 (20H, brm, ArC$\underline{H}$), 7.8-8.7 (25H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 21.8 (C$\underline{H}_3$), 23.1 (C$\underline{H}_3$), 24.2 (Leu-C$\underline{H}$), 40.6 (Leu-C$\underline{H}_2$), 50.8 (α-C$\underline{H}$), 51.1 (α-C$\underline{H}$), 64.3 (C$\underline{H}_2$O), 127.9 (ArC$\underline{H}$), 128.5 (ArC$\underline{H}$), 136.4 (Ar *ipso*C); GPC (*m*-cresol) M_n 3,220, M_w 3,720, M_w/M_n 1.2.

*Poly(propylamine(((S)-Leu)$_8$-(S)-Lys-((S)-Ala)$_{14}$-(S)-Lys), poly**(59)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(58)** (0.3g, 0.2 mmoles, 1.0eq.) in dried and distilled DMF (80 ml). Yield 0.3g (73 %); δ_H (DMSO-d_6) 0.7-1.0 (51H, brs, 16x Leu-C$\underline{H}_3$ + C$\underline{H}_3$), 1.2-2.2 (88H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 9x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$, + 14x Ala-C$\underline{H}_3$), 2.9-3.1 (6H, brs, *N*C$\underline{H}_2$), 3.8-4.5 (25H, brm, 8x Leu-α-C$\underline{H}$, 3x Lys-α-C$\underline{H}$ + 14x Ala-α-C$\underline{H}$), 7.2-8.4 (33H, brm, CON$\underline{H}$ + 4x N$\underline{H}_2$).

*Poly(propylamine(((S)-Leu)$_8$-(S)-Lys-((S)-Ala)$_{14}$-((S)-Phe)$_{16}$-N-Z, N′-Z-(S)-Lys), poly**(60)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(52)** (0.3g, 1.6 mmoles, 16.0eq.), initiated by poly**(59)** (0.3g, 0.1 mmoles, 1.0eq.) and capped with *N*, *N*′-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.3g, 0.5 mmoles, 5.0eq.) in dried and distilled DMF (50 ml). Yield 0.5g (77 %); υ_{max} (KBr) 3279 (br), 2957 (s), 1659 (s), 1543 (s), 1470 (m), 1392 (m), 1368 (s), 1220 (s) and 1170 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-2.2 (163H, brm, 16x Leu-C$\underline{H}_3$, C$\underline{H}_3$, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 21x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$ + 14x Ala-C$\underline{H}_3$), 2.6-3.1 (46H, brs, 7x *N*C$\underline{H}_2$ +16x C$\underline{H}_2$Ph), 3.7-4.7 (45H, brm, 7x Lys-α-C$\underline{H}$, 8x Leu-α-C$\underline{H}$, 14x Ala-α-C$\underline{H}$ + 16x Phe-α-C$\underline{H}$,), 4.8-5.2 (16H, brs, 8x C$\underline{H}_2$O), 6.8-7.5 (120H, brm, ArC$\underline{H}$), 7.6-8.6 (45H, brm, CON$\underline{H}$); δ_C (solid state) 12.0 (Lys-$\underline{C}$H$_2$), 16.1 (Ala-$\underline{C}$H$_3$), 24.3 (Leu-$\underline{C}$H$_3$), 25.4 (Lys-$\underline{C}$H$_2$), 35.7 ($\underline{C}$H$_2$Ph, (Leu-$\underline{C}$H + $\underline{C}$H$_2$)), 52.9 (α-$\underline{C}$H), 61.9 ($\underline{C}$H$_2$O), 128.8 (Ar$\underline{C}$H), 139.3 (Ar *ipso*$\underline{C}$), 140.6 (Ar *ipso*$\underline{C}$), 175.8 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 5,240, M_w 7,820, M_w/M_n 1.5.

*Poly(propylamine(((S)-Leu)$_{10}$-N-Z, N′-Z-(S)-Lys), poly**(61)**.*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(50)** (2.5g, 16.0 mmoles, 10.0eq.), initiated by propylamine **(1a)** (0.1 ml, 1.6 mmoles, 1.0eq.) and capped with *N*, *N*′-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (2.6g, 4.8 mmoles, 3.0eq.) in dried and distilled DMF (80 ml). Yield 1.9g (58 %);

υ_{max} (KBr) 3290 (br), 3055 (s), 2958 (s), 2870 (s), 1654 (s), 1544 (s), 1468 (m), 1400 (m), 1386 (m), 1334 (m), 1283 (s) and 1192 cm^{-1} (w); δ_H (DMSO-d_6) 0.8-1.0 (63H, brs, 20x Leu-C$\underline{H}_3$ + C$\underline{H}_3$), 1.2-1.8 (40H, brm, 10x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 3x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.9-3.1 (2H, brs, *N*C$\underline{H}_2$), 3.7-3.9 (1H, brs, Lys-α-C$\underline{H}$), 4.1-4.5 (10H, brm, 10x Leu-α-C$\underline{H}$), 4.9-5.1 (4H, brs, 2x C$\underline{H}_2$O), 7.1-7.4 (10H, brm, ArC$\underline{H}$), 7.6-8.7 (9H, brm, CON$\underline{H}$); δ_C (solid state) 11.7 (C$\underline{H}_3$), 24.4 (Leu-C$\underline{H}_3$), 25.8 (Leu-C$\underline{H}_3$), 31.8 (C$\underline{H}_2$), 37.1 (C$\underline{H}_2$), 44.1 (Leu-C$\underline{H}_2$ + C$\underline{H}$), 51.5 (Leu-α-C$\underline{H}$), 55.9 (α-C$\underline{H}$), 128.5 (ArC$\underline{H}$), 164.1 (C$\underline{O}$NH), 171.2 (C$\underline{O}$NH), 176.4 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 2,400, M_w 2,800, M_w/M_n 1.1.

*Poly(propylamine(((S)-Leu)$_{10}$-(S)-Lys), poly**(62)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(61)** (0.7g, 0.4 mmoles, 1.0eq.) in dried and distilled DMF (150 ml). Yield 0.5g (84 %); δ_H (DMSO-d_6) 0.7-1.0 (63H, brs, 20x Leu-C$\underline{H}_3$ + C$\underline{H}_3$), 1.2-2.1 (40H, brm, 10x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 3x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.9-3.1 (2H, brs, *N*C$\underline{H}_2$), 3.8-4.0 (1H, brs, Lys-α-C$\underline{H}$), 4.1-4.6 (10H, brm, 10x Leu-α-C$\underline{H}$), 7.5-8.2 (15H, brm, CON$\underline{H}$ + 2x N$\underline{H}_2$).

*Poly(propylamine(((S)-Leu)$_{10}$-(S)-Lys-((S)-Phe)$_{14}$-N-Z, N'-Z-(S)-Lys), poly**(63)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(52)** (0.9g, 4.5 mmoles, 14.0eq.), initiated by poly**(62)** (0.4g, 0.3 mmoles, 1.0eq.) and capped with *N*, *N*'-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.9g, 1.7 mmoles, 6.0eq.) in dried and distilled DMF (80 ml). Yield 1.2g (78 %); υ_{max} (KBr) 3300 (br), 2968 (s), 1635 (s), 1541 (s), 1456 (m), 1368 (s), 1250 (s) and 1050 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (63H, brs, 20x Leu-C$\underline{H}_3$, C$\underline{H}_3$), 1.1-2.0 (52H, brm, 10x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 9x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$), 2.6-3.1 (34H, brs, 3x *N*C$\underline{H}_2$ +14x C$\underline{H}_2$Ph), 3.7-4.7 (27H, brm, 3x Lys-α-C$\underline{H}$, 10x Leu-α-C$\underline{H}$, + 14x Phe-α-C$\underline{H}$,), 4.9-5.2 (8H, brs, 4x C$\underline{H}_2$O), 6.8-7.4 (90H, brm, ArC$\underline{H}$), 7.6-8.6 (27H, brm, CON$\underline{H}$); δ_C (solid state) 24.8 (Leu-C$\underline{H}_3$), 25.8 (Lys-C$\underline{H}_2$), 35.4 (C$\underline{H}_2$Ph, (Leu-C$\underline{H}$ + C$\underline{H}_2$)), 54.9 (α-C$\underline{H}$), 56.0 (α-C$\underline{H}$), 61.9 (C$\underline{H}_2$O), 128.8 (ArC$\underline{H}$), 139.3 (Ar *ipso*C$\underline{}$), 140.7 (Ar *ipso*C$\underline{}$), 175.7

(CONH); GPC (*m*-cresol) M_n 5,600, M_w 7,400, M_w/M_n 1.3.

Poly(propylamine(((S)-Leu)$_{10}$-(S)-Lys-((S)-Phe)$_{14}$-(S)-Lys), poly ***(64)***.

This polymer was obtained by the hydrogenation **(Method P)** of poly**(63)** (0.5g, 0.1 mmoles, 1.0eq.) in dried and distilled DMF (150 ml). Yield 0.3g (73 %); δ_H (DMSO-d_6) 0.7-1.0 (63H, brs, 20x Leu-C$\underline{H}_3$, C$\underline{H}_3$), 1.1-2.0 (52H, brm, 10x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 9x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$), 2.7-3.1 (34H, brs, 3x *N*C$\underline{H}_2$ +14x C$\underline{H}_2$Ph), 3.8-4.6 (27H, brm, 3x Lys-α-C$\underline{H}$, 10x Leu-α-C$\underline{H}$, + 14x Phe-α-C$\underline{H}$,), 6.8-7.4 (70H, brm, ArC$\underline{H}$), 7.4-8.8 (35H, brm, CON$\underline{H}$ + N$\underline{H}_2$).

Poly(propylamine(((S)-Leu)$_{10}$-(S)-Lys-((S)-Phe)$_{14}$-((S)-Ala)$_{20}$-N-Z, N′-Z-(S)-Lys), poly ***(65)***.

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(51)** (0.1g, 0.6 mmoles, 20.0eq.), initiated by poly**(64)** (0.1g, 30μmoles, 1.0eq.) and capped with *N*, *N*′-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (62μg, 0.1 mmoles, 4.0eq.) in dried and distilled DMF (60 ml). Yield 0.2g (78 %); δ_H (DMSO-d_6) 0.7-1.0 (63H, brm, 20x Leu-C$\underline{H}_3$, C$\underline{H}_3$), 1.1-1.9 (117H, brm, 10x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 21x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$ + 20x Ala-C$\underline{H}_3$), 2.7-3.1 (42H, brs, 7x *N*C$\underline{H}_2$ +14x C$\underline{H}_2$Ph), 3.7-4.4 (51H, brm, 7x Lys-α-C$\underline{H}$, 10x Leu-α-C$\underline{H}$, 20x Ala-α-C$\underline{H}$ + 14x Phe-α-C$\underline{H}$,), 4.9-5.1 (16H, brs, 8x C$\underline{H}_2$O), 6.9-7.4 (110H, brm, ArC$\underline{H}$), 7.6-8.6 (45H, brm, CON$\underline{H}$); δ_C (solid state) 15.8 (Ala-C$\underline{H}_3$), 23.4 (Leu-C$\underline{H}_3$), 41.6 (C$\underline{H}_2$Ph, + (Leu-C$\underline{H}$ + C$\underline{H}_2$)), 49.2 (α-C$\underline{H}$), 53.0 (α-C$\underline{H}$), 66.1 (C$\underline{H}_2$O), 128.5 (ArC$\underline{H}$), 136.9 (Ar *ipso*C), 157.2 (NC$\underline{O}_2$), 172.4 (C$\underline{O}$NH), 176.8 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 960, M_w 2,020, M_w/M_n 2.1.

*Poly(propylamine(((S)-Phe)$_8$-N-Z, N'-Z-(S)-Lys), poly**(66)**.*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(52)** (2.0g, 10.5 mmoles, 8.0eq.), initiated by propylamine **(1a)** (0.1 ml, 1.3 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.4g, 2.6 mmoles, 2.0eq.) in dried and distilled DMF (50 ml). Yield 1.5g (71 %); υ_{max} (KBr) 3289 (br), 3028 (s), 2978 (s), 1633 (s), 1515 (s), 1455 (s), 1409 (s), 1224 (s), 1078 (w) and 1030 cm^{-1} (w); δ_H (DMSO-d_6) 0.8-1.0 (3H, brs, C$\underline{H}_3$),1.2-1.9 (10H, brm, 3x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.3 (18H, brm, 8x C$\underline{H}_2$Ph + *N*C$\underline{H}_2$), 4.1-4.3 (1H, brm, Lys-α-C$\underline{H}$), 4.5-4.8 (8H, brs, Phe-α-C$\underline{H}$), 5.1-5.2 (4H, brs, C$\underline{H}_2$O), 7.0-7.5 (50H, brm, ArC$\underline{H}$), 7.9-9.1 (10H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 11.4 (C$\underline{H}_3$), 22.3 (Lys-C$\underline{H}_2$), 26.3 (Lys-C$\underline{H}_2$), 30.1 (Lys-C$\underline{H}_2$), 35.9 (NC$\underline{H}_2$), 37.6 (C$\underline{H}_2$Ph), 53.2 (α-C$\underline{H}$), 53.8 (α-C$\underline{H}$), 65.2 (C$\underline{H}_2$O), 126.3 (ArC$\underline{H}$), 127.8 (ArC$\underline{H}$), 128.1 (ArC$\underline{H}$), 128.5 (ArC$\underline{H}$), 129.3 (ArC$\underline{H}$), 129.8 (ArC$\underline{H}$), 137.6 (Ar *ipso*C), 137.7 (Ar *ipso*C), 167.8 (C$\underline{O}$NH), 170.5 (C$\underline{O}$NH), 170.7 (C$\underline{O}$NH), δ_C (solid state) 11.8 (C$\underline{H}_3$), 22.4 (Lys-C$\underline{H}_2$), 29.1 (Lys-C$\underline{H}_2$), 31.5 (NC$\underline{H}_2$), 40.7 (C$\underline{H}_2$Ph), 54.2 (α-C$\underline{H}$), 65.2 (C$\underline{H}_2$O), 126.9 (ArC$\underline{H}$), 129.2 (ArC$\underline{H}$), 136.8 (Ar *ipso*C), 157.6 (Z-C$\underline{O}_2$), 169.9 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 1,800, M_w 2,000, M_w/M_n 1.1.

*Poly(propylamine(((S)-Phe)$_8$-(S)-Lys), poly**(67)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(66)** (0.6g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (150 ml). Yield 0.5g (78 %); δ_H (DMSO-d_6) 0.9-1.1 (3H, brs, C$\underline{H}_3$),1.2-1.9 (10H, brm, 3x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.2 (18H, brm, 8x C$\underline{H}_2$Ph + *N*C$\underline{H}_2$), 3.8-3.9 (1H, brm, Lys-α-C$\underline{H}$), 4.1-4.5 (8H, brs, Phe-α-C$\underline{H}$), 6.8-7.1 (40H, brm, ArC$\underline{H}$), 7.4-8.1 (14H, brm, CON$\underline{H}$ + N$\underline{H}_2$).

*Poly(propylamine(((S)-Phe)$_8$-(S)-Lys-((S)-Leu)$_{16}$-N-Z, N'-Z-(S)-Lys), poly**(68)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(50)** (0.3g, 2.2 mmoles, 16.0eq.), initiated by poly**(67)** (0.2g, 0.1 mmoles, 1.0eq.) and

capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.2g, 0.4 mmoles, 3.0eq.) in dried and distilled DMF (50 ml). Yield 0.5g (78 %); υ_{max} (KBr) 3279 (br), 2957 (s), 1658 (s), 1543 (s), 1489 (m), 1407 (m), 1387 (m), 1368 (s), 1315 (m), 1280 (m), 1220 (s), 1170 (m) and 1004 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (99H, brs, 32x Leu-C$\underline{H}_3$, C$\underline{H}_3$), 1.1-1.9 (70H, brm, 16x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 9x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$), 2.7-3.1 (22H, brs, 3x *N*C$\underline{H}_2$ +8x C$\underline{H}_2$Ph), 3.9-4.1 (3H, brm, Lys-α-C$\underline{H}$), 4.2-4.7 (24H, brm, 16x Leu-α-C$\underline{H}$, + 8x Phe-α-C$\underline{H}$,), 4.9-5.1 (8H, brs, 4x C$\underline{H}_2$O), 7.0-7.4 (60H, brm, ArC$\underline{H}$), 7.7-8.8 (27H, brm, CON$\underline{H}$); δ_C (solid state) 12.0 (C$\underline{H}_3$), 22.4 (Lys-C$\underline{H}_2$), 24.7 (Leu-C$\underline{H}_3$), 34.1 (C$\underline{H}_2$Ph, (Leu-C$\underline{H}$ + C$\underline{H}_2$)), 53.2 (α-C$\underline{H}$), 66.2 (C$\underline{H}_2$O), 128.9 (ArC$\underline{H}$), 137.0 (Ar *ipso*C), 170.0 (C$\underline{O}$NH), 176.4 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 1,700, M_w 2,000, M_w/M_n 1.2.

*Poly(propylamine(((S)-Phe)$_8$-(S)-Lys-((S)-Leu)$_{16}$-(S)-Lys), poly**(69)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(68)** (150mg, 36μmoles, 1.0eq.) in dried and distilled DMF (150 ml). Yield 130mg (98 %); δ_H (DMSO-d_6) 0.7-1.0 (99H, brs, 32x Leu-C$\underline{H}_3$, C$\underline{H}_3$), 1.1-1.9 (70H, brm, 16x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 9x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$), 2.7-3.0 (22H, brs, 3x *N*C$\underline{H}_2$ +8x C$\underline{H}_2$Ph), 3.9-4.1 (3H, brm, Lys-α-C$\underline{H}$), 4.1-4.5 (24H, brm, 16x Leu-α-C$\underline{H}$, + 8x Phe-α-C$\underline{H}$,), 7.0-7.4 (40H, brm, ArC$\underline{H}$), 7.5-8.6 (35H, brm, CON$\underline{H}$ + N$\underline{H}_2$).

*Poly(propylamine(((S)-Phe)$_8$-(S)-Lys-((S)-Leu)$_{16}$-((S)-Ala)$_{16}$-N-Z, N'-Z-(S)-Lys), poly**(70)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(51)** (60mg, 0.4 mmoles, 16.0eq.), initiated by poly**(69)** (0.1g, 30μmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (90μg, 0.2 mmoles, 6.0eq.) in dried and distilled DMF (50 ml). Yield 0.2g (96 %); υ_{max} (KBr) 3429 (br), 3237 (br), 2959 (s), 1654 (s), 1540 (s), 1457 (s), 1368 (s), 1264 (m), 1192 (m) and 1050 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (99H, brm, 32x Leu-C$\underline{H}_3$, C$\underline{H}_3$), 1.1-1.9 (142H, brm, 16x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 21x Lys-C$\underline{H}_2$, 2x C$\underline{H}_2$ + 16x Ala-C$\underline{H}_3$), 2.7-3.1

(30H, brs, 7x $N\underline{C}H_2$ +8x $C\underline{H}_2Ph$), 3.8-4.0 (7H, brs, Lys-α-C$\underline{H}$), 4.0-4.6 (30H, brm, Leu-α-C$\underline{H}$, Ala-α-C$\underline{H}$ + Phe-α-C$\underline{H}$,), 4.9-5.1 (16H, brs, 8x $C\underline{H}_2O$), 6.9-7.5 (80H, brm, Ar$\underline{C}$H), 7.7-8.6 (45H, brm, CON$\underline{H}$); δ_C (solid state) 15.8 (Ala-$\underline{C}H_3$), 23.6 (Leu-$\underline{C}H_3$), 31.1 (Lys-$N\underline{C}H_2$), 40.7 ($\underline{C}H_2Ph$, + (Leu-$\underline{C}$H + $\underline{C}H_2$)), 53.1 (α-$\underline{C}$H), 65.4 ($\underline{C}H_2O$), 128.7 (Ar$\underline{C}$H), 136.9 (Ar *ipso*$\underline{C}$), 157.2 (Z-$\underline{C}O_2$), 172.0 ($\underline{C}$ONH), 176.7 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 2,200, M_w 2,200, M_w/M_n 1.0.

*Poly(1,4 diaminobutane(((S)-Leu)$_8$-N-Z, N'-Z-(S)-Lys), poly(**71**).*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(50)** (2.0g, 12.7 mmoles, 8.0eq.), initiated by 1,4 diaminobutane **(1b)** (0.2 ml, 1.6 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (2.1g, 4.0 mmoles, 2.5eq.) in dried and distilled DMF (40 ml). Yield 2.0g (71 %); υ_{max} (KBr) 3358 (br), 3067 (br), 2956 (s), 1650 (s), 1539 (s), 1467 (m), 1384 (m), 1367 (m), 1339 (m), 1256 (s), 1167 (m) and 1128 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (48H, brs, 16x Leu-C$\underline{H}_3$), 1.2-1.9 (40H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 6x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.1 (8H, brs, $N\underline{C}H_2$), 3.8-4.0 (2H, brs, Lys-α-C$\underline{H}$), 4.1-4.5 (8H, brm, 8x Leu-α-C$\underline{H}$), 4.9-5.1 (8H, brs, 4x $C\underline{H}_2O$), 7.1-7.5 (20H, brm, Ar$\underline{C}$H), 7.6-8.7 (10H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 21.7 ($\underline{C}H_3$), 23.0 ($\underline{C}H_3$), 24.1 ($\underline{C}$H), 26.4 (Lys-$\underline{C}H_2$), 29.2 (Lys-$\underline{C}H_2$), 31.6 (Lys-$\underline{C}H_2$), 38.2 (Lys-N$\underline{C}H_2$), 40.4 (Leu-$\underline{C}H_2$), 51.1 (α-$\underline{C}$H), 54.9 (α-$\underline{C}$H), 65.2 ($\underline{C}H_2O$), 65.5 ($\underline{C}H_2O$), 126.2 (Ar$\underline{C}$H), 127.8 (Ar$\underline{C}$H), 128.4 (Ar$\underline{C}$H), 136.4 (Ar *ipso*$\underline{C}$), 168.6 ($\underline{C}$ONH), 171.6 ($\underline{C}$ONH); δ_C (solid state) 24.0 ($\underline{C}H_3$), 25.7 (Lys-$\underline{C}H_2$), 31.8 (Lys-$\underline{C}H_2$), 36.9 (Lys-N$\underline{C}H_2$), 43.9 (Leu-$\underline{C}H_2$ +$\underline{C}$H), 51.8 (α-$\underline{C}$H), 66.4 ($\underline{C}H_2O$), 128.4 (Ar$\underline{C}$H), 137.1 (Ar *ipso*$\underline{C}$), 157.1 (Z-$\underline{C}O_2$), 163.8 ($\underline{C}$ONH), 171.5 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 2,300, M_w 2,640, M_w/M_n 1.1.

*Poly(1,4 diaminobutane(((S)-Leu)$_8$-(S)-Lys), poly(**72**).*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(71)** (1.5g, 0.8 mmoles, 1.0eq.) in dried and distilled DMF (80 ml). Yield 1.0g (82 %); δ_H (DMSO-d_6) 0.7-1.0 (48H, brs, 16x Leu-C$\underline{H}_3$), 1.2-1.7 (88H, brm, 8x (Leu-C$\underline{H}_2$), 6x Lys-C$\underline{H}_2$ + 2x

C$\underline{H}_2$), 1.8-2.2 (8H, brm, Leu-C$\underline{H}$), 2.9-3.1 (8H, brs, *N*C$\underline{H}_2$), 3.8-4.5 (10H, brm, 8x Leu-α-C$\underline{H}$, 2x Lys-α-C$\underline{H}$), 7.7-8.5 (18H, brm, CON$\underline{H}$ + 4x N$\underline{H}_2$).

*Poly(1,4 diaminobutane(((S)-Leu)$_8$-(S)-Lys-((S)-Phe)$_{16}$-N-Z, N'-Z-(S)-Lys), poly(**73**).*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(52)** (1.9g, 10.0 mmoles, 16.0eq.), initiated by poly(**72**) (0.9g, 0.6 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.7g, 3.1 mmoles, 5.0eq.) in dried and distilled DMF (75 ml). Yield 2.5g (78 %); υ_{max} (KBr) 3288 (br), 2957 (s), 1629 (s), 1542 (s), 1469 (m), 1387 (m), 1368 (s), 1257 (s) and 1171 cm^{-1} (s); δ_H (DMSO-d$_6$) 0.7-1.0 (48H, brs, 16x Leu-C$\underline{H}_3$), 1.2-2.1 (64H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.2 (48H, brm, 8x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.0 (6H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (8H, brs, 8x Leu-α-C$\underline{H}$), 4.4-4.7 (16H, brs, Phe-α-C$\underline{H}$), 4.9-5.2 (16H, brs, 8x C$\underline{H}_2$O), 6.9-7.5 (120H, brm, ArC$\underline{H}$), 7.6-8.6 (30H, brm, CON$\underline{H}$); δ_C (DMSO-d$_6$) 21.6 (C$\underline{H}_3$), 23.0 (C$\underline{H}_3$), 24.1 (C$\underline{H}$), 26.4 (Lys-C$\underline{H}_2$), 29.2 (Lys-C$\underline{H}_2$), 31.8 (Lys-C$\underline{H}_2$), 36.8 (Lys-NC$\underline{H}_2$), 38.2 (C$\underline{H}_2$Ph), 41.4 (Leu-C$\underline{H}_2$), 51.2 (α-C$\underline{H}$), 53.8 (α-C$\underline{H}$), 65.3 (C$\underline{H}_2$O), 65.6 (C$\underline{H}_2$O), 126.3 (ArC$\underline{H}$), 128.1 (ArC$\underline{H}$), 129.4 (ArC$\underline{H}$), 137.5 (Ar *ipso*C), 157.4 (Z-C$\underline{O}_2$), 170.6 (C$\underline{O}$NH), 171.6 (C$\underline{O}$NH); δ_C (solid state) 24.5 (C$\underline{H}_3$), 25.1 (Lys-C$\underline{H}_2$), 40.3 ((Leu-C$\underline{H}_2$, C$\underline{H}$) + C$\underline{H}_2$Ph), 53.7 (α-C$\underline{H}$), 65.9 (C$\underline{H}_2$O), 128.6 (ArC$\underline{H}$), 137.3 (Ar *ipso*C), 157.0 (Z-C$\underline{O}_2$), 171.7 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 3,870, M_w 5,300, M_w/M_n 1.4.

*Poly(1,4 diaminobutane(((S)-Leu)$_8$-(S)-Lys-((S)-Phe)$_{16}$-(S)-Lys), poly(**74**).*

This polymer was obtained by the hydrogenation **(Method P)** of poly(**73**) (1.8g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (120 ml). Yield 1.2g (75 %); δ_H (DMSO-d$_6$) 0.7-1.0 (48H, brs, 16x Leu-C$\underline{H}_3$), 1.1-2.2 (96H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 6x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.7-3.2 (48H, brs, 8x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.0 (6H, brm, Lys-α-C$\underline{H}$), 4.1-4.3 (8H, brs, Leu-α-C$\underline{H}$), 4.4-4.6 (16H, brs, Phe-α-C$\underline{H}$), 7.1-7.4 (80H, brm, ArC$\underline{H}$), 7.8-8.5 (46H, brm, CON$\underline{H}$ + 8x N$\underline{H}_2$).

*Poly(1,4 diaminobutane(((S)-Leu)$_8$-(S)-Lys-((S)-Phe)$_{16}$-((S)-Ala)$_{32}$-N-Z, N'-Z-(S)-Lys), poly(**75**).*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(51)** (0.7g, 6.0 mmoles, 32.0eq.), initiated by poly**(74)** (0.9g, 0.2 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.0g, 1.9 mmoles, 10.0eq.) in dried and distilled DMF (95 ml). Yield 1.4g (76 %); δ_H (DMSO-d_6) 0.7-1.0 (48H, brs, 16x Leu-C$\underline{H}_3$), 1.2-2.2 (240H, brm, 8x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 32x Ala-C$\underline{H}_3$, 42x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.2 (64H, brm, 16x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.4-3.9 (46H, brm, Ala-α-C$\underline{H}$ + Lys-α-C$\underline{H}$), 4.0-4.7 (24H, brm, Leu-α-C$\underline{H}$, + Phe-α-C$\underline{H}$), 4.9-5.2 (32H, brs, 16x C$\underline{H}_2$O), 6.8-7.5 (160H, brm, ArC$\underline{H}$), 7.6-8.6 (70H, brm, CON$\underline{H}$); δ_C (solid state) 15.7 (Ala-$\underline{C}H_3$), 23.7 (Leu-$\underline{C}H_3$), 24.7 (Lys-$\underline{C}H_2$), 31.7 (Lys-$\underline{C}H_2$), 40.7 ((Leu-$\underline{C}H_2$, $\underline{C}$H) + $\underline{C}H_2$Ph), 53.0 (α-$\underline{C}$H), 65.9 ($\underline{C}H_2$O), 128.6 (Ar$\underline{C}$H), 136.7 (Ar *ipso*$\underline{C}$), 157.1 (Z-$\underline{C}O_2$), 172.6 ($\underline{C}$ONH), 176.9 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 3,570, M_w 5,340, M_w/M_n 1.5.

*Poly(1,4 diaminobutane(((S)-Phe)$_8$-N-Z, N'-Z-(S)-Lys), poly(**76**).*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(52)** (2.0g, 10.5 mmoles, 8.0eq.), initiated by 1,4 diaminobutane **(1b)** (0.1 ml, 1.3 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (2.1g, 3.9 mmoles, 3.0eq.) in dried and distilled DMF (50 ml). Yield 1.8g (65 %); υ_{max} (KBr) 3300 (br), 2927 (s), 1696 (s), 1647 (s), 1540 (s), 1456 (m), 1259 (s) and 1049 cm^{-1} (s); δ_H (DMSO-d_6) 1.1-1.6 (16H, brm, 6x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.2 (24H, brm, 8x C$\underline{H}_2$Ph + 4x *N*C$\underline{H}_2$), 3.8-4.0 (2H, brm, Lys-α-C$\underline{H}$), 4.4-4.6 (8H, brs, Phe-α-C$\underline{H}$), 4.9-5.1 (8H, brs, C$\underline{H}_2$O), 7.0-7.4 (60H, brm, ArC$\underline{H}$), 7.8-8.4 (10H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 22.9 (Lys-$\underline{C}H_2$), 26.3 (Lys-$\underline{C}H_2$), 29.2 (Lys-$\underline{C}H_2$), 31.8 (N$\underline{C}H_2$), 38.2 ($\underline{C}H_2$Ph), 39.2 ($\underline{C}H_2$Ph), 54.0 (α-$\underline{C}$H), 54.2 (α-$\underline{C}$H), 65.3 ($\underline{C}H_2$O), 65.6 ($\underline{C}H_2$O), 126.3 (Ar$\underline{C}$H), 127.9 (Ar$\underline{C}$H), 128.5 (Ar$\underline{C}$H), 137.1 (Ar *ipso*$\underline{C}$), 137.4 (Ar *ipso*$\underline{C}$), 137.7 (Ar *ipso*$\underline{C}$), 156.0 (Z-$\underline{C}O_2$), 156.2 (Z-$\underline{C}O_2$), 170.5 ($\underline{C}$ONH), 170.8 ($\underline{C}$ONH), 171.8 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 2,200, M_w 2,680, M_w/M_n 1.2.

Poly(1,4 diaminobutane(((S)-Phe)$_8$-(S)-Lys), poly(77).

This polymer was obtained by the hydrogenation **(Method P)** of poly**(76)** (1.5g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (90 ml). Yield 1.3g (100 %); δ_H (DMSO-d_6) 1.1-2.2 (16H, brm, 6x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.5 (24H, brm, 8x C$\underline{H}_2$Ph + 4x *N*C$\underline{H}_2$), 3.9-4.1 (2H, brm, Lys-α-C$\underline{H}$), 4.4-4.7 (8H, brs, Phe-α-C$\underline{H}$), 7.0-7.4 (40H, brm, ArC$\underline{H}$), 7.6-8.6 (18H, brm, CON$\underline{H}$ + N$\underline{H}_2$).

Poly(1,4 diaminobutane(((S)-Phe)$_8$-(S)-Lys-((S)-Leu)$_{16}$-N-Z, N'-Z-(S)-Lys), poly(78).

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(50)** (1.7g, 10.9 mmoles, 16.0eq.), initiated by poly**(77)** (1.2g, 0.7 mmoles, 1.0eq.) and capped with *N*, *N*'-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.8g, 3.4 mmoles, 5.0eq.) in dried and distilled DMF (90 ml). Yield 2.9g (86 %); υ_{max} (KBr) 3311 (br), 2943 (s), 1654 (s), 1541 (s), 1447 (m), 1392 (m), 1368 (s), 1249 (s) and 1160 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (96H, brs, 32x Leu-C$\underline{H}_3$), 1.2-2.1 (88H, brm, 16x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.2 (32H, brm, 8x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.0 (6H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (16H, brs, 16x Leu-α-C$\underline{H}$), 4.4-4.7 (8H, brs, Phe-α-C$\underline{H}$), 4.9-5.2 (16H, brs, 8x C$\underline{H}_2$O), 6.9-7.5 (80H, brm, ArC$\underline{H}$), 7.6-8.6 (30H, brm, CON$\underline{H}$); δ_C (solid state) 23.8 (Leu-$\underline{C}H_3$), 25.0 (Lys-$\underline{C}H_2$), 40.0 ((Leu-$\underline{C}H_2$, $\underline{C}$H) + $\underline{C}H_2$Ph),48.1 (α-$\underline{C}$H), 56.2 (α-$\underline{C}$H), 65.8 ($\underline{C}H_2$O), 128.6 (Ar$\underline{C}$H), 137.4 (Ar *ipso*$\underline{C}$), 157.0 (Z-$\underline{C}O_2$), 172.5 ($\underline{C}$ONH), 176.0 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 3,810, M_w 4,890, M_w/M_n 1.3.

Poly(1,4 diaminobutane(((S)-Phe)$_8$-(S)-Lys-((S)-Leu)$_{16}$-(S)-Lys), poly(79).

This polymer was obtained by the hydrogenation **(Method P)** of poly**(78)** (1.7g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (120 ml). Yield 1.3g (88 %); δ_H (DMSO-d_6) 0.7-1.0 (96H, brs, 32x Leu-C$\underline{H}_3$), 1.2-2.1 (88H, brm, 16x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.2 (32H, brm, 8x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.0 (6H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (16H, brs, 16x Leu-α-C$\underline{H}$), 4.4-4.7 (8H, brs, Phe-α-C$\underline{H}$), 6.9-7.5 (40H,

brm, ArC<u>H</u>), 7.6-8.6 (46H, brm, CON<u>H</u> + N<u>H</u>$_2$).

*Poly(1,4 diaminobutane(((S)-Phe)$_8$-(S)-Lys-((S)-Leu)$_{16}$-((S)-Ala)$_{32}$-N-Z, N'-Z-(S)-Lys), poly(**80**).*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(51)** (0.4g, 3.7 mmoles, 32.0eq.), initiated by poly(**79**) (0.5g, 0.1 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.6g, 1.0 mmoles, 9.0eq.) in dried and distilled DMF (95 ml). Yield 0.9g (85 %); δ_H (DMSO-d$_6$) 0.6-0.9 (96H, brs, 32x Leu-C<u>H</u>$_3$), 1.1-2.1 (264H, brm, 16x (Leu-C<u>H</u>$_2$ + C<u>H</u>), 32x Ala-C<u>H</u>$_3$, 42x Lys-C<u>H</u>$_2$ + 2x C<u>H</u>$_2$), 2.6-3.0 (64H, brm, 16x *N*C<u>H</u>$_2$ + C<u>H</u>$_2$Ph), 3.2-3.6 (32H, brm, Ala-α-C<u>H</u>), 3.8-4.0 (14H,brs, Lys-α-C<u>H</u>), 4.0-4.6 (24H, brm, Leu-α-C<u>H</u>, + Phe-α-C<u>H</u>), 4.8-5.0 (32H, brs, 16x C<u>H</u>$_2$O), 6.8-7.4 (120H, brm, ArC<u>H</u>), 7.6-8.6 (70H, brm, CON<u>H</u>); δ_C (solid state) 15.7 (Ala-<u>C</u>H$_3$), 23.7 (Leu-<u>C</u>H$_3$), 24.9 (Lys-<u>C</u>H$_2$), 31.5 (Lys-<u>C</u>H$_2$), 36.5 (Lys-<u>C</u>H$_2$), 40.0 ((Leu-<u>C</u>H$_2$, <u>C</u>H) + <u>C</u>H$_2$Ph), 48.7 (α-<u>C</u>H), 53.1 (α-<u>C</u>H), 55.9 (α-<u>C</u>H), 66.5 (<u>C</u>H$_2$O), 128.5 (Ar<u>C</u>H), 137.1 (Ar *ipso*<u>C</u>), 157.3 (Z-<u>C</u>O$_2$), 172.4 (<u>C</u>ONH), 176.5 (<u>C</u>ONH); GPC (*m*-cresol) M_n 2,430, M_w 4,420, M_w/M_n 1.8.

*Poly(1,4 diaminobutane(((S)-Ala)$_{10}$-N-Z, N'-Z-(S)-Lys), poly(**81**).*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(51)** (0.7g, 6.1 mmoles, 10.0eq.), initiated by 1,4 diaminobutane **(1b)** (63μl, 0.6 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.2g, 2.3 mmoles, 3.8eq.) in dried and distilled DMF (45 ml). Yield 1.0g (96 %); υ_{max} (KBr) 3278 (br), 3067 (br), 2978 (s), 2933 (s), 1730 (s), 1656 (s), 1628 (s), 1533 (s), 1450 (m), 1378 (m), 1244 (s) and 1168 cm^{-1} (s); δ_H (DMSO-d$_6$) 1.1-1.7 (46H, brm, 10x Ala-C<u>H</u>$_3$, 6x Lys-C<u>H</u>$_2$ + 2x C<u>H</u>$_2$), 2.9-3.1 (8H, brm, 4x *N*C<u>H</u>$_2$), 3.8-3.9 (2H, brm, Lys-α-C<u>H</u>), 4.1-4.4 (10H, brm, Ala-α-C<u>H</u>), 4.9-5.1 (8H, brs, C<u>H</u>$_2$O), 7.2-7.4 (20H, brm, ArC<u>H</u>), 7.7-8.4 (12H, brm, CON<u>H</u>); δ_C (DMSO-d$_6$) 18.1 (Ala-<u>C</u>H$_3$), 22.9 (Lys-<u>C</u>H$_2$), 26.4 (Lys-<u>C</u>H$_2$), 31.6 (Lys-<u>C</u>H$_2$), 38.3 (N<u>C</u>H$_2$), 48.3 (Ala-α-<u>C</u>H), 54.7 (Lys-α-<u>C</u>H), 65.2 (<u>C</u>H$_2$O), 65.5 (<u>C</u>H$_2$O), 127.8 (Ar<u>C</u>H), 127.9 (Ar<u>C</u>H), 128.5 (Ar<u>C</u>H), 137.1

(Ar *ipso*C), 137.4 (Ar *ipso*C), 156.2 (Z-CO$_2$), 171.7 (CONH), 171.9 (CONH); δ_C (solid state) 20.4 (Ala-CH$_3$), 27.8 (Lys-CH$_2$), 31.5 (Lys-CH$_2$), 39.6 (NCH$_2$), 49.0 (α-CH), 64.9 (CH$_2$O), 128.1 (ArCH), 137.1 (Ar *ipso*C), 157.5 (Z-CO$_2$), 163.7 (CONH), 172.2 (CONH); GPC (*m*-cresol) M_n 2,400, M_w 2,900, M_w/M_n 1.2.

*Poly(1,4 diaminobutane(((S)-Ala)$_{10}$-(S)-Lys), poly(**82**).*

This polymer was obtained by the hydrogenation **(Method P)** of poly(**81**) (0.5g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (50 ml). Yield 0.3g (95 %); δ_H (DMSO-d$_6$) 1.1-1.7 (46H, brm, 10x Ala-CH$_3$, 6x Lys-CH$_2$ + 2x CH$_2$), 2.9-3.1 (8H, brm, 4x *N*CH$_2$), 3.8-3.9 (2H, brm, Lys-α-CH), 4.1-4.4 (10H, brm, Ala-α-CH), 7.5-8.4 (20H, brm, CONH + NH$_2$).

*Poly(1,4 diaminobutane(((S)-Ala)$_{10}$-(S)-Lys-((S)-Leu)$_{20}$-N-Z, N'-Z-(S)-Lys), poly(**83**).*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(50)** (1.0g, 6.5 mmoles, 20.0eq.), initiated by poly(**82**) (0.3g, 0.3 mmoles, 1.0eq.) and capped with *N*, *N*'-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.1g, 1.9 mmoles, 6.0eq.) in dried and distilled DMF (70 ml). Yield 0.9g (57 %); υ_{max} (KBr) 3358 (br), 2978 (s), 1655 (s), 1525 (s), 1455 (m), 1392 (m), 1368 (s), 1251 (s) and 1160 cm^{-1} (s); δ_H (DMSO-d$_6$) 0.7-1.0 (120H, brs, 40x Leu-CH$_3$), 1.0-1.9 (130H, brm, 20x (Leu-CH$_2$ + CH), 10x Ala-CH$_3$, 18x Lys-CH$_2$ + 2x CH$_2$), 2.8-3.1 (16H, brm, 8x *N*CH$_2$), 3.8-4.0 (6H, brs, Lys-α-CH), 4.1-4.6 (30H, brm, Leu-α-CH + Ala-α-CH), 4.9-5.1 (16H, brs, 8x CH$_2$O), 7.1-7.5 (40H, brm, ArCH), 7.6-8.8 (36H, brm, CONH); δ_C (solid state) 20.8 (Ala-CH$_3$), 23.4 (Leu-CH$_3$), 25.0 (Lys-CH$_2$), 39.7 (Leu-CH$_2$, CH), 49.0 (Ala-α-CH), 56.2 (Leu-α-CH), 65.8 (CH$_2$O), 128.7 (ArCH), 157.5 (Z-CO$_2$), 172.2 (CONH), 176.0 (CONH); GPC (*m*-cresol) M_n 2,200, M_w 2,700, M_w/M_n 1.2.

*Poly(1,4 diaminobutane(((S)-Ala)$_{10}$-(S)-Lys-((S)-Leu)$_{20}$-(S)-Lys), poly**(84)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(83)** (0.3g, 60μmoles, 1.0eq.) in dried and distilled DMF (150 ml). Yield 0.2g (98 %); δ_H (DMSO-d_6) 0.7-0.9 (120H, brs, 40x Leu-C$\underline{H}_3$), 1.0-1.9 (130H, brm, 20x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 10x Ala-C$\underline{H}_3$, 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.1 (16H, brm, 8x *N*C$\underline{H}_2$), 3.8-4.0 (6H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (30H, brm, Leu-α-C$\underline{H}$ + Ala-α-C$\underline{H}$), 7.6-8.8 (52H, brm, CON$\underline{H}$ + N$\underline{H}_2$).

*Poly(1,4 diaminobutane(((S)-Ala)$_{10}$-(S)-Lys-((S)-Leu)$_{20}$-((S)-Phe)$_{32}$-N-Z, N'-Z-(S)-Lys), poly**(85)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(52)** (0.4g, 2.2 mmoles, 32.0eq.), initiated by poly**(84)** (0.2g, 68μmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.3g, 0.5 mmoles, 8.0eq.) in dried and distilled DMF (60 ml). Yield 0.5g (67 %); υ_{max} (KBr) 3358 (br), 2978 (s), 2932 (s), 1730 (s), 1655 (s), 1525 (s), 1455 (m), 1392 (m), 1368 (s), 1251 (s) and 1160 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (120H, brs, 40x Leu-C$\underline{H}_3$), 1.1-1.9 (158H, brm, 20x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 10x Ala-C$\underline{H}_3$, 42x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.1 (96H, brm, 16x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.0 (14H,brs, Lys-α-C$\underline{H}$), 4.0-4.6 (64H, brm, Ala-α-C$\underline{H}$, Leu-α-C$\underline{H}$, + Phe-α-C$\underline{H}$), 4.8-5.0 (32H, brs, 16x C$\underline{H}_2$O), 6.8-7.4 (240H, brm, ArC$\underline{H}$), 7.6-8.6 (70H, brm, CON$\underline{H}$); δ_C (solid state) 15.7 (Ala-$\underline{C}H_3$), 23.7 (Leu-$\underline{C}H_3$), 24.9 (Lys-$\underline{C}H_2$), 31.5 (Lys-$\underline{C}H_2$), 36.5 (Lys-$\underline{C}H_2$), 40.0 ((Leu-$\underline{C}H_2$, $\underline{C}$H) + $\underline{C}H_2$Ph), 48.7 (α-$\underline{C}$H), 53.1 (α-$\underline{C}$H), 55.9 (α-$\underline{C}$H), 66.5 ($\underline{C}H_2$O), 128.5 (Ar$\underline{C}$H), 137.1 (Ar *ipso*$\underline{C}$), 157.3 (Z-$\underline{C}O_2$), 172.4 ($\underline{C}$ONH), 176.5 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 4,300, M_w 7,900, M_w/M_n 1.8. **Insert IR!**

1,3,5 Tribromomesitylene **(87)**.

To a solution of mesitylene **(86)** (2.0g, 16.6 mmoles, 1.0eq.) in benzene (50 ml) was added AIBN (0.1g, 0.6 mmoles, 0.04eq.) and *N*-bromosuccinimide (9.4g, 52.3

mmoles, 3.2eq.). Subsequently the reaction mixture was refluxed at 80 ° C for 21 hours. The reaction mixture was filtered to remove a white solid (succinimide) and subsequently washed with $NaHCO_3$ (3x 50 ml) and water (1x 30 ml), dried over $MgSO_4$ and the solvent removed *in vacuo* to obtain a yellow oil. This was recrystallised from EtOH (50 ml) to obtain the title compound as a white crystalline solid. Yield 4.5g (75 %); δ_H ($CDCl_3$) 4.44 (6H, s, $C\underline{H}_2Br$), 7.4 (3H, s, $ArC\underline{H}$).

1,3,5 Triazidomesitylene **(88)**.

To a solution of compound **(87)** (3.2g, 9.0 mmoles, 1.0eq.) in dried acetone (100 ml) was added sodium azide (6.4g, 97.5 mmoles, 10.8eq.). Subsequently the reaction mixture was refluxed at 85 °C for 21 hours under an argon atmosphere. The solvent was removed *in vacuo* and subsequently taken up in dried and distilled ether (105 ml). The reaction mixture was washed with water (105 ml), saturated NaCl (3x 50 ml), dried ($MgSO_4$) and the solvent removed *in vacuo* to obtain a yellow oil. Yield 2.1g (100 %); δ_H ($CDCl_3$) 4.40 (6H, s, $C\underline{H}_2N_3$), 7.3 (3H, s, $ArC\underline{H}$).

1,3,5 Triaminomesitylene **(89)**.

A solution of compound **(88)** (1.6g, 6.7 mmoles, 1.0eq.) in dry and distilled THF (20 ml) was added dropwise *via* a syringe to a solution of $LiAlH_4$ (0.8g, 22.0 mmoles, 3.3eq.) in dried and distilled THF (35 ml) cooled to 0 °C. Subsequently the reaction mixture was refluxed at 90 °C for 20 hours under an argon atmosphere. The reaction mixture was cooled to 0 °C and water (1 ml) was added dropwise. Subsequently the reaction mixture was filtered through a pad of celite and the solvent removed *in vacuo*. The residue was taken up in CH_2Cl_2 (50 ml) and filtered to remove a white precipitate. The solvent was removed *in vacuo* to obtain a wet white solid which was recrystallised from dry and distilled THF (5 ml) to obtain the title compound as a fine white solid. Yield 0.6g (76 %); δ_H (D_2O) 3.65 (6H, s, $C\underline{H}_2NH_2$), 4.7 (6H, s, $N\underline{H}_2$), 7.1 (3H, s, $ArC\underline{H}$).

*Poly(1,3,5 triaminomestiylene(((S)-Phe)$_{12}$-N-Z, N'-Z-(S)-Lys), poly**(90)**.*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(52)** (0.8g, 4.4 mmoles, 12.0eq.), initiated by compound **(89)** (60mg, 0.4 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.0g, 1.8 mmoles, 5.0eq.) in dried and distilled DMF (40 ml). Yield 0.9g (79 %); υ_{max} (KBr) 3292 (br), 2958 (s), 1655 (s), 1540 (s), 1468 (m), 1387 (m), 1368 (s), 1257 (s) and 1169 cm^{-1} (s); δ_H (DMSO-d_6) 1.0-1.4 (18H, brm, 9x Lys-C$\underline{H}_2$), 2.7-3.2 (30H, brm, 12x C$\underline{H}_2$Ph + 3x *N*C$\underline{H}_2$), 3.8-4.0 (3H, brm, Lys-α-C$\underline{H}$), 4.1-4.4 (6H, brs, ArC$\underline{H}_2$), 4.4-4.7 (12H, brs, Phe-α-C$\underline{H}$), 4.9-5.1 (12H, brs, C$\underline{H}_2$O), 6.8-7.0 (3H, brm, CH$_2$N$\underline{H}$), 7.0-7.5 (93H, brm, ArC$\underline{H}$), 7.7-8.6 (15H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 22.9 (Lys-$\underline{C}H_2$), 24.6 (Lys-$\underline{C}H_2$), 29.2 (Lys-$\underline{C}H_2$), 31.8 (N$\underline{C}H_2$), 37.8 ($\underline{C}H_2$Ph), 42.3 ($\underline{C}H_2$NH), 53.8 (Phe-α-$\underline{C}$H), 55.0 (Lys-α-$\underline{C}$H), 65.3 ($\underline{C}H_2$O), 65.6 ($\underline{C}H_2$O), 126.3 (Ar$\underline{C}$H), 127.1 (Ar$\underline{C}$H), 127.9 (Ar$\underline{C}$H), 128.1 (Ar$\underline{C}$H), 128.5 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 137.2 (Ar *ipso*$\underline{C}$), 137.7 (Ar *ipso*$\underline{C}$), 156.2 (Z-$\underline{C}O_2$), 168.1 ($\underline{C}$ONH), 170.8 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 2,910, M_w 3,740, M_w/M_n 1.3.

*Poly(1,3,5 triaminomestiylene(((S)-Phe)$_{12}$-(S)-Lys), poly**(91)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(90)** (0.4g, 0.1 mmoles, 1.0eq.) in dried and distilled DMF (100 ml). Yield 0.3g (92 %); δ_H (DMSO-d_6) 0.9-1.7 (18H, brm, 9x Lys-C$\underline{H}_2$), 2.7-3.2 (30H, brm, 12x C$\underline{H}_2$Ph + 3x *N*C$\underline{H}_2$), 3.8-4.0 (3H, brm, Lys-α-C$\underline{H}$), 4.1-4.4 (6H, brs, ArC$\underline{H}_2$), 4.4-4.7 (12H, brs, Phe-α-C$\underline{H}$), 6.8-7.0 (3H, brm, CH$_2$N$\underline{H}$), 7.2-7.3 (3H, brm, ArC$\underline{H}$), 7.7-8.7 (27H, brm, CON$\underline{H}$ +N$\underline{H}_2$).

*Poly(1,3,5 triaminomesitylene(((S)-Phe)$_{12}$-(S)-Lys-((S)-Leu)$_{24}$-N-Z, N'-Z-(S)-Lys), poly**(92)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(50)** (0.4g, 2.7 mmoles, 24.0eq.), initiated by poly**(91)** (0.3g, 0.1 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.4g, 0.8

mmoles, 7.0eq.) in dried and distilled DMF (80 ml). Yield 0.5g (64 %); υ_{max} (KBr) 3294 (br), 3015 (br), 2958 (s), 1644 (s), 1535 (s), 1386 (m), 1367 (m), 1256 (s) and 1165 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (144H, brs, 48x Leu-C$\underline{H}_3$), 1.2-1.9 (126H, brm, 24x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 27x Lys-C$\underline{H}_2$), 2.6-3.2 (42H, brm, 9x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.1 (9H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (30H, brs, Leu-α-C$\underline{H}$ + ArC$\underline{H}_2$), 4.4-4.7 (12H, brs, Phe-α-C$\underline{H}$), 4.9-5.2 (24H, brs, 12x C$\underline{H}_2$O), 6.8-7.5 (123H, brm, ArC$\underline{H}$), 7.6-8.7 (45H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 22.9 (Lys-$\underline{C}H_2$), 24.2 (Leu-$\underline{C}H_3$), 29.2 (Lys-$\underline{C}H_2$), 31.8 (N$\underline{C}H_2$), 39.3 ($\underline{C}H_2$Ph), 42.3 ($\underline{C}H_2$NH), 54.0 (α-$\underline{C}$H), 65.2 ($\underline{C}H_2$O), 126.2 (Ar$\underline{C}$H), 127.1 (Ar$\underline{C}$H), 127.8 (Ar$\underline{C}$H), 128.0 (Ar$\underline{C}$H), 128.5 (Ar$\underline{C}$H), 129.4 (Ar$\underline{C}$H), 137.7 (Ar *ipso*$\underline{C}$), 156.2 (Z-$\underline{C}O_2$), 162.4 ($\underline{C}$ONH), 170.8 ($\underline{C}$ONH) δ_C (solid state) 23.8 (Leu-$\underline{C}H_3$), 25.0 (Lys-$\underline{C}H_2$), 40.0 ((Leu-$\underline{C}H_2$, $\underline{C}$H) + $\underline{C}H_2$Ph), 48.1 (α-$\underline{C}$H), 56.2 (α-$\underline{C}$H), 65.8 ($\underline{C}H_2$O), 128.6 (Ar$\underline{C}$H), 137.4 (Ar *ipso*$\underline{C}$), 157.0 (Z-$\underline{C}O_2$), 172.5 ($\underline{C}$ONH), 176.0 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 3,810, M_w 4,890, M_w/M_n 1.3.

*Poly(1,3,5 triaminomestiylene(((S)-Leu)$_{12}$-N-Z, N'-Z-(S)-Lys), poly(**93**).*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(50)** (0.9g, 5.5 mmoles, 12.0eq.), initiated by compound **(89)** (75mg, 0.5 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.5g, 2.7 mmoles, 6.0eq.) in dried and distilled DMF (90 ml). Yield 0.8g (63 %); υ_{max} (KBr) 3293 (br), 2957 (s), 2871 (s), 1648 (s), 1540 (s), 1468 (m), 1368 (m), 1257 (s) and 1169 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (72H, brm, 24x Leu-C$\underline{H}_3$), 1.2-1.8 (54H, brm, 12x (Leu-C$\underline{H}_2$ + C$\underline{H}$) + 9x Lys-C$\underline{H}_2$), 2.9-3.1 (6H, brs, *N*C$\underline{H}_2$), 3.9-4.1 (3H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (18H, brm, Leu-α-C$\underline{H}$ + ArC$\underline{H}_2$), 4.9-5.1 (12H, brs, 6x C$\underline{H}_2$O), 6.8-7.0 (3H, brm, ArCH$_2$N$\underline{H}$), 7.2-7.4 (33H, brm, ArC$\underline{H}$), 7.6-8.4 (15H, brm, CON$\underline{H}$); δ_C (solid state) 23.7 ($\underline{C}H_3$), 40.3 (Leu-$\underline{C}H_2$ +$\underline{C}$H), 51.4 (α-$\underline{C}$H), 55.9 (α-$\underline{C}$H), 66.4 ($\underline{C}H_2$O), 128.4 (Ar$\underline{C}$H), 138.0 (Ar *ipso*$\underline{C}$), 157.3 (Z-$\underline{C}O_2$), 171.9 ($\underline{C}$ONH), 176.1 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 3,500, M_w 4,000, M_w/M_n 1.1.

*Poly(1,3,5 triaminomestiylene(((S)-Leu)$_{12}$-(S)-Lys), poly**(94)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(93)** (0.4g, 0.1 mmoles, 1.0eq.) in dried and distilled DMF (95 ml). Yield 0.3g (100 %); δ_H (DMSO-d_6) 0.7-1.0 (72H, brm, 24x Leu-C$\underline{H}_3$), 1.2-1.8 (54H, brm, 12x (Leu-C$\underline{H}_2$ + C$\underline{H}$) + 9x Lys-C$\underline{H}_2$), 2.9-3.1 (6H, brm, *N*C$\underline{H}_2$), 3.9-4.1 (3H, brm, Lys-α-C$\underline{H}$), 4.1-4.4 (18H, brm, Leu-α-C$\underline{H}$ + ArC$\underline{H}_2$), 6.8-7.0 (3H, brm, ArCH$_2$N$\underline{H}$), 7.2-7.3 (3H, brm, ArC$\underline{H}$).

*Poly(1,3,5 triaminomesitylene(((S)-Leu)$_{12}$-(S)-Lys-((S)-Phe)$_{24}$-N-Z, N′-Z-(S)-Lys), poly**(95)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(52)** (0.6g, 3.2 mmoles, 24.0eq.), initiated by poly**(94)** (0.3g, 0.1 mmoles, 1.0eq.) and capped with *N*, *N*′-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (0.6g, 1.2 mmoles, 9.0eq.) in dried and distilled DMF (95 ml). Yield 0.9g (81 %); υ_{max} (KBr) 3358 (br), 2958 (s), 2932 (s), 1644 (s), 1525 (s), 1455 (m), 1386 (m), 1367 (s), 1256 (s) and 1035 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (72H, brs, 24x Leu-C$\underline{H}_3$), 1.2-2.0 (90H, brm, 12x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 27x Lys-C$\underline{H}_2$), 2.7-3.3 (66H, brm, 9x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.1 (9H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (18H, brs, Leu-α-C$\underline{H}$ + ArC$\underline{H}_2$), 4.4-4.7 (24H, brs, Phe-α-C$\underline{H}$), 4.9-5.1 (24H, brs, C$\underline{H}_2$O), 6.8-7.5 (186H, brm, ArC$\underline{H}$ + ArCH$_2$N$\underline{H}$), 7.6-8.7 (45H, brm, CON$\underline{H}$); δ_C (solid state) 25.0 (Leu-C$\underline{H}_3$), 41.7 ((Leu-C$\underline{H}_2$, C$\underline{H}$) + C$\underline{H}_2$Ph), 52.7 (α-C$\underline{H}$), 54.3 (α-C$\underline{H}$), 55.8 (α-C$\underline{H}$), 65.8 (C$\underline{H}_2$O), 128.9 (ArC$\underline{H}$), 136.9 (Ar *ipso*C), 157.7 (Z-C$\underline{O}_2$), 172.0 (C$\underline{O}$NH), 176.4 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 4,500, M_w 5,100, M_w/M_n 1.1.

*1,4 Diaminobutane-1,4-di(N-Z, N′-Z-(S)-Lys) **(96)**.*

To a solution of compound **(55)** (3.0g, 5.6 mmoles, 2.1eq.) in CH_2Cl_2 (50 ml) cooled to 0 °C, 1,4 diaminobutane (0.3 ml, 2.7 mmoles, 1.0eq.) was added dropwise *via* a syringe. The reaction mixture was stirred for 25 hours and the solvent removed *in vacuo*. The resulting residue was refluxed in diethyl ether (70 ml) and filtered to provide a yellow-white solid. This was washed with MeOH (2x 50 ml) to provide the

title compound as a white solid. Yield 1.8g (75 %); υ_{max} (KBr) 3358 (br), 2958 (s), 2932 (s), 1644 (s), 1525 (s), 1455 (m), 1386 (m), 1367 (s), 1256 (s) and 1035 cm^{-1} (s); δ_H (DMSO-d_6) 1.2-1.7 (16H, brm, 6x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.9-3.1 (8H, brm, 2x Lys-*N*C$\underline{H}_2$ + 2x *N*C$\underline{H}_2$), 3.8-4. (2H, brm, Lys-α-C$\underline{H}$), 4.9-5.1 (8H, brm, C$\underline{H}_2$O), 7.2-7.4 (20H, brm, ArC$\underline{H}$), 7.8-7.9 (2H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 22.9 (Lys-γ-$\underline{C}H_2$), 26.6 (Lys-β-$\underline{C}H_2$), 27.0 (Lys-β-$\underline{C}H_2$), 29.2 ($\underline{C}H_2CH_2NHCO$), 31.9 (Lys-δ-$\underline{C}H_2$), 38.3 ($\underline{C}H_2NHCO$), 40.2 (Lys-*N*$\underline{C}H_2$), 54.8 (α-$\underline{C}H$), 65.2 ($\underline{C}H_2O$), 65.5 ($\underline{C}H_2O$), 126.7 (Ar$\underline{C}H$), 127.8 (Ar$\underline{C}H$), 128.4 (Ar$\underline{C}H$), 137.0 (Ar *ipso*$\underline{C}$), 157.7 (Z-$\underline{C}O_2$), 172.0 ($\underline{C}ONH$); m/z (CI) 882 (MH^+).

1,4 Diaminobutane-1,4-di-(S)-Lys ***(97)***.

To a solution of compound **(96)** (1.2g, 1.4 mmoles, 1.0eq.) in IMS (80 ml) was added Pd / C (0.2g). Subsequently the reaction mixture was exposed to hydrogen at 1 atmosphere for 15 hours. The reaction mixture was filtered through a pad of celite and the solvent removed *in vacuo* to provide the title compound as a thick oil. Yield 0.5g (100 %); υ_{max} (KBr) 3334 (br), 2943 (s), 2931 (s), 2523 (m), 1449 (s), 1394 (s), 1116 (s) and 1028 cm^{-1} (s); δ_H (DMSO-d_6) 1.2-1.7 (16H, brm, 6x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.1 (10H, brm, 2x Lys-*N*C$\underline{H}_2$, Lys-α-C$\underline{H}$ + 2x *N*C$\underline{H}_2$), 7.5-7.8 (8H, brs, N$\underline{H}_2$); δ_C (DMSO-d_6) 27.9 (Lys-γ-$\underline{C}H_2$), 31.8 (Lys-β-$\underline{C}H_2$), 37.7 ($\underline{C}H_2CH_2NHCO$), 40.3 (Lys-δ-$\underline{C}H_2$), 43.2 ($\underline{C}H_2NHCO$), 46.4 (Lys-*N*$\underline{C}H_2$), 60.0 (α-$\underline{C}H$), 175.3 ($\underline{C}ONH$); m/z (CI) 345 (MH^+); Found 345.2991 ($C_{16}H_{37}N_6O_2$ requires 345.2978).

*Poly(1,4 diaminobutane-1,4-di-(S)-Lys(((S)-Phe)$_{16}$-N-Z, N'-Z-(S)-Lys), poly****(98)***.

This polymer was obtained by the polymerisation **(Method O)** of monomer **(52)** (1.7g, 8.8 mmoles, 16.0eq.), initiated by compound **(97)** (0.2g, 0.5 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.5g, 2.7 mmoles, 5.0eq.) in dried and distilled DMF (70 ml). Yield 1.9g (80 %); υ_{max} (KBr) 3293 (br), 2957 (s), 2871 (s), 1648 (s), 1540 (s), 1468 (m), 1368 (m), 1257 (s) and 1169 cm^{-1} (m); δ_H (DMSO-d_6) 1.1-1.9 (40H, brm, 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.7-3.2

(44H, brm, 16x C$\underline{H}_2$Ph + 6x *N*C$\underline{H}_2$), 3.8-4.0 (4H, brm, Lys-α-C$\underline{H}$), 4.1-4.3 (2H, brs, Lys-α-C$\underline{H}$), 4.4-4.7 (16H, brs, Phe-α-C$\underline{H}$), 4.9-5.1 (16H, brs, C$\underline{H}_2$O), 6.9-7.5 (100H, brm, ArC$\underline{H}$), 7.7-8.4 (26H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 22.8 (Lys-$\underline{C}H_2$), 26.4 (Lys-$\underline{C}H_2$), 29.1 (Lys-$\underline{C}H_2$), 31.7 (N$\underline{C}H_2$), 33.6 (N$\underline{C}H_2$), 37.6 ($\underline{C}H_2$Ph), 53.9 (Phe-α-$\underline{C}$H), 55.0 (Lys-α-$\underline{C}$H), 65.3 ($\underline{C}H_2$O), 65.6 ($\underline{C}H_2$O), 126.3 (Ar$\underline{C}$H), 127.8 (Ar$\underline{C}$H), 127.9 (Ar$\underline{C}$H), 128.1 (Ar$\underline{C}$H), 128.5 (Ar$\underline{C}$H), 129.3 (Ar$\underline{C}$H),137.1 (Ar *ipso*$\underline{C}$), 137.4 (Ar *ipso*$\underline{C}$), 137.7 (Ar *ipso*$\underline{C}$), 156.0 (Z-$\underline{C}O_2$), 156.2 (Z-$\underline{C}O_2$), 170.7 ($\underline{C}$ONH), 171.7 ($\underline{C}$ONH); GPC (*m*-cresol) M_n 4,530, M_w 5,440, M_w/M_n 1.2.

*Poly(1,4 diaminobutane-1,4-di-(S)-Lys(((S)-Phe)$_{16}$-(S)-Lys), poly**(99)**.*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(98)** (1.7g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (95 ml). Yield 1.2g (90 %); δ_H (DMSO-d_6) 1.0-1.9 (40H, brm, 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.6-3.1 (44H, brm, 16x C$\underline{H}_2$Ph + 6x *N*C$\underline{H}_2$), 3.8-4.0 (4H, brm, Lys-α-C$\underline{H}$), 4.0-4.2 (2H, brs, Lys-α-C$\underline{H}$), 4.4-4.7 (16H, brs, Phe-α-C$\underline{H}$), 6.9-7.5 (60H, brm, ArC$\underline{H}$), 7.7-8.4 (26H, brm, CON$\underline{H}$).

*Poly(1,4 diaminobutane-1,4-di-(S)-Lys(((S)-Phe)$_{16}$-(S)-Lys-((S)-Leu)$_{24}$-N-Z, N'-Z-(S)-Lys), poly**(100)**.*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(50)** (1.1g, 6.8 mmoles, 24.0eq.), initiated by poly**(99)** (1.1g, 0.3 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.4g, 2.6 mmoles, 9.0eq.) in dried and distilled DMF (90 ml). Yield 1.9g (72 %); υ_{max} (KBr) 3358 (br), 2955 (s), 1644 (s), 1525 (s), 1456 (m), 1386 (m), 1367 (m), 1256 (s) and 1035 cm^{-1} (w); δ_H (DMSO-d_6) 0.7-1.0 (96H, brs, 48x Leu-C$\underline{H}_3$), 1.0-2.0 (136H, brm, 24x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 42x Lys-C$\underline{H}_2$ + 2xC$\underline{H}_2$), 2.6-3.2 (60H, brm, 14x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.7-4.0 (14H, brs, Lys-α-C$\underline{H}$), 4.1-4.7 (40H, brm, Leu-α-C$\underline{H}$ + Phe-α-C$\underline{H}$), 4.8-5.1 (32H, brs, C$\underline{H}_2$O), 6.8-7.5 (140H, brm, ArC$\underline{H}$), 7.6-8.5 (58H, brm, CON$\underline{H}$); δ_C (solid state) 24.7 (Leu-$\underline{C}H_3$), 39.9 ((Leu-$\underline{C}H_2$, $\underline{C}$H) + $\underline{C}H_2$Ph), 56.1 (α-$\underline{C}$H), 66.0 ($\underline{C}H_2$O), 128.6 (Ar$\underline{C}$H), 137.0 (Ar *ipso*$\underline{C}$), 157.0 (Z-$\underline{C}O_2$), 172.0 ($\underline{C}$ONH), 176.2 ($\underline{C}$ONH); GPC

(*m*-cresol) M_n 4,590, M_w 5,920, M_w/M_n 1.3.

*Poly(1,4 diaminobutane-1,4-di-(S)-Lys(((S)-Leu)$_{16}$-N-Z, N'-Z-(S)-Lys), poly(**101**).*

This polymer was obtained by the polymerisation **(Method O)** of monomer **(50)** (1.5g, 9.5 mmoles, 16.0eq.), initiated by compound **(97)** (0.2g, 0.6 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.6g, 3.0 mmoles, 5.0eq.) in dried and distilled DMF (70 ml). Yield 1.2g (60 %); υ_{max} (KBr) 3293 (br), 2957 (s), 2871 (s), 1648 (s), 1540 (s), 1468 (m), 1368 (m), 1257 (s) and 1169 cm^{-1} (s); δ_H (DMSO-d_6) 0.7-1.0 (64H, brs, Leu-C$\underline{H}_3$), 1.1-1.9 (40H, brm, 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.1 (12H, brm, *N*C$\underline{H}_2$), 3.5-3.7 (2H, brs, Lys-α-C$\underline{H}$), 3.7-3.8 (2H, brs, Lys-α-C$\underline{H}$), 3.8-4.0 (2H, brm, Lys-α-C$\underline{H}$), 4.1-4.4 (16H, brm, Leu-α-C$\underline{H}$), 4.9-5.1 (16H, brs, C$\underline{H}_2$O), 6.9-7.3 (40H, brm, ArC$\underline{H}$), 7.6-8.7 (26H, brm, CON$\underline{H}$); δ_C (DMSO-d_6) 21.2 (C$\underline{H}_3$), 22.9 (C$\underline{H}_3$), 24.2 (Leu-C$\underline{H}_2$), 28.5 (Lys-C$\underline{H}_2$), 30.8 (NC$\underline{H}_2$), 40.2 (Leu-C$\underline{H}$), 40.9 (Leu-C$\underline{H}_2$), 51.1 (Leu-α-C$\underline{H}$), 55.0 (Lys-α-C$\underline{H}$), 65.2 (C$\underline{H}_2$O), 65.5 (C$\underline{H}_2$O), 127.8 (ArC$\underline{H}$), 128.4 (ArC$\underline{H}$),137.1 (Ar *ipso*C), 137.4 (Ar *ipso*C), 137.7 (Ar *ipso*C), 156.2 (Z-C$\underline{O}_2$), 172.1 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 3,070, M_w 4,100, M_w/M_n 1.3.

*Poly(1,4 diaminobutane-1,4-di-(S)-Lys(((S)-Leu)$_{16}$-(S)-Lys), poly(**102**).*

This polymer was obtained by the hydrogenation **(Method P)** of poly**(101)** (0.9g, 0.3 mmoles, 1.0eq.) in dried and distilled DMF (75 ml). Yield 0.8g (100 %); δ_H (DMSO-d_6) 0.7-1.0 (64H, brs, Leu-C$\underline{H}_3$), 1.1-2.2 (40H, brm, 18x Lys-C$\underline{H}_2$ + 2x C$\underline{H}_2$), 2.8-3.1 (12H, brm, *N*C$\underline{H}_2$), 3.8-4.0 (6H, brm, Lys-α-C$\underline{H}$), 4.1-4.5 (16H, brm, Leu-α-C$\underline{H}$), 7.6-8.4 (42H, brm, CON$\underline{H}$ + N$\underline{H}_2$).

*Poly(1,4 diaminobutane-1,4-di-(S)-Lys(((S)-Leu)$_{16}$-(S)-Lys-((S)-Phe)$_{24}$-N-Z, N'-Z-(S)-Lys), poly(**103**).*

This polymer was obtained by the polymerisation **(Method Q)** of monomer **(52)** (1.2g, 6.3 mmoles, 24.0eq.), initiated by poly**(102)** (0.8g, 0.3 mmoles, 1.0eq.) and capped with *N*, *N'*-di(benzyloxycarbonyl)-(*S*)-lysine *p*-nitrophenyl ester **(55)** (1.3g, 2.4 mmoles, 9.0eq.) in dried and distilled DMF (80 ml). Yield 1.9g (77 %); υ_{max} (KBr) 3325 (br), 2958 (s), 1644 (s), 1525 (s), 1455 (m), 1386 (m), 1367 (s), 1256 (s) and 1035 cm^{-1} (s); δ_H (DMSO-d$_6$) 0.7-1.0 (62H, brs, 32x Leu-C$\underline{H}_3$), 1.0-2.0 (112H, brm, 16x (Leu-C$\underline{H}_2$ + C$\underline{H}$), 42x Lys-C$\underline{H}_2$ + 2xC$\underline{H}_2$), 2.6-3.2 (72H, brm, 14x *N*C$\underline{H}_2$ + C$\underline{H}_2$Ph), 3.8-4.1 (14H, brs, Lys-α-C$\underline{H}$), 4.1-4.4 (16H, brm, Leu-α-C$\underline{H}$), 4.4-4.7 (24H, brs, Phe-α-C$\underline{H}$), 4.9-5.2 (32H, brs, C$\underline{H}_2$O), 6.9-7.6 (180H, brm, ArC$\underline{H}$), 7.7-8.5 (58H, brm, CON$\underline{H}$); δ_C (solid state) 24.9 (Leu-C$\underline{H}_3$), 31.4 (Lys-*N*C$\underline{H}_2$), 40.0 ((Leu-C$\underline{H}_2$, C$\underline{H}$) + C$\underline{H}_2$Ph), 55.7 (α-C$\underline{H}$), 61.6 (C$\underline{H}_2$O), 128.8 (ArC$\underline{H}$), 137.1 (Ar *ipso*C), 140.6 (Ar *ipso*C), 157.5 (Z-C$\underline{O}_2$), 175.6 (C$\underline{O}$NH); GPC (*m*-cresol) M_n 8,270, M_w 33,600, M_w/M_n 4.1.

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