Influence of Initiation Efficiency and Polydispersity of Primary Chains on Gelation during Atom Transfer Radical Copolymerization of Monomer and Cross-Linker

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Received November 17, 2008; Revised Manuscript Received December 22, 2008

ABSTRACT: The influence of initiation efficiency and polydispersity of primary chains on the experimental gel points was studied during atom transfer radical copolymerization (ATRcP) of monovinyl monomer and divinyl cross-linker. Three initiators with progressively increased initiation efficiency—ethyl 2-bromopropionate (EBrP) < ethyl 2-bromoisobutyrate (EBiB) < 2-bromopropionitrile (BPN)—were used for the ATRcP of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). With the least efficient EBrP initiator, experimental gelation occurred when the molar ratio of EGDMA cross-linker to EBrP was as low as 0.25 due to the low initiation efficiency of EBrP. In contrast, no gelation was observed by using the most efficient BPN initiator, even when the molar ratio of cross-linker to initiator was equal to unity. The use of a poorer solvent for copper catalyst also decreased the initiation efficiency and resulted in a gelation at lower monomer conversion. The dependence of experimental gel points on the polydispersity of primary chains was studied by using activators regenerated by electron transfer (ARGET) ATRP for copolymerization of methyl acrylate (MA) and ethylene glycol diacrylate (EGDA). Decreasing the copper concentration from tens of ppm to a few ppm broadened the molecular weight distribution of primary chains, which resulted in an earlier gelation at lower monomer conversion during the copolymerization of MA and EGDA.

Introduction

Radical copolymerization of a monovinyl monomer with a small amount of divinyl cross-linker provides a convenient method for synthesis of branched polymers and/or gels. Highly cross-linked networks with inhomogeneous structure are typically formed at low monomer conversion during most conventional radical polymerization (RP) reactions due to the slow initiation, fast chain propagation, and termination reactions.[1−4] In contrast, the recently developed controlled radical polymerization (CRP)[5,6] techniques allow the preparation of polymeric networks with more homogeneous structure and preserved chain-end functionalities because of fast initiation and quick deactivation reactions. The fast initiation reactions, relative to propagation reactions, result in a rapid conversion of all initiators into primary chains and consequently a postponed gelation in comparison to the RP processes. The dynamic equilibrium between a low concentration of growing radicals and a significantly higher fraction of dormant species ensures a slow steady chain growth and a more even incorporation of vinyl groups (from monomers, cross-linkers, and pendant vinyl groups) into the polymer chains. Therefore, the branched sols and/or gels synthesized by CRP processes have a more homogeneous structure than the polymers synthesized by RP methods at similar concentrations.[7−22]

During the copolymerization of monovinyl monomer and divinyl cross-linker, the experimental gelation occurs when the whole system changes from a viscous liquid (sol) to an elastic gel. Accurate prediction of the gel point is important when one seeks to control the gelation process. According to Flory−Stockmayer's statistical theory,[23,24] the theoretical gel point in a system is reached when the weight-average number of cross-linking units per primary chain exceeds unity. This calculation was established for an ideal polymer network with two basic assumptions: equal reactivity of all vinyl species and no intramolecular cyclization. For such an ideal case, the critical conversion of vinyl bonds at the theoretical gel point can be obtained from eq 1 (details shown in the Supporting Information).

$$p_c = \sqrt{\frac{[\mathrm{PC}]_t}{2[\mathrm{X}]_0}\frac{1}{\mathrm{PDI}}} \tag{1}$$

Equation 1 indicates that the critical conversion of vinyl bonds at the moment of gelation (p_c) is determined by the initial concentration of divinyl cross-linker ($[\mathrm{X}]_0$), the instantaneous concentration of primary chains at any time t ($[\mathrm{PC}]_t$), and the polydispersity ($\mathrm{PDI} = M_w/M_n$) of primary chains.

Recently, we used atom transfer radical polymerization (ATRP)[25−28] as an exemplary CRP technique to systematically study the experimental gelation by copolymerization of monovinyl monomer with divinyl cross-linker.[18,21,29] ATRP proceeded with fast initiation, high initiation efficiency (IE), and low polydispersity of primary chains in all performed experiments.[18,21,29] The effect of several parameters on the experimental gelation was previously explored, including the initial molar ratio of cross-linker to initiator,[18] the concentration of reagents,[21] and the relative reactivity of cross-linker compared to monomer.[29] The experimental gel points were significantly affected by the initial molar ratio of cross-linker to initiator.[18] No gelation was observed when the initial molar ratio of cross-linker to initiator was less than unity, even under bulk conditions with complete conversion of vinyl species.[21] For comparison, the theoretical gel point based on Flory−Stockmayer's theory is reached at 71% monomer conversion for the equimolar ratio of cross-linkers to monodisperse primary chains (eq 1, $[\mathrm{PC}]_t/[\mathrm{X}]_0 = 1$, $\mathrm{PDI} = 1$). The discrepancy between the delayed experimental gelation and the theoretical gelation was primarily attributed to the unavoidable intramolecular cyclization reactions, which consumed pendant vinyl groups but had no contribution to the increase of molecular weight of the branched polymers.

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10.1021/ma8025833 CCC: $40.75

It is important to note that ATRP provides further control of the relative initiation rate and the polydispersity of primary chains via rational adjustment of the experimental conditions. By varying the IE of initiators, the critical conversion of vinyl bonds at the gel point can be expressed as eq 2

$$p_c = \sqrt{\frac{[\mathrm{I}]_0\mathrm{IE}_t}{2[\mathrm{X}]_0\mathrm{PDI}}} \tag{2}$$

where $[\mathrm{I}]_0$ is the initial concentration of initiator and IE_t represents the instantaneous IE value at time t ($[\mathrm{PC}]_t = [\mathrm{I}]_0\mathrm{IE}_t$).

Herein, we report the influence of the IE and the polydispersity of primary chains on the experimental gel points by deliberately applying nonideal conditions to the ATRP processes. The dependence of experimental gel points on the IE was examined by using three ATRP initiators with progressively increased reactivity,[30,31] i.e., ethyl 2-bromopropionate (EBrP), ethyl 2-bromoisobutyrate (EBiB), and 2-bromopropionitrile (BPN), for the atom transfer radical copolymerization (ATRcP) of methyl methacrylate (MMA) and ethylene glycol dimethacrylate (EGDMA). Experimental gel points based on monomer conversions were determined and compared with each other to evaluate the effect of IE on the experimental gel point. Moreover, the recently developed activators regenerated by electron transfer (ARGET)[32,33] ATRP technique was used for the copolymerization of methyl acrylate (MA) and ethylene glycol diacrylate (EGDA) to explore the effect of the polydispersity of primary chains (PDI) on the experimental gel points. The value of PDI was affected by the concentration of Cu(II) deactivator in the system. Decreasing the amount of copper catalyst from 50 to 1 ppm increased the polydispersity of primary chains from a low PDI (~1.1) to a high PDI (~2.0) and accelerated the gelation.

Experimental Section

Materials. Methyl methacrylate (MMA, 99%), methyl acrylate (MA, 99%), ethylene glycol dimethacrylate (EGDMA, 98%), and ethylene glycol diacrylate (EGDA, 90%) were purchased from Aldrich and purified by passing through a column filled with basic alumina to remove the inhibitor and/or antioxidant and then stored at −5 °C. CuBr (98%, Acros) was purified by stirring in acetic acid; it was then filtered, washed with 2-propanol, and then dried under vacuum. 2,2′-Bipyridine (bpy, 99+%) was purchased from Acros and used as received. Tris[2-(dimethylamino)ethyl]amine ($\mathrm{Me_6TREN}$)[34] was purchased from ATRP solutions and used as received. All other reagents ethyl 2-bromoisobutyrate (EBiB, 98%), ethyl 2-bromopropionate (EBrP, 99%), 2-bromopropionitrile (BPN, 97%), $\mathrm{CuBr_2}$ (98%), tin(II) 2-ethylhexanoate ($\mathrm{Sn(EH)_2}$, 95%), and solvents were purchased from Aldrich and used as received.

Synthesis of Gels by ATRcP of MMA and EGDMA. Similar procedures were used for the synthesis of various gels. In a typical experiment, MMA (2 mL, 19 mmol), EGDMA (0.071 mL, 0.38 mmol), $\mathrm{CuBr_2}$ (8.4 mg, 0.038 mmol), bpy (58.4 mg, 0.38 mmol), acetone (1.63 mL), and anisole (0.1 mL, as internal standard for determination of monomer conversion by GC) were added to a Schlenk flask. The flask was sealed and then degassed by five cycles of freeze−pump−thaw. During the final cycle, the flask was filled with nitrogen before CuBr (21.5 mg, 0.15 mmol) was added to the frozen mixture. The flask was sealed with a glass stopper and then evacuated and back-filled with nitrogen several times before it was immersed in an oil bath thermostated at 50 °C. Finally, the $\mathrm{N_2}$-purged initiator EBiB (0.055 mL, 0.38 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 MMA conversions by GC and to determine molecular weights of the sols by GPC. Gelation moment was defined when the reaction fluid lost its mobility at an upside-down position for 10 s.

Synthesis of Gels by ARGET ATRcP of MA and EGDA. In polymerizations conducted with several ppm of Cu, a stock solution of Cu(II)/$\mathrm{Me_6TREN}$ was prepared by dissolving $\mathrm{CuBr_2}$ (0.0223 g, 0.1 mmol) and $\mathrm{Me_6TREN}$ (200 μL, 0.75 mmol) in 5 mL of DMF. In a typical run with 5 ppm copper, EBiB (32.6 μL, 0.222 mmol), MA (4 mL, 44.4 mmol), EGDA (38 μL, 0.222 mmol), $\mathrm{Me_6TREN}$ (5.8 μL, 0.022 mmol), 11.2 μL of the Cu(II) stock solution, and anisole (1.3 mL) were added to a 10 mL Schlenk flask. The flask was sealed and then degassed by several freeze−pump−thaw cycles. After immersing the flask in an oil bath thermostated at 60 °C, 72 μL of $\mathrm{N_2}$-purged anisole solution containing 7.2 μL of $\mathrm{Sn(EH)_2}$ (0.022 mmol) was added to the flask to initiate polymerization. Samples were taken at timed intervals to measure conversion and to examine the evolution of molecular weight. Gelation moment was defined when the reaction fluid lost its mobility at an upside-down position for 10 s.

Characterization. Monomer conversions were determined by gas chromatography (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). Anisole or 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 polydispersities (M_w/M_n) were determined with a calibration based on linear polyMMA standards using WinGPC 6.0 software from PSS.

Results and Discussion

We have previously used divinyl cross-linker to prepare well-defined star polymers containing a cross-linked core by using either "arm-first"[35−38] or "core-first"[39] methods. In these procedures, the cross-linker was added either after or before the polymerization of monovinyl monomer. More recently, we used ATRP to synthesize series of gels via simultaneous copolymerization of monovinyl monomer and divinyl cross-linker.[18,21,29] When an efficient ATRP initiator was used, all added initiators quickly converted into short primary chains at low monomer conversion. The propagating chain ends reacted with monomers, cross-linkers, and also the pendant vinyl groups in a statistical manner, based on their concentrations and reactivities. Intermolecular reactions between propagating radicals and pendant vinyl groups generated branched polymers that grew from small molecules to larger ones and finally formed a polymer network, when the average number of cross-linkage (cross-linker with both vinyl groups reacted) per primary chain reached a critical value.[18]

It is important to note that the initiation rate can dramatically change the copolymerization process and the gelation behavior in ATRP. The use of an ATRP initiator with slow initiation would result in a slow but continuous transformation of the added initiators into primary chains during the polymerization (Scheme 1). Some unreacted initiators could be left in the system even after gelation, if the initiation rate is slow enough. Thus, the initiation rate directly determines the fraction of initiators transformed into polymer chains, i.e., the cumulative number of primary chains formed in the system. In ATRP, the initiation rate depends on several factors, including the chemical structure and reactivity of initiators, monomers, and also the catalyst and solvent quality. The effect of IE on the experimental gel point was studied in the presence of different initiators and solvents for the ATRcP of MMA and EGDMA.

Influence of IE on Experimental Gelation. Three ATRP initiators with progressively increased reactivities, EBrP, EBiB, and BPN, were used for the ATRcP reactions. Their IE was first evaluated during the homopolymerization of MMA monomer by using CuBr/bpy as the catalyst (20 mol % $\mathrm{CuBr_2}$ vs total copper species was added to the system) and acetone as

Scheme 1. Gel Formation Process during the ATRcP of Monovinyl Monomer and Divinyl Cross-Linker Using an Initiator with Low Initiation Efficiency

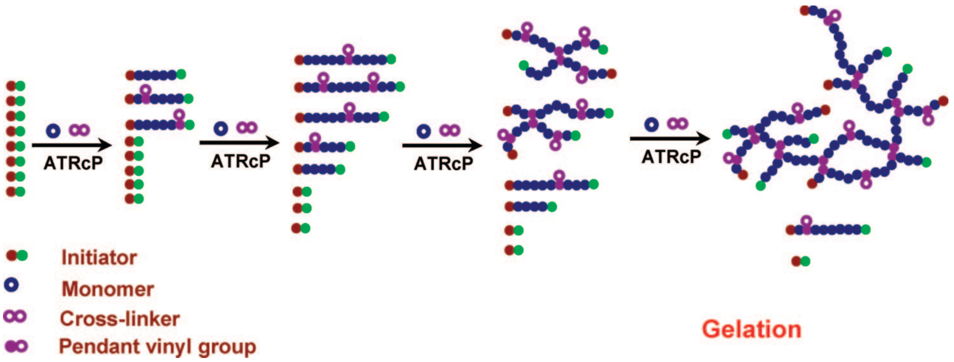

Table 1. Homopolymerization of MMA with Various Initiators by ATRP[a]

entry	initiator	reaction time (h)	$\mathrm{Conv}_{\mathrm{MMA}}$	$M_n{}^b$	$M_{\mathrm{theor}}{}^b$	PDI[b]	IE[c]
HI1	EBrP	18.4	0.99	15200	5100	1.54	0.34
HI2	EBiB	17.0	0.93	7100	4850	1.47	0.68
HI3	BPN	6.0	0.65	3600	3400	1.19	0.95

[a] Polymerization conditions: $[\mathrm{MMA}]_0/[\mathrm{initiator}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr}_2]_0/[\mathrm{bpy}]_0 = 50/1/0.4/0.1/1$, $[\mathrm{MMA}]_0 = 5.0$ M in acetone at 50 °C. [b] M_n: number-average molecular weight of polyMMA, determined by THF GPC with RI detector using linear polyMMA standards; M_{theor}: theoretical molecular weight of polyMMA, determined by $M_{\mathrm{theor}} = 50 \times \mathrm{MW}_{\mathrm{MMA}} \times \mathrm{Conv}_{\mathrm{MMA}} + \mathrm{MW}_{\mathrm{initiator}}$; PDI $= M_w/M_n$ determined by THF GPC with RI detector (M_w: weight-average molecular weight of polyMMA). [c] IE $= M_{\mathrm{theor}}/M_n$.

the solvent (Table 1). The molar ratios of reagents were set at $[\mathrm{MMA}]_0/[\mathrm{initiator}]_0/[\mathrm{CuBr}]_0/[\mathrm{CuBr}_2]_0/[\mathrm{bpy}]_0 = 50/1/0.4/0.1/1$ ($[\mathrm{MMA}]_0 = 5.0$ M). When EBrP and EBiB were used as initiators, the polymerizations proceeded with slow initiation, and the value of IE progressively increased with MMA conversion. For example, the IE of EBiB reached 68% (= 1/1.46) when the polymerization was stopped at 93% MMA conversion (HI2, Table 1), since the number-average molecular weight, determined by THF GPC with polyMMA standard, was 1.46 times higher than the theoretical value (Figure 1a). The incomplete initiation of EBiB during the ATRP of MMA is ascribed to the effect of the penultimate MMA unit on the reactivity of chain-end alkyl bromide. The activation rate of polyMMA-Br is ca. 8 times higher than that of EBiB initiator.[40,41] At similar conversions, the IE of EBiB was always higher than that of EBrP (IE = 34% at 99% MMA conversion, HI1 in Table 1) but lower than that of BPN (IE = 95%, at <65% MMA conversion, HI3 in Table 1). With BPN as initiator, the number-average molecular weight of linear polyMMA polymers overlapped with the theoretical value throughout the polymerization, indicating a fast initiation and high IE value even at the beginning of the polymerization (Figure 1a). This order of initiator reactivity agrees well with the reported values of K_{ATRP} (ATRP equilibrium constant) and k_{act} (activation rate constant) for various initiators.[31,42]

After the IE were obtained for three initiators during the ATRP of MMA, a series of ATRcP of MMA and EGDMA were performed under similar experimental conditions to study the influence of IE on the experimental gel points. Results are summarized in Table 2 and Figure 2. For the equimolar ratio of EGDMA to initiator, gelation occurred at 25% MMA conversion with the least efficient EBrP ($\mathrm{EBrP}_{1.00}$, Table 2). This value was much lower than the gel point observed at 75% MMA conversion, when EBiB was used as the initiator under similar conditions ($\mathrm{EBiB}_{1.00}$ in Table 2). In contrast, no gel was formed when the most efficient initiator BPN was used at $[\mathrm{EGDMA}]_0/[\mathrm{BPN}]_0 = 1.00$. This is in agreement with our previous report that, in an ATRcP reaction using initiators with high IE, gelation occurred only when the molar ratio of cross-linker to initiator exceeded unity.[18] By using EBrP or EBiB as the initiator, insoluble gels formed at higher MMA conversions when the initial molar ratio of EGDMA to initiator decreased to less than unity. Figure 2 shows that no gelation was observed even at complete MMA conversion, when the molar ratio of EGDMA to EBiB was lower than 0.7 (the red vertical line in Figure 2). In contrast, with EBrP as the initiator, gelation could be avoided only when the molar ratio of EGDMA to EBrP was lower than 0.2 (the black vertical line in Figure 2). These results indicate that using the least efficient EBrP as initiator for the ATRcP of MMA and EGDMA significantly accelerated the experimental gelation, in agreement with eq 2. In other words, gelation could occur at a substoichiometric amount of cross-linker to initiator, if the initiation is incomplete.

Influence of Solvent Quality on IE and Experimental Gelation. In addition to the effect of initiator structure on the IE value, the solvent quality could also influence the IE by affecting the activation rate of dormant species and the deactivation rate of propagating radicals. A poor solvent for Cu(II) deactivator in an ATRP system would decrease the solubility of Cu(II) complex and reduce the overall deactivation rate of propagating radicals.[43,44] Three solvents with increasing solubility of CuBr_2/bpy deactivator, anisole < acetone < DMF, were used in a series of ATRcP reactions with EBiB as initiator. The reaction with EBiB as initiator showed a medium value of initiation efficiency (IE = 68% at 93% MMA conversion) when acetone was used as the solvent, which provided a tuning opportunity to further increase the initiation efficiency of EBiB when the polymerization was conducted in a better solvent (DMF) for Cu complex and decrease the initiation efficiency by using a less efficient solvent (anisole). The IE of EBiB for the homopolymerization of MMA indeed increased from 39% to 68%, when the solvent was changed from anisole to acetone. The IE value further increased to 80% at ca. 90% MMA conversion when DMF was used as the solvent (Table S1 and Figure S1 in the Supporting Information). Copolymerizations of MMA and EGDMA with fixed molar ratios of $[\mathrm{MMA}]_0/[\mathrm{EGDMA}]_0/[\mathrm{EBiB}]_0 = 50/1/1$ were conducted under similar conditions. The results in Table 3 show that the monomer conversions at the gel points increased from 60% to 75% and 91% when the solvent was changed from anisole to acetone and DMF. A progressively delayed gelation could be ascribed to the increased IE value, but also lower polydispersity of primary chains, which will be discussed below.

Influence of Polydispersity of Primary Chains on Experimental Gelation. In addition to the IE, the polydispersity of primary chains should also affect the experimental gelation process, based on eq 2. In a system with broadly distributed primary chains, the polymers with higher molecular weight

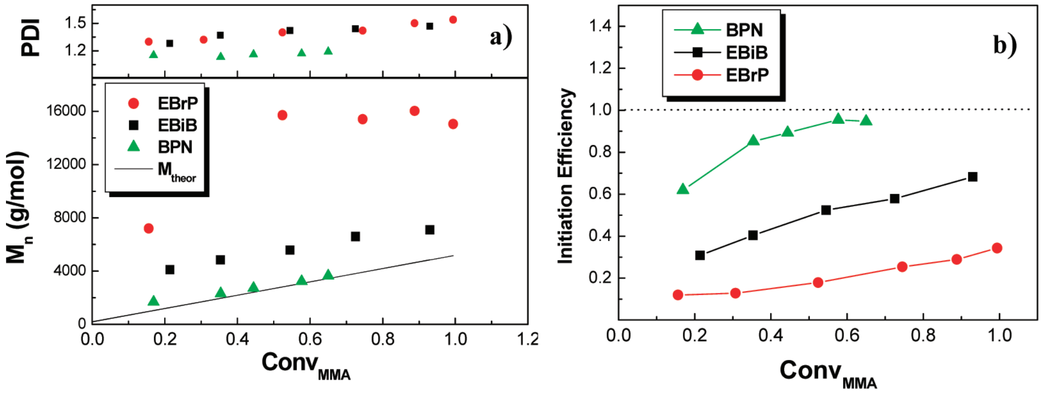

Figure 1. Dependence of (a) number-average molecular weights (M_n) and polydispersity (PDI = M_w/M_n) on MMA conversion and (b) initiation efficiency of ATRP initiators on MMA conversion during ATRP of MMA using EBrP, EBiB, and BPN as initiators. Polymerization conditions are listed in Table 1.

Table 2. Synthesis of Poly(MMA−EGDMA) Gels Using Different Initiators[a]

entry[b]	initiator	$[EGDMA]_0/[initiator]_0$ (X)	gelation time (h)	$Conv_{MMA}$ at gel point[c]
$EBrP_{1.00}$	EBrP	1.00	1.4	0.25
$EBrP_{0.90}$	EBrP	0.90	1.6	0.30
$EBrP_{0.80}$	EBrP	0.80	2.4	0.40
$EBrP_{0.50}$	EBrP	0.50	2.6	0.62
$EBrP_{0.35}$	EBrP	0.35	3.8	0.83
$EBrP_{0.25}$	EBrP	0.25	9.0	0.92
$EBrP_{0.20}$	EBrP	0.20	no gelation	
$EBiB_{1.00}$	EBiB	1.00	2.8	0.75
$EBiB_{0.90}$	EBiB	0.90	4.0	0.80
$EBiB_{0.80}$	EBiB	0.80	5.0	0.83
$EBiB_{0.70}$	EBiB	0.70	no gelation	
$BPN_{1.00}$	BPN	1.00	no gelation	

[a] Polymerization conditions: $[MMA]_0/[EGDMA]_0/[initiator]_0/[CuBr]_0/[CuBr_2]_0/[bpy]_0 = 50/X/1/0.4/0.1/1$, $[MMA]_0 = 5.0$ M in acetone at 50 °C. [b] The subscript number indicates the initial molar ratio of EGDMA to initiator (X). [c] Conversions of MMA immediately before gelation.

Table 3. Synthesis of Poly(MMA−EGDMA) Gels in Different Solvents[a]

entry	initiator	DP	solvent	gelation time (h)	$Conv_{MMA}$[b]
$EBiB_{1An}$	EBiB	50	anisole	4.0	0.60
$EBiB_{1Ac}$	EBiB	50	acetone	2.8	0.75
$EBiB_{1DMF}$	EBiB	50	DMF	5.0	0.91

[a] Polymerization conditions: $[MMA]_0/[EGDMA]_0/[EBiB]_0/[CuBr]_0/[CuBr_2]_0/[bpy]_0 = 50/1/1/0.4/0.1/1$, $[MMA]_0 = 5.0$ M in various solvents at 50 °C. [b] Conversions of MMA immediately before gelation.

Table 4. ARGET ATRP of MA with EBiB as Initiator[a]

entry	initiator	copper (ppm)[a]	reaction time (h)	$Conv_{MA}$	M_n[b]	M_{theor}[b]	PDI[b]	IE[c]
$H_{ARGET}1$	EBiB	50	21.5	0.99	16 200	17 400	1.12	1.00
$H_{ARGET}2$	EBiB	5	21.5	0.99	19 200	17 400	1.47	0.91
$H_{ARGET}3$	EBiB	1	19.3	0.99	19 000	17 400	2.01	0.91

[a] Polymerization conditions: $[MA]_0/[EBiB]_0/[Me_6TREN]_0/[Sn(EH)_2]_0 = 200/1/0.1/0.1$, $[MA]_0 = 8.2$ M in anisole at 60 °C, copper concentration is based on the molar ratio vs monomer. [b] M_n: number-average molecular weight of polyMA, determined by THF GPC with RI detector using linear polyMMA standards; M_{theor}: theoretical molecular weight of polyMA, determined by $M_{theor} = 200 \times MW_{MA} \times Conv_{MA} + MW_{initiator}$; PDI = M_w/M_n determined by THF GPC with RI detector (M_w: weight-average molecular weight of polyMA). [c] IE = M_{theor}/M_n.

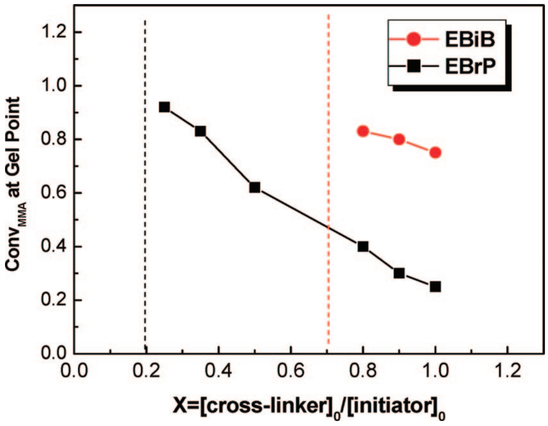

Figure 2. Comparison of experimental gel points based on monomer conversions during ATRcP of MMA and EGDMA by using different initiators with various molar ratios of $X = [cross\text{-}linker]_0/[initiator]_0$. Vertical lines show the critical values of X when the experimental gelation could be avoided at complete conversion. Polymerization conditions are listed in Table 2.

contain more pendant vinyl groups. Consequently, they have a higher opportunity to react with each other and form larger branched polymers, which could result in an earlier gelation, as compared to a system with narrowly distributed chains.

The recently developed ARGET ATRP technique provides the possibility to tailor the polydispersity of polymer chains by simply changing the copper catalyst amount in a system.[45,46] In order to study the effect of polydispersity of primary chains on the experimental gel points, ARGET ATRcP of MA and EGDA was conducted by using EBiB as initiator and various amounts of copper from 50 to 1 ppm. The reason for the selection of MA and EGDA, instead of MMA and EGDMA, as the monomer and cross-linker is the overall better control that can be exerted over the ATRP of acrylate-based monomers than methacrylate-based monomers. Methacrylate-based monomers in ATRP have much lower deactivation rate constant and also higher activation rate constant than acrylate-based monomers.

Homopolymerization of MA was first conducted by using ARGET ATRP to study the effect of copper concentration on the polydispersity of linear polymers. Polymerization conditions were set as $[MA]_0/[EBiB]_0/[Me_6TREN]_0/[Sn(EH)_2]_0 = 200/1/0.1/0.1$ in anisole at 60 °C. Decreasing the copper concentration from 50 to 1 ppm (molar ratio vs monomer) resulted in an increase of the polydispersity of polymers from $M_w/M_n = 1.12$ to 2.01 (Table 4 and Figure 3). When 50 ppm copper was used, the IE value of EBiB was essentially 100% from the beginning of polymerization and the polydispersity of resulting polymers was quite low ($M_w/M_n = \sim 1.1$). In contrast, when the polymerizations were performed by using 5 and 1 ppm copper, the IE value of EBiB was low at the beginning and gradually increased to reach >90% at high monomer conversion.

To study the effect of the polydispersity of primary chains on the experimental gel points, similar polymerization conditions

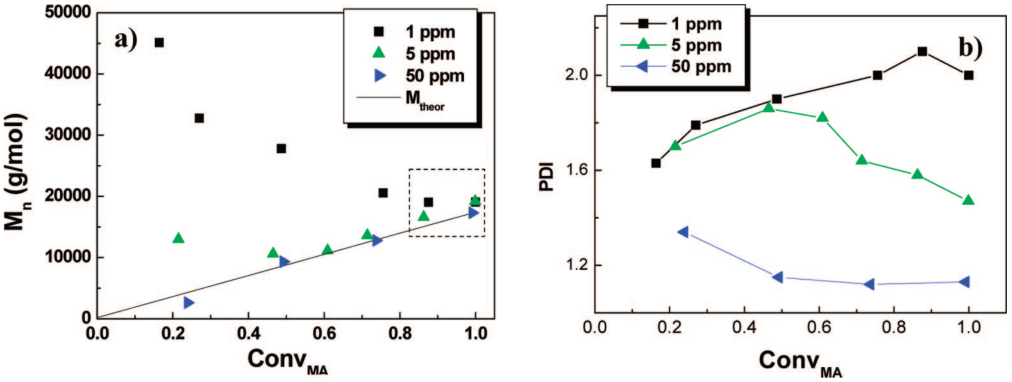

Figure 3. Dependence of (a) number-average molecular weights (M_n) and (b) PDI on MA conversion during ARGET ATRP of MA with EBiB as initiator. A dashed square in Figure 3a marks the high IE of EBiB at high MA conversion in reactions with 1 and 5 ppm copper. Polymerization conditions are listed in Table 4.

Table 5. ARGET ATRcP of MA and EGDA[a]

entry	X^a	copper (ppm)[b]	gelation time (h)	$Conv_{MA}$[c]	$Conv_{EGDA}$[c]
$AR_{50,3}$	3.0	50	2.6	0.66	0.93
$AR_{5,3}$	3.0	5	0.9	0.28	0.61
$AR_{1,3}$	3.0	1	0.4	0.14	0.38
$AR_{50,1}$	1.0	50	no gelation (20 h)	0.99	~1.00
$AR_{5,1}$	1.0	5	3.7	0.86	~1.00
$AR_{1,1}$	1.0	1	1.6	0.64	~1.00
$AR_{5,0.4}$	0.4	5	no gelation (18 h)	0.99	~1.00
$AR_{1,0.4}$	0.4	1	5.7	0.93	~1.00

[a] Polymerization conditions: $[MA]_0/[EGDA]_0/[EBiB]_0/[Me_6TREN]_0/[Sn(EH)_2] = 200/X/1/0.1/0.1$, $[MA]_0 = 8.2$ M in anisole at 60 °C. [b] Copper concentration is based on the molar ratio vs MA. [c] Conversions of MA and EGDA immediately before gelation.

were used for the copolymerization of MA and EGDA in the ARGET ATRcP system (Table 5) at various molar ratios of EGDA to EBiB. However, at higher molar ratio of EGDA to EBiB ($[EGDA]_0/[EBiB]_0 = 3.0$), gelation occurred at very low monomer conversion when less copper was used, i.e., $Conv_{MA,gel} = 28\%$ with 5 ppm copper and $Conv_{MA,gel} = 14\%$ with 1 ppm copper (Table 5, $AR_{5,3}$ and $AR_{1,3}$). At this range of monomer conversion, the initiation of EBiB was incomplete when 1 or 5 ppm amount of copper was used (Figure 3a). Thus, it is difficult to determine whether the accelerated gelation with lower amount of copper originated in the increased polydispersity of primary chains or the low IE. Since the IE of EBiB in both reactions, with 1 and 5 ppm copper, increased steadily with MA conversion and reached nearly the quantitative value at high conversion (dashed square in Figure 3a), the gelation at high monomer conversion could eliminate the effect of IE on the experimental gel point. Decreasing the initial molar ratio of EGDA to EBiB to $[EGDA]_0/[EBiB]_0 = 1.0$ resulted in gelation at higher MA conversion, $Conv_{MA,gel} = 86\%$, for the reaction with 5 ppm copper. In contrast, no gelation was observed even at 99% MA conversion when 50 ppm copper was used. Under such high MA conversions, the IE value of EBiB was similar in both reactions ($AR_{50,1}$ and $AR_{5,1}$, Table 5). Thus, the formation of gel in the reaction with 5 ppm copper was attributed to the higher polydispersity of the primary chains. Similarly, the different gelation behavior between the reactions with 1 and 5 ppm copper was compared by using an even lower molar ratio of EGDA to EBiB, i.e., $[EGDA]_0/[EBiB]_0 = 0.4$. Under such conditions, no gelation was observed at 99% MA conversion when 5 ppm amount of copper was used. In contrast, gelation occurred at $Conv_{MA,gel} = 93\%$ in the reaction with 1 ppm copper, which is again ascribed to the higher polydispersity of the primary chains (Table 5, $AR_{5,0.4}$ and $AR_{1,0.4}$).

Conclusion

A series of polyMMA- and polyMA-based gels were successfully prepared through the copolymerization of monovinyl monomer and divinyl cross-linker using ATRP. The experimental gel points were determined based on monomer conversions and compared with each other in order to study their dependence on the initiation efficiency and the polydispersity of primary chains. The use of less efficient initiators or poorer solvents accelerated the formation of gels to occur at lower monomer conversion. The effect of polydispersity of primary chains on the experimental gelation was studied by using the ARGET ATRcP of MA and EGDA with different amounts of copper catalyst. Gelation occurred at lower monomer conversion when a system with lower amount of copper was used and formed primary chains with higher polydispersity. These results expand our knowledge and capacity to control the experimental gel points during the ATRcP of monomer and divinyl cross-linker by rationally adjusting different parameters. The results also point out that gelation depends not only on the initial molar ratio of used reagents but also on their reactivity, exchange rate, amount of additives, and other parameters.

Acknowledgment. The financial support from NSF Grant DMR 05-49353 and the CRP Consortium at Carnegie Mellon University is appreciated. W. Li acknowledges support from a Bayer Fellowship.

Supporting Information Available: Derivation of eq 1 and the ATRP of MMA in different solvents. This material is available free of charge via the Internet at http://pubs.acs.org.

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MA8025833