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Gelation in ATRP Using Structurally Different Branching Reagents: Comparison of Inimer, Divinyl and Trivinyl Cross-Linkers

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ABSTRACT: Inimer and multivinyl cross-linkers were used as branching reagents for gelation in atom transfer radical (co)polymerization (ATRP) with methyl acrylate (MA). A fully reacted 2-((2-bromopropionyl)oxy)ethyl acrylate (BrA) inimer produced a "T" shaped cross-linkage, from which three chains emanated out. In contrast, the reactions of divinyl cross-linker, ethylene glycol diacrylate (**2A**), and trivinyl cross-linker, 1,1,1,-trimethylolpropane triacrylate (**3A**), generated "X" shaped and "X̶" shaped cross-linkages, respectively, from which 4 and 6 chains radiated out. The ATRP of MA and BrA produced soluble branched polymers, but the addition of a small amount of **2A** into the reaction induced gelation and produced gels containing both "T" shaped and "X" shaped cross-linkages ("T&X" reaction). Three types of ATRP reactions, "T&X", "X" and "X̶" reactions, were performed to study the effect of cross-linkage structure on the experimental gel points and the properties of gels. Under the same molar ratio of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$, the "T&X" reactions had an experimental gelation occurred at lower MA conversions (earlier gelation) than the "X" reactions because of the faster intermolecular reactions in the "T&X" reactions. The earlier gelation in the "X̶" reaction, with respect to a comparable "X" reaction, was ascribed to the higher cross-linking efficiency and less required cross-linker amount for gelation when using trivinyl cross-linker. At complete conversion gels obtained in these comparable reactions showed an order of gel fraction: "T&X" ~ "X̶" > "X" and of gel swelling ratio: "T&X" > "X" > "X̶", due to the difference in the structure of branching reagents.

Introduction

The application of controlled radical polymerization (CRP)[1,2] techniques allows synthesis of branched polymers and gels with more homogeneous structure and preserved chain-end functionalities, mainly because of the features of fast initiation and reversible deactivation of propagating chains. Several groups have reported their results on the experimental gelation in the CRP processes by applying a divinyl cross-linker as the branching comonomer.[3−11] During the copolymerization of monovinyl monomer with divinyl cross-linker, the pendant vinyl group in the polymer chain is generated by the incorporation of a free cross-linker and consumed via its reaction with propagating radicals to produce an "X" shaped cross-linkage (cross-linker with both vinyl groups reacted), from which four polymer chains radiate out (Scheme 1). During the reactions, the distribution of cross-linkages among the primary chains is statistical and the feed ratio of cross-linker to initiator is adjustable. A system with high feed amount of cross-linker could experience gelation at certain conversion when the average number of cross-linkage per primary chain reaches a critical value.[11]

The recently developed self-condensing vinyl polymerization (SCVP) of AB* inimer (*ini*tiator-mono*mer* containing double bond A and initiator fragment B* in one molecule) provides a convenient, one-pot synthesis of hyperbranched polymers by using controlled polymerization techniques.[12−15] During the polymerization, the fragment B* can be converted to an active initiating group by an external stimulus and react with the chain-end vinyl group to generate a hyperbranched polymer containing a "T" shaped cross-linkage, with three radiating polymer chains. In an ideal case, without significant chain transfer and termination reactions, the number of initiating sites in a hyperbranched molecule is equal to its degree of polymerization, while the number of pendant vinyl groups is only one. When a monovinyl comonomer, M, was copolymerized with inimer, the SCVP was extended to self-condensing vinyl copolymerization which could produce (hyper)branched polymers with various functionalities and controlled degree of branching by using different functional comonomers and ratios of comonomer to inimer in the feed.[16]

It is important to note that in the SCVP reactions, every primary chain contains one cross-linkage or two cross-linking units (one at the chain end and one statistically along the chain, Scheme 1). Since there is no distribution of "T" shaped cross-linkage among different primary chains, no gelation occurs in the SCVP reactions even at complete conversion, although the system is very close to the gel point. Therefore, addition of a small amount of divinyl cross-linker at the high conversion in a SCVP reaction is expected to induce the gelation and produce a polymeric network.

In addition to the frequently used divinyl cross-linker, the application of trivinyl cross-linker for the radical-based copolymerization with monovinyl monomer could achieve greater degree of cross-linking than the divinyl reagent.[17] For instance, when a trivinyl cross-linker is used for the copolymerization, a fully reacted cross-linker ("X̶" shaped) connects three primary chains together, from which 6 chain segments emanate out (Scheme 1). If no intramolecular cyclization is considered, the copolymerization with either 1 equiv of divinyl cross-linker or $^2/_3$ equiv of trivinyl cross-linker should have the same ultimate cross-link density at complete conversion of vinyl species.

In this paper, we report the gelation behavior by atom transfer radical polymerization (ATRP)[18−21] of methyl acrylate (MA)

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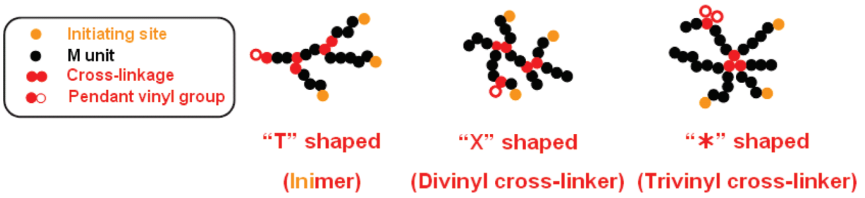
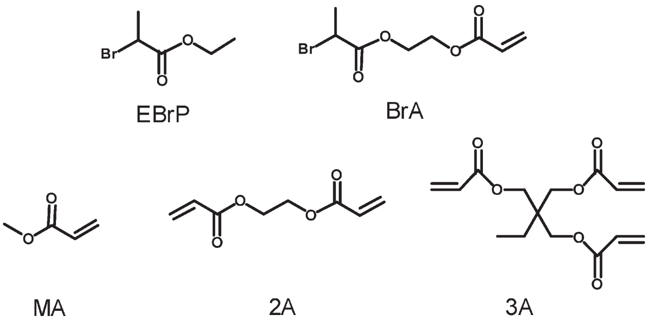
Scheme 1. Illustration of Cross-Linkage with Different Structures



Scheme 2. Synthesis of Polymer Networks by ATRP Using Different Branching Reagents



monomer with several structurally different branching reagents (Scheme 2). Inimer 2-((2-bromopropionyl)oxy)ethyl acrylate (BrA) was used as a branching reagent for gelation during copolymerization with MA and ethylene glycol diacrylate (**2A**), producing a polymer network containing both "T" shaped and "X" shaped cross-linkages. As comparison, divinyl cross-linker **2A** and trivinyl cross-linker 1,1,1,-trimethylolpropane triacrylate (**3A**), were also used as the branching comonomers for copolymerization with MA using ethyl 2-bromopropionate (EBrP) as initiator, producing insoluble networks. During the copolymerizations with different branching reagents, the total number of branching vinyl groups, i.e., the number of vinyl groups originating from the branching reagents, was kept the same. Specifically, an inimer or a divinyl cross-linker contains two branching vinyl groups because they connect two primary chains together after full reaction (Scheme 1). Similarly, a trivinyl cross-linker contains three branching vinyl groups. The experimental gel points based on the monomer conversion were determined and compared to each other in a systematic study when the species and molar ratios of branching reagents to initiator were varied. The gel fraction and the gel swelling ratio (GSR), determined at complete conversion of vinyl bonds, were compared with each other to illustrate the effect of cross-linkage structure on the gel properties.

Results and Discussion

As the first experiment, SCVP of BrA inimer and MA monomer was performed by using CuBr/*N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA) as the catalyst (10 mol % $CuBr_2$ of total copper species was preadded to the system) and *N*,*N*-dimethylformamide (DMF) as the solvent at 60 °C. This system is efficient for ATRP of acrylate-based monomers and provides fast initiation, high initiation efficiency and low polydispersity of primary chains.[22,23] During the SCVP reaction, the conversions of MA determined by GC increased with time and reached 99% at 21 h (Figure 1A).

The GPC measurement of polymer samples at different times confirmed formation of branched polymers with high molecular weight and broad molecular weight distribution (Figure 1B). At the same time, a sharp lower molecular-weight peak was still visible, representing the linear primary chains in the system. Therefore, the GPC-measured polymers indicate the presence of two types of polymer species: linear polymers and branched polymers. The peak-value molecular weight ($M_{p,GPC}$) of the linear polymers increased smoothly with MA conversion, indicating a "living" nature of the ATRP system. The intensity of the linear chain peak decreased with reaction time, suggesting the progressive incorporation of linear chains into the branched polymers. Determined by the multipeak splitting of the GPC curve using Gaussian function, the weight fraction of branched polymers among the GPC-measured polymers (f_{branch}) increased with the reaction time and reached f_{branch} = 95% at 21 h.

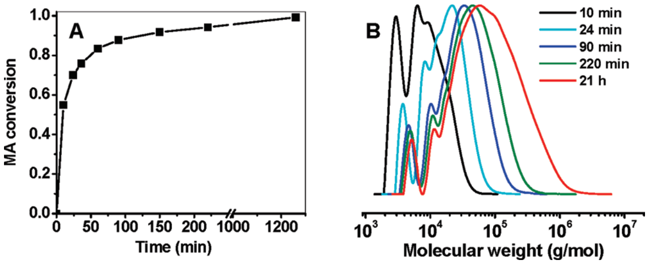
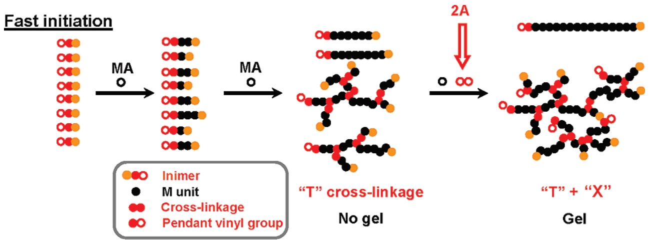


Figure 1. (A) Dependence of MA conversion on reaction time and (B) the GPC traces during the synthesis of polyMA-based branched polymers by SCVP of BrA and MA via ATRP; experimental conditions: $[MA]_0/[BrA]_0/[CuBr]_0/[CuBr_2]_0/[PMDETA]_0$ = 50/1/0.45/0.05/0.5, $[MA]_0$ = 6.0 M, in DMF at 60 °C; linear poly(methyl methacrylate) (polyMMA) standards were used for THF GPC calibration.

Scheme 3. Illustration of Branched Polymers Synthesized by SCVP of MA and BrA Using ATRP and the Subsequent Gelation Triggered by Addition of Small Amount of Divinyl Cross-Linker, 2A



Gelation during ATRP of Inimer, Monomer, and Divinyl Cross-Linker. Although SCVP of BrA and MA alone could only produce soluble branched polymers during the ATRP reaction, addition of small amount of divinyl cross-linker, such as 0.1 equiv of **2A**, at high conversion of MA induced gelation in the system (Scheme 3). After addition of **2A**, the system became a copolymerization of BrA, MA and **2A**. The reactions of **2A**, especially the reaction of pendant vinyl groups, statistically introduced extra "X" shaped cross-linkage into the branched polymers and resulted in a macroscopic gelation in the system.

Since "T" shaped cross-linkage alone cannot induce gelation, a gel formed after the addition of **2A** in the ATRP system must contain both "T" shaped and "X" shaped cross-linkages. During these processes, two parameters are considered to affect the experimental gel points, the gel fraction and the GSR. The first parameter is the distribution of "X"

Table 1. Synthesis of PolyMA-Based Gels by ATRP of BrA, MA, and 2A [a]

entry	$[\mathbf{2A}]_0/[\mathrm{BrA}]_0$	$\mathrm{convn_{MA}}$ (adding **2A**)[b]	$\mathrm{convn_{MA,gel,expt}}$[c]	gel fraction (r_{gel})[d]	GSR[e]
1	0	no gelation			
2	0.1	0.99	~1	0.42 ± 0.11	48.9 ± 5.6
3	0.1	0.94	~1	0.49 ± 0.08	27.7 ± 3.2
4	0.1	0.80	~1	0.64 ± 0.05	24.2 ± 1.4
5	0.1	0.00	0.98	0.69 ± 0.05	21.5 ± 1.5

[a] Experimental conditions: $[\mathrm{MA}]_0/[\mathbf{2A}]_0/[\mathrm{BrA}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{PMDETA}]_0$ = 50/0.1/1/0.45/0.05/0.5, $[\mathrm{MA}]_0$ = 6.0 M; all reactions were stopped after 2 days in order to reach the complete conversion of vinyl species. [b] Conversion of MA when 0.1 equiv of **2A** was added. [c] Conversions of MA immediately before gelation. [d] The averaged value of gel fraction (r_{gel}) based on four parallel measurements (Supporting Information). [e] The averaged value of gel swelling ratio (GSR) in THF based on four parallel measurements (Supporting Information).

shaped and "T" shaped cross-linkages within the gels, which can be controlled by varying the addition time of a fixed amount of **2A** cross-linker. The second parameter is the molar fraction of "X" shaped to "T" shaped cross-linkages, which can be adjusted by changing the molar ratio of added cross-linker to inimer in the system.

2A (0.1 equiv) was added into four ATRP reactions at different MA conversions varying from 99% to 0% (Table 1). The terpolymerization of inimer, monomer and divinyl cross-linker with molar ratios of $[\mathrm{MA}]_0/[\mathbf{2A}]_0/[\mathrm{BrA}]_0$ = 50/0.1/1 resulted in gelation in all of these four reactions. After stopping the reactions at complete conversion of double bonds, the gel fraction and GSR were determined and compared with each other (Table 1 and Figure 2). The results indicate that an earlier addition of 0.1 equiv of **2A** into the system resulted in a gel with more compact structure because the "X" shaped cross-linkage, originating from the fully reacted **2A**, was more homogeneously mixed with the "T" shaped cross-linkage in the network. In other words, a higher gel fraction and a lower GSR were obtained when 0.1 equiv of **2A** was added at lower MA conversion.

Effect of Cross-Linkage Structure on Experimental Gel Points. The addition of **2A** cross-linker into the ATRP of inimer and monovinyl monomer produced insoluble gels containing both "T" shaped and "X" shaped cross-linkages. The fractions of these two cross-linkages in the gels could be changed by varying the amount of added **2A**. On the other hand, the use of trivinyl cross-linker, e.g., **3A**, for radical copolymerization with monovinyl monomer could also produce a polymer network with a more compact structure, as compared to the use of 1.5 equiv amount of divinyl cross-linker under similar conditions. The incorporation of a trivinyl cross-linker into polymer chain generates two pendant vinyl groups. If one of them is consumed by intramolecular cyclization, the other one could still have chance to connect a second chain and form an intermolecular cross-linkage. In contrast, if the pendant vinyl group from an incorporated divinyl cross-linker reacts intramolecularly, this cross-linker would have no contribution to the increase of the molecular weight of branched polymers. Therefore, the use of trivinyl cross-linker for the copolymerization could achieve a network with higher intermolecular cross-link density than the use of 1.5 equiv amount of divinyl cross-linker under similar conditions.[17,24]

By systematically varying the amounts of **2A** and/or **3A** cross-linkers during the ATRP reactions, the effect of cross-linkage structure on the experimental gel points were studied. Three systems with different cross-linkages were explored, including (1) "T&X" reactions by ATRP of BrA, MA and **2A**, (2) "X" reactions by ATRP of MA and **2A** using EBrP as initiator, and (3) "~~X~~" reactions by ATRP of MA and **3A** using EBrP as initiator. The molar ratio of $[\mathrm{vinyl_{branch}}]_0/[\mathrm{R{-}Br}]_0$ was kept constant in the comparable reactions, where $[\mathrm{vinyl_{branch}}]_0$ is the initial concentration of equivalent double bonds residing from the branching reagents, e.g., BrA, **2A** and **3A**. Since a fully reacted BrA forms a "T" shaped cross-linkage and connects two primary chains together, the number of equivalent vinyl groups from a BrA inimer is 2. In other words, an inimer can be regarded as the product of monofunctional initiator and divinyl cross-linker after a one-step addition reaction, which combines the pendant vinyl group and chain-end initiating site together. The effect of cross-linkage structure on the experimental gelation during the series of ATRP reactions were studied by applying various values of $[\mathrm{vinyl_{branch}}]_0/[\mathrm{R{-}Br}]_0$ and the results are listed in Table 2.

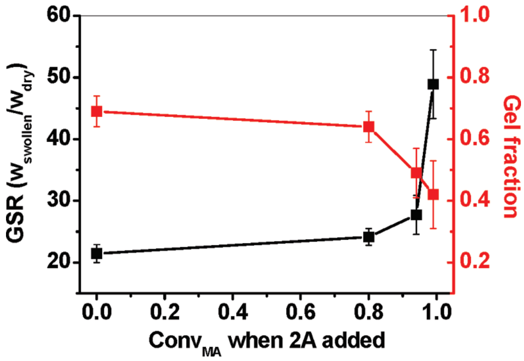


Figure 2. Effect of addition time of **2A** (0.1 equiv) on gel fraction and GSR during the ATRP reactions; experimental conditions: $[\mathrm{MA}]_0/[\mathbf{2A}]_0/[\mathrm{BrA}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr_2}]_0/[\mathrm{PMDETA}]_0$ = 50/0.1/1/0.45/0.05/0.5, $[\mathrm{MA}]_0$ = 6.0 M in DMF (Table 1).

An efficient ATRP system with high initiation efficiency and low polydispersity of primary chains was used in all reactions, which ensured the added initiators were quickly converted into primary chains at low MA conversion, i.e., $[\mathrm{P{-}Br}]_t \sim [\mathrm{R{-}Br}]_0$ = 0.12 M. During the copolymerization of MA and various amounts of **2A** by using BrA as initiator, all free BrA molecules were quickly consumed and generated a pendant vinyl group at the α-chain end (Scheme 3). Reaction of this α-end acrylate group with propagating radical generated a "T" shaped cross-linkage, and its conversion was equal to the conversion of MA monomer, since all acrylate groups in the system have the similar reactivity.[8,25] Thus, the ratio of "T" shaped cross-linkage to primary chain is proportional to MA conversion. This situation is different from the ATRP of **2A** and MA by using EBrP as initiator, where the ratio of "X" shaped cross-linkage (a **2A** with both vinyl bonds reacted) to primary chain is proportional to the square of MA conversion.[25] Therefore, the generation rate of the total cross-linkage (both "T" and "X") in a "T&X" reaction was faster than that during the ATRP of MA and comparable amount of **2A** in an "X" reaction. This possible reason explained the earlier experimental gelation at lower MA conversion in the "T&X" reactions than in the "X" reactions under the same value of $[\mathrm{vinyl_{branch}}]_0/[\mathrm{R{-}Br}]_0$ (Figure 3). It is important to note that the use of inimer as a branching

Table 2. Comparison of ATRP Reactions by Using Different Branching Reagents[a]

$[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$[b]	$\text{convn}_{\text{MA,gel,expt}}$[c]			gel fraction (r_{gel})[d]			GSR[e]		
	T&X	X	~~X~~	T&X	X	~~X~~	T&X	X	~~X~~
1.92			0.98						
2.20	0.98	0.97	0.94	0.64 ± 0.07	0.45 ± 0.10	0.53 ± 0.09	21.5 ± 1.8	17.9 ± 1.5	15.3 ± 1.6
2.67	0.91	0.92	0.84	0.74 ± 0.06	0.58 ± 0.07	0.71 ± 0.05	10.6 ± 1.4	8.16 ± 1.48	6.50 ± 1.45
3.00	0.80	0.86	0.78	0.84 ± 0.05	0.77 ± 0.05	0.86 ± 0.03	5.71 ± 1.06	5.81 ± 0.91	4.75 ± 1.15
4.00	0.69	0.79	0.67	0.90 ± 0.03	0.85 ± 0.03	0.90 ± 0.03	4.18 ± 1.04	3.71 ± 0.84	3.45 ± 0.90
6.00	0.55	0.65	0.55	0.91 ± 0.03	0.89 ± 0.03	0.93 ± 0.01	2.78 ± 0.71	2.68 ± 0.82	2.40 ± 0.60
10.0	0.41	0.48	0.40	0.97 ± 0.01	0.95 ± 0.02	0.97 ± 0.02	2.17 ± 0.60	2.04 ± 0.58	2.14 ± 0.55
20.0	0.32	0.38	0.30	1.00 ± 0.03	0.98 ± 0.02	1.00 ± 0.02	1.80 ± 0.34	1.80 ± 0.22	1.85 ± 0.37

[a] Experimental conditions. (1) "T&X" reaction: ATRP of MA, BrA and **2A** with $[\text{MA}]_0/[\mathbf{2A}]_0/[\text{BrA}]_0/[\text{CuBr}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 50/A/1/0.45/0.05/0.5$; 2). "X" reaction: ATRP of MA and **2A** with $[\text{MA}]_0/[\mathbf{2A}]_0/[\text{EBrP}]_0/[\text{CuBr}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 50/B/1/0.45/0.05/0.5$; 3). "~~X~~" reaction: ATRP of MA and **3A**: $[\text{MA}]_0/[\mathbf{3A}]_0/[\text{EBrP}]_0/[\text{CuBr}]_0/[\text{CuBr}_2]_0/[\text{PMDETA}]_0 = 50/C/1/0.45/0.05/0.5$. All reactions were performed with $[\text{MA}]_0 = 6.0$ M in DMF at 60 °C and stopped after 2 days in order to reach the complete conversions. [b] $[\text{Vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0 = (2 + 2 \times \text{A})$ for "T&X" reaction, $(2 \times \text{B})$ for "X" reaction, and $(3 \times \text{C})$ for "~~X~~" reaction. For comparable reactions with the same value of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$, $A = \text{B-1}$ and $C = 2\text{B}/3$. [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. [d] The averaged value of gel fraction based on four parallel measurements (Supporting Information). [e] The averaged value of gel swelling ratio (GSR) in THF based on four parallel measurements (Supporting Information).

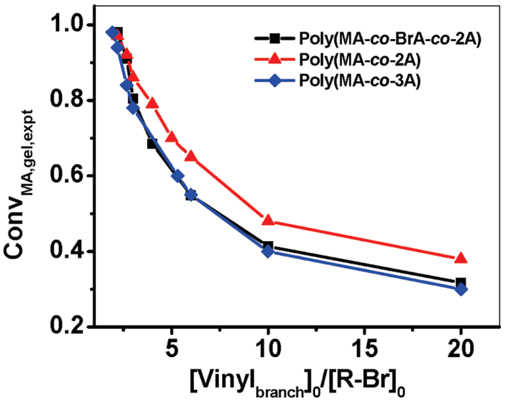


Figure 3. Comparison of experimental gel points based on MA conversions ($\text{Conv}_{\text{MA,gel,expt}}$) in three ATRP reactions: "T&X" reactions for synthesis of poly(MA-*co*-BrA-*co*-**2A**), "X" reactions for synthesis of poly(MA-*co*-**2A**), and "~~X~~" reactions for synthesis of poly(MA-*co*-**3A**); experimental conditions and results are listed in Table 2.

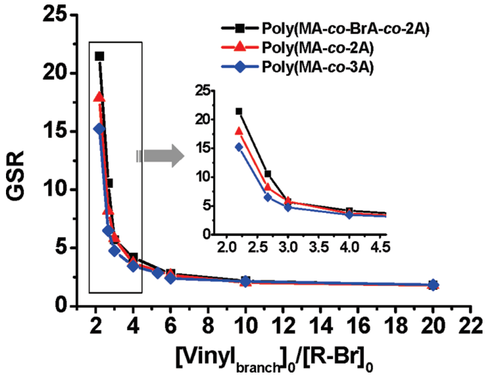


Figure 4. Comparison of GSR among the three comparable ATRP reactions: "T&X" reactions for synthesis of poly(MA-*co*-BrA-*co*-**2A**), "X" reactions for synthesis of poly(MA-*co*-**2A**), and "~~X~~" reactions for synthesis of poly(MA-*co*-**3A**). Experimental conditions and results are listed in Table 2.

reagent is not considered in Flory's classic gel theory. The incorporation of "T" shaped cross-linkage into primary chain is not statistical and the sole use of inimer as branching reagent can not produce gels.

Compared to the model "X" reactions by ATRP of MA and **2A**, the use of two-thirds the amount of **3A** as cross-linker in the "~~X~~" reactions also resulted in an earlier experimental gelation at lower MA conversion, which was in agreement to Flory's theory. On the basis of Flory's statement, the critical gel point in the "~~X~~" reactions by using trivinyl cross-linker should be reached when the weight-average number of cross-linking units per primary chain is half.[26] This is lower than the unity value required for the gelation in the "X" reactions. All reported CRP reactions showed a delayed experimental gelation, as compared to the Flory's theoretical expectation, primarily due to the inevitable intramolecular cyclization reactions. Nevertheless, the general trend of experimental gel points still follows the theory that the gelation in a reaction with trivinyl cross-linker as branching reagent occurs at a lower monomer conversion than that using 1.5 equiv of divinyl cross-linker under similar conditions.

Effect of Cross-Linkage Structure on Gel Fraction and GSR. The different branching reagents used for the ATRP with monovinyl monomer affect the structure of the obtained gels, and consequently the gel fraction and the value of GSR. When low molar ratio of branching reagents to initiating sites was used (e.g., $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0 = 2.20$, Table 2), the fraction of gels obtained in the "T&X" reactions by ATRP of MA, BrA and **2A**, showed a higher value ($r_{gel} = 0.64$) than that in the "X" reactions by ATRP of MA and **2A** ($r_{gel} = 0.45$). This result indicates that the use of inimer as a branching comonomer increased the intermolecular cross-linking efficiency in the "T&X" reactions, as compared to the "X" reactions under the same value of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$.

The yield of intermolecular cross-linking by using **3A** as branching comonomer was also higher than that with **2A** because the incorporation of a free **3A** into polymer chain generates two pendant vinyl groups (Scheme 1). Intermolecular reaction of either one of the two pendant vinyl groups produces an intermolecular cross-linkage, which has a higher possibility than the intermolecular reaction by using **2A** cross-linker.[17] This difference explains the higher gel fraction in the "~~X~~" reactions, as compared to the "X" reactions during the ATRP reactions.

In all of the three systems, the gel fraction increased with the initial molar ratio of branching reagent to initiator and approached unity when $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0 = 20.0$ (Table 2). Consequently, the difference in gel fractions among these three reactions became smaller, indicating a diminished effect of cross-linkage structure on gel fraction when the cross-link density was high.

The effect of cross-linkage structure on the GSR among these three systems is shown in Figure 4. The results indicate that the difference in the values of GSR is larger when less branching reagents were used. For example, the value of GSR was 21.5 in the "T&X" reaction when $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0 = 2.2$, which was higher than the values in the "X" reaction (GSR = 17.9) and in the "Ӿ" reaction (GSR = 15.3). The differences in gel swelling could be ascribed to the different structure of the cross-linkage in the polymeric network, since 3, 4, and 6 chains radiate from the "T" shaped, "X" shaped and "Ӿ" shaped cross-linkages, respectively. As expected, the effect of cross-linkage structure on GSR became weaker with the increase of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$ in the systems and finally became undetectable when the ratio of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$ was larger than 10.0 (Figure 4).

Conclusions

Experimental gelation in a series of reactions by ATRP of MA with different branching reagents was studied. When BrA inimer was used as the sole branching reagent, its ATRP with MA monomer generated soluble branched polymers containing "T" shaped cross-linkage. Addition of a small amount of divinyl cross-linker **2A** in the system induced gelation and produced network containing both "T" shaped and "X" shaped cross-linkages. The molar ratio and distribution of these two cross-linkages in the network affected the gel fraction and the GSR, depending on the addition time and added amount of **2A**. The effect of cross-linkage structure on the experimental gel points were systemically studied by applying three types of ATRP reactions with various molar ratios of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$, including "T&X", "X", and "Ӿ" reactions by using inimer and divinyl cross-linker mixture, divinyl cross-linker, and trivinyl cross-linker, respectively, as branching reagents. Under the same molar ratio of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$, the experimental gel points based on MA conversions were earlier in the "T&X" and "Ӿ" reactions than in the "X" reactions. The gel fraction and the GSR were also affected by the cross-linkage structure. For parallel reactions under the same molar ratio of $[\text{vinyl}_{\text{branch}}]_0/[\text{R}-\text{Br}]_0$, the gel fraction followed an order: "T&X" ~ "Ӿ" > "X" and the GSR decreased progressively as "T&X" > "X" > "Ӿ". These results illustrated the application of inimer for gelation during controlled radical polymerization and expanded our knowledge of gelation behavior by using branching comonomers with various structures.

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Supporting Information Available: Text giving details on synthesis and characterization of polymers by using different branching reagents. This material is available free of charge via the Internet at http://pubs.acs.org.

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