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Atom Transfer Radical Copolymerization of Monomer and Cross-Linker under Highly Dilute Conditions

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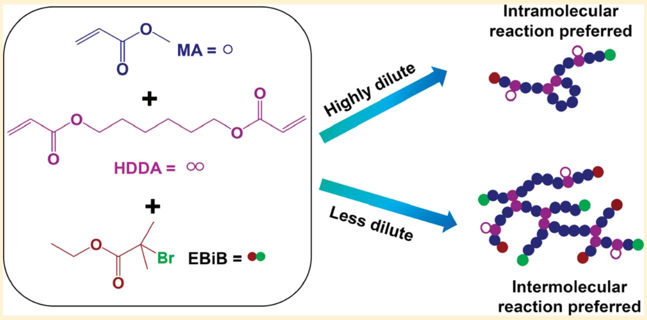

ABSTRACT: The influence of dilution on the degree of intra- or intermolecular cross-linking reactions during the copolymerization of a monomer and a divinyl cross-linker via atom transfer radical polymerization (ATRP) technique was studied. To maximize intramolecular cross-linking, highly dilute systems with 0.5−10 vol % of monomer plus cross-linker vs solvent were used. The fraction of branched polymers formed through intermolecular consumption of pendant vinyl groups was calculated for each system through multipeak splitting of the gel permeation chromatography (GPC) curves. Progressive dilution of the reaction media resulted in the formation of products containing less branched polymers. Absolute molecular weights and compactness of the formed polymers determined by GPC with a multiangle laser light scattering (MALLS) detector further confirmed the formation of majority nonbranched polymer structures in more dilute systems, indicating an enhanced level of intramolecular cross-linking reactions in this case.

INTRODUCTION

The continuous development of controlled radical polymerization (CRP)[1,2] techniques, such as atom transfer radical polymerization (ATRP),[3−6] during the past decade not only facilitated the preparation of linear polymers with predetermined molecular weights and narrow molecular weight distribution but also allowed the facile synthesis of copolymers with various branched architectures, including star polymers, graft/brush polymers, randomly branched polymers, and even cross-linked polymer networks or insoluble gels.[7,8] Continuing studies disclosed that randomly branched polymers, or insoluble gels, obtained from the simple copolymerization of a monovinyl monomer and a small amount of divinyl cross-linker via CRP resulted in a more homogeneous network microstructure and an absence of microgel generation, as compared to networks prepared by conventional free radical polymerization (FRP).[9−20] This can be attributed to the slower but concurrent growth of all polymer chains in a CRP, which gives chains sufficient time for relaxation and diffusion during the periods of dormancy. The chain diffusion facilitates intermolecular contact of functional groups, i.e., radical centers and pendant vinyl groups, in the polymerization system allowing them to react with each other, thereby ensuring the evolution of a more ordered copolymer network.

Although a polymer network with more evenly distributed cross-linking units along the polymer chain can be achieved by CRP, the branching copolymerization process usually exhibits nonideal gelation behavior.[13−15,21−27] The monomer conversion at the experimental gelation point was commonly higher than the value predicted by classical Flory−Stockmayer theory.[28,29] Furthermore, the average number of cross-linkage per primary chain, i.e., cross-linker with both vinyl groups reacted, present at the experimental gel point was typically 1 or 2 orders of magnitude larger than those predicted by Flory's theory. This discrepancy is mainly attributed to the occurrence of intramolecular cross-linking reactions, which are neglected during theoretical predictions. The intramolecular cross-linking reactions can be suppressed when using CRP compared to FRP, but they cannot be avoided, especially when the copolymerization is conducted under relatively dilute conditions, since the polymer chains cannot readily interpenetrate each other. Thus, it is critically important to study the effect of concentration of reactive reagents in a copolymerization system on intramolecular reaction, which would then provide guidelines for the design of suitable reaction conditions to generate different targeted structures, soluble branched polymers, or insoluble gels. Recently, various models and methods have been used to evaluate the effect of dilution on gelation processes, especially the probabilities of intra- or intermolecular cross-linking.[19,26,30−33] These reports confirm the aforementioned point: dilution enhances the possibility of intramolecular cross-linking reactions. However, most of these studies focused on the copolymerization conducted in relatively concentrated systems and sought to determine the critical concentration above which the intramolecular reactions could be significantly limited. In other words, most reports concentrated on improving the quality of the branching copolymerization reaction and ensuring that the majority of the pendant vinyl groups were consumed by intermolecular cross-linkage. Few reports studied cross-linking reactions occurring under highly dilute conditions.[34]

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In the present work, we conducted a systematic study on the copolymerization of a monovinyl monomer and a divinyl cross-linker under highly dilute conditions, trying to evaluate how efficiently can dilution enhance intramolecular cross-linking and determine the critical concentration under which the intermolecular cross-linking reactions can be significantly suppressed, resulting in the formation of uniform linear copolymers with some intracyclic structures along the polymer chains. To achieve these goals, methyl acrylate (MA) was copolymerized with 1,6-hexanediol diacrylate (HDDA) under a series of dilute conditions, 0.5−10 vol % of monomer and cross-linker compared to solvent, using activators generated by electron transfer (AGET) ATRP.[35,36] The fraction of branched polymers formed through intermolecular cross-linking was calculated for each concentration at different monomer conversions. In addition, chain extension of *n*-butyl acrylate (BA) from the polymers generated in the dilute systems was also conducted to further compare the different polymer structures.

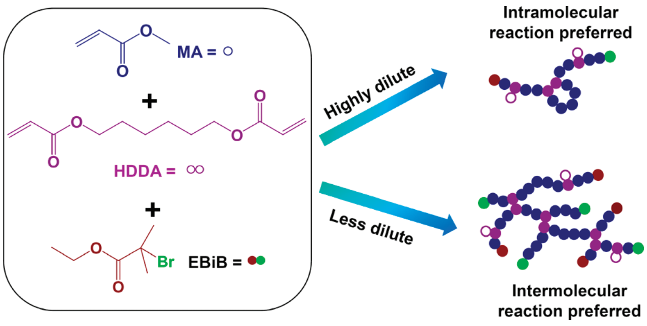
EXPERIMENTAL SECTION

Materials. Methyl acrylate (MA, 99%), *n*-butyl acrylate (BA, 99%), and 1,6-hexanediol diacrylate (HDDA) were purchased from Aldrich, purified by passing through a column filled with basic alumina to remove the inhibitor and/or antioxidant, and then stored at −5 °C. Tris-(2-(dimethylamino)ethyl)amine (Me_6TREN)[37] was purchased from ATRP Solutions and used as received. All other reagents, ethyl 2-bromoisobutyrate (EBiB, 98%), $CuBr_2$ (98%), copper powder (<75 μm, Cu(0), 99%), and solvents were purchased from Aldrich and used as received.

Copolymerization of MA and HDDA by ATRP under Dilute Conditions. Similar procedures were used for the copolymerization under different degrees of dilution. In a typical experiment, the copolymerization of 1 vol % of MA and HDDA compared to dimethyl sulfoxide (DMSO) was conducted by adding MA (0.21 mL, 2.3 mmol), HDDA (0.15 mL, 0.67 mmol), $CuBr_2$ (3.1 mg, 0.014 mmol), Me_6TREN (18 μL, 0.069 mmol), and DMSO (2 mL) to a Schlenk flask. The flask was sealed and then degassed by five freeze−pump−thaw cycles. During the final cycle, the flask was filled with nitrogen before copper powder (2.9 mg, 0.046 mmol) was added to the frozen mixture. The flask was sealed with a glass stopper, then evacuated, and backfilled with nitrogen several times; an additional 34 mL of deoxygenated DMSO was added to the flask before it was immersed in an oil bath thermostated at 30 °C. Finally, the deoxygenated initiator EBiB (6.7 μL, 0.046 mmol) was injected into the reaction system via a syringe through the side arm of the Schlenk flask to initiate the polymerization. Samples were taken at timed intervals to measure MA conversions by gas chromatography (GC) and to determine molecular weights of the formed polymers by gel permeation chromatography (GPC).

Characterization. Monomer conversions were determined by GC with a Shimadzu GC-14A gas chromatograph equipped with a capillary column (DB-Wax, 30 m × 0.54 mm × 0.5 μm, J&W Scientific). DMSO was used as internal standard for calculation of monomer conversions. After being diluted with THF and filtration through 200 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 index (M_w/M_n) were determined with a calibration based on linear polyMMA standards using WinGPC 6.0 software from PSS. Area fractions of different polymer species in one GPC curve were determined by multipeak splitting of the GPC curve using Gaussian functions. The detectors employed to measure the absolute molecular weights were a triple detector system containing RI detector (Wyatt Technology, Optilab REX), viscometer detector (Wyatt Technology, ViscoStar), and a multiangle laser light scattering (MALLS) detector (Wyatt Technology, DAWN EOS) with the light wavelength at 690 nm. Absolute molecular weights were determined using ASTRA software from Wyatt Technology.

Scheme 1. Copolymerization of MA and HDDA by ATRP under Different Dilution Conditions



RESULTS AND DISCUSSION

As stated in the Introduction, the concentration of the monomers and cross-linkers in the reaction media can significantly affect the copolymerization process of monovinyl monomers and divinyl cross-linkers via CRP, especially the mode of consumption of pendant vinyl groups by either an intra- or intermolecular cross-linking reaction. A more concentrated system can promote intermolecular reactions, initially resulting in the formation of branched polymers which can further generate a gel network at high monomer conversion. A highly dilute system reduces the possibility for overlapping of polymer chains in solution, thereby limiting interchain cross-linking and formation of highly branched polymers, while generating polymer chains with intrachain cyclic structures along the polymer chain (Scheme 1). In this paper, the copolymerization of MA and HDDA was conducted under relatively dilute conditions to determine the effect of concentration on the degree of intra- and intermolecular reactions of pendant vinyl groups in the more dilute systems. The performance, or level of control, of the polymerization in a highly dilute ATRP system was also studied.

Homopolymerization of MA under Dilute Conditions. The active Cu(0)/$CuBr_2$/Me_6TREN catalyst was selected for the current system in order to complete the polymerization in a reasonable time and to reach high monomer conversion, up to 90%, under high dilution conditions. The control of polymerization, including the polymerization kinetics, initiation efficiency, and uniformity of polymer chain, was first evaluated though the homopolymerization of MA under a series of different concentrations of monomer. The molar ratios of reagents were set at $[MA]_0/[EBiB]_0/[Cu(0)]_0/[CuBr_2]_0/[Me_6TREN]_0 = 80/1/1/0.3/1.5$, and polymerization was conducted in DMSO at 30 °C, with 0.5, 1.0, or 5.0 vol % of monomer compared to solvent. The trends of the kinetic plots for the three experiments are similar: polymerization was initially relatively fast, then slowed down, and even stopped after a certain time, which was probably caused by termination reactions and loss of end-group functionality. In order to maintain a reasonable and comparable polymerization rates, reactions were carried out in the presence of Cu(0) as a reducing agent. Although the concentration of radicals and

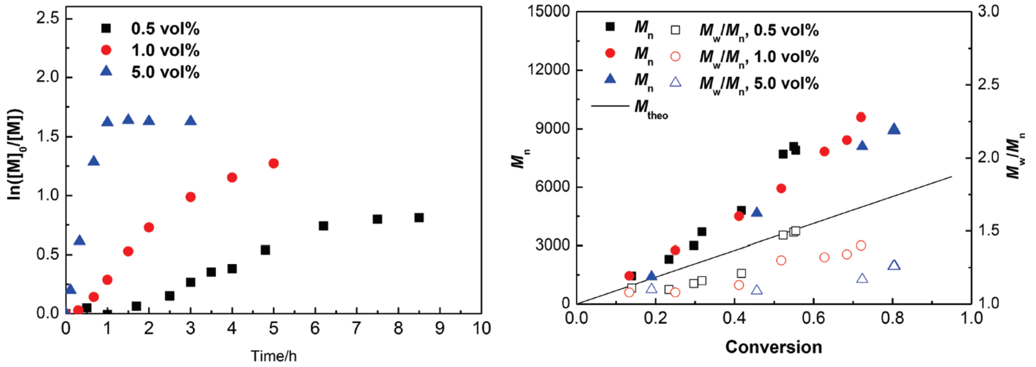


Figure 1. Homopolymerization of MA under a series of dilutions via AGET ATRP. Polymerization conditions: $[MA]_0/[EBiB]_0/[Cu(0)]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 80/1/1/0.3/1.5, in DMSO, 30 °C, 0.5, 1.0, and 5.0 vol % of MA vs DMSO.

Table 1. Fraction of Branched Polymers Formed under Various Dilutions

			fraction of branched polymers (%)[c]		
entry	$[MA]_0/[HDDA]_0/[EBiB]_0$[a]	concn (vol %)[b]	$conv_{MA}$ ~20%	$conv_{MA}$ ~50%	$conv_{MA}$ ~70%
S1-0.5	50/15/1	0.5	0	0	0
S1-1.0	50/15/1	1.0	12	38	48
S1-2.4	50/15/1	2.4	50	n/a	80
S2-2.4	50/10/1	2.4	37	58	65
S2-5.0	50/10/1	5.0	42	70	82
S2-10.0	50/10/1	10.0	n/a	76	gel

[a] $[MA]_0/[HDDA]_0/[EBiB]_0/[Cu(0)]_0/[CuBr_2]_0/[Me_6TREN]_0$ = 50/−/1/1/0.3/1.5 in DMSO at 30 °C. [b] The volume percentage of MA plus HDDA vs DMSO. [c] The area percentage of the branched polymer peak according to the multipeak splitting of the GPC curve using Gaussian function.

consequently the rate of termination were similar in all systems, the fraction of dead chains increased with dilution. This is so because the absolute concentration of dead chains was approximately constant (similar termination rates), but the concentration of dormant species or initiators was progressively decreased with dilution, resulting in a larger fraction of terminated chains.[38]

Moreover, as expected, the polymerization was slower under more dilute conditions, 0.5 vol %. While the initiation efficiency was essentially 100% for the less dilute system, 5.0 vol %, it was progressively limited in the more dilute systems, 0.5 or 1 vol %, to 65−70%. The formed polymers displayed uniform structure at low monomer conversion, with M_w/M_n around 1.1, but this value gradually increased as the polymerization continued to ca. 1.4−1.5 at the end of the polymerization. This should be caused by the loss of end-group functionality: certain polymer chains stopped growing and coupled with each other. The termination reactions, as well as low initiation efficiency, also resulted in formation of polymers with much higher molecular weight than the theoretically calculated value, as shown in Figure 1. However, considering the highly diluted polymerization in these experiments, the level of control over the polymerization was still acceptable.

Copolymerization of MA and HDDA under Dilute Conditions. The copolymerizations were conducted under similar conditions to those used for the homopolymerization. The only difference was that the targeted degree of polymerization for MA was set as 50, and divinyl cross-linkers, HDDA, were introduced to the system, with molar ratio of $[MA]_0/[HDDA]_0$ set at 50/15 (S1-0.5, S1-1.0, and S1-2.4, Table 1) or 50/10 (S2-2.4, S2-5.0, and S2-10.0, Table 1). Note that the total vinyl group amount in the former system was kept the same as that employed for the homopolymerization. Typical polymerization conditions and results are summarized in Table 1 and Figures 2 and 3.

The results were similar to those obtained in the homopolymerization process. The polymerization rate gradually decreased as the polymerization progressed and finally reached an almost steady state after certain monomer conversion for all the reactions. These results can also be explained by the relatively high radical concentration and increased termination reactions, as discussed above (Figure 2a). The reaction was faster in the relatively more concentrated system, 5.0 vol %, and the molecular weight of the primary polymer chains, obtained from the GPC peak value (M_p), smoothly increased as the polymerization continued. Only slightly higher M_p than the theoretically calculated molecular weights (assuming the pendant vinyl groups did not react) indicated relatively high initiation efficiency and a well-controlled polymerization process. The M_p of polymers formed in the more dilute systems were higher than the calculated value (Figure 2b), indicating poorer control, as expected. However, the molecular weight distribution of the primary chains was still narrow.

A fast increase of the weight-average molecular weight M_w and M_w/M_n of formed polymers was observed, especially for the polymers obtained in a more concentrated system, even in the presence of less amount of cross-linking agent (S2-5.0, Figure 3a). This is due to the formation of branched polymers through intermolecular reactions between the pendant vinyl groups along one polymer chain with the Br end group from another polymer chain. The generation of the branched polymers through the interchain cross-linking reactions was further

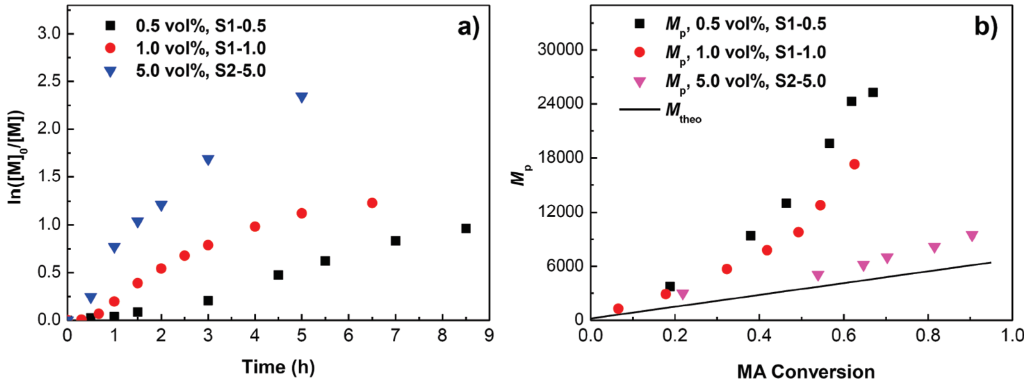


Figure 2. Copolymerization of MA and HDDA under high dilution: (a) kinetic plots ln([M]$_0$/[M]) vs time; (b) peak value of the apparent molecular weight for the primary chains M_p vs MA conversion. Polymerization conditions are summarized in Table 1.

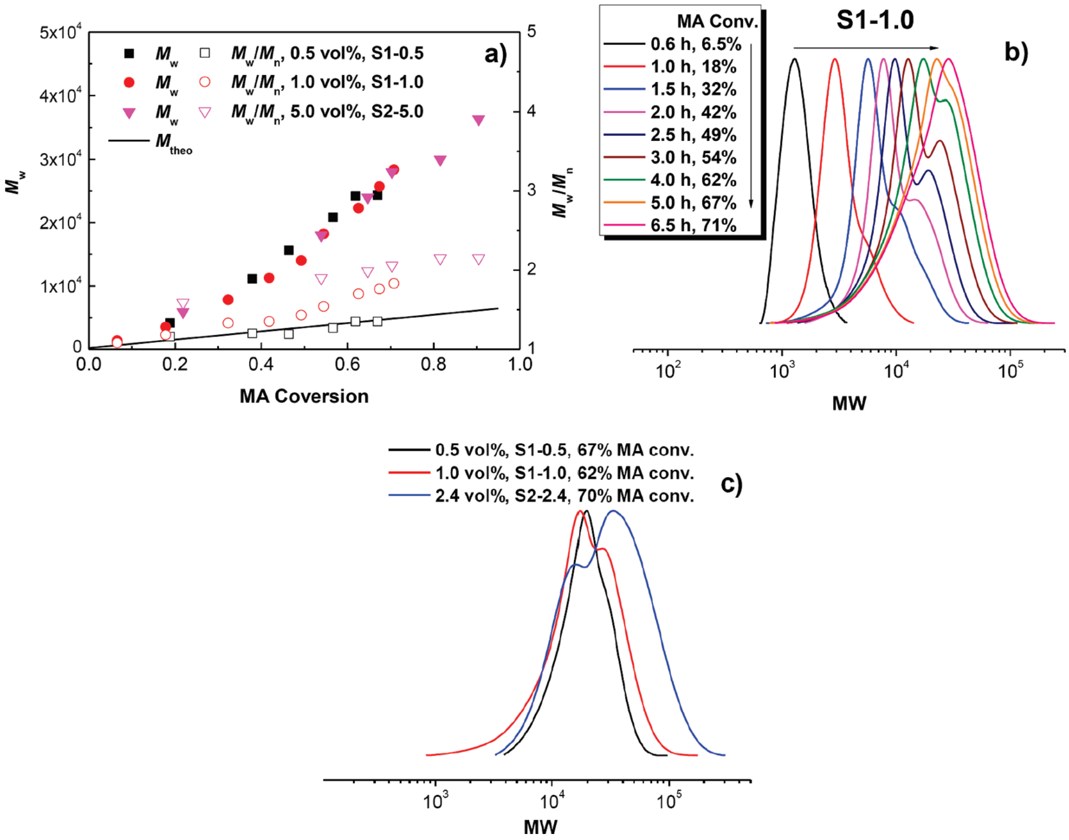


Figure 3. Copolymerization of MA and HDDA under high dilution: (a) weight-average molecular weight M_w of the formed polymers vs MA conversion; (b) typical GPC traces of copolymers formed during the polymerization, S1-1.0; (c) GPC traces of polymers formed under different dilution conditions at similar MA conversion. Polymerization conditions are summarized in Table 1.

confirmed by the appearance of a shoulder in the GPC traces at higher monomer conversion. Typical GPC traces of the polymers formed during the copolymerization process are shown in Figure 3b for the copolymers prepared at 1 vol % of comonomers vs solvent. Two peaks appeared in the GPC traces after a certain reaction time. It is worth noting that the peak shown at the higher molecular weight region was assumed to represent the branched polymers formed through the intermolecular cross-linking reactions, while the peak at low molecular weight region was assigned to represent the primary polymer chains and/or polymer chains containing intramolecular cyclic structures. The area percentage of the peak at higher molecular weight slowly increased with the monomer conversion, indicating more branched polymers were generated as the reaction continued. Comparing the GPC traces of polymers formed under different dilutions at similar monomer conversion (Figure 3c), one can observe less branched polymers generated in the more dilute systems, even in the presence of more cross-linker, 0.5 and 1.0 vol %, whereas a larger branched polymer peak can be observed in the GPC traces for 2.4 vol % case, in which less cross-linking agent was used.

For a better comparison of the amount of branched polymers formed in different systems, the fraction of branched polymers formed through interchain reactions was calculated by peak splitting the GPC curves of polymers formed at different dilutions at various monomer conversions. As summarized in Figure 4 and Table 1, with the molar ratio $[\mathrm{MA}]_0/[\mathrm{HDDA}]_0/[\mathrm{EBiB}]_0 = 50/15/1$, increase of the concentration of the comonomers from 1.0 to 2.4 vol % resulted in an increase in the fraction of branched polymers from 48% to nearly 80% (at ca. 70% monomer conversion), whereas there is almost no branched polymers present in the highly dilute 0.5 vol % system, at similar monomer conversion, 70%. This is also observed for the relatively more concentrated systems in which less HDDA was introduced to the system to reduce the cross-linking reactions. The ratio of $[\mathrm{MA}]_0/[\mathrm{HDDA}]_0/[\mathrm{EBiB}]_0$ was changed to 50/10/1, and in these cases, at 70% MA conversion, 65% and 82% of branched polymers were obtained in the 2.4 and 5.0 vol % systems, respectively, while insoluble gels were generated in the more concentrated system, 10 vol % of monomer and cross-linker compared to solvent. The larger fraction of branched polymers obtained from the more concentrated systems, even with less cross-linking agent, can be attributed to the enhanced number of interchain reactions.

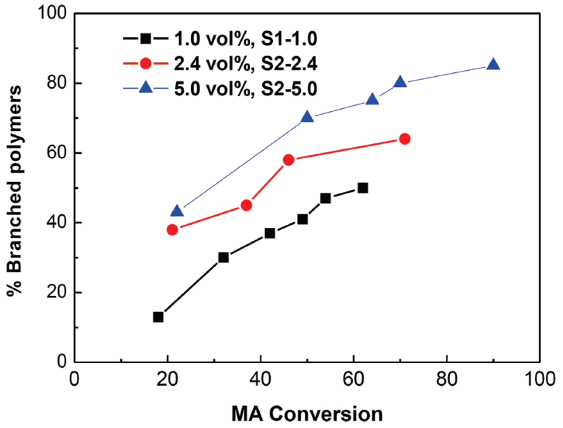


Figure 4. Percentage of branched polymers present in the products formed under different dilution conditions calculated by peak splitting of GPC curves vs MA conversion.

Table 2. Comparison of Branched Polymers Formed under Various Dilutions

entry	concn (vol %)[a]	$M_{\mathrm{w,RI}}$[c]	$M_{\mathrm{w,MALLS}}$[d]	$M_{\mathrm{w}}/M_{\mathrm{n}}$[d]	$M_{\mathrm{w,MALLS}}/M_{\mathrm{w,RI}}$
S1-0.5	0.5	2.43×10^4	4.15×10^4	1.27	1.7
S2-5.0	5.0	3.64×10^4	1.32×10^5	1.59	3.6
extending BA from S1-0.5[b]		4.84×10^4	5.79×10^4	1.72	1.2
extending BA from S2-5.0[b]		7.27×10^4	1.97×10^5	1.27	2.7

[a] Volume percentage of MA plus HDDA vs DMSO. [b] $[\mathrm{S1\text{-}0.5\ or\ S2\text{-}5.0}]_0/[\mathrm{BA}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = 1/500/2/2$, 20 vol % of DMF compared to BA, 60 °C. [c] Weight-average molecular weight determined by THF GPC with RI detector, calibration with linear polyMMA as standard. [d] Weight-average molecular weight $M_{\mathrm{w,MALLS}}$ and molecular weight distribution $M_{\mathrm{w}}/M_{\mathrm{n}}$ of the branched polymers determined by THF GPC with MALLS detector.

These results show that dilution promotes intramolecular cross-linking reactions with pendant vinyl groups and sufficiently suppresses the formation of highly branched polymers through intermolecular incorporation of the second vinyl group in the cross-linker to an adjacent growing polymer chain. The critical concentration, to efficiently limit the interchain reactions in the current system, was determined to be 0.5 vol % of monomer and cross-linker vs solvent, since apparently almost no branched polymer peak was observed in the GPC traces of copolymers prepared under this condition. In other words, a significantly lower amount of branched polymers was formed in the highly dilute 0.5 vol % system, and they could not be separated from the GPC curves of the primary polymer chains. Predominately linear polymer chains, with intramolecular cyclic structure along the polymer chains, should be obtained in this system. These conclusions are confirmed by a comparison of absolute molecular weights and compactness of polymers formed in different systems.

A GPC with a MALLS detector was utilized to determine the absolute molecular weights of the branched polymers obtained from the 0.5 and 5 vol % systems, S1-0.5 and S2-5.0 (Table 2). Branched polymers with much higher weight-average molecular weight $M_{\mathrm{w,MALLS}} = 1.32 \times 10^5$, and also broader molecular weight distribution, $M_{\mathrm{w}}/M_{\mathrm{n}} = 1.59$, were obtained in the more concentrated 5 vol % system. The polymers generated in this system had a more compact structure, as proved by the larger ratio between the absolute molecular weight and apparent molecular weight $M_{\mathrm{w,MALLS}}/M_{\mathrm{w,RI}}$ 3.6, compared to the value 1.7 for polymers prepared in the 0.5 vol % system. The lower value indicates that a very loosely cross-linked polymer network was achieved or limited amount of branched polymers existed in the product formed under high dilution conditions.

To further compare the different structures, chain extension of BA was conducted from these two kinds of polymers obtained from the copolymerization. The efficiency of the chain extension

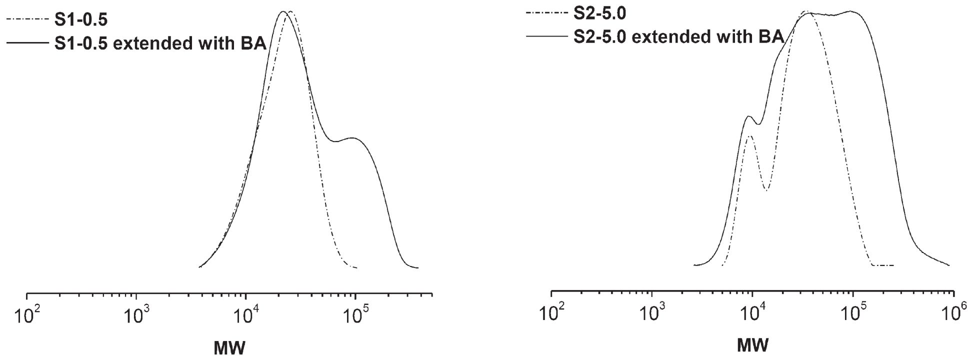


Figure 5. Chain extension of BA from the branched polymers formed under different dilutions. Polymerization conditions: $[\mathrm{S1{-}0.5\ or\ S2{-}5.0}]_0/[\mathrm{BA}]_0/[\mathrm{CuBr}]_0/[\mathrm{PMDETA}]_0 = 1{:}500{:}2{:}2$, 20 vol % of DMF compared to BA, 60 °C, 20 h.

reaction was relatively poor, as shown in the GPC traces (Figure 5); a large fraction of polymer chains were not successfully extended with BA. These results confirm the loss of some end-group functionalities during the synthesis under dilute conditions. The polymeric structure became less compact after the chain extension reaction due to the introduction of a linear polymer "shell", as indicated by the decrease of $M_{w,MALLS}/M_{w,RI}$ ratio in both cases (Table 2). The low $M_{w,MALLS}/M_{w,RI}$ value, 1.2, for the polymers obtained from the extension of BA from S1-0.5 indicated that predominately nonbranched structures existed in the system.

CONCLUSION

Atom transfer radical copolymerization of a monovinyl monomer, MA, and a divinyl cross-linker, HDDA, was conducted in a series of highly diluted systems. The copolymerization process was moderately well controlled with predominate formation of relatively uniform primary chains. The fraction of branched polymers formed through intermolecular reactions was calculated for the different systems to study the effect of dilution on the bimolecular cross-linking process. The occurrence of intramolecular pendant vinyl group cross-linking reactions can be significantly enhanced under high dilution, and limited amounts of branched polymers can be seen in the GPC traces of the copolymers even at high monomer conversion, when the reaction was carried out with only 0.5 vol % of MA and HDDA vs DMSO. Conducting the copolymerization of monomer and cross-linker under high dilution conditions results in polymers with intramolecular cyclic structures along the predominately linear polymer backbone.

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