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Effect of Cross-Linker Reactivity on Experimental Gel Points during ATRcP of Monomer and Cross-Linker

Haifeng Gao, Anna Miasnikova, and Krzysztof Matyjaszewski*

Department of Chemistry, Carnegie Mellon University, 4400 Fifth Avenue,
Pittsburgh, Pennsylvania 15213

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ABSTRACT: A systematic study of the effect of cross-linker reactivity on experimental gel points was conducted using the atom transfer radical copolymerization (ATRcP) of methyl acrylate (MA) with different types and amounts of divinyl cross-linkers, including ethylene glycol diacrylate (EGDA), ethylene glycol dimethacrylate (EGDMA), and an asymmetric cross-linker EGAMA containing one acrylate group and one methacrylate group. The variations of experimental gel points based on the monomer conversions were determined and compared with each other. Compared to the equivalent reactivity of the acrylate groups in MA and EGDA, the methacrylate groups from EGDMA had higher reactivity and led to faster incorporation of cross-linker unit into polymers and quicker generation of branching points (acceleration effect). However, the branched polymers containing the gradient distribution of pendant vinyl groups and branching points resembled a starlike structure, in which the pendant vinyl groups, located in the more densely cross-linked core, were isolated by the surrounded shell and reduced probability of the intermolecular reaction, which retarded the gelation (deceleration effect). These two effects intercorrelated with each other and significantly affected the experimental gel points of the poly(MA-*co*-EGDMA) system, depending on the amount of added EGDMA. With more EGDMA added, the acceleration effect became dominant, which led to a quicker gelation at lower MA conversion compared to the ATRcP by using the same molar amount of EGDA. When the asymmetric cross-linker EGAMA was used, these two effects became much weaker because the pendant vinyl groups were mainly acrylate groups, which had a similar reactivity to free MA monomer and slower branching compared to methacrylate pendant groups.

Introduction

The introduction of a small amount of divinyl cross-linker into the controlled radical copolymerization of vinyl monomers is a convenient method to produce polymers with branched architectures. The structures of polymers obtained from such copolymerization reactions can be varied from soluble starlike polymers containing a cross-linked core and linear radiating arms to highly branched copolymers or insoluble gels, depending on the initiation technique, amount of cross-linker added, and timing of the addition of the cross-linker.[1−3] For instance, using the atom transfer radical polymerization (ATRP)[4−7] technique, the polymerization of monomer before the addition of cross-linker (“arm-first” method)[8−12] or polymerization of monomer after cross-linker[3] (“core-first” method)[13−17] resulted in formation of starlike polymers with a cross-linked core, while copolymerization of monomer and cross-linker together with the same molar ratios of reagents generated insoluble gels with variable mesh size.[18−21]

Highly branched polymers and/or gels with inhomogeneous structures are formed at very early stage (low monomer conversions) during most conventional free radical polymerization (RP) reactions due to the slow continuous initiation, fast chain propagation, and termination reactions.[22−25] Consequently, the experimental gel points show a large deviations from the classic Flory and Stockmayer’s mean-field theory,[26,27] mainly attributed to the intramolecular cyclization (i.e., formation of cycles) in the RP reactions. In contrast, recently developed controlled radical polymerization (CRP)[28−30] methods prepare more homogeneous polymer networks. The fast initiation reactions, relative to propagation reactions, result in all polymer chains being initiated at approximately the same time and a 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 monomer units 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. This results in a more random spatial distribution of the pendant vinyl groups in the polymer chains than that in the conventional RP system. Therefore, the branched sols and/or gels synthesized by CRP methods[1,18−21,31−46] have a more homogeneous distribution of branching points than the polymers synthesized by RP methods at similar concentrations.[1,18,20]

In our previous study, we used ATRP as an exemplary CRP technique to copolymerize methyl acrylate (MA) monomer with ethylene glycol diacrylate (EGDA) cross-linker at high monomer concentration (e.g., $[MA]_0 = 6.0$ M, 55 vol %) and studied the gelation behavior.[20] The use of an appropriate ATRP initiator, an efficient catalyst and a good solvent for the copolymerization, resulted in fast initiation, high initiation efficiency, and good control in the system. The experimental gel points, determined as the conversion of monomer and/or cross-linker at the moment of gelation, were significantly affected by the initial molar ratio of cross-linker to initiator. For instance, the experimental gelation occurred at 97% MA conversion when the $[\text{cross-linker}]_0/[\text{initiator}]_0$ ratio = 1.1. Increasing the amount of cross-linker in the copolymerization led to gelation at lower MA conversions.

It is worth noting that these atom transfer radical copolymerization (ATRcP) reactions were performed after satisfying several factors: high monomer concentration, high initiation efficiency, low polydispersity of the primary chain, and equal reactivity of all vinyl species. Consequently, changing one or several of these factors should lead to changes in the gelation behavior. For example, gelation was significantly delayed, even prevented, by simply decreasing the initial concentration of monomers in the reaction, while keeping all other conditions the same. Dilution of the copolymerization system decreased

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

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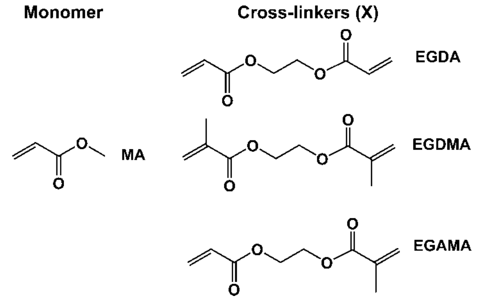
Scheme 1. Structures of Monomer and Cross-Linkers for Synthesis of Poly(MA-*co*-X) Network by ATRcP



the concentration of copolymer in solution and increased the fraction of intramolecular cyclization reactions compared to the intermolecular cross-linking reactions. Since intramolecular cyclization consumed pendant vinyl groups but had no contribution to increasing the molecular weight of the branched polymers, the effect of dilution was to delay the occurrence of experimental gelation.[44]

Herein, we report the effect of another important factor on the experimentally determined gel point: a difference in the reactivity of vinyl groups present in the cross-linker and monomer. In order to keep the current system comparable to the previously studied systems, MA was used as the monovinyl monomer which was copolymerized with three types of cross-linkers. Two cross-linkers had a symmetric structure, EGDA and ethylene glycol dimethacrylate (EGDMA), while the third had an asymmetric structure and contained one acrylate group and one methacrylate group (Scheme 1). The experimental gel points based on the conversions of monomer were determined in a systematic study where the species and ratios of cross-linker to initiator were varied in order to understand the influence of different cross-linker reactivity.

Experimental Section

Materials. Methyl acrylate (MA, 99%), ethylene glycol diacrylate (EGDA, 90%), and ethylene glycol dimethacrylate (EGDMA, 98%) were purchased from Aldrich and purified by passing through a column filled with basic alumina twice to remove the inhibitor. CuBr (98%, Acros) was purified using a modified literature procedure.[47] All other reagents—ethyl 2-bromoisobutyrate (EBiB), *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA), $CuBr_2$, and solvents—were the highest purity reagents that could be purchased from Aldrich and were used as received without further purification.

Synthesis of Asymmetric Cross-Linker Acryloyloxyethyl Methacrylate (EGAMA). Triethylamine (40.16 mL, 0.288 mol) and 2-hydroxyethyl methacrylate (25.00 g, 0.192 mol) were added sequentially to a clean, dry round-bottom flask containing 150 mL of methylene chloride (dried overnight with $MgSO_4$) that had been cooled to 0 °C in an ice−water bath. The heterogeneous mixture was magnetically stirred for 10 min before dropwise addition of acryloyl chloride (23.41 mL, 0.288 mol) over a period of 30 min. The flask was then removed from the ice−water bath, and the reaction was allowed to proceed for 24 h at room temperature. During this period, the reaction mixture slowly changed from a yellowish color to brown. The reaction mixture was washed successively with 300 mL of 1 M HCl, 300 mL of 1 M NaOH, and 300 mL of deionized water and then dried overnight over anhydrous $MgSO_4$. After removing the solvent via rotary evaporation, the product was purified via silica column chromatography with mixture of hexane/ethyl acetate 8/2 by volume as the spreading solvent. The final product was a colorless liquid with yield 26.9 g (76%). The structure was verified by ^1H NMR spectroscopy (δ, 300 MHz, $CDCl_3$ as solvent): 6.39−6.43 ppm (2d, H, $\mathrm{C}H_2\mathrm{{=}CHC(O)O}$), 6.05−6.20 ppm (m, 2H, $\mathrm{CH_2{=}C}H\mathrm{C(O)O}$ and $\mathrm{C}H_2\mathrm{{=}C(CH_3)}$), 5.80−5.90 ppm (2d, H, $\mathrm{C}H_2\mathrm{{=}CHC(O)O}$), 5.57 ppm (br s, H, $\mathrm{C}H_2\mathrm{{=}C(CH_3)}$), 4.30−4.45 ppm (m, 4H, $\mathrm{OC}H_2\mathrm{C}H_2\mathrm{O}$), 1.94 ppm (s, 3H, $\mathrm{CH_2{=}C(C}H_3\mathrm{)}$).

Synthesis of Poly(MA-*co*-X) Cross-Linked Copolymers Prepared by ATRcP of MA with Different Cross-Linkers (X). All experimental procedures for synthesis of various kinds of cross-linked copolymers were conducted under similar conditions. A typical procedure for ATRcP of MA and EGDMA is briefly described. The copolymerization started with the ratio of reagents $[MA]_0/[EGDMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1.5/1/0.45/0.05/0.5$, $[MA]_0 = 6.0$ M. A clean and dry Schlenk flask was charged with MA (3.50 mL, 0.039 mol), EGDMA (0.220 mL, 1.17 mmol), PMDETA (81.2 μL, 0.39 mmol), and *N,N*-dimethylformamide (DMF, 2.60 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. The flask was sealed with a glass stopper 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 EBiB (0.114 mL, 0.78 mmol) was injected into the reaction system via a syringe through the side arm of the Schlenk flask. Samples were withdrawn via a syringe at timed intervals for GC measurements of monomer conversions and GPC measurements of the molecular weight of the soluble copolymers. Gelation occurred at certain moment and was measured as the time 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.

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 separated 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)). The apparent molecular weights and polydispersity (M_w/M_n) were determined with a calibration based on linear poly(methyl methacrylate) (polyMMA) standards using WinGPC 6.0 software from PSS. Area fractions of both branched and linear polymers were determined by multipeak splitting of the GPC curve using Gaussian function in Origin 6.0 software. The GPC curves obtained with flat baseline were imported into the WinGPC software for calculation of their apparent molecular weights and polydispersity. ^1H NMR spectra, using $CDCl_3$ as solvent, were measured on a Bruker Avance 300 MHz spectrometer at 27 °C.

Results and Discussion

Several parameters are expected to have an influence on the experimental gel points determined for the ATRcP of a monovinyl monomer with specific amounts of divinyl cross-linker. Variables include concentration of polymer in solution, initiation efficiency of ATRP initiator, polydispersity of the primary chain, and the reactivity of each vinyl group in the cross-linker compared to the reactivity of the monomer. In order to exclusively explore the effect of unequal reactivity of the different vinyl species present in the cross-linker on the experimental gel points, the effects of all other factors on the copolymerization should be controlled or at least minimized.

Therefore, the ATRcP reactions were performed under fairly concentrated conditions ($[MA]_0 = 6.0$ M, 55 vol %). The initial molar ratio of MA to initiator was kept constant, $[MA]_0/[R\text{-}Br]_0 = 50/1$. DMF was used as the solvent due to the high solubility of copper catalyst in it. EBiB was used as the initiator, instead of ethyl 2-bromopropionate (EBrP), for the copolymerization of MA with three types of cross-linkers in order to

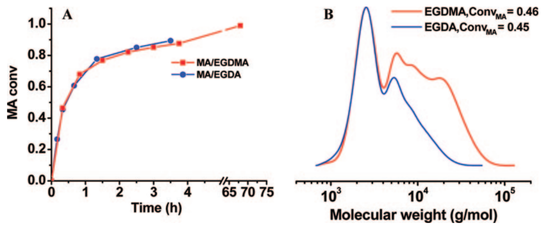


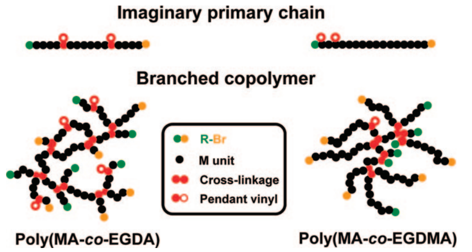
Figure 1. (A) Dependence of MA conversion on reaction time and (B) GPC traces of copolymers formed at ca. 45% MA conversion during the synthesis of poly(MA-*co*-EGDA) and poly(MA-*co*-EGDMA) copolymers by ATRcP of MA with different divinyl cross-linkers. Experimental conditions: $[MA]_0/[X]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/1.5/1/0.45/0.05/0.5$, $[MA]_0 = 6.0$ M, in DMF at 60 °C, linear polyMMA standards for THF GPC calibration.

obtain a high initiation efficiency and good control over the polydispersity of primary chains during the ATRcP of MA and methacrylate-containing cross-linker.[48]

Effect of Cross-Linker Reactivity on Experimental Gel Points. In order to illustrate the effect of cross-linker reactivity on the experimental gel points, two ATRcP reactions were performed using the same molar ratios of reagents but different cross-linker species. In the first reaction a diacrylate cross-linker, EGDA, was used for the copolymerization with MA, in which all vinyl species have a similar reactivity toward propagating radicals.[20] In contrast, the second experiment used a dimethacrylate cross-linker, EGDMA, for the copolymerization. Since the methacrylate has a higher reactivity than an acrylate during their radical copolymerization ($r_{12} = 0.3$, $r_{21} = 2.2$ for MA (**1**) and MMA (**2**) radical copolymerization),[49] it is expected that the rate of incorporation of EGDMA and the generation rate of cross-linkage (the cross-linker with both vinyl groups reacted) should be faster during the ATRcP of MA and EGDMA compared to using EGDA as a cross-linker.

The ATRcP of 50 equiv of MA and 1.5 equiv of cross-linker (EGDA or EGDMA) was conducted using EBiB as initiator, CuBr/PMDETA as catalyst (10 mol % $CuBr_2$ of total copper species was added into the system), and DMF as solvent. The polymerization rates of MA in both reactions were similar, evidenced by the two overlapped curves of MA conversion versus time (Figure 1A). This result indicates that the addition of 1.5 equiv of cross-linker with differing reactivity had no significant effect on the kinetics of MA polymerization. On the other hand, the GPC traces of both poly(MA-*co*-EGDA) and poly(MA-*co*-EGDMA) copolymers at ca. 45% MA conversion show the effects of different degrees of branching, i.e., different molecular weights and area fractions of branched copolymers (Figure 1B). At 45% MA conversion, branched copolymers with high molecular weight and broad molecular weight distribution formed in both reactions while, at the same time, a sharp lower molecular-weight peak is still visible, representing the linear primary chains in the system. Therefore, the GPC-measured sols indicate the presence of two types of polymers: linear polymers and branched polymers. The linear chains in the two reactions had the same molecular weight at the same conversion (Figure 1B), demonstrating the good control over the polymerization in both cases. The branched copolymers formed in the copolymerization of MA and EGDMA had higher molecular weight than that in the poly(MA-*co*-EGDA) reaction. Multipeak splitting of the GPC curve, using Gaussian function, determined that the area fraction of branched copolymers versus total GPC-measured sols was 59.2% in the poly(MA-*co*-EGDMA), which is larger than the value (38.0%) for the poly(MA-*co*-EGDA). These differences in the extent of branching between the two copolymerization reactions, poly(MA-*co*-EGDA) and poly(MA-*co*-EGDMA), are ascribed to the higher reactivity of methacrylate groups in EGDMA cross-linker than the acrylate groups in EGDA.

Scheme 2. Initial Stages of Gel Formation Process by ATRcP of MA with Different Cross-Linker (EGDA or EGDMA)



During the copolymerization of MA and EGDA, all vinyl groups, including the free monomer, each double bond in the cross-linker, and the pendant vinyl group, have a similar reactivity at the initial stage.[20] Therefore, the propagating radicals react with monomer, cross-linker, and pendant vinyl group in a statistical manner based on their relative concentration. In other words, the branching points are distributed along the polymer chains in a more homogeneous manner (Scheme 2). In contrast, the cross-linker EGDMA contains two methacrylate groups, which are expected to have reactivity similar to MMA during the copolymerization with MA. Because of the higher reactivity of a methacrylate group, both the incorporation rate of EGDMA into the polymer chain and the consumption rate of pendant methacrylate group were faster (or accelerated) than the copolymerization using EGDA as cross-linker. Therefore, at the same conversion of MA, more EGDMA reacted and more branching points were generated during the ATRcP of MA and EGDMA, which explains the difference between the GPC curves in Figure 1B.

The conversions of monomer and cross-linkers (EGDA and EGDMA), during the radical copolymerization, could be calculated based on the initial molar ratio of MA to cross-linker and their reactivity; the detailed calculation is shown in the Supporting Information. Figure 2 shows that the conversion of EGDMA was much higher than that of EGDA at any MA conversion, simply due to the higher reactivity of methacrylate groups than acrylate groups. At the same MA conversion, the averaged EGDMA cross-linkage per primary chain was higher than when EGDA was used as the cross-linker. For example, the ratio of EGDMA cross-linkage to $[R-Br]_0$ reached a value 1.0 at 40.1% MA conversion for the ATRcP of MA and EGDMA, while this value was not reached until after 82.0% MA conversion during the ATRcP of MA and EGDA.

Taking only these results into account, it was expected that gelation should occur earlier, or at lower MA conversion, in the case of poly(MA-*co*-EGDMA) when compared to poly(MA-*co*-EGDA). However, it was initially a surprise to find that no gel was formed in the ATRcP reaction of MA and EGDMA after 68 h, when the conversion of MA reached 99%. In contrast,

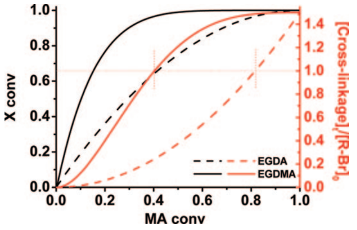


Figure 2. Calculated results for dependence of cross-linker conversion and $[\text{cross-linkage}]_t/[R-Br]_0$ on MA conversion during the copolymerization of MA with EGDA and EGDMA. Copolymerization conditions: $[MA]_0/[X]_0/[R-Br]_0 = 50/1.5/1$; the detailed calculation is shown in the Supporting Information.

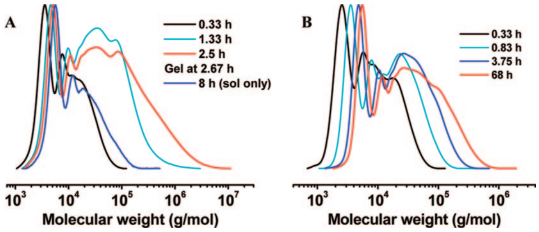


Figure 3. Evolution of GPC traces during the synthesis of (A) poly(MA-*co*-EGDA) and (B) poly(MA-*co*-EGDMA) branched copolymers or gels by ATRcP of MA with different divinyl cross-linkers. Experimental conditions: $[\mathrm{MA}]_0/[\mathrm{X}]_0/[\mathrm{EBiB}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{PMDETA}]_0 = 50/1.5/1/0.45/0.05/0.5$, $[\mathrm{MA}]_0 = 6.0$ M, in DMF at 60 °C, linear polyMMA standards for THF GPC calibration.

Table 1. Synthesis of Poly(MA-*co*-X) by Using Various Cross-Linkers at $[\mathrm{MA}]_0 = 6.0$ M[a]

entry[b]	X	$[\mathrm{X}]_0/[\mathrm{R{-}Br}]_0$	$\mathrm{conv_{MA,gel}}$[c]
$\mathrm{MA_{6.0}DA_{1.0}}$	EGDA	1.0	no gelation
$\mathrm{MA_{6.0}DA_{1.1}}$	EGDA	1.1	0.97
$\mathrm{MA_{6.0}DA_{1.5}}$	EGDA	1.5	0.86
$\mathrm{MA_{6.0}DA_{2.0}}$	EGDA	2.0	0.79
$\mathrm{MA_{6.0}DA_{2.5}}$	EGDA	2.5	0.70
$\mathrm{MA_{6.0}DA_{3.0}}$	EGDA	3.0	0.65
$\mathrm{MA_{6.0}DA_{5.0}}$	EGDA	5.0	0.48
$\mathrm{MA_{6.0}DA_{10.0}}$	EGDA	10.0	0.38
$\mathrm{MA_{6.0}DMA_{1.5}}$	EGDMA	1.5	no gelation
$\mathrm{MA_{6.0}DMA_{2.0}}$	EGDMA	2.0	0.95
$\mathrm{MA_{6.0}DMA_{2.5}}$	EGDMA	2.5	0.53
$\mathrm{MA_{6.0}DMA_{3.0}}$	EGDMA	3.0	0.39
$\mathrm{MA_{6.0}DMA_{5.0}}$	EGDMA	5.0	0.29
$\mathrm{MA_{6.0}DMA_{6.0}}$	EGDMA	6.0	0.25
$\mathrm{MA_{6.0}DMA_{8.0}}$	EGDMA	8.0	0.16
$\mathrm{MA_{6.0}DMA_{10.0}}$	EGDMA	10.0	0.12
$\mathrm{MA_{6.0}AMA_{1.1}}$	EGAMA	1.1	no gelation
$\mathrm{MA_{6.0}AMA_{1.2}}$	EGAMA	1.2	0.96
$\mathrm{MA_{6.0}AMA_{1.5}}$	EGAMA	1.5	0.86
$\mathrm{MA_{6.0}AMA_{3.0}}$	EGAMA	3.0	0.59
$\mathrm{MA_{6.0}AMA_{5.0}}$	EGAMA	5.0	0.42
$\mathrm{MA_{6.0}AMA_{10.0}}$	EGAMA	10.0	0.30

[a] Experimental conditions: $[\mathrm{MA}]_0/[\mathrm{X}]_0/[\mathrm{EBiB}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{PMDETA}]_0 = 50/\mathrm{X}/1/0.45/0.05/0.5$, in DMF at 60 °C, $[\mathrm{MA}]_0 = 6.0$ M, linear polyMMA standards were used for THF GPC calibration. [b] The code "$\mathrm{MA_{\alpha}X_{\beta}}$" represents an experimental ATRcP with $\alpha = [\mathrm{MA}]_0$ and $\beta = [\mathrm{X}]_0/[\mathrm{EBiB}]_0$, where DA, DMA, and AMA represent cross-linker EGDA, EGDMA, and EGAMA, respectively. [c] Conversions of MA immediately before gelation. The experimental gel point was the moment when the reaction fluid lost its mobility when held at an upside-down position for 10 s.

the ATRcP of MA and EGDA with the same molar ratio of reagents reached gelation after 2.7 h with MA conversion as 86% (Figure 3). In both cases, the linear chains in the GPC-measured sols showed a narrow distribution and smoothly increased molecular weights with MA conversions, indicating both polymerizations were under a good control within the range of MA conversions. However, analysis of the evolution of branched polymers in the reaction of poly(MA-*co*-EGDMA) shows that the increase of molecular weight and area fraction of the branched copolymers gradually slowed down with the increase of MA conversion, which could be due to the intramolecular cyclization at high MA conversion and produced nanogels with more compact structure. This result is different from the steady progress of the branched polymers and an earlier gelation at 2.7 h in the case of poly(MA-*co*-EGDA) reaction. After 2.7 h, the largest branched polymers were incorporated into the network and only sols with smaller size were left and measured by GPC. Therefore, the apparent molecular weight of the poly(MA-*co*-EGDA) branched polymers in the sols at 8 h decreased (Figure 3A).

The absence of gelation in the reaction of poly(MA-*co*-EGDMA) can be ascribed to another consequence of faster incorporation of the methacrylate units into the copolymer: a steric isolation effect.[50,51] This steric isolation effect hindered the reaction between two branched polymers and decelerated the experimental gelation process. The accelerated incorporation of EGDMA into the polymer chains led to a gradient distribution of the methacrylate units along the primary chain and a gradient distribution of the pendant vinyl groups within the branched polymers from inside to outside (Scheme 2). Most of the pendant methacrylate groups were located in the core section of the branched polymer and were protected by the surrounded shell from reacting with the propagating radicals in another branched polymer, the intermolecular cross-linking reaction required for gel formation. As a result of the shell isolation, intramolecular cyclization, the reaction of pendant vinyl groups with a radical in the same branched molecule was enhanced, which consumed the pendant vinyl groups but did not contribute to an increase in the molecular weight of the branched copolymers. Thus, it is reasonable to envision that the spontaneous gradient ATRcP of MA and EGDMA resulted in formation of poly(MA-*co*-EGDMA) branched copolymers that resembled a starlike polymer containing a more densely cross-linked core and a loosely cross-linked shell (Scheme 2).

The gelation behavior during the ATRcP of MA and EGDMA is concurrently influenced by both an acceleration effect, due to the higher reactivity of methacrylate group, and a deceleration effect, due to the steric protection of dangling chains, compared to the ATRcP of MA and EGDA. The higher reactivity of methacrylate groups leads to a faster consumption of EGDMA and an earlier generation of branched structures. However, the initially formed poly(MA-*co*-EGDMA) branched copolymer has to overcome a higher steric isolation from the surrounded shell to react intermolecularly and form larger branched polymers and gels.

To systematically explore the impact of these two intercorrelated factors on the experimental gel point during the ATRcP of MA and EGDMA, a series of poly(MA-*co*-EGDMA) branched/cross-linked copolymers with constant MA concentration ($[\mathrm{MA}]_0 = 6.0$ M) and various amounts of EGDMA were carried out. The experimental gel points based on the conversion of MA at gelation were determined and compared to poly(MA-*co*-EGDA) formed under similar conditions.

ATRcP of MA and EGDMA Using Different Amounts of Cross-Linker. The initial molar ratios of EGDMA to EBiB were systematically varied, and it was determined that no gelation occurred when the initial molar ratio of $X = [\mathrm{EGDMA}]_0/[\mathrm{EBiB}]_0 \leq 1.5$ ($\mathrm{MA_{6.0}DMA_{1.5}}$, Table 1), which contrasted with gelation at 86% MA conversion when 1.5 equiv of EGDA was used as cross-linker for ATRcP with 50 equiv of MA ($\mathrm{MA_{6.0}DA_{1.5}}$, Table 1). As discussed above, these results indicate that when a small amount of EGDMA, such as 1.5 equiv, was added to the copolymerization, the steric isolation effect was dominant over the acceleration effect. This phenomenon enhanced intramolecular cyclization reactions and consequently prevented gelation. When 2.0 equiv of EGDMA was used as cross-linker ($\mathrm{MA_{6.0}DMA_{2.0}}$, Table 1), gelation was observed at 95% MA conversion. This was still higher than the gel point ($\mathrm{conv_{MA,gel}} = 79\%$) determined for the ATRcP of MA and 2.0 equiv of EGDA ($\mathrm{MA_{6.0}DA_{2.0}}$, Table 1), indicating that the cumulative effect of these two factors at 2.0 equiv of EGDMA still retarded gelation compared to the ATRcP of MA and EGDA. In other words, the higher reactivity of cross-linker did not compensate for the enhanced cyclization reaction induced by the protective shell. The system had to reach higher MA conversion and required a longer reaction time to form a gel.

When the amount of EGDMA was increased to $X = [\mathrm{EGDMA}]_0/[\mathrm{EBiB}]_0 = 2.5$, the experimental gel point was

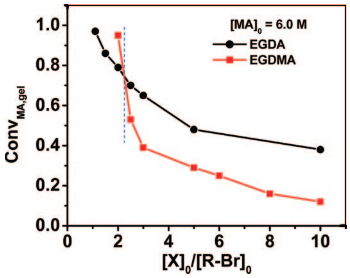


Figure 4. Comparison of experimental gel points, based on MA conversions, during ATRcP of MA with two types of cross-linkers. Experimental conditions: $[MA]_0/[X]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C, $[MA]_0 = 6.0$ M.

observed at $conv_{MA,gel} = 53\%$ ($MA_{6.0}DMA_{2.5}$, Table 1), which was lower than the gel point for the $MA_{6.0}DA_{2.5}$ reaction ($conv_{MA,gel} = 70\%$). This result indicates that during the ATRcP of MA with 2.5 equiv of EGDMA the acceleration effect became dominant and led to gelation at lower MA conversion. From this point on, further increase in the initial molar ratio of $[EGDMA]_0/[EBiB]_0$ resulted in increasing evidence for the acceleration effect during the ATRcP of MA and EGDMA. The use of a large amount of EGDMA increased the average cross-linking density within the branched polymers, which overwhelmed the steric isolation effect and led to earlier formation of poly(MA-*co*-EGDMA) gel at lower MA conversion than the control poly(MA-*co*-EGDA) reaction. For instance, when $X = [EGDMA]_0/[EBiB]_0 = 10.0$, gelation was observed at only 12% MA conversion while the same amount of EGDA cross-linker to initiator resulted in gelation at 38% MA conversion ($MA_{6.0}DA_{10.0}$, Table 1).

Figure 4 shows the overall effect of these two factors on the experimental gel points of poly(MA-*co*-EGDMA) copolymer compared to model reactions of poly(MA-*co*-EGDA) with the same molar ratio of cross-linker. It is seen that these two lines crossed around $X = [EGDMA]_0/[EBiB]_0 = 2.3$ (the dashed blue line). When the initial ratio of cross-linker to initiator was below this value, the steric isolation effect was dominant, which prevented or delayed the gelation during the ATRcP of MA and EGDMA. When higher amounts of EGDMA were used ($X > 2.3$), the dangling chains (i.e., shell) were shorter and the steric isolation effect became less important. Therefore, the acceleration effect became dominant leading to faster formation of cross-linkage and gelation at lower MA conversion.

Use of an Asymmetric Cross-Linker: Synthesis of Poly(MA-*co*-EGAMA) Copolymers. In order to confirm our observation of the combined acceleration and deceleration effects during the ATRcP of MA and the dimethacrylate cross-linker EGDMA, an asymmetric cross-linker, containing one acrylate group and one methacrylate group, EGAMA was used for the ATRcP with MA.

Since the asymmetric cross-linker contains one methacrylate group, which has higher reactivity than the acrylate group, the faster incorporation of the EGAMA unit into the polymer chains, compared to the ATRcP of MA and EGDA system, should still induce a gradient distribution of the pendant vinyl groups along the primary chain. On the other hand, after the incorporation of EGAMA into the primary chain, the pendant vinyl groups, mainly acrylate groups, have a similar reactivity toward unreacted MA monomer. Therefore, the branching rate, which depends only on the reaction of the pendant vinyl group with propagating radical, should be comparable to that in the ATRcP of MA and EGDA system. In other words, the steric congestion effect and the acceleration effect should still affect the experimental gel points based on the conversion of MA during the ATRcP of MA and EGAMA, but the extent could be weaker than that observed in the ATRcP of MA and EGDMA.

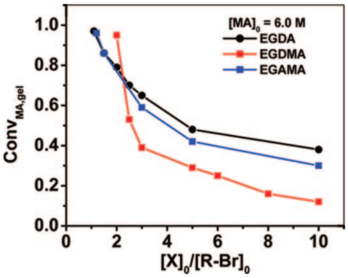


Figure 5. Comparison of experimental gel points based on MA conversion during ATRcP of MA and EGAMA with those using EGDA or EGDMA as cross-linker. Experimental conditions: $[MA]_0/[X]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/X/1/0.45/0.05/0.5$, in DMF at 60 °C, $[MA]_0 = 6.0$ M.

To determine the overall result of these two competing effects on the experimental gel points, a series of ATRcP of MA and EGAMA with varied amounts of cross-linker were performed at a molar ratio of $[MA]_0/[EBiB]_0 = 50$ and $[MA]_0 = 6.0$ M. The experimental gel points, based on the MA conversion, are listed in Table 1 and plotted in Figure 5 to compare the results with the observations made during the ATRcP of MA and EGDA and ATRcP of MA and EGDMA.

In Figure 5, the gelation behavior observed with EGAMA as cross-linker showed a combined effect of the MA/EGDA and MA/EGDMA systems. This is due to the asymmetric nature of EGAMA which contains one acrylate group and one methacrylate group. Compared to the ATRcP of MA and EGDA, which showed a gel point at $conv_{MA,gel} = 97\%$ when $X = [EGDA]_0/[EBiB]_0 = 1.1$, there was no gelation in the reaction of $MA_{6.0}AMA_{1.1}$ when 1.1 equiv of EGAMA was used. This result indicates that the gradient distribution of EGAMA unit, at low amount cross-linker, still resulted in some steric isolation effect on the intermolecular branching reaction, which prevented gelation. However, this deceleration effect was so weak that a small increase in the amount of the cross-linker to $X = [EGAMA]_0/[EBiB]_0 = 1.2$ induced gelation at $conv_{MA,gel} = 96\%$. Further increase of the EGAMA cross-linker amount from $X = 1.5$ to 10.0 led to gelation at lower MA conversions compared to experiments using EGDA as cross-linker, indicating the higher reactivity of methacrylate group in EGAMA accelerated the incorporation of cross-linker into polymer chain and increased the rate of branching.

On the other hand, the gel points based on MA conversion during the ATRcP of MA and EGAMA were much later than those from the ATRcP of MA and EGDMA system. When 10 equiv of cross-linker was used, the gel point in $MA_{6.0}AMA_{10.0}$ reaction occurred at ($conv_{MA,gel} = 30\%$), significantly later than gel formation at $conv_{MA,gel} = 12\%$ in $MA_{6.0}DMA_{10.0}$. Since the consumption of pendant vinyl group is the only way to generate cross-linkage and induce the gelation, this observation could be ascribed to the lower reactivity of the predominantly acrylate pendant vinyl groups. Therefore, it was important to experimentally determine the existence and structure of the pendant vinyl groups, both pendant acrylate and methacrylate groups, at different reaction times and compare their reactivity and concentrations to the calculated values based on the assumption that pendant acrylate and methacrylate groups have the same reactivity as free acrylate and methacrylate monomers.

Polymer samples were periodically withdrawn from the ATRcP of MA and 5.0 equiv of EGAMA before gelation. The conversions of both MA and EGAMA were directly determined by GC analyses before purification of the remaining sample to remove the unreacted monomer and cross-linker by repeated precipitation of the polymer from THF solution into hexane.

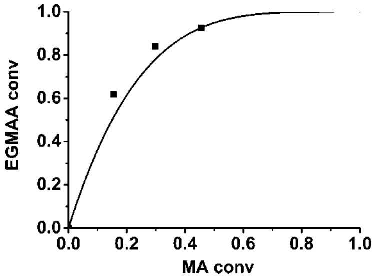


Figure 6. Comparison of experimental and calculated conversions of MA and EGAMA at different intervals. The detailed calculation is shown in the Supporting Information. Experimental conditions: $[MA]_0/[EGAMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/5.0/1/0.45/0.05/0.5$, in DMF at 60 °C, $[MA]_0 = 6.0$ M.

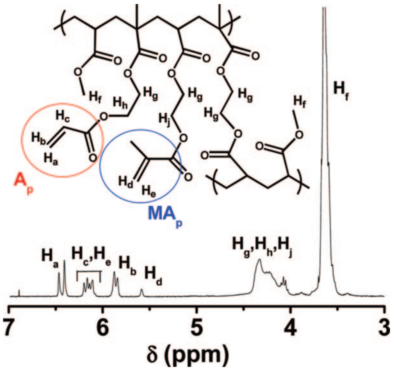


Figure 7. ^{1}H NMR spectrum of the monomer-free poly(MA-*co*-EGAMA) copolymer obtained at 30% MA conversion. Experimental conditions: $[MA]_0/[EGAMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/5.0/1/0.45/0.05/0.5$, in DMF at 60 °C, $[MA]_0 = 6.0$ M. ^{1}H NMR conditions: 27 °C, $CDCl_3$ as solvent.

Because of the fact that each EGAMA contains one acrylate group and one methacrylate group, the kinetics during the copolymerization of MA and EGAMA with ratio of $[MA]_0/[EGAMA]_0 = 50/5$ is assumed to be equal to that of copolymerization of MA and MMA with $[MA]_0/[MMA]_0 = 55/5$. EGAMA conversion was calculated based on the conversions of MMA and MA; the detailed calculation is shown in the Supporting Information, and its dependence on MA conversion was plotted and compared to the experimental results. Figure 6 indicates that the GC-determined experimental conversions of MA and EGAMA were very close to the calculated value, indicating that the vinyl groups (one acrylate and one methacrylate) in the free EGAMA cross-linker have similar reactivity to the corresponding monomers, at least in the period before gelation.

The purified poly(MA-*co*-EGAMA) copolymer, which was free of unreacted monomer and cross-linker, was dried under vacuum and analyzed by ^{1}H NMR spectroscopy to quantitatively determine the concentration of pendant vinyl groups. Figure 7 shows a typical ^{1}H NMR spectrum of the purified copolymer at 30% MA conversion. The integration results determined the molar ratios of pendant acrylate groups A_p (peaks H_a, H_b, and H_c) and pendant methacrylate groups MA_p (peaks H_d and H_e) to reacted MA monomer units in the polymer backbone (peak H_f), which were further converted into the fractions of $f_{A,p}$ (molar fraction of pendant acrylate groups to initially added EGAMA) and $f_{MA,p}$ (molar fraction of pendant methacrylate groups to initially added EGAMA) when considering the conversions of MA.

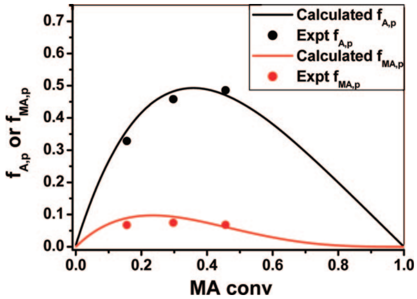


Figure 8. Comparison of calculated results (solid lines) and experimental results (dots) of the fraction of pendant acrylate group ($f_{A,p}$) and methacrylate group ($f_{MA,p}$) as a function of MA conversions during the ATRcP of MA and EGAMA. Experimental conditions: $[MA]_0/[EGAMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0 = 50/5.0/1/0.45/0.05/0.5$, in DMF at 60 °C, $[MA]_0 = 6.0$ M.

The results in Figure 8 suggest that the experimental results overlapped with the calculated fractions of these two pendant vinyl groups at different times, which proved the pendant vinyl groups had reactivity similar to the corresponding free monomers within the investigated range of monomer conversions. The fraction (or concentration) of pendant acrylate group was larger than that of pendant methacrylate group, indicating the consumption of free EGAMA cross-linker predominantly proceeded by the reaction of methacrylate group, which generated a pendant acrylate group. Because of the similar reactivity of pendant acrylate group to the free MA monomer, the rate of generation of cross-linkage during ATRcP of MA and EGAMA was much slower than with EGDMA as cross-linker, which led to a weaker acceleration effect and consequently a weaker steric isolation effect.

Conclusion

A series of poly(MA-*co*-X) branched/cross-linked copolymers were synthesized by ATRcP of MA with three different cross-linkers to study the effect of unequal reactivity of vinyl groups on the experimental gel points. The divinyl cross-linkers employed for the ATRcP reactions included a diacrylate cross-linker, EGDA, with vinyl groups possessing the similar reactivity as the MA monomer, a dimethacrylate cross-linker, EGDMA, whose vinyl groups have higher reactivity than the MA comonomer, and an asymmetric cross-linker containing one acrylate group and one methacrylate group. The experimental gel points, based on the MA conversions at the moment of gelation, were compared to each other. When EGDMA was used as the cross-linker, the experimental gelation behavior was concurrently affected by two intercorrelated factors: (1) an acceleration effect due to the higher reactivity of methacrylate groups, which led to branching and gelation at lower monomer conversion, and (2) a deceleration effect due to the steric isolation induced by the surrounded dangling chains, which retarded or in some cases even prevented the gel formation. The deceleration effect was dominant when the initial molar ratio of $X = [EGDMA]_0/[EBiB]_0 < 2.3$. While the acceleration effect became dominant when higher amounts of EGDMA were used, leading to gelation at lower MA conversion compared to the ATRcP of MA and EGDA. When the asymmetric cross-linker, EGAMA, was used, these two effects became much weaker because the pendant vinyl groups were mainly acrylate groups, which had similar reactivity to free MA monomer. These results elucidate the effect of cross-linker reactivity on the spatial distribution of pendant vinyl groups and the experimental gel points, which can be used as a guide for further exploration of other gelation systems via ATRcP of different monomers and cross-linkers.

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Supporting Information Available: Details on the methods employed for calculation of cross-linker conversion, fraction of cross-linkage, and pendant vinyl groups at any MA conversion. This material is available free of charge via the Internet at http://pubs.acs.org.

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