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Gelation in Living Copolymerization of Monomer and Divinyl Cross-Linker: Comparison of ATRP Experiments with Monte Carlo Simulations

Haifeng Gao,[†] Piotr Polanowski,[‡] and Krzysztof Matyjaszewski*,[†]

[†]*Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue, Pittsburgh, Pennsylvania 15213, and* [‡]*Department of Molecular Physics, Technical University of Lodz, 90-924 Lodz, Poland*

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ABSTRACT: Two types of Monte Carlo simulations were carried out to simulate gelation in a living copolymerization of monovinyl monomer and divinyl cross-linker. The simulated gel points under various conditions were compared to the experimental gel points obtained in series of ATRP reactions and the calculated gel points based on Flory−Stockmayer (FS) theory. The first simulation was based on an off-lattice (OL) model, simplified by ignoring the geometry of macromolecules. The second more complex simulation was based on the dynamic lattice liquid (DLL) model. Both OL model and FS mean-field theory were capable to count on the influence of molar ratios of cross-linker to initiator and initiation rate on the gel points. However, the simulated gel points occurred at much lower monomer conversion, as compared to the experimental results. Furthermore, the solvent dilution, an important parameter to adjust the experimental gel points, had no effect on the gel points in both OL simulation and FS theory. In contrast, the DLL simulation based on a cooperative motion of elements on a lattice successfully predicted the effect of solvent dilution on the gel points. Addition of solvent beads in the DLL system decreased the concentrations of initiator, cross-linker, and monomer and significantly postponed the gel points. A decreasing targeted DP of primary chains, while keeping the molar concentrations of initiator and cross-linker constant, also resulted in a delayed gelation, which was confirmed by the ATRP experiments under similar conditions. These results provide means to understand the dependence of gel points on various parameters and can serve as a basis for the development of more advanced simulation models of the controlled/living copolymerization systems.

Introduction

Chain growth copolymerization of a monovinyl monomer with a divinyl cross-linker has been broadly used for synthesis of various branched copolymers and gels. Experimentally, gelation occurs when the system changes from a viscous liquid (sol) to an elastic gel. To predict the gel point, Flory and Stockmayer developed a statistical mean-field theory (FS theory) and pointed out that the theoretical gel point should occur when the weight-average number of cross-linking unit per primary chain reaches unity.[1,2] It is important to note that the cross-linking unit is different from cross-linkage. These two terms are sometimes incorrectly used in the literature. Based on Flory's statement,[2] a cross-linkage, provided by a divinyl cross-linker with both vinyl groups reacted, is formed in the polymer chains via reaction of pendent vinyl group with a propagating chain-end radical. One cross-linkage, a bridge connected two chains, consists of two cross-linking units. The FS theory was established for an ideal polymer network with two assumptions: (1) equal reactivity of all vinyl species and (2) absence of intramolecular cyclization reactions. Equation 1, derived from FS theory, indicates that the theoretical gel point (p_c) based on the conversion of total vinyl groups is determined only by the initial molar ratio of an initiator to a divinyl cross-linker ($[Ini]_0/[X]_0$), the initiation efficiency of initiator (IE_t), and the polydispersity of primary chains ($PDI = M_w/M_n$).[3]

$$p_c = \sqrt{\frac{[Ini]_0 IE_t}{2[X]_0}\frac{1}{M_w/M_n}} \quad (1)$$

The conventional radical polymerization (RP) technique is widely used for synthesis of polymeric networks via copolymerization of monovinyl monomer and divinyl cross-linker. The experimental gel point is significantly deviated from the theoretical FS value mainly because of the severe intramolecular cyclization reactions in RP reactions, which are ignored in the classic FS theory. The intrinsic features of RP, such as slow initiation and fast chain propagation, result in the formation of polymer chains with high molecular weight at very low conversion (highly dilute condition). These polymer chains contain numerous pendent vinyl groups but seldom overlap with each other due to the low concentration, excluded volume effect and slow diffusion/relaxation of long chains. Consequently, most of the pendent vinyl groups are consumed via intramolecular cyclization reactions, producing a less-swollen nanogel with highly cross-linked nanodomains. As the reaction proceeds, the number of these nanogels increases and radicals generated later in the reaction connect these preformed overlapped nanogels into a macroscopic and heterogeneous network.[3−5]

Recently, controlled radical polymerization (CRP)[6,7] techniques have been increasingly applied for synthesis of branched

*Corresponding author. E-mail: km3b@andrew.cmu.edu.

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polymers and gels with preserved chain-end functionalities and more homogeneous structures than in conventional RP.[8−23] In CRP, fast initiation, relative to propagation, results in a quick conversion of all initiators into primary chains and a retarded gelation. Moreover, the dynamic equilibrium between a low concentration of growing radicals and a significantly higher fraction of dormant species, established in CRP, ensures a slow steady chain growth and a more even incorporation of vinyl groups (from monomers, cross-linkers, and pendent vinyl groups) into the polymer chains. Therefore, the branched sols and/or gels synthesized by CRP processes have a more homogeneous structure than the polymers synthesized by RP methods at similar concentrations.[8]

Nitroxide-mediated polymerization (NMP),[24] atom transfer radical polymerization (ATRP),[25−28] and reversible addition−fragmentation chain transfer (RAFT)[29] polymerization have been used to study the gelation kinetics during the copolymerization of monomer and divinyl cross-linker.[8−16,18,19,30−40] For instance, our group systematically studied the experimental gelation in series of atom transfer radical copolymerization (ATRcP) reactions. The experimental gel points based on monomer conversion were affected by several parameters,[18,37,41,42] including the initial molar ratio of cross-linker to initiator, the initiation efficiency, and polydispersity of primary chains, as predicted by FS theory (eq 1). However, gelation was additionally influenced by the concentration of the involved reagents and the reactivity of vinyl groups, although eq 1 does not take this into account.[37,41] In an ATRP system with high initiation efficiency and low polydispersity of primary chains, no experimental gelation was observed when the initial molar ratio of cross-linker to initiator was less than unity, even under bulk conditions and at complete conversion. For comparison, the theoretical gel point based on FS theory (eq 1) is reached at 71% monomer conversion for the equimolar ratio of cross-linker to initiator. The discrepancy between the predicted theoretical gelation and the postponed experimental gelation was primarily attributed to the occurrence of unavoidable intramolecular cyclization reactions. As the two complementary reactions in chain growth copolymerization, intermolecular cross-linking reactions increase the molar mass of branched polymers and lead to gelation, whereas intramolecular cyclization reactions account for the formation of three-dimensional network via the formation of loops.

Kinetic modeling of the CRP systems was also attempted, e.g., in the presence of RAFT agents as radical mediators, showing the dependence of gel point and gel structure on several parameters.[43] However, the kinetic methods take into account only rate constants and concentrations of the involved reagents and cannot consider the statistical distribution of pendent vinyl groups among different polymer populations.

In the past decades, computational simulation has become one of the major tools in polymer science that helps understanding the molecular structure and dynamics of the polymer chains.[44,45] It can be applied to study complex gelation processes under various conditions. The gelation in the simulated system depends not only on the parameters used but also on the applied model. A systematic variation of the kinetic parameters and concentrations of the involved reagents should help to better understand and predict the experimental gelation process.

Herein, we present two types of Monte Carlo simulations of the living copolymerization of monovinyl monomers and divinyl cross-linkers. The first simulation was based on the off-lattice (OL) model, simplified by ignoring the geometry of macromolecules. The second more complex simulation was based on the dynamic lattice liquid (DLL) model. Several assumptions reflecting an ideal living copolymerization were applied in both simulations, including (i) no termination and chain transfer reactions were considered and (ii) the reactivity of functional groups (probability of being selected to react) was set constant, independent of chain length. All compounds, including initiators (Ini), monovinyl monomers (M), divinyl cross-linkers (X), solvent (S, if applicable), and polymer molecules, had no detailed chemical structures. Each step of the reaction resulted in irreversible formation of a link between two elements that reduced the number of molecules in the system by one. The reaction scheme is shown in Scheme 1. The bielemental reactions took place at random between initiating ends, e.g., initiators (**1**), the generated active centers (**5**, **7**, **9**, **10**), and elements containing double bonds, e.g., monomers (**2**), divinyl cross-linkers (**3**), and pendent vinyl groups (**7**, **8**). Nonreactive solvent elements, if applicable, were not included in the reaction scheme. A complete chart including all elemental reactions is also listed in Scheme 1.

The difference between these two simulations is in their treatment of chain geometry in the systems. The OL model ignores the geometry of macromolecules, which essentially corresponds to FS mean-field theory but is supplemented by the possibility of *statistical* intramolecular cyclization. In other words, the cyclization in OL model is solely dependent on the concentrations of reagents without considering any geometry of the polymer chains and the effect of excluded volume. In contrast, the DLL model takes into account elementary molecular movements in a densely occupied lattice, resulting in local cooperative structural transformations.[46,47] As compared to the OL model and the models based on kinetic equations,[43] the DLL model represents a self-fitting system, which needs no adjustable parameters to define the structure of branched chains.

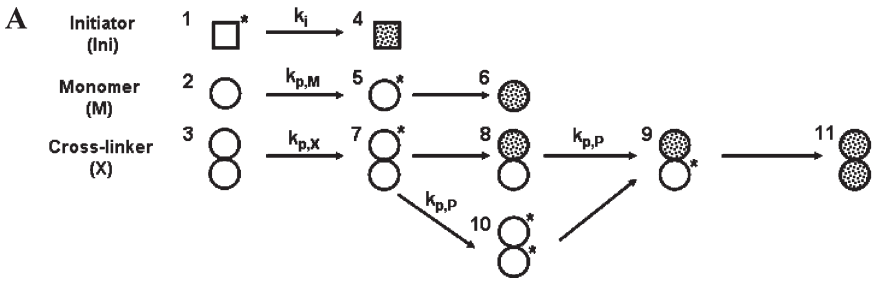
The gel points under various simulating conditions using OL and DLL models were compared with the theoretical gel points calculated based on FS theory (eq 1) and with the experimental gel points reported previously for a series of ATRcP of acrylates and divinyl cross-linkers. The comparison between the simulated gelation and experimental gelation under ATRP conditions provided a comprehensive understanding of the dependence of the gel points on various parameters, including molar ratios of cross-linker to initiator, concentrations of different reagents, initiation rate, and solvent dilution.

Experimental Section

Materials. Methyl acrylate (MA, 99%) and ethylene glycol diacrylate (EGDA, 90%) were purchased from Aldrich and purified twice by passing through a column filled with basic alumina to remove the inhibitor. CuBr (98%, Acros) was purified using a modified literature procedure.[48] All other reagents—ethyl 2-bromopropionate (EBrP), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), and $CuBr_2$—and solvents were purchased from Aldrich with the highest purity and used as received without further purification.

Synthesis of Poly(M-*co*-X) Gels by ATRcP of Monomer (M) and Cross-Linker (X). A series of ATRcP reactions by copolymerization of monovinyl monomer and divinyl cross-linkers were performed. Some of the experimental results have been recently reported.[37,41] Additional experiments were conducted by systematically changing the targeted degree of polymerization (DP) of primary chains during the ATRcP reactions using similar procedures. A typical experimental procedure for ATRcP of MA and EGDA started with the ratios of reagents $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 71/3/1/0.45/0.05/0.5$, $[MA]_0 = 8.5$ M. A clean and dry Schlenk flask was charged with MA (3.50 mL, 0.039 mol), EGDA (0.284 mL, 1.65 mmol of cross-linker given the purity of EGDA as 90%), PMDETA (57.3 μL, 0.27 mmol), and *N*,*N*-dimethylformamide (DMF, 0.73 mL). The flask was deoxygenated by five freeze−pump−thaw cycles. During the final cycle, the flask was filled with nitrogen before CuBr (35.4 mg, 0.25 mmol) and $CuBr_2$ (6.1 mg, 0.027 mmol) were quickly added to the frozen mixture. The flask was sealed with a glass stopper, then evacuated, and backfilled with

Scheme 1. (A) Schematic Illustration of Living Copolymerization of Monovinyl Monomer (M) and Divinyl Cross-Linker (X) in Monte Carlo Simulations and (B) the Complete Chart of Elemental Reactions[a]



B

$1+2 \xrightarrow{k_i} 4-5$	$5+2 \xrightarrow{k_{p,M}} 6-5$	$7+2 \xrightarrow{k_{p,M}} 8-5$
$1+3 \xrightarrow{2k_i} 4-7$	$5+3 \xrightarrow{k_{p,X}} 6-7$	$7+3 \xrightarrow{k_{p,X}} 8-7$
$1+7 \xrightarrow{k_i} 4-10$	$5+7 \xrightarrow{k_{p,P}} 6-10$	$7+7 \xrightarrow{2k_{p,P}} 8-10$
$1+8 \xrightarrow{k_i} 4-9$	$5+8 \xrightarrow{k_{p,P}} 6-9$	$7+8 \xrightarrow{k_{p,P}} 8-9$
$10+2 \xrightarrow{2k_{p,M}} 9-5$	$9+2 \xrightarrow{k_{p,M}} 11-5$	
$10+3 \xrightarrow{2k_{p,X}} 9-7$	$9+3 \xrightarrow{k_{p,X}} 11-7$	
$10+7 \xrightarrow{2k_{p,P}} 9-10$	$9+7 \xrightarrow{k_{p,P}} 11-10$	
$10+8 \xrightarrow{2k_{p,P}} 9-9$	$9+8 \xrightarrow{k_{p,P}} 11-9$	

[a] Open symbols show unreacted species and filled symbols show reacted species. Asterisk indicates species capable of reacting with a vinyl bond. Probability of involved reactions is defined by the rate constants of initiation (k_i), propagation with monomer ($k_{p,M}$), divinyl cross-linker ($k_{p,X}$), and pendent vinyl group ($k_{p,P}$). All these parameters can be independently changed. The value of $k_{p,X}$ was twice larger than those of $k_{p,M}$ and $k_{p,P}$ in most simulations, unless stated otherwise.

nitrogen five times before it was immersed in an oil bath at 60 °C. Finally, the N_2-purged initiator EBrP (71.3 μL, 0.55 mmol) was injected into the reaction system via a syringe through the side arm of the Schlenk flask. At timed intervals, samples were withdrawn via a syringe for GC measurements of MA and EGDA conversions and GPC measurements of sol molecular weights. At a certain moment, gelation occurred when the reaction fluid lost its mobility at an upside-down position for 10 s. After gelation, the reaction was kept at 60 °C for another 2 days before stopping the reaction via exposure to air. The catalyst was removed from the gel by repeated THF extraction and filtration.

Monte Carlo Simulations. Both OL model and DLL model ignored the detailed chemical structures of the compounds, including initiators, monomers, divinyl cross-linkers, solvents, and polymer molecules. The unit was considered as the elementary structure, and its status changed as a result of conversion. Each step of reaction resulted in irreversible formation of a link that reduced the number of molecules in the system by one. The change in the size distribution of molecules present in the system was monitored with conversion. Two assumptions reflecting an ideal living copolymerization were applied in both simulations, including (i) no termination and chain transfer reactions were considered and (ii) the reactivity of functional groups (probability of being selected to react) was set constant, independent of chain length. The simulated gel point was defined as the moment when the weight-average DP of all macromolecules, except the biggest chain (the highest DP), reached a peak value.

1. Off-Lattice (OL) Model. The molecules were placed in a virtual reaction space without defining its size and dimension. In other words, the molecules were dimensionless and had no coordinates or specific positions in space. The model corresponds to the mean-field classical approach where many collisions between molecules occur before an active collision results in bond formation.[49,50] Results obtained by simulations gave normalized second moment of the probability density function of molecular weight $\Phi(\alpha, n)$

$$DP_w = \frac{\sum_{n=1}^{\infty} n^2 \Phi(\alpha, n)}{\sum_{n=1}^{\infty} n \Phi(\alpha, n)} \quad (2)$$

where α is the conversion, n represents the DP of each polymer population, and DP_w is the weight-average DP of polymer chains.[51]

2. Dynamic Lattice Liquid (DLL) Model. Most lattice models are based on movement of elements into vacancies with comparable size to the mobile elements and regarded as free volume fluctuations.[52] In contrast, the DLL model used a cooperative motion concept, based on rearrangements of beads within closed dynamic loops and enabled efficient treatment of the diffusion problems in mixtures.[53] A specific feature of the DLL model is the possibility of simulations with density factor $\rho = 1$ (i.e., all lattice sites are occupied by microscopic units). Molecular systems are treated by the dynamics, consisting of local vibrations and occasional diffusion steps, resulting from coincidental attempts of the neighboring elements to displace the occupied positions. At longer time interval, the dynamics produced by DLL model leads to a displacement of individual beads along the random walk trajectories with steps distributed randomly in time. Earlier application of this model indicates that this kind of algorithm reflects very well the dynamic behavior of a complex system, such as the aggregation and diffusion of polymer chains (particles) in a solution.[46,47,54,55] The fundamentals of this model were described in detail previously.[46,53] In the DLL simulations, an $N_x \times N_y \times N_z$ fcc lattice with box dimension as $100 \times 100 \times 100$ was used. At the initial moment,

the initiator, monomer, and divinyl cross-linker were randomly distributed in the system with concentrations $[Ini]_0$, $[M]_0$, and $[X]_0$.

Results and Discussion

We recently studied the dependence of experimental gel points on various parameters by using ATRcP of monovinyl monomers and divinyl cross-linkers.[18,37,41,42] In the present study, a series of computational Monte Carlo simulations were performed based on two types of models (OL and DLL) with systematically varied parameters. During the simulations, the chemical structures of all molecules were not considered, and each step of reaction resulted in irreversible formation of a link that reduced the number of molecules in the system by one. By systematically changing the initial molar ratios of initiator, monovinyl monomer, and divinyl cross-linker, the simulated gel points were compared to the experimental gel points obtained under ATRP conditions and values calculated based on FS theory (eq 1).

It is worth noting that a dynamic equilibrium between a low concentration of growing radicals and a significantly higher fraction of dormant species is established in all CRP reactions. The exchange reactions affect polymerization kinetics but should not influence the gelation process, if they are fast enough (generating chains with low polydispersity) and provided that termination can be neglected. In a typical ATRcP of acrylates, concentration of radicals is very low, and the proportion of terminated chains is below 1%.[56,57] Also, exchange reactions are fast generating primary chains with $M_w/M_n < 1.2$. Thus, in order to simplify Monte Carlo simulations, we adopted the living polymerization model without termination and without equilibria between active and dormant species.

Effect of Cross-Linker Amounts on Gel Points: Comparison of Gel Points Simulated by OL and DLL with the Experimental and FS Values. The OL model was first applied for simulating the bulk copolymerization of monovinyl monomer (M) and various amounts of divinyl cross-linker (X) under a living polymerization condition with fast initiation and no termination reactions. During the simulation, the molecular weight of each polymer population was determined. The simulated gel point was defined as the moment, when the weight-average degree of polymerization (DP) of all macromolecules, except the biggest chain (the highest DP), reached a peak value. Such a definition is similar to that suggested by Eichinger[58] and is in agreement with our previous experimental results, where the experimental gelation occurred when the molecular weight of GPC-measured sols reached a maximum value and then started to decrease (Figure 1A).[18] Figure 1B shows the evolution of weight-average DP of polymers without the biggest chain during OL simulations at various molar ratios of cross-linker to initiator ($[X]_0/[Ini]_0$), indicating that the simulated gelation occurred earlier (at lower monomer conversion), when more X was used.

The simulated gel points in series of OL simulations were compared to the experimental results and the calculated results based on eq 1, shown in Table 1. By fixing the initial fraction of initiator as $[Ini]_0 = 2\%$ and systematically varying the X amounts, the simulated gel points using OL model were in agreement with the calculated results based on the FS theory. Both FS theory and OL model ignore the geometry of the polymer chains and the spatial distribution of pendent vinyl groups, as discussed above. Any chain-end propagating center, i.e., radical, in the virtual reaction space can react with any double bond with probability solely depending on their concentrations and reactivity. A small difference between the OL simulated gel points and the FS calculated values was due to the fact that a limited statistical cyclization

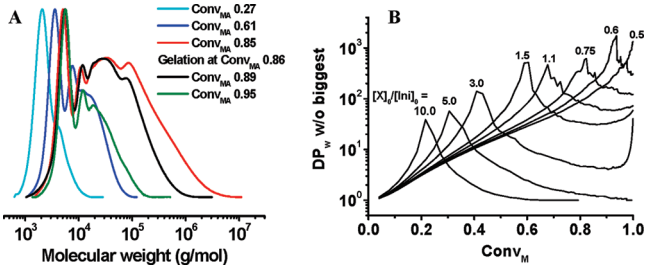


Figure 1. (A) Evolutions of GPC curves during synthesis of poly(MA-*co*-EGDA) by ATRcP of MA and EGDA and (B) evolution of weight-average DP of polymers without the biggest chain during OL simulations with different amounts of X. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1.5/1.0/0.45/0.05/0.5$, $[MA]_0 = 6.0$ M, in DMF at 60 °C, linear polyMMA standards for THF GPC calibration, data taken from ref 18. OL simulation conditions: $[M]_0/[X]_0/[Ini]_0 = (98 - X)/X/2$ with total number of element as 10^6.

was considered in the OL simulation, while it was completely excluded in the FS theory. Therefore, the OL gel points based on M and/or X conversions were slightly higher than the values from FS theory under the same molar ratios of reagents.

The simulated OL gel points always occurred at lower conversions than the experimental results obtained in ATRP reactions with high monomer concentrations ($[MA]_0 = 8.5$ M with 10 vol % of solvent, Figure 2) because spatial distribution of pendent vinyl groups was neglected in the OL simulation. The simulated gelation occurred when the ratio of cross-linkage to primary chains was slightly higher than 0.5, whereas experimentally no gelation occurred if this ratio was less than unity.

To consider the polymer geometry and the distribution of pendent vinyl groups along the polymer chains, a more advanced DLL model based on the lattice structure was applied for simulating the living copolymerization of M and X. All elements in the DLL model, including the reacted beads and unreacted beads, were placed in a fully packed fcc lattice. The chain-end propagating center could only react with the double bonds at its neighbor, depending on the coordination number of the lattice, e.g., coordination number = 12 for fcc lattice. The limited availability of unreacted double bonds around each chain end isolates propagating centers and delays the growth of branched polymers. Therefore, as expected, the simulated gel points in the DLL model occur at higher monomer conversion than those in the OL model.

The method to determine the simulated gel point in the DLL model was similar to that in the OL model: the moment when the weight-average DP of all molecules, except the biggest chain (the highest DP), reached a peak value. By varying the initial molar ratios of $[X]_0/[Ini]_0$, the DLL simulated gel points (Table 1) were compared to the experimental gel points as well as to the OL gel points and calculated values based on FS theory (Figure 2). The results indicate that the DLL simulated gel points occurred at the highest monomer conversion than all other gel points under similar molar ratios of cross-linker to initiator. For example, at $[X]_0/[Ini]_0 = 3/2 = 1.5$ the DLL gel point was $conv_M = 0.83$, later than the OL gel point ($conv_M = 0.61$) and the FS gel point ($conv_M = 0.58$). Compared to the ATRP experimental gel points under concentrated conditions ($[MA]_0 = 8.5$ M), the DLL simulated gel points were slightly later when the same molar ratios of $[M]_0/[X]_0/[Ini]_0$ were used. During the DLL simulation, it was found that whenever the ratios of $[M]_0/[X]_0/[Ini]_0$ were fixed, the mobility of particles has little

Table 1. Comparison of the Gel Points in Four Different Systems (X Amount Effect)

			ATRP exp[a]		FS calc[b]		OL sim[c]		DLL sim[d]	
$[Ini]_0$ (%)	$[X]_0$ (%)	$[M]_0$ (%)	$conv_M$	$conv_X$	$conv_M$	$conv_X$	$conv_M$	$conv_X$	$conv_M$	$conv_X$
2	1	97	no gelation		1.00	1.00	no gelation		no gelation	
2	1.2	96.8	no gelation		0.91	0.99	0.94	1.00	no gelation	
2	1.5	96.5	no gelation		0.82	0.97	0.82	0.97	no gelation	
2	2	96	no gelation		0.71	0.91	0.74	0.92	no gelation	
2	2.2	95.8	0.97	1.00	0.67	0.89	0.70	0.91	0.94	0.98
2	3	95	0.78	1.00	0.58	0.82	0.61	0.84	0.83	0.95
2	6	92	0.61	0.81	0.41	0.65	0.42	0.67	0.64	0.83
2	10	88	0.42	0.66	0.32	0.53	0.34	0.56	0.49	0.71
2	20	78	0.32	0.43	0.22	0.40	0.23	0.40	0.37	0.57

[a] Experimental gel points obtained under ATRP conditions. The experimental gel point was the moment when the reaction fluid lost its mobility at an upside-down position for 10 s. Conversions of MA ($conv_M$) and EGDA ($conv_X$) immediately before gelation; experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C, $[MA]_0 = 8.5$ M. These experimental results were recently published elsewhere.[37] [b] Calculated gel points based on FS theory. Assuming monodisperse primary chains and quantitative initiation efficiency. [c] Simulated gel points by using OL model. Total number of elements: 10^6. [d] Simulated gel points by using DLL model. Total number of elements: 10^6.

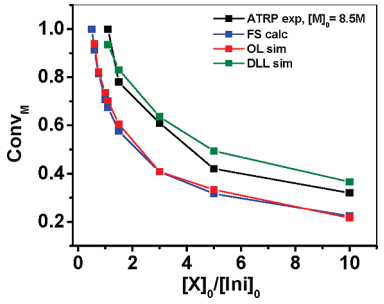


Figure 2. Comparison of OL and DLL simulated gel points with ATRP experimental and FS calculated values for systematic variation of the initial molar ratios of divinyl cross-linker to initiator $[X]_0/[Ini]_0$ (Table 1).

effect on the DLL gel points. These results indicate that during the DLL simulation the spatial distribution of chain-end propagating centers and pendent vinyl groups in the system was more heterogeneous than in the experiments. Some pendent vinyl groups and chain-end centers could be trapped in the 3D lattice, becoming less reactive or even nonreactive. The application of DLL lattice model in the Monte Carlo simulation resulted in a much better correlation with the experimental ATRcP of MA and EGDA because it takes into account the spatial distribution and geometry of the polymer chains.

Effect of Dilution on the Gel Points: Comparison of DLL Simulated Gel Points to ATRP Experimental Values. Experimental results of ATRcP clearly showed the significant influence of solvent dilution on the experimental gel points. Diluting a system by adding more solvent, while keeping all other conditions the same, dramatically postponed the experimental gelation and shifted to higher monomer conversion.[37,39] However, dilution showed no effect on the gel points simulated by OL because the OL model ignores the spatial distribution of vinyl groups along the polymer chains and the dimension of polymer chains in the virtual reaction system. In order to study the effect of dilution on the gel points during the Monte Carlo simulation, the DLL model based on the lattice structure was used. The addition of inert solvent beads into the DLL lattice dilutes the reactive beads and decreases the overlap between primary chains, similar to the experimental situation.

In order to compare the experimental ATRcP of MA and EGDA, a series of DLL simulations were performed at two molar ratios of $[M]_0/[X]_0/[Ini]_0$ and different dilution conditions. The DLL simulated gel points under various dilution levels (Table 2) showed a trend similar to the experimental

Table 2. Solvent (S) Effect on Gel Points at Two Constant $[M]_0/[X]_0/[Ini]_0$ Ratios

$[M]_0$ (M)	$[Ini]_0$ (%)	$[X]_0$ (%)	$[M]_0$ (%)	$[S]_0$ (%)	DLL sim[a]		ATRP exp[b]	
					$conv_M$	$conv_X$	$conv_M$	$conv_X$
$[M]_0/[X]_0/[Ini]_0 = 50/3/1$								
bulk	1.85	5.56	92.59	0.00	0.61	0.81		
8.5	1.70	5.10	85.00	8.20	0.64	0.84	0.61	0.81
6.0	1.20	3.60	60.00	35.20	0.70	0.87	0.65	0.90
2.5	0.50	1.50	25.00	73.00	0.97	0.99	0.84	~1
1.0	0.20	0.60	10.00	89.20	no gelation		no gelation	
$[M]_0/[X]_0/[Ini]_0 = 50/5/1$								
bulk	1.79	8.93	89.29	0.00	0.51	0.71		
8.5	1.70	8.50	85.00	4.80	0.51	0.73	0.42	0.66
6.0	1.20	6.00	60.00	32.80	0.57	0.77	0.48	0.76
2.5	0.50	2.50	25.00	72.00	0.79	0.94	0.71	0.95
1.0	0.20	1.00	10.00	88.80	no gelation		no gelation	

[a] Simulated gel points by using DLL model. Total number of elements: 10^6. [b] Experimental gel points obtained under ATRP conditions. The experimental gel point was the moment when the reaction fluid lost its mobility at an upside-down position for 10 s. Conversions of MA ($conv_M$) and EGDA ($conv_X$) immediately before gelation. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C. These experimental results were recently published elsewhere.[37]

results. Solvent dilution delayed the gelation that occurred at a progressively higher monomer conversion (Figure 3). Some differences between the DLL simulated gel points and the experimental gel points are noticed, since no further adjustments to the model were made. As an important comparison, the solvent dilution had no effect during the OL simulation and FS calculation, demonstrating that the lattice-based DLL simulation is a powerful method to mimic the experimental conditions (Figure 3).

Dependence of Gel Points on Replacing Monomer by Solvent: Comparison of DLL Simulated Gel Points to ATRP Experimental Values. In the previous system, the concentrations of monomer, cross-linker, and initiator were simultaneously decreased due to the addition of solvent, but their ratios were constant. Another situation occurs when concentrations of initiator and cross-linker are constant, but only monomer is diluted by adding solvent. In this system, the molar concentration of primary chains is constant but the targeted DP of primary chains is decreased.

The extent of intermolecular cross-linking reaction depends on the interactions of two overlapped polymeric molecules. Since the critical overlapping concentration of

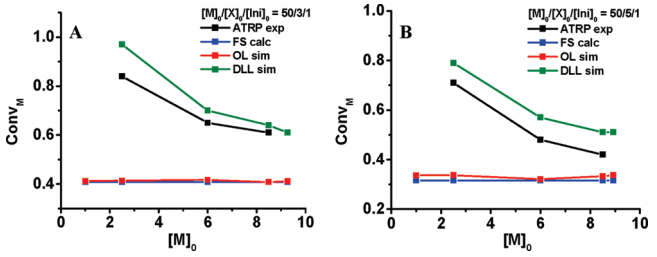


Figure 3. Effect of solvent dilution on the DLL simulated gel points and the ATRP experimental gel points under two conditions (Table 2): (A) $[M]_0/[X]_0/[Ini]_0 = 50/3/1$ and (B) 50/5/1. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C. The experimental results were recently published elsewhere.[37]

Table 3. Solvent (S) Effect on Gel Points: Replacing M by S

$[Ini]_0$ (M)	$[Ini]_0$ (%)	$[X]_0$ (%)	$[M]_0$ (%)	$[S]_0$ (%)	DLL sim[a]		ATRP exp[b]	
					$conv_M$	$conv_X$	$conv_M$	$conv_X$
0.12	1.20	3.60	95.20	0.00	0.63	0.82		
0.12	1.20	3.60	85.00	10.20	0.65	0.84	0.64	0.85
0.12	1.20	3.60	60.00	35.20	0.70	0.87	0.65	0.90
0.12	1.20	3.60	40.00	55.20	0.78	0.93	0.75	0.90
0.12	1.20	3.60	25.00	70.20	0.94	0.99	0.78	0.95
0.12	1.20	3.60	10.00	85.20	no gelation		no gelation	

[a] Simulated gel points by using DLL model. Total number of elements: 10^6. [b] Experimental gel points obtained under ATRP conditions. The experimental gel point was the moment when the reaction fluid lost its mobility at an upside-down position for 10 s. Conversions of MA ($conv_M$) and EGDA ($conv_X$) immediately before gelation. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = M/3/1/0.45/0.05/0.5$, in DMF at 60 °C, $[EBrP]_0 = 0.12$ M.

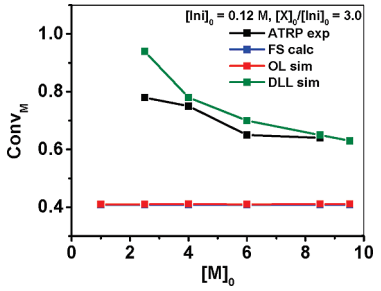


Figure 4. Comparison of the gel points in DLL simulation and ATRcP experiments: replacing monomer (M) by solvent (S) (Table 3). Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = M/3/1/0.45/0.05/0.5$, in DMF at 60 °C, $[EBrP]_0 = 0.12$ M.

polymers in solution depends on the weight fraction of polymer in solution, a lower targeted DP of primary chains should decrease the polymer weight concentration and the probability for overlapping.[39] Therefore, when more solvent was added to replace monomer in ATRP, gel points occur later, i.e., at higher monomer conversions (Table 3).

The results in Table 3 and Figure 4 indicate that when the concentrations of initiator and divinyl cross-linker in the system were constant, the gradual monomer dilution (lower DP) resulted in a gelation at higher monomer conversion. The trends in both DLL simulation and ATRP experiments were similar and very different from those in the OL simulation and the FS calculation, where addition of solvent had no effect on the gel points.

Effect of the Initiator Amount on Gel Points: Comparison of Gel Points Simulated by OL with FS Values. It is worth stressing that, in contrast to FS theory, OL simulations take into account statistical intramolecular cyclization. Therefore, gel points simulated by OL can differ from the FS calculated values. For instance, when the concentration of initiator, $[Ini]_0$, is progressively decreased, but the concentration of cross-linker, $[X]_0$, is kept constant, the targeted DP of the primary chains increases: $DP_{target} = ([M]_0 + 2[X]_0)/[Ini]_0$. According to eq 1, the variation of targeted DP should have no effect on the calculated gel points. However, in the OL simulation the contribution of statistical intramolecular cyclization, as compared to intermolecular cross-linking reaction, is determined by the number of pendent vinyl groups per primary chain as well as the concentration of primary chains. When a very low amount of initiator was used, such as $[Ini]_0 = 0.00002\%$ (Table 4), the gel point in the OL simulation, based on M conversion, was 10 times higher than the FS value. Such a result indicates that the intramolecular cyclization in this OL simulation became statistically more significant due to the increased ratio $[X]_0/[Ini]_0$. When the total number of elements during the simulation was enlarged to $N = 10^7$, the number of primary chains in the system ($N_{PC} = 2$) was still much lower than the average number of pendent vinyl groups per chain. When the initiator amount was progressively increased, the simulated gel point became closer to the FS calculated one (Figure 5).

Table 4. Effect of Initiator Amount on the Simulated Gel Points

$[Ini]_0$ (%)	$[X]_0$ (%)	$[M]_0$ (%)	FS calc[a]		OL sim[b]	
			$conv_M$	$conv_X$	$conv_M$	$conv_X$
0.00002[c]	2	97.999 98	0.002	0.004	0.021	0.042
0.02	2	97.98	0.071	0.136	0.084	0.159
0.2	2	97.8	0.224	0.397	0.236	0.415
2	2	96.0	0.707	0.914	0.736	0.920
20	2	78.0	no gelation		no gelation	

[a] Assuming monodisperse primary chains and quantitative initiation efficiency. [b] Simulated gel points by using OL model. Total number of elements: 10^6. [c] Simulated gel points by using OL model. Total number of elements: 10^7.

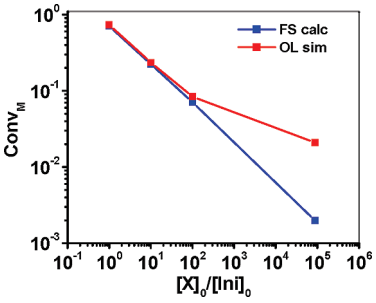


Figure 5. Comparison of OL simulated gel points to the FS calculated values under various amounts of initiator with a constant $[X]_0 = 2\%$ (Table 5).

Effect of Initiation Rates on Gel Points Simulated by OL. It was previously reported that the efficiency of initiation in ATRcP of monomer and divinyl cross-linker also affects the gel points[42] The OL simulation, although it ignores the spatial geometry of the polymeric chains, can be still used to qualitatively illustrate the influence of the $k_i/k_{p,M}$ ratio on the simulated gel points.

During the ATRcP reactions, the reactivity of initiator directly determines its consumption rate and the number of primary chains at any time. When an efficient ATRP initiator is used, all added initiators quickly convert into primary chains at low monomer conversion, resulting in a nearly constant number of primary growing chains throughout the polymerization. In contrast, for systems with slow initiation, initiation efficiency progressively increases with

Table 5. Effect of Initiation Rates on the OL Simulated Gel Points

				OL sim[b]	
$[Ini]_0$ (%)	$[X]_0$ (%)	$[M]_0$ (%)	$k_i/k_{p,M}$[a]	$conv_M$	$conv_X$
2	2	96	10^{-4}	0.137	0.255
2	2	96	0.01	0.533	0.778
2	2	96	0.1	0.701	0.911
2	2	96	1	0.736	0.920
2	2	96	10	0.730	0.924

[a] Ratio of rate constants of initiation to propagation with monomer. The ratios of $k_{p,M}/k_{p,X}/k_{p,P}$ = 1/2/1 were kept constant. [b] Simulated gel points by using the OL model. Total number of element: 10^6.

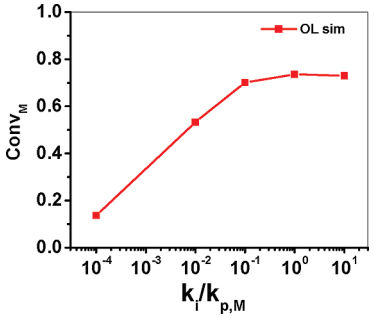


Figure 6. Dependence of OL simulated gel points on initiation rates ($k_i/k_{p,M}$) with fixed molar ratios of $[M]_0/[X]_0/[Ini]_0$ = 96/2/2 (Table 5).

monomer conversion. Thus, the relative initiation rate directly affects the fraction of initiators transformed into polymer chains, i.e., the number of primary chains formed in the system.[42]

The effect of initiation rate, as compared to the propagating rate, on the gel points was studied by performing a series of OL simulation for the constant molar ratio of $[M]_0/[X]_0/[Ini]_0$ = 96/2/2. The simulated gel points were nearly identical for the two systems with $k_i/k_{p,M}$ = 1.0 and 10. However, they became progressively lower for the value of $k_i/k_{p,M} < 0.1$. When a very low $k_i/k_{p,M}$ value was used, such as $k_i/k_{p,M} = 10^{-4}$, the conversion of initiator into primary chains was very slow, which directly decreased the number of primary chains at gel point and resulted in a much earlier simulated gel points (Table 5, Figure 6). These OL results reflect a similar trend as demonstrated in the recent experiments where an initiator with slower initiation resulted in a gelation at lower monomer conversion.[42]

Conclusions

In this article, two models of Monte Carlo simulations were used to study a living copolymerization of monovinyl monomer and divinyl cross-linker. The first simulation was an off-lattice (OL) model simplified by ignoring the geometry of macromolecules, while the second more complex simulation was based on the dynamic lattice liquid (DLL) model. The simulated gel points under various conditions were compared to the experimental gel points obtained in series of ATRcP reactions and to the calculated gel points based on Flory−Stockmayer (FS) theory. These comparisons provided a better understanding of the dependence of the gel points on various parameters in a controlled "living" system. They can be summarized as follows: (1) Off-lattice simulation by ignoring the geometry of polymer chains essentially corresponded to FS mean-field theory. Both systems take into account the influence of molar ratios of cross-linker to initiator and initiation rate on the gel points. However, the OL and FS gel points were at much lower monomer conversion than the experimental results. Furthermore, the solvent dilution, an important parameter to adjust the experimental gel points, had no effect on the gel points in both OL simulation and FS theory. (2) The DLL simulation based on a cooperative motion concept successfully predicted the effect of solvent dilution on the gel points. Addition of solvent beads in the DLL system decreased the concentrations of initiator, cross-linker, and monomer and significantly postponed the gel points, in agreement with the experimental results. Additionally, a decreasing targeted DP of primary chains, while keeping the molar concentrations of initiator and cross-linker constant, also resulted in a delayed gelation, as confirmed by the ATRcP experiments under similar conditions. A more powerful simulation model should be developed in the future to account for all possible reactions (pathways) in the CRPs, such as termination, activation/deactivation, as well as solvation processes, and various aspects of molecular structure. The evolution of polymer topology as a function of conversion could also provide additional information on the gelation process.

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