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Supporting Information:

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

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Figure S1. Simulation for ATRcP of monovinyl monomers and divinyl monomers.

The dependence of RDP plotted vs. double bond conversion, obtained from (a) **w.c.** model and (b) **wo.c.** model for various $[X]_0/[M]_0/[Ini]_0$.

Figure S2. Comparison of the gel points ($Conv_x$) for various initial molar ratios of divinyl monomer to initiator $[X]_0/[Ini]_0$, obtained from ATRcP, FRcP simulations and F-S theory.

Figure S3. Simulation for ATRcP of monovinyl monomers and divinyl monomers. The growth of P_n with double bond conversion for (a) **w.c.** model and (d) **wo.c.** model. The growth of P_w with double bond conversion for (b) **w.c.** model and (e) **wo.c.** model. The growth of $\bar{D}$ with double bond conversion for (c) **w.c.** model and (f) **wo.c.** model.

Figure S4. Simulation for ATRP of monovinyl monomers. The linear growth of P_n and P_w with monovinyl monomer conversion.

Table S1. Comparison of gel points of ATRcP of monovinyl and divinyl monomers obtained from experiments, F-S theory and different simulation models.

$[X]_0/[M]_0/[Ini]_0$	w.c. ^a $_{sim}$		wo.c. ^a $_{sim}$		ATRP $_{exp}$ ^b	F-S $_{calc}$ ^b		DLL w.c. ^b		DLL wo.c. ^b	
	$Conv_d$	$Conv_x$	$Conv_d$	$Conv_x$		$Conv_d$	$Conv_x$	$Conv_d$	$Conv_x$	$Conv_d$	$Conv_x$
20/78/2	0.24	0.42	0.23	0.41	0.43	0.22	0.40	0.38	0.57	0.34	0.55
10/88/2	0.33	0.56	0.32	0.55	0.66	0.32	0.53	0.50	0.71	0.46	0.68
6/92/2	0.44	0.70	0.43	0.67	0.81	0.41	0.65	0.62	0.83	0.56	0.78
3/95/2	0.64	0.87	0.62	0.85	1.0	0.58	0.82	0.83	0.95	0.76	0.90

^aThe values were calculated in this work. ^bThe values for $Conv_x$ were taken from ref.

^[1,2], and the values for $Conv_d$ were calculated in this work.

Figure S5. Simulation for ATRcP of monovinyl monomers and 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 double bond conversion. Arrows indicate gel points.

Reference:

- (1) H. Gao, P. Polanowski, K. Matyjaszewski, *Macromolecules* **2009**, *42*, 5925-5932.
- (2) P. Polanowski, J. K. Jeszka, K. Krysiak, K. Matyjaszewski, *Polym. (United Kingdom)* **2015**, *79*, 171-178.