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Monte Carlo Simulations of Atom Transfer Radical (Homo)Polymerization of Divinyl Monomers:

Applicability of Flory-Stockmayer Theory

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KEYWORDS. Monte Carlo, ATRP, F-S theory, intramolecular cyclization

ABSTRACT. It is well known that free radical (co)polymerization of multivinyl monomers (MVMs) leads to insoluble gels even at a low monomer conversion and the gelation point can be predicted by Flory-Stockmayer theory (F-S theory) based on two assumptions: (1) equal reactivity of all vinyl groups and (2) the absence of intramolecular cyclization. This theory has been experimentally studied and verified with conventional free radical (co)polymerization (FRP) of several MVMs (e.g. divinyl benzene, DVB). However, it is still debatable whether this theory is applicable for the polymerization of MVMs using reversible deactivation radical polymerization (RDRP) approaches, such as atom transfer radical polymerization (ATRP). Herein, Monte Carlo simulations using two statistical models - with cyclization (w.c.) and without cyclization (wo.c. - corresponding to F-S theory) and dynamic lattice liquid (DLL) models were conducted to study ATRP of divinyl monomers. The simulated gel points using w.c. and wo.c. models were compared with those obtained from ATRP experiments, from calculation using F-S theory and from simulations using DLL models. The molecular weights, dispersity and extent of intermolecular/intramolecular crosslinking were calculated as function of double bond and crosslinker conversion. The results demonstrated that the gel points obtained from both w.c. and wo.c. models were lower than the values from DLL models and experiments. This indicates that F-S theory cannot be used to accurately predict the polymerization of divinyl monomers via ATRP. Our study shows that the limitation of F-S theory in predicting ATRP reaction of divinyl monomers is not only due to neglecting intramolecular cyclization, but also due to spatial restrictions which can cause the reactivity and accessibility of vinyl groups becoming non-equivalent in ATRP of divinyl monomers.
INTRODUCTION

Conventional free radical polymerization (FRP) of multivinyl monomers (MVMs) is commonly used for the preparation of polymer networks, because such reactions inevitably lead to gelation even at a low monomer conversion, as predicted by the classic Flory-Stockmayer theory (F-S theory).\(^1\)–\(^4\) F-S theory is based on two fundamental assumptions: (1) equal reactivity of all vinyl groups and (2) absence of the intramolecular cyclization. The pioneers were aware of the fact that these assumptions are not fully correct but argued that in concentrated system, at least up to the gel point, the error is small in FRP (as verified in our previous work\(^5\)). Stockmayer concluded that the gel point should occur when the number of crosslinked units per primary chain reaches unity,\(^1\)–\(^4,6\) and related this value to dispersity (\(D\)).\(^2\) Flory also studied the effect of \(D\) on gel point and concluded that for the most probable distribution (\(D \sim 2\)), the number of crosslinked units per chain should be 0.5.\(^4\) Thus, in FRP of MVMs, it is difficult to control the polymerization processes and the structure of the polymers produced.\(^7\)

The advent of reversible-deactivation radical polymerizations (RDRPs), such as atom transfer radical polymerization (ATRP), nitroxide mediated polymerization (NMP), and reversible addition fragmentation chain transfer (RAFT) polymerization, allows the facile synthesis of polymers with well controlled molecular weight and polymers/copolymers of various architectures (e.g. randomly branched polymers, single-chain cyclized polymers, graft/brush polymers, star polymers and polymer gels).\(^8\)–\(^10\) However, the applicability of F-S theory to RDRP is still under
discussion. Ide and Fukuda\textsuperscript{11} investigated the critical number density of crosslinks at the gel point in NMP of styrene with 4,4\textsuperscript{-}divinylbiphenyl (DVBP) and found that it is ca. twice higher than that predicted by the F-S theory (although much lower than in FRP). Matyjaszewski et al\textsuperscript{12,13} reported the differences between the gel points obtained from ATRP experiments and one with F-S theoretical values, and attributed them to the intramolecular cyclization, neglected in F-S theory. Vo et al\textsuperscript{14}, in the synthesis of branched acrylic copolymers via RAFT polymerization, reported that a substantially higher fraction of ethylene glycol diacrylate (EGDA) could be tolerated without causing gelation, due to the existence of intramolecular cyclization. Wang et al\textsuperscript{10,15–19} prepared single-chain cyclized polymers from homopolymerization of MVMs via in situ deactivation enhanced ATRP (in situ DE-ATRP), RAFT and Cu\textsuperscript{0}&Cu\textsuperscript{II} - mediated RDRP. All aforementioned results confirm the presence of intramolecular cyclization, which should not be neglected. On the other hand, there are experimental data showing that the gel points of the RDRPs of MVMs are consistent with the values predicted by the F-S theory. Rosselgong et al\textsuperscript{20} synthesized highly branched methacrylic copolymers through RAFT copolymerization at a high crosslinker concentration, the crosslinking degree of which was close to prediction by the classical F-S theory. The copolymerization of 2-hydroxypropyl methacrylate (HPMA) with ethylene glycol dimethacrylate (EGDMA), carried out by Bannister et al\textsuperscript{21} using ATRP, demonstrated that the network formation in ATRP is well fitted by the F-S model for gelation. In summary, the applicability of F-S theory to RDRPs of MVMs is controversial, and the extent of intramolecular cyclization and its effect on gel point are still under debate.

Indeed, it is challenging to study and clarify the reaction mechanism and kinetics of RDRPs of MVMs by conventional experimental methods. Thus, developing a reliable and powerful approach is required in order to investigate the extent of intramolecular cyclization in RDRP of MVMs.
Johnson and co-workers\textsuperscript{22–26} proposed a new method termed symmetric isotopic labeling disassembly spectrometry (SILDaS) for counting loops in $A_2+B_f$ polymer network (where $f$ represents the network branch functionality) from isotopically labelled and degradable monomers. The network degradation and analysis of the disassembly products gives the average number of primary loops per junction. Then a computer simulation method - Monte Carlo (MC) was further used to link the primary loop densities to high order loop densities. In principle, this strategy should be applicable to any type of polymer networks including those from chain addition polymerization.

Computer simulations can provide important information on parameters which are not easily obtained experimentally, and MC method is a convenient simulation technique\textsuperscript{27} that can be used to simulate polymerization processes.\textsuperscript{28–31} Three approaches are possible. In the first one, a MC method (e.g. Gillespie’s method\textsuperscript{32,33}) is used to replace solving kinetic equations by a stochastic master equation. It is assumed that all reagents of a certain type are equally reactive (like in the Flory and Stockmayer theory), i.e., the diffusion rate is high comparing to reaction rates and local interactions can be averaged, so these are in fact mean-field models. Al-Harthi et al.\textsuperscript{31} used this method to study an ATRP system, where the molecular weight distributions, the effect of control volume, and equilibrium constant on polymer properties were simulated. In the second approach, some initial sets of elements are chosen and a selected element can react (or not) with others according to predefined probabilities\textsuperscript{12,13,28,34}. The position and surroundings of reacting molecules are not specified, so this method can be classified as off-lattice (OL) and mean-field model. Bannister et al.\textsuperscript{28} introduced this method to branching copolymerization of methacrylic monomers under living conditions. In the third approach, the reactions proceed with certain probability between elements moving on a lattice (e.g., dynamic lattice liquid (DLL),\textsuperscript{12,13,34,35} or bond fluctuation models\textsuperscript{36}), where the reaction rate is not exactly the same for all elements of a given
type, but depends on their positions and detailed surrounding, thus changes in space and time. Matyjaszewski and co-workers studied the copolymerization of monomer and divinyl crosslinker by ATRP using OL model\textsuperscript{12,13,34} and DLL model\textsuperscript{12,13,34,35} and provided an insight into the gelation process in various systems. Thus, computer simulations have become a powerful tool to study the mechanism of RDRPs. However, the homopolymerization of MVMs using RDRP has not yet been studied based on the exact F-S model and MC simulations.

In this work, in order to test whether the F-S theory is suitable for RDRP of MVMs and to determine the extent of the intramolecular cyclization in RDRP of MVMs, MC simulations (Gillespie’s method) were used to study ATRP of divinyl monomers using a model without cyclization (\textit{wo.c}) corresponding to the F-S theory, or a model with cyclization (\textit{w.c}) (Scheme 1). The simulation results from these two models were compared with the F-S theoretical gel points, DLL results and the experimental values obtained from ATRP of divinyl monomers.
Scheme 1. Schematic representation of the simulation of homopolymerization of divinyl monomers by ATRP. The macromolecules contain closed loops if intramolecular crosslinking is allowed (with cyclization). (w.c. - with cyclization model, wo.c. - without cyclization model).

EXPERIMENTAL SECTION

Materials. Ethylene glycol dimethacrylate (EGDMA) was purchased from Sigma-Aldrich. Ethyl 2-bromoisobutyrate (EBriB, 98%, Sigma-Aldrich) was used as the initiator. Copper (I) chloride (CuCl, 97%, Sigma-Aldrich) was purified before use (washed with acetic acid four times, ethanol and diethyl ether once, respectively). Pentamethyldiethylenetriamine (PMDETA, 99%, Sigma-Aldrich), d-chloroform (99.8%, Sigma-Aldrich), 2-butanone (HPLC grade, Sigma-Aldrich) were used as received.

Polymerization Procedures. Homopolymerizations of EGDMA by ATRP were carried out in a two-necked round-bottom flask, the ratio of divinyl monomer and initiator was set as 100/1 and 100/10. Here, the typical reaction conditions and procedures were used. For the ratio of 100/1, EBriB (97.53 mg, 0.5 mmol, 1 equiv), EGDMA (9.91 g, 50 mmol, 100 equiv), 2-butanone (24.93 ml, [EGDMA] = 1.45 M or 28% w/v) and PMDETA (34.66 mg, 0.2 mmol, 0.4 equiv) were added into the flask and oxygen was removed by bubbling argon through the solutions for 15 min. CuCl (19.80 mg, 0.2 mmol, 0.4 equiv) was added into the flask under positive pressure of argon before the flask was immersed in a preheated oil bath at 50 °C. The solution was stirred at 700 rpm and the polymerization was conducted for the desired reaction time. For the ratio of 100/10, the same polymerization procedures were used.
**H NMR analysis.** $^1$H NMR spectrum was obtained using a Varian NMR 400 MHz spectrometer and processed with MestRenova 9.09 software. The reported chemical shifts were in parts per million (ppm) relative to CDCl$_3$ (7.26 ppm) and tetramethylsilane (0.00 ppm).

**SIMULATION METHODS**

**Algorithm Description.** In an ATRP system, the fast initiation relative to propagation results in all initiators being converted into primary polymer growing chains at the very early stage of the polymerization process.$^{8,37,38}$ Thus in the simulations, one assumption is that all initiators were consumed at very low monomer conversion. In addition, no termination was considered. In typical ATRP systems, a fast dynamic equilibrium between a low concentration of active radicals and a significantly higher concentration of dormant species is established. The probability of these reactions could be sometimes larger than that of propagation. Exact simulation of such a process would require a very long computation time.$^{39}$ Therefore, to accelerate MC simulations, instead of considering the reversible exchange reactions between propagating radicals and dormant species in the simulation scheme, we assumed that this equilibrium was established at the beginning of the polymerization and a fast exchange process between the active radicals and dormant species were maintained throughout the reaction. Based on Equation (1), and assuming ideal terminationless process ([Cu(II)] = [R]), low fraction of active radicals was calculated (0.02% of the dormant species). In real systems, termination does happen and every act of irreversible termination will generate Cu(II) species, which concentration will increase, following persistent radical effect$^{40}$.

$$[R] = K_{eq} \frac{[P_n - X][Cu(I)]}{[Cu(II)]}$$

(1)

[R] is the concentration of the radicals in active state, $K_{eq}$ is the equilibrium constant - the ratio of activation rate constant ($k_{act}$) to deactivation rate constant ($k_{deact}$), $[P_n-X]$ denotes the concentration...
of dormant species, [Cu(I)] and [Cu(II)] represent the concentrations of copper(I) and copper(II), respectively (for propagation rate coefficient $k_{pm} = 100 \text{ M}^{-1}\text{s}^{-1}$ and deactivation rate coefficient $k_{deact} = 5 \times 10^7 \text{ M}^{-1}\text{s}^{-1}$, intermittent deactivation would happen after one monomer addition).

For w.c. and wo.c. models, the simulation approach followed Gillespie’s algorithm$^{32,33}$ which is based on the master equation for dynamic MC simulation: in a defined volume $V$, a large amount of random numbers distributed uniformly in the interval [0, 1] were generated to determine which type of reaction would take place. The probability of each elementary reaction was determined based on its reaction rate constant and the number of molecules participated in the reaction process.

The reaction probabilities were calculated as following:

$$R_{pm} = k_{pm} \times N_m \times N_r$$  \hspace{1cm} (2)

$$R_{pp} = k_{pp} \times N_p \times N_r$$  \hspace{1cm} (3)

$$S = R_{pm} + R_{pp}$$  \hspace{1cm} (4)

$$P_{pm} = R_{pm}/S$$  \hspace{1cm} (5)

$$P_{pp} = R_{pp}/S$$  \hspace{1cm} (6)

$k_{pm}$ and $k_{pp}$ are the microscopic reaction rate constants of the propagations with monomers ($pm$) and pendent double bonds ($pp$) respectively. $R_v$ and $P_v$ are the rate and the reaction probability for the reaction $v$ ($v = pm, pp$) respectively. $N_m$, $N_r$ and $N_p$ are the number of divinyl monomers, active radicals and pendent double bonds in the system, respectively. $S$ represents the sum of all reaction rates.
All polymerization conditions used in w.c. and wo.c. models for homopolymerization of divinyl monomers via ATRP are listed in Table 1. The monomer concentration was set as 1.45 M representing a relatively high concentration. In addition, the effect of different simulation volumes on the gel points which are indicated by the sharp maximum\(^\text{12}\) in Figure 1 (the detailed definition of gel point is presented in the following sections) were tested, it can be seen that the size of the system has a negligible effect on the predicted gel point. Therefore, in this work, 10\(^7\) and 10\(^6\) were used as \(N_m\) for the two simulation systems (100/1 and 100/10) respectively - which were sufficient to obtain the accurate prediction.

**Table 1.** Summary of the parameters used in the simulation for homopolymerization of divinyl monomers via ATRP

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
<th>Sources/Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>([X]_0/[\text{Ini}]_0/[\text{Cu(I)}]_0^a)</td>
<td>100/1/0.4, 100/10/0.4</td>
<td>5</td>
</tr>
<tr>
<td>([X] (M)^a)</td>
<td>1.45, 1.45</td>
<td>5</td>
</tr>
<tr>
<td>number of monomer elements ((N_m))^b</td>
<td>10(^7), 10(^6)</td>
<td>this work</td>
</tr>
<tr>
<td>number of initiator elements ((N_a))^b</td>
<td>10(^5), 10(^5)</td>
<td>this work</td>
</tr>
<tr>
<td>number of Cu(I) elements ((N_{\text{Cu(I)}}))^b</td>
<td>4(\times)10(^4), 4(\times)10(^3)</td>
<td>this work</td>
</tr>
<tr>
<td>(K_{eq}^c)</td>
<td>10(^{-7}), 10(^{-7})</td>
<td>41,42</td>
</tr>
<tr>
<td>(k_{pm}, k_{pp} (\text{M}^{-1}\text{s}^{-1})^d)</td>
<td>(k_{pm}/k_{pp} = 2/1), (k_{pm}/k_{pp} = 2/1)</td>
<td>12</td>
</tr>
</tbody>
</table>

\(^a\)The simulation system ([X]_0/[Ini]_0/[Cu(I)]_0 and [X]) corresponds to ref. 5. X represents divinyl monomers, i.e. crosslinkers, Ini represents initiators.\(^b\)The value of \(N_m\) (system size) was estimated in this work, the values of \(N_a\) and \(N_{\text{Cu(I)}}\) were calculated based on \(N_m\) - 100/1/0.4 or 100/10/0.4.\(^c\)The value for \(K_{eq}\) was taken from ref. 41,42.\(^d\)The ratio of \(k_{pm}\) and \(k_{pp}\) was set as 2/1 according to ref. 12.
Figure 1. The changes of reduced degree of polymerization ($RDP$) with divinyl monomer conversion ($Conv_x$). This demonstrates a negligible effect of the size of the system ($N_m$) on the predictions of gel point in ATRP of divinyl monomers.

**Model Description.** The coarse-grain approach, two statistical models (with/without cyclization model - w.c./wo.c. model) and DLL models (with/without cyclization) were used in this work. The w.c./wo.c. model was treated in similar way as in the simulations of FRP of divinyl monomers except for the difference in dealing with the elementary reactions, such as the fast initiation, no termination, and especially, the consideration of the fast exchange reactions between active radicals and dormant species and the significantly low concentration of propagating radicals. Briefly, all reactants were randomly placed within a virtual reaction space with no specific coordinate or position. The size, dimensions and details of chemical structure of the species in the space were all disregarded. Moreover, all components in the system were assumed to be fully accessible to each other. Corresponding to F-S theory, no substitution effects was considered in this work - the reactivity of all vinyl groups (probability of being selected to react) was assumed to be constant, thus the probability of a reaction with all molecules belonging to a given class was considered to be the same. All elementary reactions took place between two reactants selected...
randomly in the system. In both models, the information regarding the individual chains and radicals was recorded using a series of consecutive numbers, by which, different chains and radicals could be distinguished.

1) w.c. model

If the propagation with pendent double bonds is chosen, a radical in active state will be selected at random followed by the calculations of the fraction of pendent double bonds on the chain where the chosen radical is located in (denoted by \( m \)), and the fraction of pendent double bonds on other chains can also be obtained (\( 1-m \)). Then a random number \( r \) uniformly distributed in the interval [0, 1] will be generated. If \( r < m \), the radical will react with a pendent double bond on its own chain, otherwise it will select a pendent double bond on other chains to react. After every reaction cycle, the information of all components in the system will be updated.

2) wo.c. model

This model exactly corresponds to the F-S theory where intramolecular cyclization is strictly forbidden. Also, if the propagation with pendent double bond is selected to occur, an active radical will be chosen randomly, then the corresponding number for the chain which this chosen radical belongs to will be recorded. For example, if chain 1 is chosen, we then randomly select a chain number (such as chain \( x \)) in the simulation system. If \( x = 1 \), we will have to re-select a chain because no intramolecular cyclization is allowed in this model, otherwise, the chosen active radical will react with one pendent double bond on chain \( x \).

In the DLL models, possible cooperative motions of beads (monomeric units) on a lattice are analyzed when the random attempt-to-move vector fields are generated in successive MC steps.
Excluded volume condition and integrity of polymer chains are observed (only those attempts can be successful - the selected vectors which attempt to move should make a closed loop, the sum of displacements is equal to zero and the move does not lead to breaking polymer bonds). Polymerization reactions are simulated by forming new bonds between beads representing active radicals and monomers or crosslinkers with a predefined probability. The algorithm was described in more detail in ref. 12,13,34,35. In this work, DLL with/without cyclization models are established for the ATRP homopolymerizations of divinyl monomers.

**Determination of Parameters Showing the Structure Properties of Polymer Chains.** The following parameters were monitored and calculated to obtain the structural properties of chains in the simulations:

- Number average degree of polymerization as a function of monomer conversion - $P_n(\alpha)$. For all macromolecules in the simulation system.

\[
P_n(\alpha) = \frac{\sum_i i \cdot n_i}{\sum_i n_i}
\]

(7)

- Weight average degree of polymerization as a function of monomer conversion - $P_w(\alpha)$.

\[
P_w(\alpha) = \frac{\sum_i i^2 \cdot n_i}{\sum_i i \cdot n_i}
\]

(8)

- Dispersity as a function of monomer conversion - $D(\alpha)$.

\[
D(\alpha) = \frac{P_w(\alpha)}{P_n(\alpha)}
\]

(9)
where $\alpha$ is the monomer conversion, $i$ denotes chain length of each polymer population in the system, $n_i$ represents the number of molecules with the chain length of $i$.

- Reduced degree of polymerization as a function of monomer conversion - $RDP(\alpha)$. $RDP$ is the weight average degree of polymerization excluding the longest chain, which is analogous to $P_w(\alpha)$, but without the biggest chain in the system:

$$RDP(\alpha) = \frac{\sum_l i^2 \cdot n_i - i_{\text{max}}^2}{\sum_l i \cdot n_i - i_{\text{max}}}$$

where $i_{\text{max}}$ represents the biggest macromolecular chain length in the system. This parameter was proposed by Hoshen and Koppelman$^{43}$ and effectively used in the analysis of gelation processes.$^{44,45}$

**RESULT AND DISCUSSION**

Here, we present the experimental results and a series of simulation results of ATRP of divinyl monomers based on w.c., wo.c. as well as DLL models. The evolution of $RDP$, $P_n$, $P_w$, $D$ and the ratio of intermolecular crosslinking and intramolecular cyclization are systematically analyzed. The gel points of ATRP of divinyl monomers obtained from experiments, w.c./wo.c. model, F-S theory and DLL models are compared. The extent of intramolecular cyclization in ATRP of divinyl monomers and the relationship of F-S theory with ATRP of divinyl monomers are discussed. Moreover, our previous results for FRP of divinyl monomers$^5$ are also presented for comparison. The simulations of ATRP copolymerization (ATRcP) for a series of ratios of monovinyl and divinyl monomers using w.c. and wo.c. models are also conducted and analyzed (see Supporting Information).
Gel Points - Experimental Results: Homopolymerization of EGDMA via ATRP. In order to compare with the simulated gel points and F-S theoretical values, the ATRP of EGDMA was carried out experimentally. $^1$H NMR spectroscopy was used to monitor the progress of the polymerization (Figure 2). For $[X]_0/[\text{Ini}]_0=100/1$, the experimental gel point (eq 11) was obtained at 14% based on the conversion of vinyl groups ($\text{Conv}_d$), which is much higher than the F-S theoretical gel point $^5$ - 7.07% ($\text{Conv}_d$). Similarly, the experimental gel point for $[X]_0/[\text{Ini}]_0=100/10$ is 31% ($\text{Conv}_d$) which is also higher than the value calculated from F-S theory - 22%.

The vinyl conversion is defined as the ratio of consumed vinyl groups to all the original vinyl groups, as shown in eq 11:

$$Vinyl \text{ Conversion} = \frac{\text{consumed vinyl groups}}{\text{original vinyl groups}} = 1 - \frac{\text{current vinyl groups}}{\text{original vinyl groups}}$$

$$= 1 - \frac{2 \times \text{integrals of A}}{\text{integral of C}} \quad (11)$$
**Figure 2.** $^1$H NMR spectrum of polyEGDMA prepared via ATRP in CDCl$_3$ at 400 MHz. The resonances of protons A and B relative to proton C demonstrate the presence of unreacted vinyl functionalities ([X]$_0$/[Ini]$_0$=100/1).

**Gel Points - w.c./wo.c. Simulations.** Given the discrepancy observed between the gel points obtained from ATRP experiments and F-S theory, the ability of F-S theory to predict the gel points of ATRP of divinyl monomers was investigated using the simulation method. Figure 3 illustrates RDP for w.c. and wo.c. simulations at different molar ratios of divinyl monomer to initiator (100/1 and 100/10) (Table 1). The simulation results of FRP of divinyl monomers for the ratio of 100/1 are also shown for comparison.$^5$

For wo.c. (F-S) model, Figure 3 shows that the gel points are around 7.16% and 23% ($\text{Conv}_d$) for [X]$_0$/[Ini]$_0$=100/1 and 100/10 respectively, which are consistent with the value 7.07% and 22% ($\text{Conv}_d$) calculated using F-S theory.$^5$ However, the simulated (7.16% and 23%) or the F-S theory predicted gelation (7.07% and 22%) takes place at much lower conversion of vinyl groups compared to the experimental value - 14% (for the ratio of 100/1) and 31% (for the ratio of 100/10), and it is close to the simulated gel point of FRP system (7.03%).$^5$ Moreover, though the probability of intramolecular cyclization would be much lower for the lower ratio of 100/10 due to the shorter length and higher concentration of primary chains, the experimental gel point under this condition is still higher than that calculated from F-S theory and w.c./wo.c. simulations. Therefore, it can be concluded that F-S theory cannot successfully predict the gel point of ATRP of divinyl monomers.
Figure 3. Evolution of the RDP with double bond conversion, obtained from w.c. and wo.c. models of ATRP and FRP simulations ([X]₀/[Ini]₀=100/1 or 100/10).

Furthermore, to clarify whether the reason for the inapplicability of F-S theory to ATRP system is the neglect of intramolecular cyclization, the simulated gel points using w.c. model were also analyzed. It can be clearly observed in Figure 3 that even though the intramolecular cyclization is allowed to occur in w.c. model, the gel point is still the same as that predicted by wo.c. model - consistent with F-S theory and much lower than the experimental value. In summary, the neglected intramolecular cyclization is not the only reason for the underestimation of gel points in F-S theory.

ATRP systems were also simulated using w.c. and wo.c. models for various ratios of [X]₀/[M]₀/[Ini]₀. In these simulations, two reactants were involved - monovinyl monomers and divinyl monomers. The evolution of RDP was investigated (Figure S1 and S2). Consistent with the conclusions deduced from the homopolymerization of divinyl monomers, nearly no difference between the gel points obtained from w.c. and wo.c. models was observed (the corresponding curves almost completely coincide). In addition, compared with FReP system, the gel points of
ATRcP simulations are only a little higher but still much lower than the experimental values (Table S1). Overall, similar to the conclusion obtained from homopolymerization system, F-S theory is not suitable for the prediction of gel points in ATRcP of monovinyl and divinyl monomers, and this invalidation cannot only be attributed to the neglected intramolecular cyclization.

**Polymerization Process - w.c./wo.c. Simulations.** In addition to the gel points, the prediction of the polymerization process of ATRP of divinyl monomers by F-S theory was also studied. Figure 4 shows the homopolymerization process of ATRP of divinyl monomers from two simulation conditions (with/without cyclization) for the ratio of 100/1. For comparison, the results of FRP of divinyl monomers under the same conditions are also shown. The degree of polymerization and $D$ are displayed as a function of $Conv_d$. 

![Graph showing polymerization process](image-url)
Figure 4. Evolution of the (a) number average degree of polymerization ($P_n$), (b) weight average degree of polymerization ($P_w$), (c) $\bar{D}$ with double bond conversion, obtained from ATRP and FRP homopolymerization of divinyl monomers.

For both cases (w.c. and wo.c. models) of ATRP systems, a fast increase of $P_w$ and $\bar{D}$ can be observed characterizing the crosslinking process (the inflection points roughly coincide with the sharp maximum of RDP, indicating the gel point). However, for both w.c. and wo.c. models, the rapid increase of $P_w$ and $\bar{D}$ still takes place at the same $Conv_d$ - ca. 7% as in FRP of MVMs, which is consistent with the gel point calculated from F-S theory (7.07%) but much lower than the experimental value - 14% based on $Conv_d$. Moreover, the polymerization processes obtained from the two models are almost identical before the gel point, and deviations only appear above the gel point - an abrupt increase of $P_n$ and decrease of $\bar{D}$ in wo.c. model. This discrepancy could be due to not considering intramolecular cyclization in the wo.c. simulation model, so the consumption of the pendent vinyls is entirely from intermolecular crosslinking reactions, which results in the quick decrease in the number of polymer chains above the gel point when most chains are crosslinked (although not all belong to the biggest gel network). Reactions between the crosslinked chains and the largest one, formed at gel point, lead to an abrupt increase of $P_n$ and the formation of one giant network. Thus, similar to the conclusions in above sections, we show that F-S theory (wo.c. model) is not suitable for the prediction of the homopolymerization process of ATRP of divinyl monomers before the gel point, and even the w.c. model cannot demonstrate any effect of intramolecular reaction on the gel point or the polymerization process (before the gel point). The neglected intramolecular cyclization is not the only main cause for the discrepancy with F-S theory.
The polymerization processes of ATRcP of monovinyl monomers and divinyl monomers for various ratios of $[X]_0/[M]_0/[Ini]_0$ were also simulated using w.c. and wo.c. models (Figure S3). The case of linear chains ($[X]_0 = 0$) is presented for comparison and indicates that without crosslinker, $P_n$ and $P_w$ both show a linear increase with $Conv_d$ (Figure S4) and low $D$. In both w.c. and wo.c. models, the fast increase of $P_n$, $P_w$ and $D$ (characteristic of the intermolecular crosslinking process) appears earlier and deviates from linearity more significantly with the increasing concentrations of crosslinker. However, similar to the ATRP homopolymerization system, the rapid growth still takes place at the same conversion in different models (w.c./wo.c.), which is consistent with the F-S theoretical value but lower than the results obtained from experiments (Table S1), and only above the gel point, the difference between w.c. and wo.c. models appears.

**Analysis of the Reasons for the Inapplicability of F-S theory to ATRP of Divinyl Monomers.**

In Figure 4, one can observe that though the models used for FRP and ATRP simulations are both mean-field statistical models, unlike the typical polymerization process of FRP of divinyl monomers (the degree of polymerization rapidly increases to a high value at the beginning), a typical slow and steady growth of $P_w$ and $P_n$ at the early stages can be correctly predicted by both w.c. and wo.c. models. These differences are caused by the different settings for elementary reactions (slow/fast initiation and propagation, the consideration of termination or activation/deactivation equilibrium) of ATRP and FRP models. Thus, in the simulations, the rate of ATRP reactions is much slower than that of FRP reactions. Nonetheless, the predicted gel points between them are very similar. This phenomenon promoted us to make a further analysis of the polymerization process of ATRP of divinyl monomers.

For the ATRP homopolymerization of divinyl monomers ($[X]_0/[Ini]_0=100$), Figure 5 shows the ratios of inter-chain crosslinked units to all fully reacted divinyl monomers as a function of $Conv_x$.
and Conv for the model with cyclization. This analysis permits us to track how the intramolecular cyclization/intermolecular crosslinking occurred during the whole polymerization process of ATRP of divinyl monomers. The arrows correspond to the gel points (Conv = 7.16%, Conv = 13.80%) which are consistent with the results we discussed above. Besides, one can see that similar to the trend in FRP of divinyl monomers, before the gel point, almost no intramolecular cyclization occurred in ATRP of divinyl monomers though it was permitted. Similar trend can also be observed for ATRcP of monovinyl monomers and divinyl crosslinkers for various ratios of [X]₀/[M]₀/[Ini]₀ (Figure S5).

**Figure 5.** Simulation for FRP and ATRP homopolymerization of divinyl monomers using w.c. model shows the ratio of intermolecular crosslinking formed at different conversions. Ratio of
intermolecular crosslinks per chain to all crosslinks per chain versus (a) double bond conversion, 
(b) divinyl monomer conversion. Arrows indicate gel points.

Overall, in the w.c. model for ATRP of divinyl monomers, even though the polymerization rate is 
slower than that of FRP of divinyl monomers, intramolecular cyclizations have not been promoted, 
that is, the probabilities of intermolecular crosslinking and intramolecular cyclization have not 
changed. In these mean-field statistical models, the determination of the probability of each 
elementary reaction only depends on the amount of the reactants, which implies the fact that not 
only the F-S theory, but also all other pure statistical models are not suitable for ATRP of divinyl 
monomers. Note that, in Figure 4, \( P_n \) above \( \text{Conv}_d = 0.09 \) (\( \text{Conv}_x = 0.19 \)) is ca. \( 2 \times 10^6 \), which is very 
close to all polymer mass \( (10^7 \times 0.19) \) and the \( \mathcal{D} \) is equal to one, which means that we have one 
molecule in the system. In real systems, the reaction between such clusters is much slower because 
their diffusion is slow and most double bonds on a micro gel are not accessible for reaction with a 
selected radical. By contrast, reaction with the divinyl monomer is still fast because of its fast 
diffusion. In other words, the failure of F-S theory in predicting ATRP of divinyl monomers can 
also be attributed to not considering the effect of diffusion, which plays an important role in ATRP 
systems.

To further prove this conclusion, we also studied the gel points of ATRP homopolymerization of 
divinyl monomers using DLL with/without cyclization models which involve the position 
restraints. The gel points obtained from different models are summarized in Table 2. One can 
observe that the gel points simulated by DLL models are in good agreement with the ATRP 
experimental value, while the results from w.c. and wo.c. models are closer to the values obtained 
from F-S theory, which are much lower than the results obtained from the experiments and 
simulations using the DLL models. Moreover, comparing with the \( RDP \) and \( \mathcal{D} \) of DLL simulations
(Figure 6), the abrupt decrease of $D$ is not observed. In addition, the effect of intramolecular cyclization on the gel points and polymerization process can be found which was not predicted by the statistical models (w.c. and wo.c. models). The difference between the DLL w.c. and DLL wo.c. models can be observed which become more obvious when $RDP$ and $D$ are analyzed as the function of $Conv_d$. This is because that partially reacted and fully reacted divinyl monomers cannot be distinguished in $Conv_x$, so only the promoted linear propagations due to the suppression of intermolecular crosslinking in w.c. model can be reflected. While in terms of $Conv_d$, besides the vinyl groups consumed by promoted linear propagation, the number of pendent vinyl groups consumed by intramolecular cyclizations was also counted, which led to a more significant discrepancy on the gel point and the evolution trend after the gel point was reached.

In summary, through these comparisons, it is further confirmed that those purely statistical models cannot correctly predict gelation. It can be concluded that the assumption of full availability of all substrates or no spatial restrictions (which leads to the underestimation of intramolecular cyclizations) could be the main reason for causing F-S model not being able to correctly describe well neither the gel points nor $P_n/D$ evolution after gelation. This assumption is realistic for low molecular weight substrates because their diffusion is fast compared with the reaction rate. It is far from the reality for large molecules e.g. nanogels, which diffuse slowly and thus, for a given radical, most of the vinyl bonds on a distant nanogel are not accessible. In other words, the coupling of large branched molecules, which is critical for gelation, is not kinetically controlled but diffusion controlled, thus it does not fulfill assumptions of the F-S model.

Table 2. Comparison of gel points of ATRP of divinyl monomers obtained from experiments, F-S theory and different simulation models.
Note: all the values were calculated in this work.

<table>
<thead>
<tr>
<th>[X]₀/[Ini]₀</th>
<th>w.c. sim Conv</th>
<th>Conv</th>
<th>w.o.c. sim Conv</th>
<th>Conv</th>
<th>ATRP exp Conv</th>
<th>Conv</th>
<th>F-S calc Conv</th>
<th>Conv</th>
<th>DLL w.c. Conv</th>
<th>Conv</th>
<th>DLL w.o.c. Conv</th>
<th>Conv</th>
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<td>0.07</td>
<td>0.14</td>
<td>0.14</td>
<td>0.14</td>
<td>0.07</td>
<td>0.14</td>
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</tr>
<tr>
<td>100/10</td>
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<td>0.42</td>
<td>0.23</td>
<td>0.41</td>
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<td>0.22</td>
<td>0.34</td>
<td>0.57</td>
<td>0.31</td>
<td>0.56</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Figure 6. DLL simulation for homopolymerization of divinyl monomers via ATRP. The changes in RDP, and D with the increasing (a) double bond conversion and (b) divinyl monomer conversion.

CONCLUSIONS

Two simulation models (w.c. and w.o.c.) were adopted to study ATRP of divinyl monomers. These results were compared with the corresponding simulation results obtained for FRP of divinyl monomers, ATRP experimental values, F-S theory and DLL models (conducted regarding ATRP homopolymerization systems in this work). In the case of ATRP of divinyl monomers, it is demonstrated that the gel points obtained using both models (w.c. and w.o.c.) are much lower than the values obtained from experiments and using DLL models. Both models cannot give a correct
description of the effect of gelation. By conducting DLL simulations, we conclude that the spatial correlations are also responsible for the discrepancies between gel points obtained from F-S model and experiments. As the number of large branched molecules increases (even before gel point), the polymerization process passes from kinetically controlled (described by F-S model) into diffusion controlled, in which F-S assumptions are no longer fulfilled. The reactive elements are not fully accessible, and thereby F-S model leads to underestimated values of gel point and predicts another sharp transition in $P_n$ above gel point, which to our best knowledge was never observed.

In summary, F-S theory and all other purely statistical models which ignore the intramolecular reaction and spatial restrictions cannot provide correct prediction and explanation of the gel point and gelation process of ATRP of divinyl monomers. An advanced model taking into account the spatial effect should be developed to better simulate the RDRP systems.

ASSOCIATED CONTENT

**Supporting Information**

Supporting Information Available: [The gel point and polymerization process of ATRP copolymerization of monovinyl monomer and divinyl crosslinker.] This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
The authors declare no competing financial interest.

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Monte Carlo Simulations of Atom Transfer Radical (Homo)Polymerization of Divinyl Monomers: Applicability of Flory-Stockmayer Theory

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