Synthesis of Polyacrylate Networks by ATRP: Parameters Influencing Experimental Gel Points

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ABSTRACT: Series of poly(M-*co*-X) cross-linked polymers were synthesized by atom transfer radical copolymerization (ATRcP) of different acrylate monomers (M) and diacrylate cross-linkers (X). The variation of experimental gel points based on monomer and/or cross-linker conversions was systematically studied by changing three parameters: monomer concentration, structure of cross-linkers, and structure of monomers. Under constant molar ratios of reagents, decreasing monomer concentration significantly increased the intramolecular cyclization reactions and delayed the occurrence of macroscopic gelation. Three types of acrylate monomers and five types of diacrylate cross-linkers with different structures were used for the copolymerization to explore the structural effect of monomers and cross-linkers on the experimental gel points. The results indicated that the experimental gel points based on conversions and the gel structural compactness did not change significantly by varying the monomer and/or cross-linker species within the scale of our investigation.

Introduction

The conventional free radical polymerization (FRP) method has been broadly used for synthesis of branched polymers and gels by copolymerization of monovinyl monomers with a small amount of divinyl cross-linkers. The branching points are generated in the polymer chains via reaction of pendant vinyl groups with the propagating radicals. Highly branched polymers and/or gels with inhomogeneous structures are formed at a very early stage (low monomer conversions) during most FRP reactions due to the slow initiation, fast chain propagation, and termination reactions.[1–3] In contrast to FRP, recently developed controlled radical polymerization (CRP)[4–7] methods have advantages in preparing homogeneous polymer networks because of the fast initiation and quick deactivation reactions. The fast initiation reactions, relative to propagation reactions, result in all polymer chains being initiated at approximately the same time and the nearly constant number of primary growing chains throughout the polymerization. The dynamic equilibrium, established between a low concentration of active propagating chains and a large number of "dormant" chains, ensures that only a few monomers are incorporated into the polymer chains in every activation/deactivation cycle. During the long "dormant" period, the polymer chains cannot propagate but can diffuse and relax, which results in the fact that the reaction possibility of each vinyl species (from monomer, cross-linker, and pendant vinyl group) is statistically determined by their concentrations. Therefore, the sols and/or gels synthesized by CRP methods[8–25] have a more homogeneous distribution of branching points than the polymers synthesized by FRP methods at similar concentrations.[8,9,17]

Recently, our group used the atom transfer radical polymerization (ATRP)[26–29] technique to synthesize series of poly(MA-*co*-EGDA) cross-linked polymers via copolymerization of methyl acrylate (MA) and ethylene glycol diacrylate (EGDA).[24] The concentration of MA was kept constant at $[\mathrm{MA}]_0 = 6.0$ M, and the molar ratios of cross-linker to initiator were varied systematically. The experimental gel points, determined as the conversion of MA ($\mathrm{conv}_{\mathrm{MA,gel}}$) or EGDA ($\mathrm{conv}_{\mathrm{EGDA,gel}}$) at the moment of gelation, were compared to the simulated values based on Predici simulation.[24,30–32]

It should be noted that currently there are two opinions on the gel points during the CRP of vinyl monomer and divinyl cross-linker. The first view is that the critical gelation happens when the average number of cross-linkage (cross-linker with both vinyl groups reacted) per primary chain exceeds unity if the primary chains are uniform and the intramolecular cyclization reactions are neglected. This opinion has been confirmed in various experiments performed by different groups,[11,20,24] indicating that no gelation occurred in ATRP systems with high initiation efficiency when the initial molar ratio of cross-linker to initiator was less than 1, even at complete monomer conversion. The second view[9,17] directly applies Flory's statistical gelation theory,[33] which was developed based on condensation and vulcanization of preformed polymers. Herein, the gelation occurs when two primary chains contain an averaged one cross-linkage; i.e., the average number of cross-linkage per primary chain is half. This was first described in ref 9. However, the experimental gel points were 2 times larger than the 0.5 theoretical expectations.[9]

In our study, by defining the simulated gel point as the moment when the average number of cross-linkage per primary chain exceeded unity, we found that the experimental gel points were very close to but slightly higher than the simulated values when the initial monomer concentration was $[\mathrm{MA}]_0 = 6.0$ M.[24] The small difference between the experimental gel points and the simulated values was caused by the inevitable intramolecular cyclization reactions, which were neglected during the Predici simulation. The intramolecular cyclization consumed pendant vinyl groups but had no contribution to the increase of molecular weights of branched polymers. In other words, the competition between intermolecular cross-linking reaction and intramolecular cyclization reaction is a main factor in determining the variation of experimental gel points.

Although the discrepancy between the two views on the gel points in CRP systems still exists, the values of experimental gel points determined as the conversions of monomer and divinyl cross-linker at the gelation moment are undisputed. Herein, we systematically studied the influence of three parameters on the experimental gel points, e.g., monomer concentration, structure of cross-linkers, and structure of monomers, during atom transfer radical copolymerization (ATRcP) of acrylate monomers and diacrylate cross-linkers.

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Three types of acrylate monomers and five types of diacrylate cross-linkers with different structures were employed for series of ATRcP reactions at various concentrations and molar ratios of reagents. The experimental gel points based on the conversions of monomers and/or cross-linkers were determined and compared with each other in order to understand the influence of each parameter on the experimental gel points.

Experimental Section

Materials. Three types of acrylate monomers, including methyl acrylate (MA, 99%), *n*-butyl acrylate (BA, 99%), and 2-ethylhexyl acrylate (EHA, 98%), and five types of diacrylate cross-linkers, including ethylene glycol diacrylate (EGDA, 90%), 1,4-butanediol diacrylate (BDDA, 90%), 1,6-hexanediol diacrylate (HDDA, 80%), 1,6-hexanediol ethoxylated diacrylate (HEDA, $M_n \sim 314$ g/mol), and bisphenol A ethoxylated diacrylate (BEDA, $M_n \sim 468$ g/mol), 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.[34] 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). All experimental procedures for synthesis of various kinds of cross-linked copolymers were similar. A typical procedure for ATRcP of MA and EGDA is briefly described, starting with the ratios of reagents $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/5/1/0.45/0.05/0.5$, $[MA]_0 = 6.0$ M. A clean and dry Schlenk flask was charged with MA (3.50 mL, 0.039 mol), EGDA (0.670 mL, 3.9 mmol of cross-linker given a purity of EGDA of 90%), PMDETA (81.2 μL, 0.39 mmol), and *N,N*-dimethylformamide (DMF, 2.20 mL). The flask was deoxygenated by five freeze–pump–thaw cycles. During the final cycle, the flask was filled with nitrogen before CuBr (50.2 mg, 0.35 mmol) and $CuBr_2$ (8.7 mg, 0.039 mmol) were quickly added to the frozen mixture. Special care was not taken to avoid moisture condensation. The flask was sealed with a glass stopper and then evacuated and back-filled with nitrogen five times before it was immersed in an oil bath at 60 °C. Finally, the N_2-purged initiator EBrP (0.10 mL, 0.78 mmol) was injected into the reaction system via a syringe through the sidearm 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 tetrahydrofuran (THF) extraction and filtration.

Characterization. Monomer conversions were determined from the concentration of the unreacted monomer in the samples periodically removed from the reactions using a Shimadzu GC-17A gas chromatograph, equipped with a capillary column (DB-Wax, 30 m × 0.54 mm × 0.5 μm, J&W Scientific). DMF was used as an internal standard for calculation of monomer conversions. After filtration through a 220 nm poly(tetrafluoroethylene) (PTFE) filter, the polymer samples were separated by gel permeation chromatography (GPC) (Polymer Standards Services (PSS) columns (guard, 10^5, 10^3, and 10^2 Å), with THF eluent at 35 °C, flow rate = 1.00 mL/min, and a differential refractive index (RI) detector (Waters, 2410)). The apparent molecular weights and polydispersities (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) (polyMMA) standards using WinGPC 6.0 software from PSS. The detectors employed to measure the absolute molecular weights ($M_{w,MALLS}$) were a triple detector system containing a RI detector (Wyatt Technology, Optilab REX), a viscometer detector (Wyatt Technology, ViscoStar), and a multi-angle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology. ^1H NMR spectra by using $CDCl_3$ as the solvent were collected on a Bruker Avance 300 MHz spectrometer at 27 °C. The conversions of monomers determined by using the NMR technique were in excellent agreement with GC results, which were primarily used in this study.

Determination of Gel Points by Predici Simulation. The Predici program (version 6.3.1) was used for kinetic modeling of copolymerization of monovinyl monomer and divinyl cross-linker.[24,30–32] It employs an adaptive Rothe method as a numerical strategy for time discretization. The simulated gelation occurred when the average number of cross-linkage (cross-linkers with both vinyl groups reacted) per primary chain exceeded unity. The concentrations of all species can be followed with time. During simulation, the copolymerization of acrylate monomer and diacrylate cross-linker was simplified as a terpolymerization reaction, in which M_1 was acrylate monomer, M_2 was cross-linker, and the third monomer was the pendant vinyl group M_{2P}, which was generated stoichiometrically when a cross-linker reacted with a propagating radical (eq 1).[24]

$$P_i^\bullet + M_2 \rightarrow P_2^\bullet + M_{2P} \qquad (i = 1, 2, 2P) \qquad (1)$$

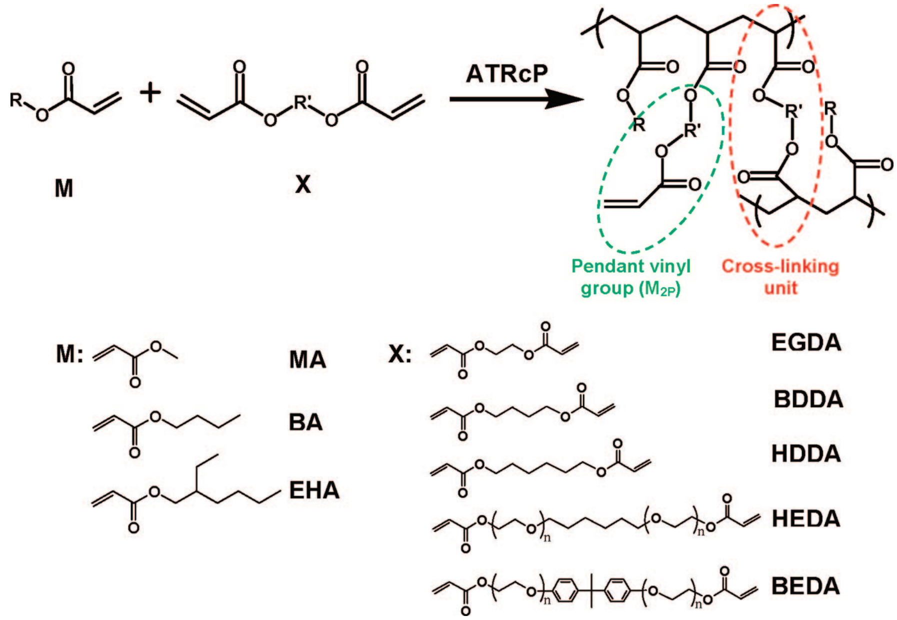
Results and Discussion

With EBrP as the initiator, CuBr/PMDETA as the catalyst (10 mol % $CuBr_2$ of total copper species was preadded in the system), and DMF as the solvent, ATRP of acrylate showed a fast initiation and high initiation efficiency.[24] During ATRcP of acrylate monomer and diacrylate cross-linker, the initiators are consumed quickly and converted into short primary chains containing pendant vinyl groups and halogen chain-end functionality. The fast activation/deactivation equilibrium ensures that only a very low concentration of primary chains is active. Since all vinyl species have a similar reactivity during copolymerization of acrylate monomer and diacrylate cross-linker,[24] the propagating radicals react with free monomers, cross-linkers, and the pendant vinyl groups in a statistical manner based on their concentrations. The intermolecular reactions between propagating radicals and pendant vinyl groups generate branched polymers, which have a higher probability to react with each other than the linear primary chains because the branched polymers contain more pendant vinyl groups and/or chain-end active centers. Therefore, branched polymers grow from smaller molecules to larger molecules and finally form a polymer network when the number of reacted pendant vinyl groups per primary chain reaches a critical value (Scheme 1).[24] The transition point (moment) from sols to gels is defined as the "gel point".[33]

To determine the gel points based on the conversions of monomer and/or cross-linker, the Predici simulation does not consider the intramolecular cyclization reaction, although it inevitably occurs in all experiments. The extent of intramolecular cyclization compared to intermolecular cross-linking reaction depends on the concentration of reagents in the system, as well as the chemical structures of cross-linkers and monomers. In order to study the effect of these parameters on the experimental gel points, three types of acrylate monomers and five types of diacrylate cross-linkers were employed for syntheses of series of poly(M-*co*-X) cross-linked copolymers at various concentrations and molar ratios of reagents (Scheme 1). The experimental gel points based on the conversions of monomer and/or cross-linker were obtained in each reaction and compared with each other systematically.

Effect of Concentrations on Experimental Gel Points. As discussed above, the intramolecular cyclization reactions consume pendant vinyl groups but have no contribution to the increase of molecular weights of branched polymers. Since polymer solution under diluted conditions is more inhomoge-

Scheme 1. Synthesis of Poly(M-*co*-X) Network by ATRcP of Acrylate Monomer and Diacrylate Cross-Linker



neous, it is expected that the enhanced intramolecular cyclization reactions under diluted conditions delays or even prevents the occurrence of experimental gelation.[35,36] For example, the Predici simulation of ATRcP of MA and EGDA with $[\mathrm{MA}]_0/[\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0 = 50/5/1$ indicates that the molar ratio of reacted pendant vinyl groups to primary chains exceeded unity at $\mathrm{conv}_{\mathrm{MA,gel,simu}} = 43\%$ (S-5.0, Table 1).[24] As a comparison to the simulation, two ATRcP reactions by using the same molar ratios of reagents but different MA concentrations were performed, and their GPC results are shown in Figure 1. In both reactions, broad elution peaks in the high-molecular-weight region were detected, whose molecular weights increased with the MA conversions, indicating the formation of branched polymers. Since the molecular weights of branched polymers in the system with $[\mathrm{MA}]_0 = 6.0$ M increased much faster than those in the more diluted reaction ($[\mathrm{MA}]_0 = 1.0$ M), gelation occurred in the former system at 60 min with $\mathrm{conv}_{\mathrm{MA,gel,expt}} = 48\%$ ($\mathrm{MA}_{6.0}\mathrm{EG}_{5.0}$, Table 1), which was slightly higher than the simulated gelation point (43%). In contrast, no gelation occurred in the system with $[\mathrm{MA}]_0 = 1.0$ M even after 70 h when the conversion of MA reached 94% ($\mathrm{MA}_{1.0}\mathrm{EG}_{5.0}$, Table 1). Such a result suggests that when a system is diluted enough, the enhanced intramolecular cyclization consumed so many pendant vinyl groups that no gelation occurred in the system.

Table 1. Summary of Poly(MA-*co*-EGDA) Gels by Using Different MA Concentrations[a]

entry[b]	$[\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0$	$[\mathrm{MA}]_0$ (mol/L)	$\mathrm{conv}_{\mathrm{MA,gel}}$[c]	$\mathrm{conv}_{\mathrm{EGDA,gel}}$[c]
S-1.1	1.1		0.95	1.00
$\mathrm{MA}_{8.5}\mathrm{EG}_{1.1}$	1.1	8.5	~1	~1
$\mathrm{MA}_{6.0}\mathrm{EG}_{1.1}$	1.1	6.0	0.97	~1
$\mathrm{MA}_{2.5}\mathrm{EG}_{1.1}$	1.1	2.5	no gelation	
$\mathrm{MA}_{1.0}\mathrm{EG}_{1.1}$	1.1	1.0	no gelation	
S-1.5	1.5		0.81	0.96
$\mathrm{MA}_{8.5}\mathrm{EG}_{1.5}$	1.5	8.5	0.78	~1
$\mathrm{MA}_{6.0}\mathrm{EG}_{1.5}$	1.5	6.0	0.86	~1
$\mathrm{MA}_{2.5}\mathrm{EG}_{1.5}$	1.5	2.5	no gelation	
$\mathrm{MA}_{1.0}\mathrm{EG}_{1.5}$	1.5	1.0	no gelation	
S-3.0	3.0		0.57	0.81
$\mathrm{MA}_{8.5}\mathrm{EG}_{3.0}$	3.0	8.5	0.61	0.81
$\mathrm{MA}_{6.0}\mathrm{EG}_{3.0}$	3.0	6.0	0.65	0.90
$\mathrm{MA}_{2.5}\mathrm{EG}_{3.0}$	3.0	2.5	0.84	~1
$\mathrm{MA}_{1.0}\mathrm{EG}_{3.0}$	3.0	1.0	no gelation	
S-5.0	5.0		0.43	0.67
$\mathrm{MA}_{8.5}\mathrm{EG}_{5.0}$	5.0	8.5	0.42	0.66
$\mathrm{MA}_{6.0}\mathrm{EG}_{5.0}$	5.0	6.0	0.48	0.76
$\mathrm{MA}_{2.5}\mathrm{EG}_{5.0}$	5.0	2.5	0.71	0.95
$\mathrm{MA}_{1.0}\mathrm{EG}_{5.0}$	5.0	1.0	no gelation	
S-10.0	10.0		0.28	0.49
$\mathrm{MA}_{7.2}\mathrm{EG}_{10.0}$[d]	10.0	7.2	0.32	0.43
$\mathrm{MA}_{6.0}\mathrm{EG}_{10.0}$	10.0	6.0	0.38	0.60
$\mathrm{MA}_{2.5}\mathrm{EG}_{10.0}$	10.0	2.5	0.48	0.76
$\mathrm{MA}_{1.0}\mathrm{EG}_{10.0}$	10.0	1.0	0.81	~1

[a] Experimental conditions: $[\mathrm{MA}]_0/[\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{PMDETA}]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C. Linear polyMMA standards were used for THF GPC calibration. [b] The code "S-*X*" represents the result from Predici simulation[24] with $X = [\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0$, in which the simulated gelation occurred when the average number of reacted pendant vinyl groups to primary chains (number of cross-linkage per chain) exceeded unity. The code "$\mathrm{MA}_\alpha\mathrm{EG}_\beta$" represents an experimental ATRcP with $\alpha = [\mathrm{MA}]_0$ and $\beta = [\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0$. [c] Conversions of MA and EGDA immediately before gelation. The experimental gel point was the moment when the reaction fluid lost its mobility at an upside-down position for 10 s. [d] The concentration of MA was $[\mathrm{MA}]_0 = 7.2$ M due to the dilution of a large amount of EGDA.[37]

In order to systematically study the effect of concentration on experimental gel points, the ATRcP of MA and EGDA with various MA concentrations and molar ratios of $X = [\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0$ were performed (Table 1). When $[\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0 = 1.1$ or 1.5, only systems with $[\mathrm{MA}]_0 = 8.5$ and 6.0 M formed gels, while the copolymerization with $[\mathrm{MA}]_0 = 2.5$ and 1.0 M only formed branched polymers before the MA conversion stopped growing, which was ascribed to the enhanced intramolecular cyclization reactions under diluted conditions. When a higher molar ratio of EGDA to EBrP was used, e.g., $[\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0 = 10.0$, the copolymerization reactions with $[\mathrm{MA}]_0 = 1.0$ and 2.5 M formed gels at 81 and 48% MA conversions, respectively ($\mathrm{MA}_{1.0}\mathrm{EG}_{10.0}$ and $\mathrm{MA}_{2.5}\mathrm{EG}_{10.0}$, Table 1), which were higher than the experimental gel points at concentrated conditions ($\mathrm{conv}_{\mathrm{MA,gel,expt}} = 32\%$ for $[\mathrm{MA}]_0 = 7.2$ M and $\mathrm{conv}_{\mathrm{MA,gel,expt}} = 38\%$ for $[\mathrm{MA}]_0 = 6.0$ M) and the simulated value ($\mathrm{conv}_{\mathrm{MA,gel,simu}} = 28\%$). All of these results proved that dilution enhanced the intramolecular cyclization reactions, which significantly varied the experimental gel points, and even prevented the occurrence of gelation in some ATRcP experiments. When the copolymerizations of MA and EGDA with various molar ratios of $X = [\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0$ were performed at a higher concentration, such as $[\mathrm{MA}]_0 = 8.5$ M,[37] the experimental gel points based on MA conversion were in good

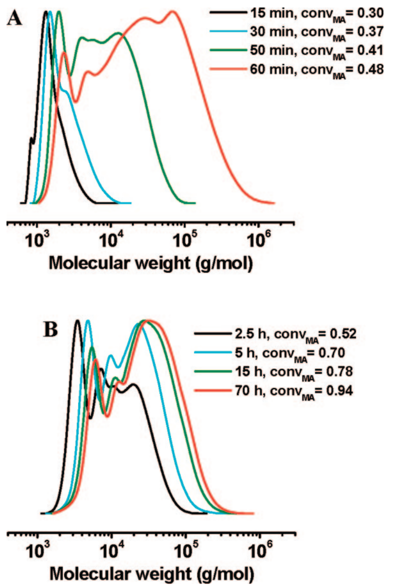


Figure 1. GPC curves of the sols during synthesis of poly(MA-*co*-EGDA) cross-linked copolymers under different MA concentrations: (A) $[MA]_0 = 6.0$ M ($MA_{6.0}EG_{5.0}$ in Table 1) and (B) $[MA]_0 = 1.0$ M ($MA_{1.0}EG_{5.0}$ in Table 1). Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/5/1/0.45/0.05/0.5$, in DMF at 60 °C. Linear polyMMA standards were used for THF GPC calibration.

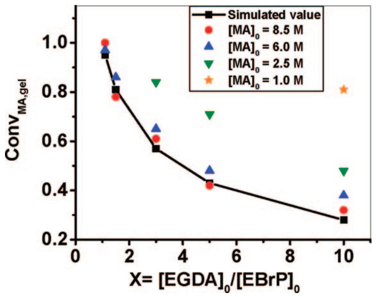


Figure 2. Comparison of simulated gel points and experimental gel points at different concentrations and molar ratios of $X = [EGDA]_0/[EBrP]_0$ by ATRcP of MA and EGDA.

agreement with the simulated values, indicating an insignificant effect of the cyclization side reactions (Figure 2).

Effect of Cross-Linker Structures on Experimental Gel Points. Besides the concentration effect on the variation of experimental gel points, the influence of cross-linker structures, i.e., the structures of the spacers between two acrylate groups, on the experimental gel points were also studied. Five types of diacrylate cross-linkers with different alkoxylated spacers (Scheme 1) were used for copolymerization with constant MA concentration ($[MA]_0 = 6.0$ M) at two molar ratios of cross-linker to initiator ($X = [X]_0/[EBrP]_0 = 3.0$ or 1.5). The results in Table 2 indicate that, by simply changing the spacer in the cross-linker from C_2H_4 (EGDA) to C_4H_8 (BDDA), C_6H_{12} (HDDA), and (C_6H_{12} + $(CH_2CH_2O)_2$) (HEDA, the averaged DP of the CH_2CH_2O unit is ca. 2 determined by ^1H NMR measurement), the experimental gel points based on the conversion of MA were similar in each series. When a diacrylate cross-linker with a longer and more rigid spacer (BEDA, $M_n \sim 468$ g/mol) was used, the conversions of MA at gelation were only slightly higher ($conv_{MA,gel} = 75$ and 90% for $[BEDA]_0/[EBrP]_0 = 3.0$ and 1.5, respectively) than the values obtained by using the other four cross-linkers (Table 2). In other words, the structural difference among all investigated diacrylate cross-linkers had no significant effect on the intramolecular cyclization of pendant vinyl groups and the experimental gel points during ATRcP with MA monomer.

Table 2. **Summary of Poly(MA-*co*-X) Gels by Using Different Diacrylate Cross-Linkers**[a]

entry[b]	X	$[X]_0/[EBrP]_0$	$conv_{MA}$ at gel point[c]
$MA_{6.0}EG_{3.0}$	EGDA	3.0	0.65
$MA_{6.0}BD_{3.0}$	BDDA	3.0	0.67
$MA_{6.0}HD_{3.0}$	HDDA	3.0	0.70
$MA_{6.0}HE_{3.0}$	HEDA	3.0	0.68
$MA_{6.0}BE_{3.0}$	BEDA	3.0	0.75
$MA_{6.0}EG_{1.5}$	EGDA	1.5	0.86
$MA_{6.0}BD_{1.5}$	BDDA	1.5	0.85
$MA_{6.0}HD_{1.5}$	HDDA	1.5	0.82
$MA_{6.0}HE_{1.5}$	HEDA	1.5	0.86
$MA_{6.0}BE_{1.5}$	BEDA	1.5	0.90

[a] Experimental conditions: $[MA]_0/[X]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, $[MA]_0 = 6.0$ M, in DMF at 60 °C. [b] The code "$MA_\alpha X_\beta$" represents a copolymerization with $\alpha = [MA]_0$ and $\beta = [X]_0/[EBrP]_0$. [c] Conversions of MA immediately before gelation. The experimental gel point was the moment when the reaction fluid lost its mobility at an upside-down position for 10 s.

Recently, Armes et al. used the reversible addition fragmentation chain transfer (RAFT)[38,39] polymerization technique to copolymerize 2-hydroxyisopropyl acrylate (HPA) and diacrylate cross-linkers.[23] They found that during the RAFT synthesis of branched copolymers, one primary chain could contain more than one cross-linkage before macroscopic gelation occurred. By using three kinds of diacrylate cross-linkers with different structures to study the critical amount of cross-linker on gelation, they concluded that the bulkier and less flexible cross-linker, BEDA, was less likely to undergo intramolecular cyclization than shorter and more flexible EGDA. Therefore, by using BEDA as a cross-linker for RAFT copolymerization with HPA ($[HPA]_0 \sim 2.8$ M),[23] they found that gelation occurred when $[BEDA]_0/[CTA]_0 \geq 1.35$. In contrast, when EGDA was used as a cross-linker under the same concentration of HPA, no gelation was observed, even at quantitative conversion, until $[EGDA]_0/[CTA]_0 \geq 2.25$.

The discrepancy between results from ATRP and RAFT is plausibly due to the fundamental difference in the initiation/activation mechanism between the ATRP and RAFT techniques.[20,23,40] Furthermore, the initial concentration of HPA in the paper reported by Armes' group was $[HPA]_0 \sim 2.8$ M,[23] lower than the concentration of MA used in the present study ($[MA]_0 = 6.0$ M, Table 2). Therefore, it is reasonable to expect that there were more intramolecular cyclization reactions in their systems, which consumed pendant vinyl groups and delayed the experimental gelation.

When different diacrylate cross-linkers were used for ATRcP with MA, another concern is the structural difference of the obtained gels and/or branched copolymers. Since gel cannot be analyzed by GPC, the branched polymers withdrawn from each reaction shortly before gelation were characterized by GPC with a MALLS detector to determine their structural compactness. Figure 3 shows the plots of weight-average molecular weight ($M_{w,MALLS}$, determined by GPC with MALLS detector) as a function of elution volume for the branched copolymers by using different cross-linkers. All branched polymers were synthesized by ATRcP of MA with different cross-linkers under the conditions of $[MA]_0/[X]_0/[EBrP]_0 = 50/1.5/1$ and $[MA]_0 = 6.0$ M (Table 2). The results indicate that the branched copolymers had similar structural compactness, because at a given value of molecular weight, the elution volumes of different branched copolymers were similar. Since the branched polymers were withdrawn shortly before gelation, their structural compactness represented the thereafter-formed gels. Such a result indicates that when $X = [X]_0/[EBrP]_0 = 1.5$, the difference of spacer

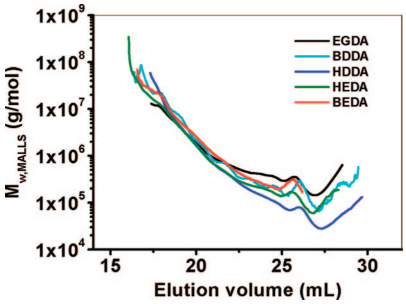


Figure 3. Absolute molecular weights ($M_{w,MALLS}$) as a function of elution volumes for various poly(MA-*co*-X) branched copolymers withdrawn from reaction shortly before gelation by using five types of different cross-linkers. Experimental conditions: $[MA]_0/[X]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1.5/1/0.45/0.05/0.5$, $[MA]_0 = 6.0$ M, in DMF at 60 °C.

Table 3. Summary of Poly(M-*co*-EGDA) Gels by Using Different Acrylate Monomers[a]

entry[b]	M	$[M]_0$ (mol/L)	$[EGDA]_0/[EBrP]_0$	gelation time[c] (h)	conv$_M$ at gel point[d]
$MA_{6.0}EG_{5.0}$	MA	6.0	5.0	1.0	0.48
$BA_{6.0}EG_{5.0}$	BA	6.0	5.0	1.6	0.47
$MA_{2.5}EG_{5.0}$	MA	2.5	5.0	2.0	0.71
$BA_{2.5}EG_{5.0}$	BA	2.5	5.0	3.2	0.67
$EHA_{2.5}EG_{5.0}$	EHA	2.5	5.0	4.0	0.67
$MA_{2.5}EG_{10.0}$	MA	2.5	10.0	1.2	0.48
$BA_{2.5}EG_{10.0}$	BA	2.5	10.0	1.9	0.49
$EHA_{2.5}EG_{10.0}$	EHA	2.5	10.0	2.7	0.53

[a] Experimental conditions: $[M]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C. [b] The code "$M_\alpha EG_\beta$" represents a copolymerization with $\alpha = [M]_0$ and $\beta = [EGDA]_0/[EBrP]_0$. [c] Gelation time was the moment when the reaction fluid lost its mobility at an upside-down position for 10 s. Although the systematic errors, such as the purity of reagents and deoxygenation procedures, could affect the experimental gelation times, they were comparable to each other within parallel reactions performed under similar conditions. [d] Conversions of M immediately before gelation.

structures in the diacrylate cross-linkers had no significant effect on the gel structural compactness.

Effect of Acrylate Monomer Structures on Experimental Gel Points. The effect of structure of acrylate monomers was also studied as a potential parameter that could affect the experimental gel points. Three types of acrylates with different structures of alkyl ester groups, MA, BA, and EHA, were used for ATRcP with EGDA to demonstrate the influence of monomer structures on the experimental gelation behaviors. It is worth noting that, by using DMF as the solvent and CuBr/PMDETA as the catalyst (10 mol % $CuBr_2$ of total copper species was preadded in each reaction), variation of acrylate monomer species during copolymerization changes the solubility of catalyst in the mixed solvent, which could affect the apparent polymerization rate and dynamics of exchange in different ATRcP reactions. It was found that, for parallel ATRcP reactions with the same monomer concentration, molar ratio of reagents, and reaction temperature, the apparent polymerization rates decreased from MA to BA to EHA during their copolymerizations with EGDA, which is plausibly due to the decreased solubility of CuBr/PMDETA activator complex in the solvent mixture.[41] Although the different polymerization rates affected the experimental gelation time in each reaction (Table 3), they had no effect on the experimental gel points based on monomer conversion, because the latter one is more sensitive to concentrations and the molar ratios of $[M]_0/[EGDA]_0/[EBrP]_0$.

The results in Table 3 indicate that when the monomer concentration and the molar ratio of $X = [EGDA]_0/[EBrP]_0$ were constant, the variation of monomer species did not affect the monomer conversions at gelation in different reactions. For example, when $X = [EGDA]_0/[EBrP]_0 = 5.0$ and $[M]_0 = 6.0$ M, the conversions of MA and BA at gelation were around 48 and 47%, respectively ($MA_{6.0}EG_{5.0}$ and $BA_{6.0}EG_{5.0}$). Since the bulk concentration of EHA (4.8 M) was lower than 6.0 M, the ATRcP reactions for comparing the effects of the three monomers on the experimental gel points were performed at a lower concentration, e.g., $[M]_0 = 2.5$ M. Under this concentration, two series of copolymerizations with $X = [EGDA]_0/[EBrP]_0 = 5.0$ and 10.0 were carried out by using different acrylate monomers. Although their gelation times were different, the conversions of different monomers at experimental gel points were quite similar in each series. Thus, during ATRcP with EGDA, the structures of acrylate monomers, either MA with a smaller ester group or EHA with a more bulky ester group, had no significant effect on the intramolecular cyclization of pendant vinyl groups and the experimental gel points.

Conclusions

Series of cross-linked copolymers were synthesized by atom transfer radical copolymerization (ATRcP) of acrylate monomers and diacrylate cross-linkers. The experimental gel points based on the monomer and/or cross-linker conversions were significantly affected by the extent of intramolecular cyclization reactions compared to intermolecular cross-linking reactions in the experiments. The effects of three experimental parameters on the variation of experimental gel points were systematically studied during the ATRcP reactions, including the monomer concentration, the structure of cross-linkers, and the structure of monomers. With fixed molar ratios of reagents, decreasing the monomer concentration significantly increased the inhomogeneity of the polymer solution and enhanced the intramolecular cyclization reactions, which delayed and even prevented the experimental gelation. Three types of acrylate monomers with different alkyl ester chains (MA, BA, and EHA) and five types of diacrylate cross-linkers with various spacers between the two acrylate groups were employed to study the effect of structures of cross-linkers and monomers on the experimental gel points. The results indicate that the extent of intramolecular cyclization was not dramatically affected by the structures of both monomers and cross-linkers within the investigation. These results provided a guideline for further exploration of the gelation process during ATRcP reactions with different monomer and cross-linker species.

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(37) Note: When $X = [\mathrm{EGDA}]_0/[\mathrm{EBrP}]_0 = 10.0$, the bulk concentration of MA is 7.8 M (lower than 8.5 M). Since a certain amount of DMF was needed as the internal standard for GC measurements of MA and EGDA conversions, a reduced concentration of $[\mathrm{MA}]_0 = 7.2$ M was used for the reaction $\mathrm{MA}_{7.2}\mathrm{EG}_{10.0}$.
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(40) Note: During RAFT copolymerization of monomer and divinyl cross-linker, an additional thermal initiator, such as AIBN, is added to generate radicals. The AIBN introduces an additional amount of primary chains into the system. In contrast, there is no thermal initiator in the ATRP system and all initiators quickly generate polymer chains. Moreover, the exchange process between active and dormant chains proceeds in different ways, and involves reaction between two polymer chains in RAFT, in contrast to the reaction with low molar mass species, e.g., activator and deactivator, in ATRP.
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