

Gel Formation in Atom Transfer Radical Polymerization of 2-(*N,N*-Dimethylamino)ethyl Methacrylate and Ethylene Glycol Dimethacrylate

CHENGFA JIANG,¹ YOUQING SHEN,¹ SHIPING ZHU,¹ DAVID HUNKELER²

¹Department of Chemical Engineering, McMaster University, Hamilton, Ontario L8S 4L7, Canada

²Department of Chemistry, Swiss Federal Institute of Technology Lausanne, Lausanne 1015, Switzerland

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ABSTRACT: Copolymers of 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) and ethylene glycol dimethacrylate (EGDMA) were synthesized via atom transfer radical polymerization using ethyl 2-bromoisobutyrate as the initiator, Cu(I)Br as the catalyst, and 1,1,4,7,10,10-hexamethyltriethylene tetramine as the ligand. At low crosslinker levels, the polymerizations followed the first-order kinetics. However, when the crosslinker level was above 10 mol %, the $\ln([M]_0/[M])$ versus time curves showed deceleration at medium conversions because of the higher reactivity of EGDMA than that of DMAEMA. An acceleration at high conversions was also observed and probably caused by the diffusion limitations of catalyst/ligand complex in the polymer network. The hydrogels were characterized by swelling experiments, and the sol polymers were characterized by the size exclusion chromatographic technique to determine the number-average molecular weight and polydispersity. The gel data were analyzed and, via a comparison to Flory's gelation theory, found to be more homogeneous than similar hydrogels prepared by conventional free-radical polymerization methods. © 2001 John Wiley & Sons, Inc. *J Polym Sci Part A: Polym Chem* 39: 3780–3788, 2001

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INTRODUCTION

A hydrogel is a crosslinked network of hydrophilic polymer that is water insoluble but can swell in polar media. The synthesis of hydrogels has become an intriguing research area, motivated in part by successful applications of hydrogels in many fields, particularly in medicine and pharmacy.^{1,2} The methods used to prepare a cross-linked polymeric network can be classified into three groups.³ In the first, a network is produced by vulcanization, peroxidation, or irradiation of pre-existing linear polymers. In the second, net-

work formation involves polycondensation-based and free-radical-based copolymerization from monomers. In the last group, the method proceeds by the end-linking of well-defined linear polymeric precursor chains. Among these methods, the free-radical copolymerization of vinyl monomers, which have hydrophilic units in its backbone and/or hydrophilic side groups with a small amount of divinyl comonomer, is an effective route because of its versatility for monomer type and mild reaction conditions as well as tolerance to water.⁴

Free-radical polymerization has many advantages over other methods. However, it offers little control over the network structure and yields a random copolymerization of monomer and crosslinking agent, leading to microgel formation

Correspondence to: S. Zhu (E-mail: zhuship@mcmaster.ca)

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and a heterogeneous network structure. A well-defined homogeneous network structure is desirable for many hydrogel applications. To overcome the drawbacks of free-radical crosslinking polymerization, various types of living polymerization have been investigated. For example, Ide and Fukuda⁵ used nitroxide-mediated radical polymerization and synthesized homogeneous gels of styrene with a small amount of 4,4'-divinylbiphenyl and found that the critical number density of crosslinks at the gel point agreed with the mean-field theoretical value of Flory and Stockmayer within a factor of two.

Recently, a new type of controlled radical polymerization, atom transfer radical polymerization (ATRP),⁶ has been developed and proven to be most robust to vinyl monomer types, such as styrene,^{7,8} methacrylates,^{9,10} acrylonitrile,¹¹ and 2-(*N,N*-dimethylamino)ethyl methacrylate,¹² particularly when the Cu-based catalytic system is used. The advantage of ATRP is that it does not require strict experimental conditions such as in the case for anionic and cationic polymerizations. A few investigations have been reported on the use of ATRP to prepare crosslinked networks by a macromonomer method or end-linking process. Matyjaszewski et al.¹³ used ATRP to produce polystyrene macromonomer first, and then the macromonomer was copolymerized with *N*-vinylpyrrolidinone to prepare polystyrene-*g*-*N*-vinylpyrrolidinone hydrogels. Asgarzadeh et al.¹⁴ obtained a linear polymer precursor of polystyrene with two reactive end groups by ATRP and then used this difunctional polystyrene precursor as a macroinitiator to prepare styrene/divinylbenzene networks.

No studies have been reported on the utilization of the ATRP method to prepare hydrogels. The objective of this work is to synthesize poly[2-(*N,N*-dimethylamino)ethyl methacrylate-co-ethylene glycol dimethacrylate] (polyDMAEMA/EGDMA) hydrogel using the ATRP method. The copolymerization kinetics was investigated systematically with respect to the crosslinker level. The hydrogels were characterized by swelling experiments, and the extractable polymers were also analyzed by sol fraction and molecular weight measurements.

EXPERIMENTAL

Materials

The monovinyl monomer of 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) (Aldrich) and

the divinyl comonomer of ethylene glycol dimethylacrylate (EGDMA) (Aldrich) were distilled under reduced pressure and stored at $-15\text{ }^{\circ}\text{C}$ before use. The catalyst of copper bromide (CuBr) (99.99%, Aldrich), the ligand of 1,1,4,7,10,10-hexamethyl triethylenetetramine (HMTETA) (Aldrich), and the initiator of ethyl 2-bromoisobutyrate (EBIB) (Aldrich) were all used as received. The solvent of tetrahydrofuran (THF) (99.8%, Aldrich), petroleum ether (Aldrich), and acetone (Aldrich) were also used without further purification.

Polymerization

A solution process was used for the copolymerization of DMAEMA with EGDMA, using THF as the solvent. The concentration of the total monomers of DMAEMA and EGDMA was fixed to 50% of the solution by weight. The CuBr:HMTETA:EBIB:DMAEMA molar ratio was 1:1:1:100. The mixture was added into a glass ampoule reactor and sealed with a septum. The reactor with its content was degassed using ultrapurified nitrogen for 15 min. The degassed reactor was placed in a water bath, and the polymerization was conducted at $60\text{ }^{\circ}\text{C}$. When the reaction proceeded for a preset time period, the reaction was stopped by immediately immersing the ampoule into an ice-water bath.

The polymer was recovered by precipitation in petroleum ether and dried in a vacuum oven at $40\text{ }^{\circ}\text{C}$ to a constant weight. The conversion of total monomer was determined by a gravimetric method.

Gel fractions were determined by the following method: A weighed amount of thoroughly dried polymer was extracted with acetone as solvent in a Soxhlet extractor for 48 h until no more extractable polymer could be detected by gel permeation chromatography. The sol-free hydrogel, if present, was dried in a vacuum oven at $40\text{ }^{\circ}\text{C}$ for a certain time until a constant weight was reached. The gel fraction, f_g , was then determined by $f_g = w_g/w_p$, where w_g is the weight of the dried sol-free hydrogel sample, and w_p is the total polymer weight.

Hydrogel Swelling

Swelling experiments were conducted to characterize the hydrogels. Because some hydrogel samples could swell to an extent that they become too fragile to handle, a sieve weighing boat was used following Chen et al.¹⁵ A weighed amount of dried sol-free hydrogel was placed in a sieve weighing

boat. The boat was immersed in deionized water at room temperature for swelling. When the swelling process reached equilibrium, the boat was taken out to drain free water, and a filter paper was used to remove excess water underneath the sieve. The weight of the swollen hydrogel was then determined gravimetrically. The swelling ratio, s_g , was defined by $s_g = (w_s - w_0)/w_0$, where w_s is the weight of the swollen hydrogel sample, and w_0 is that of the dried hydrogel.

Sol Characterization

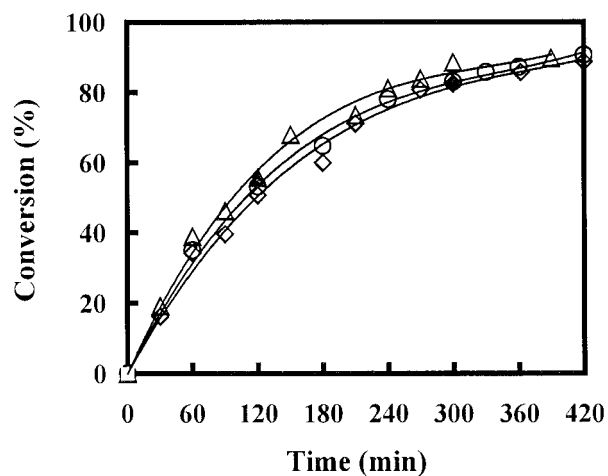
Sol was the portion of extractable uncrosslinked polymers. After extracted, the sol was precipitated from petroleum ether. The molecular weight and polydispersity of the sol polymers were measured using a Waters 590 LC with three Varian Micropark columns (G1000, 3000, and 7000 HXL) connected to a 410 differential refractometer detector. A universal calibration was performed on the basis of polystyrene standards obtained from TSK Manufacturing Co., Japan. THF was used as the solvent. All experiments were performed at 25 °C under isocratic conditions.

RESULTS AND DISCUSSION

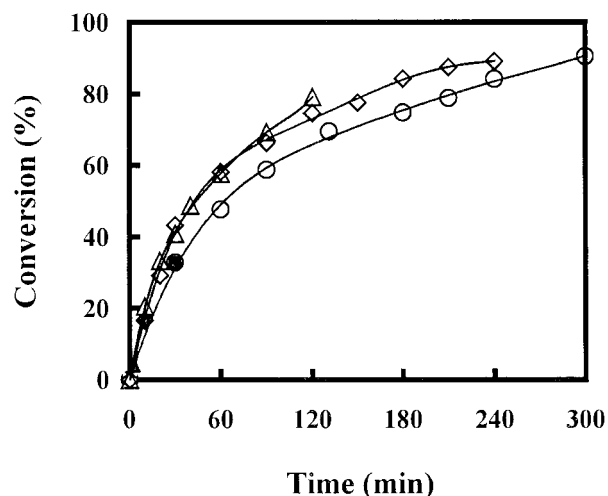
Copolymerization Kinetics

The total monomer conversion versus time data and their kinetic plots of $\ln([M]_0/[M])$ versus time for the ATRP of DMAEMA with EGDMA at six EGDMA levels ($f_2 = 0.01, 0.02, 0.05, 0.1, 0.2,$ and 0.5) are presented in Figures 1 and 2. The conversion increased smoothly with time, and there was no sharp change observed near the gel point (indicated by the solid point for each curve). At low EGDMA concentrations, the $\ln([M]_0/[M]) \sim t$ curves are linear, indicating there is neither diffusion-controlled propagation nor a significant increase in radical termination, which are the characteristics of the conventional free-radical polymerization and the nitroxide-controlled copolymerization of monovinyl monomer with divinyl monomer.^{5,16} In contrast to the conventional free-radical polymerization, most propagating centers in the ATRP process are dormant species temporarily capped by the bromine atom that minimizes possible radical termination.

The polymerization rate increased with an increased EGDMA level. The conversion determined by a gravimetric method is the weight-



(a)

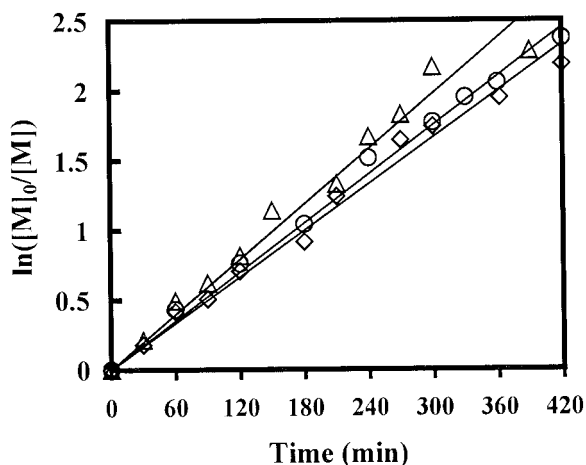


(b)

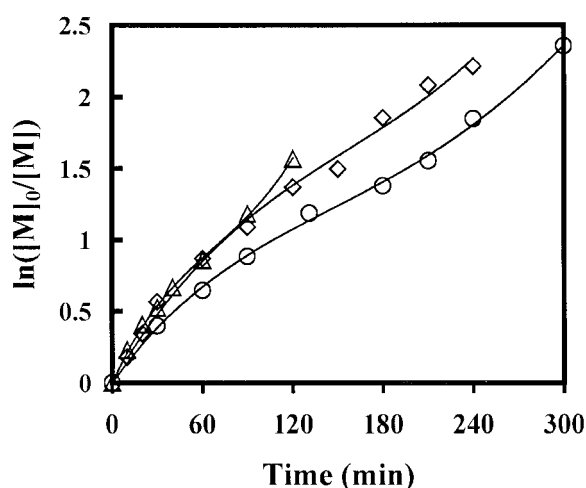
Figure 1. The conversion versus time of the copolymerization of DMAEMA with EGDMA by ATRP in THF solution at 60 °C with the total monomer concentration equal to 50% in weight and the molar ratio of CuBr/HMTETA/EBIB/monomer equal to 1:1:1:100. The EGDMA fractions are (a) 0.01 (○), 0.02 (◇), and 0.05 (△); and (b) 0.1 (○), 0.2 (◇), and 0.5 (△). The filled points are gel points.

based total conversion of vinyl and divinyl monomers. For a divinyl monomer like EGDMA, it becomes a part of the polymer population as soon as one of the two vinyl groups is reacted. The difunctional nature of EGDMA allows the monomer to be easily incorporated. The reactivity of EGDMA as a comonomer is higher than that of DMAEMA although each of its two vinyl groups may not be as reactive.

At high EGDMA levels (above 10 mol %), the kinetic curves showed some abnormal features.



(a)



(b)

Figure 2. The $\ln([M]_0/[M])$ versus time of the copolymerization of DMAEMA/EGDMA with the EGDMA fractions: (a) 0.01 (\circ), 0.02 (\diamond), and 0.05 (\triangle); and (b) 0.1 (\circ), 0.2 (\diamond), and 0.5 (\triangle). The other experimental conditions refer to Figure 1.

Taking the case of $f_2 = 0.1$ as an example [refer to Fig. 2(b)], the polymerization shows a deceleration at intermediate conversions. Three possible reasons for this decrease in rate are evident through an examination of the relationship of

$$\ln([M]_0/[M]) = kp[R]t \quad (1)$$

where in this case kp is a pseudokinetic rate constant

$$kp = kp_{11}\phi_1f_1 + kp_{12}\phi_1f_2 + kp_{21}\phi_2f_1 + kp_{22}\phi_2f_2 \quad (2)$$

where kp_{ij} is the propagation-rate constant of i -type radical with j -type monomer, ϕ_i is the molar fraction of i -type radical, f_j is the molar fraction of j -type monomer, and the subscripts 1 and 2 are the vinyl and divinyl monomers. The first possibility is the decrease of radical concentration $[R]$ as a result of termination. However, the rate acceleration in a later stage excludes this possibility. The second possibility is the diffusion limitations experienced by monomers in a polymer network, and thus the propagation reactions become diffusion controlled, resulting in a decrease in kp 's. Diffusion-controlled reactions are common in a conventional free-radical polymerization, where the formation of a polymer chain with thousands of monomeric units requires only seconds. In contrast, it takes hours for an ATRP process to grow a polymer chain with hundreds of units via a living mechanism. This is also why an ATRP process is expected to produce a more homogeneous polymer network than a conventional free-radical counterpart. In the latter process, monomer propagation is so quick that it gives no time to the polymer chain to relax and thus leads to the generation of locally concentrated microdomains of polymer network (microgels). In the ATRP process, the slow growth rate permits a polymer chain to be fully relaxed, generating a homogeneous network, and thus the propagation does not become diffusion controlled at this stage. The third explanation for the deceleration is the

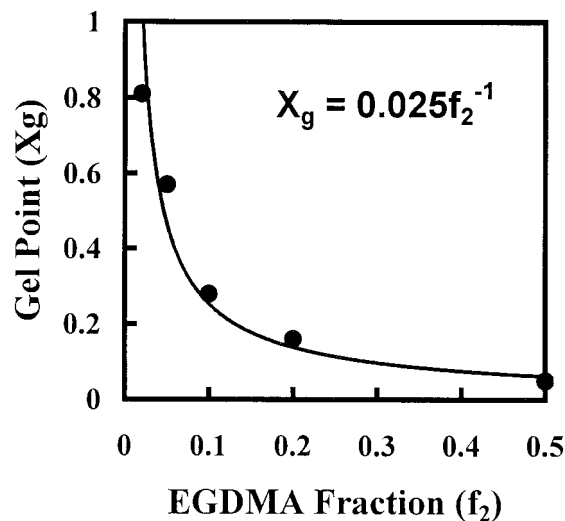


Figure 3. The gel point as a function of the EGDMA fraction. The solid line is fitted by $X_g f_2 = 0.025$. The gelation occurred at higher conversions than those calculated by Flory's equation $X_g f_2 = 0.01$.

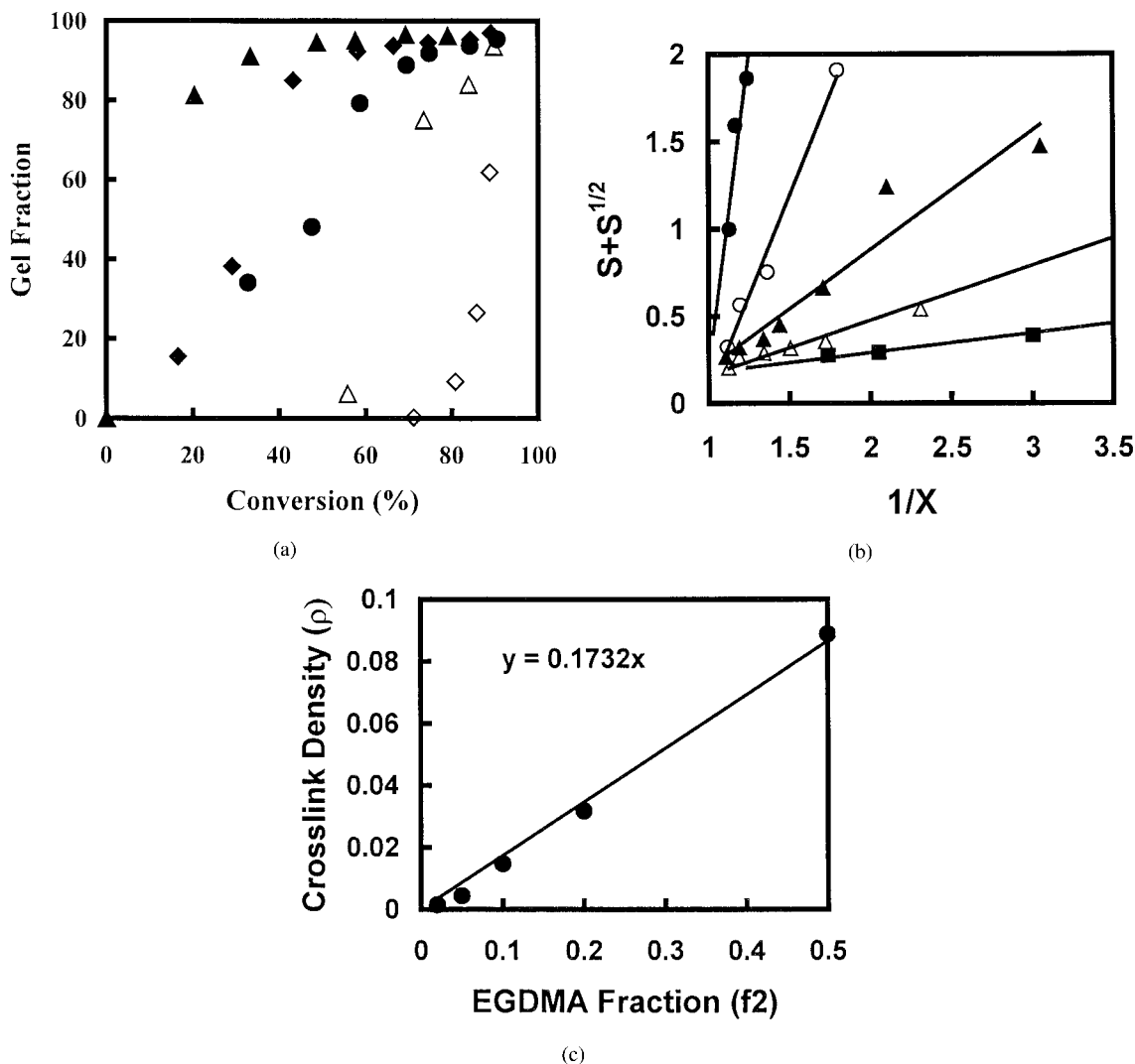


Figure 4. The gel development in the ATRP copolymerization of DMAEMA/EGDMA with the EGDMA fractions of (a) gel fraction versus conversion $f_2 = 0.02$ (\diamond), 0.05 (\triangle), 0.1 (\bullet), 0.2 (\blacklozenge), 0.5 (\blacktriangle), (b) $s + s^{1/2}$ versus $1/X$ $f_2 = 0.02$ (\bullet), 0.05 (\circ), 0.1 (\blacktriangle), 0.2 (\triangle), 0.5 (\blacksquare), and (c) crosslink density versus EGDMA fraction.

consumption of divinyl comonomers. EGDMA is more reactive than DMAEMA. In a batch process, the former monomers are consumed faster than the latter that leads to the reduction in the polymerization rate. Composition drifting in batch copolymerization is common when one comonomer is more reactive than the other.

An interesting kinetic observation is the rate acceleration at high conversions. It is unlikely that the k_p 's can increase during the polymerization [refer to $\ln([M]_0/[M]) = k_p[R]t$]. Therefore, the only factor that could potentially accelerate the rate is an increase in radical concentration. In a conventional free-radical polymerization, poly-

mer chains are entangled at high conversions, and this limits radical termination. Additionally, radicals are continuously generated by initiation. The radical population is, therefore, accumulated. This phenomenon is known as the "gel effect" or "Trommsdorff effect." However, the ATRP mechanism does not permit this molecular process to occur. In the ATRP process, propagating centers are at most time capped with the bromine atom by the atom transfer reaction with CuBr_2 complexed with the ligand. The dormant species are reactivated when the bromine atom is abstracted by the $\text{CuBr}/\text{ligand}$ complex. The only possibility is that the $\text{Cu(II)Br}_2/\text{ligand}$ complex experiences

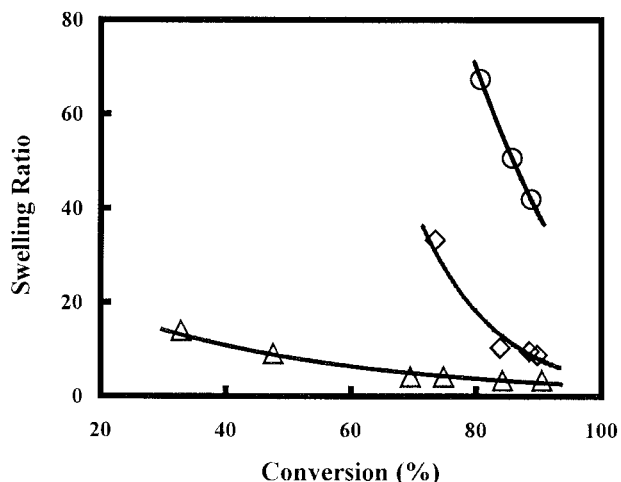


Figure 5. The swelling ratios of the gel samples in water as a function conversion for $f_2 = 0.02$ (○), 0.05 (◇), and 0.1.

diffusion limitations in the polymer network, and thus the atom transfer reactions become diffusion controlled. The equilibrium constant of $\text{P-Br} + \text{Cu(I) Br/ligand} \leftrightarrow \text{P} \cdot + \text{Cu(II)Br}_2/\text{ligand}$ is very low, and the rate constant of the backward reaction exceeds that of the forward reaction by orders of magnitude. Therefore, the backward reaction becomes diffusion controlled much earlier than the forward reaction. In this scenario, the radical concentration increases and leads to the acceleration of the polymerization rate at high conversions. Also, this phenomenon occurred much later than the gelation point and at the time when the polymer network became quite rigid.

Gel Formation and Swelling

Figure 3 depicts the dependence of the gel point (X_g is the total monomer conversion at the gel point) on the EGDMA level. Except for the $f_2 = 0.01$ case, all other conditions yielded gels. Increasing the divinyl fraction accelerated the gel formation. According to Flory,¹⁷ gelation occurs at the point where on an average basis, each primary chain contains one crosslink point. It is difficult to have a detailed model calculation on the basis of the available data at this stage. However, a brief analysis can be provided to examine the applicability of Flory's theory. Neglecting the effects of the compositional drifting during the polymerization and the unequal reactivities of vinyl, divinyl, and pendant double bonds, the

crosslink density is given by $2[\text{EGDMA}]_0/[\text{M}]_0$ (one crosslinkage consists of two crosslink points), the average chain length is given by $[\text{M}]_0X/[\text{I}]_0$, and their product is given by $2[\text{EGDMA}]_0X/[\text{I}]_0$ or $2[\text{M}]_0f_2X/[\text{I}]_0$, which should equal to 1 at the gel point according to Flory. In this work, $f_2X = [\text{I}]_0/2[\text{M}]_0 = 0.005$. The correlation shown in the figure is $f_2X = 0.025$. Flory's equation was developed for a homogeneous network, that is, a network statistically assembled from equally reactive vinyl groups. The gel points in the conventional free-radical polymerization often deviated from the prediction by orders of magnitude.^{5,18} The relatively small factor of 5 indicates that the ATRP process yields a more homogeneous network than the conventional free-radical process. Usually, the reactivity of pendant double bonds is lower than those of vinyl and divinyl, and thus the crosslink density is smaller than $2[\text{EGDMA}]_0X/[\text{I}]_0$ because of the residual pendant double bonds trapped in the network. The real value of f_2X in this work should be higher than 0.005 and closer to the theoretical 0.025.

Figure 4(a) shows the gel development during the ATRP polymerization at five EGDMA levels of 0.02, 0.05, 0.1, 0.2, and 0.5. Because of the difficulty in measuring the gel content close to gel point, the data are somewhat scattered. However, the trend is evident. The gel fraction increased rapidly in the postgelation period. The gel growth is not only caused by propagating monomers but also by incorporating sol polymers via the reactions between radicals and pendant double bonds on both gel and sol populations.

According to Charlesby and Pinner,¹⁸ the relationship of $s + s^{1/2} = (\rho r_{\text{np}})^{-1}$ should hold, where s is the sol fraction ($s = 1 - g$), ρ is the crosslink density, and r_{np} is the number-average primary chain length. However, the equation was originally derived by radiation crosslinking with primary chains having a most probable distribution and is therefore used as an approximation. For a living polymerization such as ATRP, $r_{\text{np}} = [\text{M}]_0X/[\text{I}]_0$ ($[\text{M}]_0/[\text{I}]_0 = 100$ in this work). Figure 4(b) plots $s + s^{1/2}$ against $1/X$. Their linear relationship is clear. From the slopes in Figure 4(b), one can obtain the crosslink density data as shown in Figure 4(c). It is of interest to note the weak dependence of the crosslink density on the EGDMA fraction. Only a small fraction (approximately 17%) of the comonomer was actually used for crosslinking. It appears that a significant reduction exists in the reactivity of pendant double bonds trapped in the polymer network and/or in-

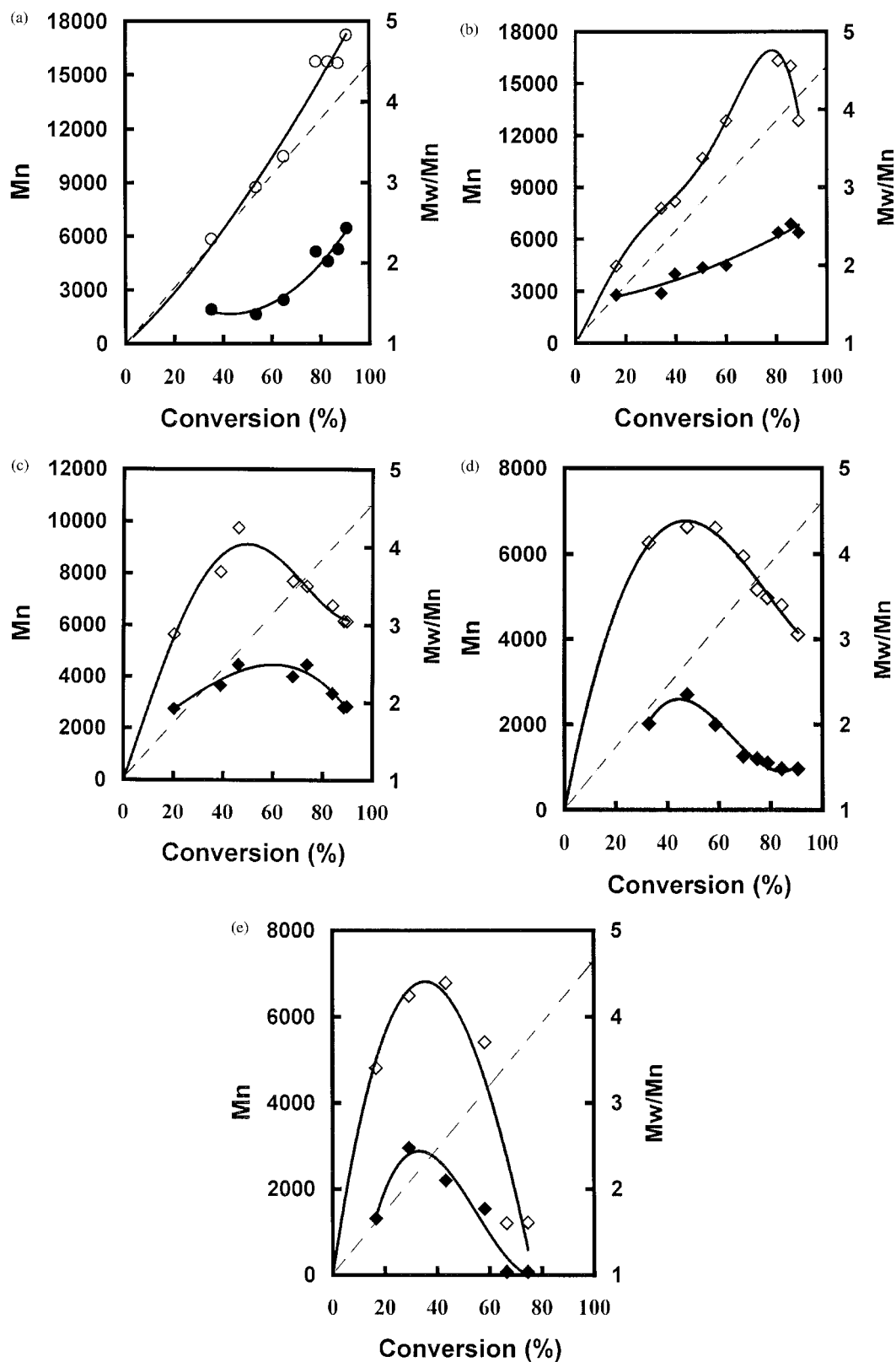


Figure 6. The molecular weight development and polydispersity of sol polymers in the copolymerization of DMAEMA/EGDMA. The EGDMA fractions are (a) 0.01, (b) 0.02, (c) 0.05, (d) 0.1, and (e) 0.2. The empty symbols are M_n . The filled symbols are M_w/M_n . The dashed lines are calculated by $[M]_0 X / [I]_0$.

tramolecular cyclization reaction. If this factor of 17% is considered in the f_2X estimate, it becomes 0.029 that is very close to the theoretical value of 0.025.

The equilibrium swelling ratios were measured for the systems of $f_2 = 0.02, 0.05, \text{ and } 0.10$. The network structure has a dramatic effect on the swelling ratio; on the other hand, the swelling result reflects the hydrogel structure. Figure 5 illustrates the swelling ratio data plotted against monomer conversion. Increasing the EGDMA content and/or monomer conversion yields a tight polymer network and results in a lower swelling ratio.

Molecular Weight of Sol Polymers

Figure 6(a–e) demonstrates the development of number-average molecular weight (M_n) and polydispersity (M_w/M_n) during the polymerization. At low EGDMA concentrations (take the case of $f_2 = 0.01$ as an example), the molecular weight agreed with the values calculated by $[M]_0X/[I]_0$ (the dashed line) at low conversions, indicating that most polymers at this stage were linear chains. However, it deviated from the predicted values at high conversions because of crosslinking. The difference between the experimental and calculated values gives the number of crosslink points, $M_n/M_{np} - 1$. At 80% conversion, this number is approximately 0.28. The M_w/M_n data also reflect the trend of crosslinking. The value was low at low conversions when the polymer chains were linear. It significantly increased when crosslinking occurred. There was no gel observed in the case of $f_2 = 0.01$.

The deviation of the M_n from $[M]_0X/[I]_0$ became evident at low conversions for $f_2 > 0.02$. The M_w/M_n was also higher from the early stage and steadily increased up to the gel point. After the gel point, the polymerization system contained both sol and gel polymers. A gel molecule is defined as an insoluble (but swellable in good solvent) three-dimensional polymer network with a theoretical infinitely large molecular weight. At the gel point, the weight-average molecular weight goes to infinity but not the M_n . However, the latter also shows a maximum at the gel point as evident in Figure 6(b–e). After the gel point, the molecular weight decreased. This is because high molecular weight sol polymers have a better chance to be consumed by gels through the reactions between radicals and pendant double bonds. The residual sol molecules are mostly linear or

slightly crosslinked. Their M_w/M_n 's approached unity, the same level as the case of $f_2 = 0.01$ in its early stage [Fig. 6(d,e)].

CONCLUSION

The copolymerization of DMAEMA with EGDMA was carried out by ATRP with CuBr as a catalyst, HMTETA as a ligand, and EBIB as an initiator. The process proceeded in a living manner. At low EGDMA levels, the kinetic plots of $\ln([M]_0/[M])$ versus t were linear. However, at high EGDMA levels, the curves showed deceleration in rate at low conversions followed by acceleration at high conversions. The former was caused by the fast consumption of EGDMA, whereas the latter was likely due to diffusion limitations of the catalyst/ligand complex $\text{Cu}(\text{I-I})\text{Br}_2$ in the polymer network. The diffusion-controlled atom transfer reaction suppressed the formation of dormant species and thus increased the radical concentration. The gel formation in the polymerization system was examined against Flory's theory. The gelation occurred at higher conversions than the predicted, indicating the presence of significant intramolecular cyclization and trapping of pendant double bonds. The crosslink densities were lower than the EGDMA fractions. The molecular weights of the sol polymers decreased in the postgel period with their M_w/M_n 's approaching unity at the final stage of polymerization.

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