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Determination of Gel Point during Atom Transfer Radical Copolymerization with Cross-Linker

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ABSTRACT: Atom transfer radical polymerization (ATRP) of methyl acrylate (MA) and ethylene glycol diacrylate (EGDA) provided a series of poly(MA-*co*-EGDA) branched and cross-linked copolymers using various initial molar ratios of cross-linker to initiator. In agreement with the Flory−Stockmayer theory, the gelation occurred when the concentration of reacted pendant vinyl groups was larger than that of primary chains. This critical point depends on the initiation efficiency and the reactivity of vinyl groups in both cross-linker and monomer. The experimental gelation point occurred when both the molecular weight and the weight fraction of branched polymers among the total sols (f_{branch}) reached the maximum, as determined by GPC measurement of the sols at different conversions. The kinetic study based on experimental results and Predici simulation demonstrated that all acrylate groups had a similar reactivity. In all reactions, the gel points theoretically predicted by Predici simulation, based on the conversions of MA and EGDA ($\mathrm{conv}_{\mathrm{MA,gel}}$ and $\mathrm{conv}_{\mathrm{EGDA,gel}}$), were only slightly lower than the experimental results. These results indicate that the gels synthesized by ATRP have a more homogeneous structure and contain a smaller amount of cyclization products in contrast to gels synthesized by conventional free radical polymerization.

Introduction

Radical copolymerization of monovinyl monomers with a small amount of divinyl cross-linkers has been widely used for synthesis of branched polymers and cross-linked gels. The branching points are generated in the polymer chains via reaction of pendant vinyl groups with the propagating radicals either intermolecularly or intramolecularly. With the progressing of intermolecular reactions, the molecular weight and/or size of the branched polymers increases exponentially and finally reaches an "infinite" value with the formation of insoluble gel. The transition from sols to gels is defined as the "gel point".[1]

On the basis of Flory−Stockmayer's mean-field theory,[2−6] the critical gel point during the copolymerization of monovinyl monomer and divinyl cross-linker is reached when the number of cross-linking units (defined as cross-linkers with both vinyl groups reacted) per primary chain equals unity. In this treatment all vinyl groups are assumed to have the same reactivity, and no intramolecular cyclization reactions are considered. It is important to note that the gel point during the copolymerization is not determined by the ratio of reacted cross-linker to primary chain but by the ratio of the reacted pendant vinyl group to primary chain. The consumption of free cross-linker only introduces potential branching point (pendant vinyl group) into the polymer chains. Only when the cumulative amount of reacted pendant vinyl groups exceeds the number of primary chains can gelation occur. When the targeted product is a soluble branched polymer (sol) instead of a cross-linked gel, the copolymerization should be properly tailored so that the number of cross-linking units per primary chain is less than 1.

Conventional free radical polymerization (FRP) method has been extensively used for copolymerization of monovinyl monomers and divinyl cross-linkers. Although the FRP method has many advantages over other polymerization mechanisms, including mild experimental conditions and various applicable monomer species, the sols and gels synthesized by FRP have little control over structures. By using FRP, highly branched polymers, including gels, are formed at a very early stage of polymerization (low monomer conversions), and the polymerization behavior largely deviates from the prediction by Flory−Stockmayer theory.[7−9] The heterogeneous structure of polymer network synthesized by FRP[10,11] is mainly ascribed to several inherent features of FRP, including slow initiation, fast chain propagation, and termination reactions. The slow initiation and unavoidable termination reactions result in the number of "dead" polymer chains increasing with time. At the early stage the polymer chains in the system are very diluted. The fast chain propagation produces polymer chains with high molecular weight and numerous pendant vinyl groups per chain within seconds. As discussed above, pendant vinyl groups can react with radicals and produce branching points by either intermolecular or intramolecular reactions. Significant intramolecular cyclization is observed at the beginning of FRP process, which is due to two reasons: high dilution of polymer chains[12] and their relatively slow diffusion compared to the fast chain propagation.[13] The former factor decreases the possibility of chain overlapping, and the latter factor increases the concentration of pendant vinyl groups at the radical vicinity. Therefore, highly cross-linked nanodomains are formed at low polymer concentration, which further react with each other by intermolecular reaction and form a heterogeneous polymer network. In order to prevent the gelation and produce soluble polymers, a large amount of chain transfer agent (comparable to that of cross-linker) is purposely added into the reaction system to decrease the number of cross-linking unit per primary chain below unity.[14−16] Soluble branched polymers were also synthesized by using a large amount of initiator, in which the gelation was avoided due to the chain transfer reaction to initiator and primary radical termination.[17]

In contrast to FRP, recently developed controlled radical polymerization (CRP)[18−20] techniques are based on fast activation/deactivation equilibrium. Because of the fast initiation reactions, relative to bimolecular termination, all polymer chains

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are initiated at approximately the same time, and the number of primary growing chains is nearly constant throughout the polymerization. The dynamic equilibrium is established between a low concentration of active propagating chains and a large number of "dormant" chains, which are unable to propagate or terminate but can be reactivated. The fast deactivation reactions between active radicals and deactivators ensure 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 that the reaction possibility of each vinyl species (from monomer, cross-linker, and pendant vinyl group) is statistically determined by their concentrations. Thus, at low monomer conversions, the possibility of the reaction of pendant vinyl groups is lower than that of free monomers and cross-linkers due to the concentration effect. On the basis of the assumption that all vinyl species have a similar reactivity, highly branched polymers are only formed when the concentration of pendant vinyl groups becomes considerable. With the increase of cross-linker conversions, the pendant vinyl groups and the branching points are introduced randomly throughout the polymer chains. Therefore, the sols or gels synthesized by CRP methods have a more homogeneous distribution of branching points than the polymers synthesized by FRP methods. The critical gel point in CRP processes agrees much better with the Flory−Stockmayer prediction than the FRP processes.[12]

Several research groups have reported the synthesis of branched polymers and/or gels by using CRP methods to copolymerize monomers and cross-linkers.[12,21−28] For example, Sherrington[23,29] and Armes[25,28] et al. used the atom transfer radical polymerization (ATRP)[30−32] method for synthesis of branched polymers by copolymerization of methacrylate monomer and dimethacrylate cross-linker. They concluded that highly branched polymers only occurred at high monomer conversions, and it is essential to keep the molar ratio of cross-linker to initiator less than 1 in order to obtain branched sols instead of gels. Zhu et al. also studied the homopolymerization[33] of ethylene glycol dimethacrylate (EGDMA) and copolymerization[13,34] of methyl methacrylate (MMA) and dimethacrylate cross-linker using bulk ATRP. They found that most of the pendant vinyl groups were consumed, and the cross-link density of the final gel network was close to the maximum values achievable for the added cross-linker amounts. These results suggested that the occurrence of gelation (gel point) in ATRP was determined by the initial molar ratio of cross-linker to initiator. When the concentration of initially added cross-linker was larger than that of initiator, insoluble gels were produced at high monomer conversions. By using other CRP techniques, including nitroxide-mediated polymerization (NMP)[35] and reversible addition fragmentation chain transfer (RAFT) polymerization,[36] various branched polymers and polymer networks were prepared.[12,21,26,27,37] These studies indicate that the gels synthesized by CRP methods have preserved chain-end functionalities[27] and a more homogeneous structure[12,26] than gels formed in FRP processes.

Although significant progress has been achieved on understanding the gelation behavior by applying CRP techniques to copolymerization of monovinyl monomers and divinyl cross-linkers, the kinetics of copolymerization and especially the consumption of pendant vinyl groups during the gel formation have not been studied in detail. It is worth noting that although the initial molar ratio of cross-linker to initiator is crucial for gelation, the gel point is actually determined by the reaction of pendant vinyl groups instead of free cross-linker itself.

Herein, we report the comparison of theoretical gel points with those determined experimentally during the copolymerization of methyl acrylate (MA) and ethylene glycol diacrylate (EGDA) under various ATRP conditions. The vinyl groups in both monomer and cross-linker have the same structure. Homopolymerization of MA produced well-controlled linear polymers with high initiation efficiency (IE). Copolymerization of MA and EGDA under similar conditions produced poly(MA-*co*-EGDA) gels when the EGDA amount was high enough. The gel points and the reactivity of pendant vinyl groups in series of reactions with variable molar ratios of cross-linker to initiator determined experimentally were in good agreement with the theoretical predictions based on Predici simulation.

Experimental Section

Materials. Methyl acrylate (MA, 99%), ethylene glycol diacrylate (EGDA, 90%), methyl methacrylate (MMA, 99%), and ethylene glycol dimethacrylate (EGDMA, 98%) 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.[38] All other reagents—ethyl 2-bromopropionate (EBrP), ethyl 2-bromoisobutyrate (EBiB), 2-bromopropionitrile (BPN), 2,2′-bipyridyl (bpy), *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA), $CuBr_2$, and solvents—were purchased from Aldrich with the highest purity and used as received without further purification.

Kinetic Study of Homopolymerization of MA by ATRP. A typical procedure is briefly described, starting with the ratio of reagents $[MA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1/0.45/0.05/0.5$. A clean and dry Schlenk flask was charged with MA (3.5 mL, 0.039 mol), PMDETA (81.2 μL, 0.39 mmol), and *N*,*N*-dimethylformamide (DMF, 3.0 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, then evacuated, and backfilled 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 side arm of the Schlenk flask. At timed intervals, samples were withdrawn via a syringe for measurements of monomer conversions and polymer molecular weights by GC and GPC, respectively. The reaction was stopped after 2.5 h via exposure to air and dilution with THF.

Synthesis of Poly(MA-*co*-EGDA) Gel by Copolymerization of MA and EGDA Using ATRP. The experimental procedures for synthesis of cross-linked copolymers were very similar to those of polyMA linear polymers, except various amounts of EGDA cross-linker were added initially. The reaction was conducted at 60 °C, and samples were withdrawn periodically for GC and GPC measurements of monomer conversions and polymer 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 until 150 h before stopping the reaction via exposure to air.

Determination of Gel Fraction and Gel Swelling Property in THF. A piece of gelled product with known weight was taken from the Schlenk flask and immersed in THF, in which the weight of polymer $w_{polymer}$ (including sol and gel) was determined on the basis of known conversions of MA and EGDA and the initial weight ratio of monomer to solvent. The sol was removed from gel by repeated THF extraction and filtration, and the sol-containing THF solution was replaced by fresh THF every 4 days for five cycles. The THF solution was analyzed by GPC to qualitatively determine the sol existence. After five cycles, the sol in THF became undetectable, indicating the complete removal of sol from gel. The fully THF-swollen gel was weighted before complete evaporation of the THF under vacuum. The gel fraction was determined as r_{gel}

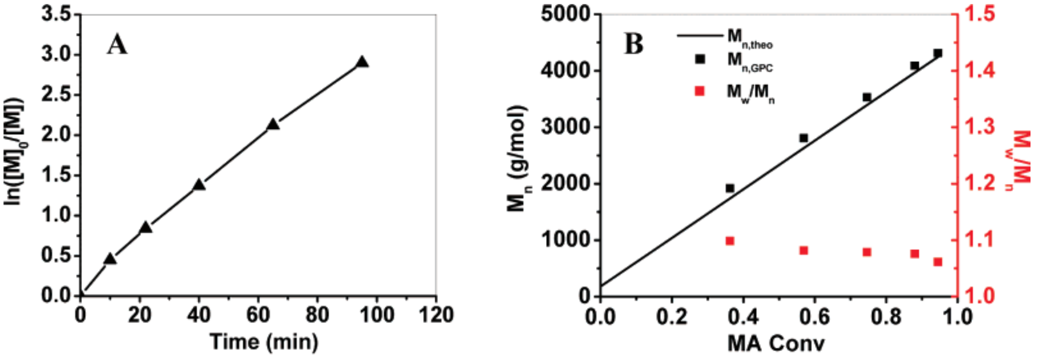


Figure 1. (A) Dependence of $\ln([M]_0/[M])$ on reaction time and (B) molecular weights and molecular weight distributions during synthesis of polyMA-Br linear polymers by ATRP. Experimental conditions: $[MA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1/0.45/0.05/0.5$, $[MA]_0 = 5.98$ M, in DMF at 60 °C; linear polyMMA standards for THF GPC calibration.

$= w_{gel}/w_{polymer}$, in which w_{gel} is the weight of dried poly(MA-*co*-EGDA) gel and the gel-swelling ratio (GSR) in THF is defined as the weight ratio of fully THF-swollen gel to dried gel.

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 internal standard for calculation of monomer conversions. After filtration through 220 nm PTFE filter, the polymer samples were measured by 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 differential refractive index (RI) detector (Waters, 2410). Toluene was used as the internal standard to correct the fluctuation of the THF flow rate. The apparent molecular weights and polydispersity were determined with a calibration based on linear polyMMA standards using WinGPC 6.0 software from PSS. ^{1}H NMR spectra of the polymer solutions in $CDCl_3$ were collected on Bruker Avance 300 MHz spectrometer at 27 °C.

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.[39,40] It employs an adaptive Rothe method as a numerical strategy for time discretization. The concentrations of all species can be followed with time. During simulation, the copolymerization of MA and EGDA was simplified as a terpolymerization reaction, in which M_1 was MA, M_2 was EGDA, and the third monomer was the pendant vinyl group M_{2P}, which was generated stoichiometrically when a EGDA cross-linker reacted with a propagating radical (eq 1).

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

Results and Discussion

Initiation Efficiency during Homopolymerization of Monomers by ATRP. As discussed before, the theoretical gel point refers to the reaction extent when primary chain contains averaged one reacted cross-linking unit (equivalent to two branching points). Even if we assume the conversion of vinyl groups is 100%, the determining factor for gelation is not the molar ratio of cross-linker to initiator, but the molar ratio of reacted cross-linking unit to primary chains. In other words, only when the IE of the initiator is high enough is the moles of formed primary chains close to that of the added initiator. In a system with low IE, polymer network can form even when the molar ratio of the added cross-linker to initiator is less than 1 because the amount of reacted cross-linking unit is larger than the amount of produced primary chains. For example, when polyMMA with a targeted degree of polymerization ($DP_{target} = [MMA]_0/[EBiB]_0$) equal to 50 was prepared via ATRP using ethyl 2-bromoisobutyrate (EBiB) as initiator, the reaction proceeded with a slow initiation, and the IE of EBiB was only 65%, as confirmed by the GPC molecular weight of polyMMA chains at 80% conversion being 1.5 times higher than the theoretical value (Figure S1 in the Supporting Information). This is due to lower reactivity of EBiB than polyMMA-Br.[41] Therefore, under similar conditions a gel was formed during the copolymerization of MMA and EGDMA when the molar ratio of $[EGDMA]_0/[EBiB]_0$ was only 0.8 because at high conversions of pendant vinyl groups the ratio of reacted cross-linking unit to primary chain was higher than 1 (= 0.8/0.65). However, when the copolymerization was initiated rapidly (by selecting BPN as an efficient initiator)[42] resulting in high IE, the number of primary chains was close to that of initiator throughout the polymerization. Thus, no gel was formed when the amount of MMA/EGDMA/BPN = 50/1/1 even at complete conversion. More detailed studies on the effect of IE on gelation are currently underway.

Figure 1 shows the results of synthesis of polyMA-Br linear chains with the initial ratios of reagents as $[MA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1/0.45/0.05/0.5$ ($[MA]_0 =$ 5.98 M and DMF as solvent). The essentially linear first-order kinetic plot (Figure 1A) indicates a constant concentration of radicals. GPC analyses of the linear polymer chains showed a symmetric, unimodal molecular weight distribution. The number-average molecular weights ($M_{n,GPC}$), based on linear polyMMA standards, increased linearly with MA conversions and overlapped with the theoretical values (Figure 1B), suggesting fast initiation and high IE of EBrP during the polymerization process. Therefore, these experimental conditions were employed for all subsequent copolymerizations of MA and EGDA to synthesize polymer networks and to determine the critical gel points.

Gelation during Copolymerization of MA and EGDA by ATRP. During copolymerization, all initiators, e.g., alkyl halide in ATRP, are consumed quickly and converted into short polymer chains containing pendant vinyl groups and halogen chain-end functionality (Scheme 1). As discussed above, the fast activation/deactivation equilibrium between a low concentration of active propagating chains and a large number of "dormant" chains provides each chain a sufficiently long "dormant" period for diffusion and relaxation and, additionally, suppresses the irreversible termination. At any time, the propagating chain ends can react with monovinyl monomers and cross-linkers but also can react with the pendant vinyl groups in polymer chains and form branched polymers. The branched polymers formed by intermolecular reactions represent a higher generation of polymer molecules with enhanced possibility to react with each other rather than the linear primary

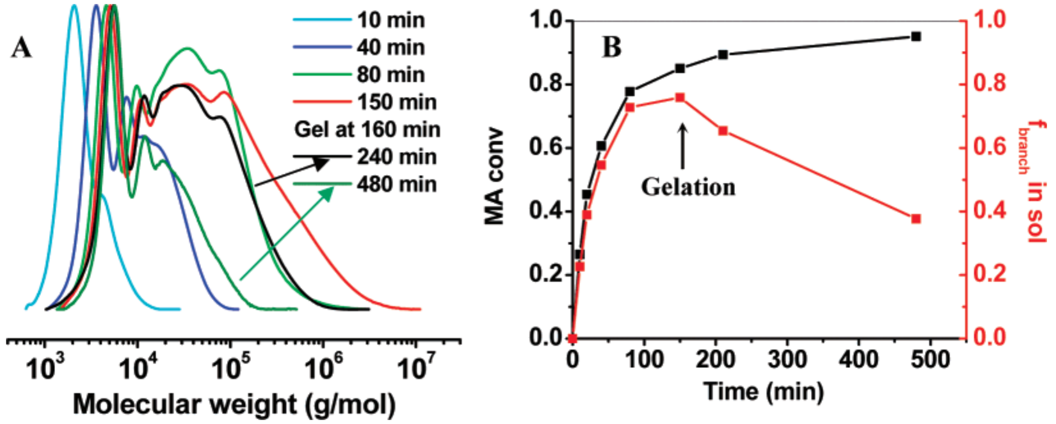
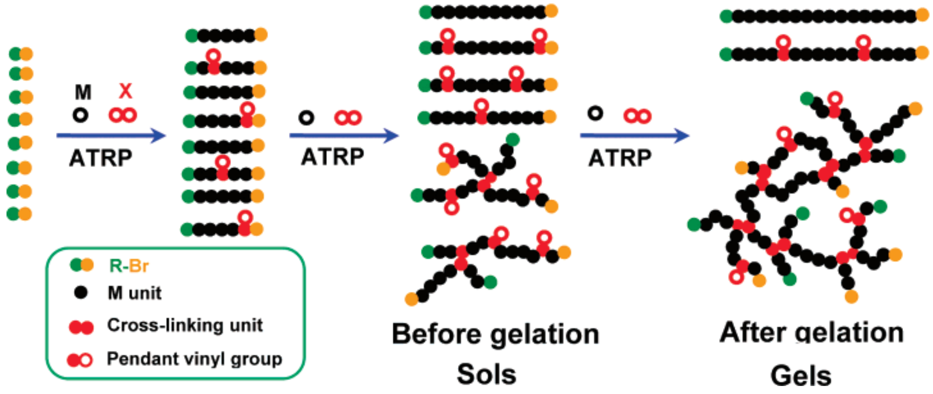


Figure 2. (A) Evolutions of GPC curves and (B) MA conversion and weight fraction of branched polymers among the total sols as a function of time during synthesis of poly(MA-*co*-EGDA) cross-linked polymers by copolymerization of MA and EGDA via ATRP. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1.5/1/0.45/0.05 /0.5$, $[MA]_0 = 5.98$ M, in DMF at 60 °C, linear polyMMA standards for THF GPC calibration.

Scheme 1. Illustration of Gel Formation Process by Copolymerization of Monomer (M) and Cross-Linker (X) Using ATRP Technique with Fast Initiation



chains because they contain more pendant vinyl groups and chain-end active centers than their linear counterparts.[43] Therefore, branched polymers grow from smaller, low-generation molecules to larger and high-generation molecules and finally form a polymer network when the number of reacted pendant vinyl groups per primary chain reaches a critical value (Scheme 1). Different from a recent publication by Billingham and Armes et al.,[28] who claimed that all linear chains disappeared at later branching stage; the gelation process in our investigation indicates that during the chain propagation and branching process linear primary chains always coexisted with branched polymers in the sols. Even after gelation, linear polymer chains were still detectable in the sols by GPC measurement, which will be discussed later in detail.

Figure 2A demonstrates the formation of branched polymers and the gelation process by GPC measurements of the sols at different times. During the copolymerization, branched polymers with high molecular weight and broad molecular weight distribution (MWD) formed with the increase of MA and EGDA conversions, as evidenced by the appearance of broad elution peaks in the higher molecular weight region. At the same time, a sharp lower molecular weight peak was observed, representing the linear primary chains in the system. Therefore, the GPC-measured sols included two species: linear polymers and branched polymers. The peak value molecular weight ($M_{p,GPC}$) of the linear polymers increased smoothly with reaction time, indicating the "livingness" of these linear primary chains. The weight fraction of branched polymers among the sols (f_{branch} in sol) also increased with the reaction time (determined by the multipeak splitting of the GPC curve using Gaussian function,[44] Figure 2B). For the copolymerization with initial molar ratio of $[EGDA]_0/[EBrP]_0 = 1.50$, gelation occurred at 160 min at conversion of MA ca. 86%, when the whole reaction mixture lost its mobility at an upside-down position for 10 s (GM-1.5, Table 1).[45,46] The signal of unreacted EGDA during GC analysis was undetectable, suggesting the conversion of EGDA at 160 min was essentially 100%.

After the gel point, the conversion of MA continued to increase with time, but the molecular weights and weight fractions of the branched polymers decreased (Figure 2B). The GPC-measured sol at 240 min had lower molecular weight and weight fraction of branched polymers (f_{branch}) than the sol at 160 min but higher than the sol at 480 min. As discussed above, branched polymers with more pendant vinyl groups and chain-end functionalities had higher possibility to react with each other than the smaller linear polymers. Thus, larger branched polymers were incorporated into the network first. Before gel point, all of the branched polymers were sols and showed increasing molecular weights and weight fractions with reaction time. After gel point, the largest branched polymers containing the largest amount of pendant vinyl groups and alkyl halide chain ends have been incorporated into the gel network, and only sols with smaller size were left and measured by GPC. Therefore, the molar fraction of branched polymers in the sols decreased (Figure 2B).[22,43] The higher possibility of branched polymers for intermolecular reactions, when compared to linear primary chains, also explained our observation that linear primary chains existed in the sols even after gel point because the linear chains containing less pendant vinyl groups and halogen chain-end functionalities had lower possibility for branching reactions.

Table 1. Synthesis of Poly(MA-*co*-EGDA) Cross-Linked Copolymers by Using Various Amounts of EGDA

			$conv_{MA}$ at gel point		$conv_{EGDA}$ at gel point				
entry[a]	X = $[EGDA]_0/[EBrP]_0$	gelation time (h)[b]	theor[c]	expt[d]	theor[c]	expt[d]	final $conv_{MA}$[d]	r_{gel} (gel fraction)[e]	GSR[f]
GM-0.9	0.9						~1		
GM-1.1	1.1	9.5	0.95	0.97	1.00	~1	~1	0.43	36.82
GM-1.5	1.5	2.7	0.81	0.86	0.96	~1	~1	0.74	9.91
GM-3.0	3.0	1.2	0.57	0.65	0.81	0.90	~0.97	0.89	3.78
GM-5.0	5.0	1.0	0.43	0.48	0.67	0.76	~1	0.94	3.07
GM-10.0	10.0	0.6	0.28	0.38	0.49	0.60	~0.97	0.98	2.75

[a] Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, $[MA]_0 = 5.98$ M, in DMF at 60 °C; linear polyMMA standards for THF GPC calibration; all reactions were stopped after 150 h in order to reach the maximum monomer conversions. [b] Gelation time was defined as the moment when the reaction fluid lost its mobility at an upside down position for 10 s. [c] Simulation results obtained by using Predici software. [d] Experimental results determined by GC analyses. [e] The final gel fraction $r_{gel} = w_{gel}/w_{polymer}$; the sol in polymer product was removed by five cycles of THF extraction and filtration. [f] After removal of sol, the gel-swelling ratio (GSR) in THF was defined as the weight ratio of fully swollen gel to dried gel.

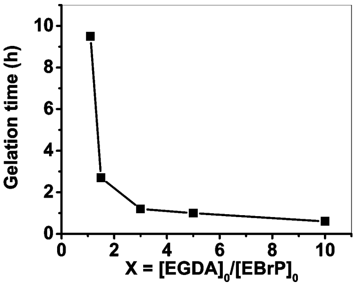


Figure 3. Gelation time at various $X = [EGDA]_0/[EBrP]_0$ during copolymerization of MA and EGDA by ATRP. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/ [CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, $[MA]_0 = 5.98$ M, in DMF at 60 °C.

By using similar procedures, a series of poly(MA-*co*-EGDA) cross-linked copolymers were synthesized by using various molar ratios of $X = [EGDA]_0/[EBrP]_0$. A general trend is that a poly(MA-*co*-EGDA) gel is formed faster at lower MA and EGDA conversions, when a higher molar ratio of $X = [EGDA]_0/[EBrP]_0$ is employed. Figure 3 indicates that at $X = 1.1$ gelation occurred after ca. 9.5 h at conversions of MA and EGDA 97% and essentially 100%, respectively. When $X = 10.0$, a gel was formed after 0.6 h at 38% MA and 60% EGDA conversion. All information about the poly(MA-*co*-EGDA) copolymers by using various molar ratios of $X = [EGDA]_0/[EBrP]_0$ is summarized in Table 1.

Determination of Reactivity of All Vinyl Groups during Copolymerization. Although several research groups have reported the synthesis of branched polymers and/or polymer networks by copolymerization of monomer and cross-linker using CRP techniques, the kinetics of the gelation has not been comprehensively studied. The conversion and the reactivity of both vinyl groups in the cross-linker have not been followed in detail.[21] As mentioned before, the determining factor for gel formation is not the conversion of monomer or cross-linker, but the amount of reacted pendant vinyl groups. ^{1}H NMR analysis of the polymers, after removal of the unreacted monomer and cross-linker, can quantitatively determine the amount of pendant vinyl groups in the polymer chains. However, integration could become imprecise when the concentration (or weight fraction) of pendant vinyl groups in the polymers is too low.[15] To reduce such an inaccuracy in NMR analysis, an experiment with high value of $X = 10.0$ (GM-10.0, Table 1) was used to study the reactivity of the vinyl groups in EGDA and the pendant vinyl groups during the copolymerization of MA and EGDA, which was also compared to the theoretical results from simulation.

During copolymerization, the conversions of MA and EGDA were determined by GC analyses of the samples periodically withdrawn from the Schlenk flask. For copolymerization with $X = 10.0$, Figure 4A indicates that before macroscopic gelation occurred at 0.6 h the first-order kinetic plots of both MA and EGDA were linear, indicating a constant radical concentration in the reaction system. The conversion of EGDA was always higher than that of MA due to the presence of two reactive vinyl bonds in EGDA.

Predici software was used to simulate the kinetics during the gel formation process. The copolymerization of MA and EGDA under ATRP conditions was simplified as a terpolymerization reaction, in which M_1 was MA, M_2 was EGDA, and the third monomer, the pendant vinyl group M_{2P}, was generated stoichiometrically by the consumption of EGDA (eq 1). On the basis of the assumption that all vinyl groups have the same reactivity, the reactivity of EGDA molecule is twice higher than that of MA and the reactivity of M_{2P} is the same as MA. The simulation results provided the conversions of MA and EGDA at any reaction time as well as the instantaneous concentration of pendant vinyl groups ($[M_{2P}]_t$) and primary chains ($[PX]_t$) in the system by using proper kinetic constants (Table S1 in the Supporting Information).[42,47] When $X = 10.0$, the simulation results about the relationship between MA and EGDA conversions at different times overlapped completely with the experimental results (Figure 4B). Such an agreement clearly suggests that the reactivity of the vinyl groups in EGDA is the same as that of MA, which verified the basic assumption used in the Predici simulation.

The reactivity of pendant vinyl groups during the copolymerization of MA and EGDA was also evaluated by comparing the experimental results to the simulation results. The red lines in Figure 5A,B indicate the instantaneous concentration of M_{2P} vs the conversions of MA and EGDA, obtained by Predici simulation. It is worth noting that the concentration of M_{2P} at any moment was determined by its generation and consumption rates. They were further affected by the concentrations of pendant vinyl groups, monomers, and cross-linkers in the system. At low conversion of monomer and cross-linker, the concentration of M_{2P} was much lower than that of unreacted MA and EGDA. Therefore, the generation rate of M_{2P} was higher than the consumption rate, and the total concentration of M_{2P} in the system increased with reaction time. At the same time, the concentration of MA and EGDA in the system decreased with conversion. At a certain moment, when the concentration of M_{2P} in the system was comparable to that of EGDA, the generation rate of M_{2P} equaled to its consumption rate, and the maximum concentration of pendant vinyl groups was reached. The red lines in Figure 5A,B indicate that for copolymerization with $X = [EGDA]_0/[EBrP]_0 = 10.0$ the maximum instantaneous concentration of M_{2P} was 0.58 mol/L

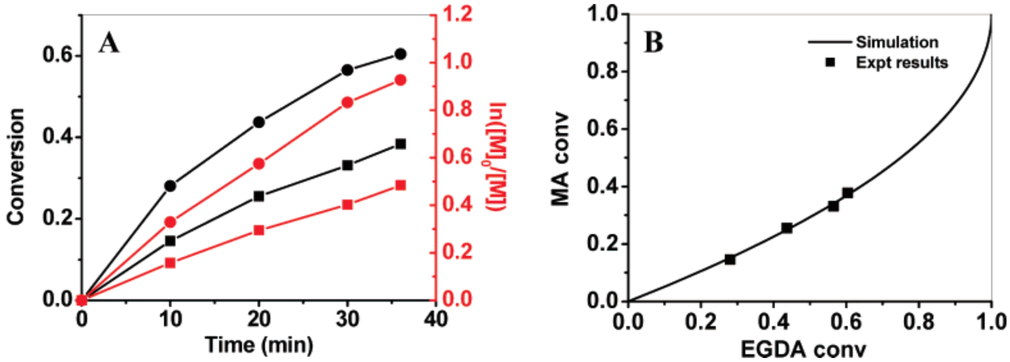


Figure 4. (A) Conversions and $\ln([M]_0/[M])$ of MA (squares) and EGDA (dots) on reaction times and (B) relationship between MA and EGDA conversions during copolymerization of MA and EGDA with $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/10/1/0.45/0.05/0.5$, $[MA]_0 = 5.98$ M, in DMF at 60 °C.

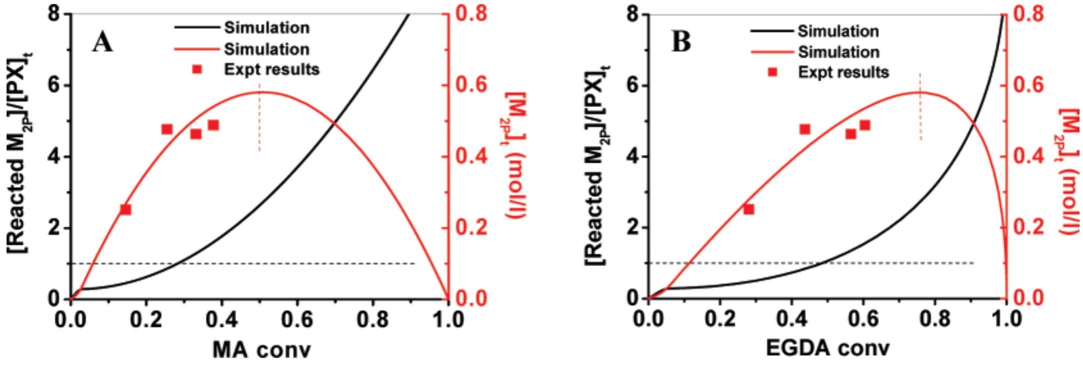


Figure 5. Simulation results (solid lines) and experimental results (dots) of copolymerization of MA and EGDA by ATRP: $[\text{reacted } M_{2P}]/[PX]_t$ and $[M_{2P}]_t$ vs (A) MA conversion and (B) EGDA conversion. Experimental conditions: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/10/1/0.45/0.05/0.5$, $[MA]_0 = 5.98$ M, at 60 °C. The kinetic constants used during Predici simulation are listed in Table S1 in the Supporting Information.

when MA conversion was 49% and EGDA conversion was 74% (red dashed lines in Figure 5A,B).

If the pendant vinyl groups have higher reactivity than MA, the experimental result of instantaneous concentration of M_{2P} ($[M_{2P}]_t$) at any time should be lower than the simulation results because the assumption of equal reactivity for all vinyl groups was applied in the Predici simulation. On the other hand, if the pendant vinyl groups have lower reactivity than MA, the experimental result of M_{2P} concentration should be higher than the simulation result. The red dots in Figure 5A,B represent the experimental results of $[M_{2P}]_t$ at different times, obtained by ^{1}H NMR analysis of the sols before gelation. Unreacted MA and EGDA were removed from the polymer samples by evaporation under vacuum and subsequent precipitation of polymer solution into cold methanol. A typical ^{1}H NMR spectrum of the monomer-free polymers at 0.6 h is shown in Figure 6. The integration results determined the molar ratio of pendant vinyl group (peaks H_a, H_b, and H_c) to reacted MA unit in the polymer backbone (peak H_d), which was further converted into the concentration of M_{2P} at different times when considering the conversion of MA. The results in Figure 5A,B show that the experimental $[M_{2P}]_t$ at any time was close to the simulation lines, indicating that the reactivity of pendant vinyl group is similar to that of MA. This result is consistent with the previous report from Fukuda's group, who claimed that the reactivity of styryl pendant vinyl group was similar to that of free styrene monomer when styrene and 4,4′-divinylbiphenyl were copolymerized by NMP.[21]

Determination of Gel Points during Copolymerization of MA and EGDA by ATRP. On the basis of the above results, the basic assumption that all vinyl groups in MA, EGDA, and pendant vinyl groups have a similar reactivity was verified. With

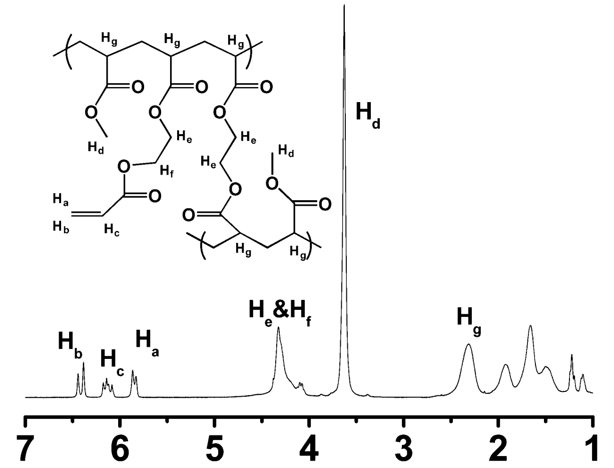


Figure 6. ^{1}H NMR spectrum of the monomer-free polymers obtained at 0.6 h during the copolymerization of MA and EGDA with $X = 10.0$ (GM-10.0, Table 1). ^{1}H NMR conditions: 27 °C, $CDCl_3$ as solvent.

the reaction of pendant vinyl groups, branching points are introduced into the polymer chains. When the cumulative amount of reacted pendant vinyl groups ($[\text{reacted } M_{2P}]$) exceeds the amount of primary chains ($[PX]_t$) in the system, statistically an averaged primary chain contains at least one reacted cross-linking unit. Thus, the theoretical gel point is reached and the gelation occurs, if no cyclization reaction is considered. In parts A and B of Figure 5, horizontal black dash lines were drawn in each plot, which intersected with the simulation plots of $[\text{reacted } M_{2P}]/[PX]_t \sim$ MA conv and $\sim$ EGDA conv, respectively. These two cross-points represent the theoretical gel point for the reaction system with $X = 10.0$, based on the conversions of MA ($\text{conv}_{MA,gel}(\text{theo}) = 28\%$) and EGDA ($\text{conv}_{EGDA,gel}(\text{theo})$

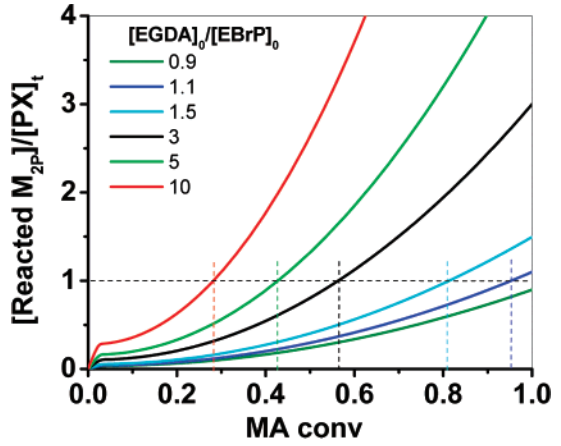


Figure 7. Dependence of [reacted M_{2P}]/$[PX]_t$ on MA conversion during copolymerization of MA and EGDA under various initial conditions by Predici simulation: $[MA]_0/[EGDA]_0/[EBrP]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, $[MA]_0 = 5.98$ M, at 60 °C. The kinetic constants are listed in Table S1 in the Supporting Information.

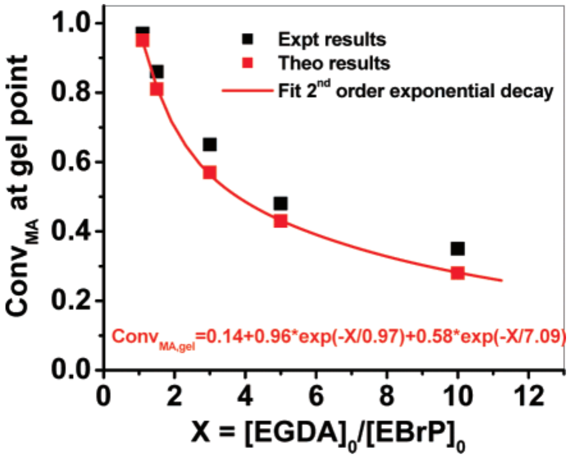


Figure 8. Comparison of experimental gel points (black dots) and theoretical gel points (red dots) based on MA conversions during copolymerization of MA and EGDA by ATRP with various $X = [EGDA]_0/[EBrP]_0$ (Table 1).

= 49%). These results provide a theoretical guideline that the reaction should be stopped before these conversions if a branched polymer instead of a gel is desired. The experimental gel point during copolymerization of MA and EGDA with $X = 10.0$ was $conv_{MA,gel}(expt) = 38\%$ and $conv_{EGDA,gel}(expt) = 60\%$, as determined by GC analysis of the sample at 0.6 h (GM-10.0, Table 1). The experimental conversions at gel point were higher than the theoretical values. This can be ascribed to the inevitable cyclization reactions, which were not considered in the Flory−Stockmayer theory and Predici simulation.

By using similar method, a series of copolymerizations of MA and EGDA with fixed concentration of MA but various molar ratios of $X = [EGDA]_0/[EBrP]_0$ were simulated by Predici. The results in Figure 7 indicate that when different amounts of EGDA were used, the simulated lines ([reacted M_{2P}]/$[PX]_t$ ∼ MA conv) had different cross-points with the horizontal dash line, indicating different theoretical gel points based on MA conversion. It is seen that when $X = 0.9$, the horizontal line has no cross-point with the simulation curve, indicating there should be no gel formation in this system even under 100% MA conversion, which was verified by the experimental results. When more EGDA was used, the cross-point appeared at lower MA conversion, indicating an earlier gelation. The cross-points at various X values are plotted in Figure 8, in which the experimental gel points are very close to the theoretical values, indicating a homogeneous structure of the gels synthesized by the ATRP technique.

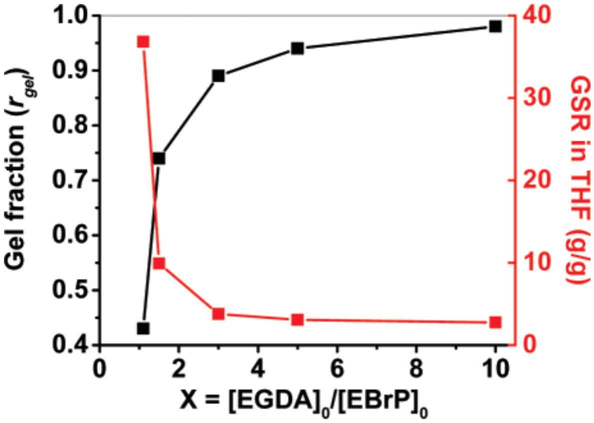


Figure 9. Dependence of poly(MA-*co*-EGDA) gel fraction (r_{gel}) and gel-swelling ratio (GSR) in THF on $X = [EGDA]_0/[EBrP]_0$ by copolymerization of MA and EGDA using ATRP.

As discussed before, the experimental results are always slightly higher than the theoretical values, which was caused by the inevitable cyclization reactions during experiments. The intramolecular cyclization consumed pendant vinyl groups but made no contribution to the increase of molecular weights. Since probability of cyclization reactions increases with a decrease of monomer concentration, it should enhance the difference between the experimental gel points and the theoretical values. When $[MA]_0 = 5.98$ M, the difference between the theoretical values and experimental values was small (Table 1), indicating that the contribution of cyclization reactions under these conditions was insignificant. This is a fundamental difference from the gel synthesized by FRP techniques.

A second-order exponential decay function fitted the theoretical gel points very well (eq 2). By using this equation, a theoretical gel point based on MA conversion can be easily calculated for any molar ratio of $X = [EGDA]_0/[EBrP]_0$ within the range of our investigations. Similarly, the theoretical gel points based on EGDA conversion under various conditions are shown in Figures S2 and S3 in the Supporting Information. A combination of these results provides us a clear guideline that, starting from the same experimental conditions, either sols or gels can be obtained as long as we know the critical dividing line (gel point) between them.

$$conv_{MA,gel} = 0.14 + 0.96\exp(-X/0.97) + 0.58\exp(-X/7.09) \quad (2)$$

Evaluation of Gel Fraction and Gel Swelling Property in THF. When $X = [EGDA]_0/[EBrP]_0 \geq 1.1$, poly(MA-*co*-EGDA) gels were formed in each reaction with different gelation time, depending on the value of X. After gelation, all reactions were kept at 60 °C for 150 h in order to reach the maximum monomer conversion. It was found that after 150 h the MA conversions (final $conv_{MA}$) in all copolymerization reactions were above 97%, and the unreacted EGDA cross-linker became undetectable during GC analysis. The gel fraction (r_{gel}) and gel-swelling ratio (GSR) in THF were measured for each poly(MA-*co*-EGDA) gel, whose results are summarized in Table 1 and plotted in Figure 9. Since the monomer conversion in all reactions after 150 h was essentially 100%, the polymer contents (gel and sol) in each sample were similar. It is shown in Figure 9 that the r_{gel} increased with the value of X, while the GSR in THF decreased. Such a result is reasonable because more added cross-linker generated more branching points per primary chain, which further facilitated more sols to be incorporated into the gels and produced a network with a higher cross-link density and a more compact structure.[12] When $X = 1.1$, the gel fraction was $r_{\text{gel}} =$ 43%, while the GSR in THF was as high as 36.82, indicating that 1 g of dry poly(MA-*co*-EGDA) gel absorbed 35.82 g of THF in the fully swollen state. For comparison, when $X = 10.0$, the gel fraction reached $r_{\text{gel}} = 98\%$, but the GSR in THF was only 2.75. These results proved that the gel swelling property was simply controlled by using various ratios of cross-linker to initiator.

Conclusions

Using the ATRP technique, a series of poly(MA-*co*-EGDA) cross-linked copolymers were successfully synthesized by copolymerization of MA and EGDA with various initial molar ratios of EGDA to EBrP ($X = [\text{EGDA}]_0/[\text{EBrP}]_0 = 1.1-10.0$). Since the gelation is determined by the molar ratio of reacted pendant vinyl groups to primary chains ($[\text{reacted M}_{2\text{P}}]/[\text{PX}]_t$), a copolymerization system with fast initiation and high IE was established, which ensured the concentration of primary chains $[\text{PX}]_t$ in the system was nearly constant throughout the polymerization. The experimental gelation process was monitored by GPC measurement of the sols at different times, indicating that gelation occurred when the weight fraction of branched polymers among the total sols (f_{branch}) reached the peak value. The kinetic study based on experimental results and Predici simulation proved that all vinyl groups had a similar reactivity during the copolymerization of MA and EGDA. The theoretical gel points ($[\text{reacted M}_{2\text{P}}]/[\text{PX}]_t = 1$) determined by Predici simulation, based on the conversions of MA and EGDA ($\text{conv}_{\text{MA,gel}}$ or $\text{conv}_{\text{EGDA,gel}}$), were very close to the experimental results in all reactions, indicating the gels synthesized by the ATRP technique contained less cyclization product and had a more homogeneous structure than the gels synthesized by FRP process. These results can be easily extended to other CRP methods and provide insight into the synthesis of cross-linked polymers by using CRP techniques.

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Supporting Information Available: Kinetic constants used during Predici simulation and experimental results of PMMA homopolymers synthesized by ATRP and gel points based on EGDA conversions. This material is available free of charge via the Internet at http://pubs.acs.org.

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