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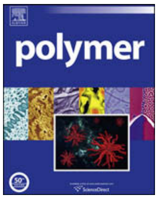

Comparison of reaction kinetics and gelation behaviors in atom transfer, reversible addition–fragmentation chain transfer and conventional free radical copolymerization of oligo(ethylene glycol) methyl ether methacrylate and oligo(ethylene glycol) dimethacrylate

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ABSTRACT

The reaction kinetics and gelation behavior in atom transfer radical polymerization (ATRP), reversible addition–fragmentation chain transfer (RAFT), and conventional free radical copolymerizations (FRP) of oligo(ethylene glycol) methyl ether methacrylate (OEGMEMA) and oligo(ethylene glycol) dimethacrylates (OEGDMAs) were investigated and compared with respect to the polymerization rate, gel point, and the evolution of network with vinyl conversion. All the three systems experienced autoacceleration in the reaction rate but occurred at different regions of vinyl conversion, caused by diffusion-controlled radical reactions: termination in the FRP, addition in the RAFT, and deactivation in the ATRP, respectively. In the FRP, significant amount of gel materials was collected by solvent extraction far before the onset of macro-gelation detected by an abrupt increase in complex viscosity. However, in the RAFT and ATRP, no gels were found until the systems approached their macro-gelation points. The observation suggests limited intramolecular crosslinking/cyclization reactions in the ATRP and RAFT systems. This is because the slow growth of primary chains (ATRP and RAFT in hours versus FRP in seconds) allowed adequate chain relaxation and diffusion of reacting species. The gel materials thus synthesized by ATRP and RAFT are expected to be more homogeneous in network structure than that by FRP.

1. Introduction

Free radical copolymerization of vinyl monomer with divinyl crosslinker has been widely used for preparation of polymer networks and gels. These polymer materials have found a variety of applications such as microelectronic devices, ophthalmic lenses, and optical fiber coatings [1–5]. Recently, there is an increasing interest in developing homogeneous polymer networks with controlled microstructure [6–16]. In the high performance applications such as controlled drug release and biomedical materials, the structural homogeneity of the networks becomes a crucial issue. However, conventional free radical polymerization (FRP) offers little control over primary polymer chains and network microstructure. FRP proceeds with slow initiation, fast propagation, and fast termination. It takes only seconds for an individual chain to fully grow from initiation to termination. Therefore, primary chains having high molecular weight and containing numerous pendant double bonds are instantaneously formed at the very beginning of polymerization. Due to high dilution of chains and relatively slow diffusion compared to fast propagation, rapid intramolecular reactions between propagating radical and pendant double bonds at vicinity are favored, generating various cycles and densely crosslinked domains (microgels). The formation of microgels leads to structural heterogeneity in the final network product [2,5,6].

In contrast to FRP, controlled/living radical polymerization (CLRP) methods have advantages in preparing homogeneous polymer networks because of their fast initiation and slow chain growth [8–10,14–17]. All primary chains are initiated at the early stage of CLRP. The fast exchange of a small number of propagating radicals with a large number of dormant chains temporarily and frequently interrupts propagation and prolongs chain growth to hours, giving sufficient time for chains to relax and for reacting species to diffuse (primary chains, monomers, crosslinkers, and pendant double bonds). The uniform distribution of reacting species minimizes microgel formation by facilitating intermolecular crosslinking, giving rise to a homogeneous polymer network.

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Several groups have reported the syntheses of crosslinked polymers with homogeneous networks by CLRPs [8–11,14–19]. For example, Ide and Fukuda used nitroxide mediated radical polymerization (NMP) [8] and reversible addition–fragmentation chain transfer (RAFT) polymerization [14] for synthesis of polystyrene gels and compared the gelation dynamics. Zhu et al. studied the kinetics of atomic transfer radical polymerization (ATRP) of oligo(ethylene glycol) dimethacrylates (OEGDMAs) [9,15,16] and their network structures [17]. It was found that the reaction proceeded in a controlled manner in the first stage of ATRP and deviated from the "living" process due to the diffusion-controlled radical deactivation as the mobility of the ATRP catalyst was severely restricted in the network. The networks prepared by ATRP were more homogeneous than those prepared by FRP. Matyjaszewki [19,20] and others [10,21,22] studied the ATRP gelation of methacrylate and dimethacrylate. They established the relationship between gel point and vinyl conversion at different crosslinker to initiator ratios and monomer concentrations. The experimental gel points were found to be in close agreement with Flory–Stockmayer theory. The structures of monomer and/or crosslinker species did not affect the experimental gel points significantly. Recently, we investigated the RAFT polymerization of dimethacrylates [18], and showed that the RAFT system had a very different reaction behavior from the FRP. The diffusion-controlled addition, which resulted in a mild autoacceleration, was caused by restricted mobilities of propagating radicals and RAFT-capped chains. Armes et al. reported on the syntheses of branched polymers by copolymerization of monovinyl monomers with a small amount of divinyl monomers using ATRP and/or RAFT [23–25]. They found the occurrence of gelation was determined by the initial molar divinyl to initiator ratio in the ATRP or by the divinyl to RAFT agent ratio in the RAFT. Insoluble gels were produced when divinyl/initiator molar ratio exceeded unity in the ATRP, while gelation occurred at much higher molar ratio of divinyl/CTA in the RAFT.

Reaction mechanism and kinetics play an important role in gelation behavior and development of network structure. A fundamental understanding of the reaction mechanism and kinetics involved in the CLRP network-forming system is essential for preparation of polymer networks with homogeneous and controlled microstructure. In this work, we report an experimental investigation on the network-forming FRP, RAFT, and ATRP systems via copolymerization of oligo(ethylene glycol) methyl ether methacrylate and oligo(ethylene glycol) dimethacrylate. The gelation behaviors in the three systems were systematically investigated and compared with respect to the polymerization rate, vinyl conversion, gel point, and the evolution of network with vinyl conversion. The relationships between autoacceleration, micro-gelation, macro-gelation to divinyl concentration were examined in order to elucidate the mechanism and kinetics of the CLRP with crosslinking.

2. Experimental part

2.1. Materials

Oligo(ethylene glycol) methyl ether methacrylate (OEGMEMA, 99%) and oligo(ethylene glycol) dimethacrylate (OEGDMA, 99%) were purchased from Aldrich and used without further purification. The number-average molecular weights measured by ^{1}H NMR for OEGMEMA and OEGDMA were 300 and 330 g/mol, respectively. The ATRP initiation system consisted of copper(I) bromide (CuBr, 98%) as the catalyst, methyl α-bromophenylacetate (MBPA, 97%) as the initiator, and *N*,*N*,*N*,*N*-tetramethylethylenediamine (TMEDA, 99.5%) as the ligand. All the chemicals were supplied by Aldrich and were used as received. Azobis-isobutyronitrile (AIBN, Aldrich, 97%), as the radical initiator in the FRP and RAFT systems, was used after purification by recrystallization from chloroform–methanol. Benzyl dithiobenzoate (BDB) was used as the RAFT agent. It was synthesized according to an established procedure [26,27].

2.2. Reaction recipe

The molar ratio of vinyl group, initiator, catalyst and ligand was set to 100:1:1:1 for the ATRP system, while in the RAFT and FRP systems the vinyl/AIBN/BDB molar ratio was set to 100:0.25:1 and 100:0.25:0, respectively. The OEGMEMA copolymerization runs with four OEGDMA molar fraction levels from 2.56, 5.26, 8.11, to 11.11% on a monomer molecule basis (equivalent to 5.0, 10, 15, and 20% on a vinyl group basis) were designed. Take the ATRP system with 2.56% OEGDMA molar fraction as a real synthetic example: 2.88 g (9.5 mmol of vinyl group) OEGMEMA, 83.3 mg (0.5 mmol of vinyl group) OEGDMA, 14.31 mg CuBr (0.1 mmol), and 11.65 mg TMEDA (0.1 mmol) were added to a dry 10 mL glass ampoule. The ampoule was then sealed with a rubber septum and degassed with ultrahigh-purity nitrogen for 10 min. 15.73 μl (0.1 mmol) MBPA was quickly added to the ampoule by a degassed syringe. In the corresponding RAFT run, 4.1 mg (0.025 mmol) AIBN and 27.1 mg (0.1 mmol) BDB were dissolved into a mixture of 2.88 g (9.5 mmol of vinyl group) OEGMEMA and 83.3 mg (0.5 mmol of vinyl group) OEGDMA in a 10 mL ampoule.

2.3. Kinetic measurement

The polymerization was carried out in a differential scanning calorimeter (DSC, Pyris-1, Perkin–Elmer). Monomer mixture samples, typically 15–20 mg with an accuracy of ±0.1 mg, were weighed in open aluminum pans and placed in the DSC cell for reaction. The DSC cell was purged with ultrahigh-purity nitrogen for 5 min before the DSC was equilibrated at reaction temperature with a heating rate of 320 °C/min. The rate of polymerization (R_p) was monitored under isothermal conditions following the heat flow ($\mathrm{d}H/\mathrm{d}t$) evolved from the highly exothermic reaction and was estimated by Equation (1). Integrating the heat flow curve versus time gave the vinyl conversion (x), as shown in Equation (2). During the isothermal DSC scanning, a 50 mL/min nitrogen flow was maintained to prevent intervention from oxygen.

$$R_\mathrm{p} = \frac{\mathrm{d}H/\mathrm{d}t}{\Delta H_0^\mathrm{theor}} \tag{1}$$

$$x = \frac{\int_0^t \mathrm{d}H/\mathrm{d}t}{\Delta H_0^\mathrm{theor}} = \frac{\Delta H_t}{\Delta H_0^\mathrm{theor}} \tag{2}$$

where ΔH_t is the reaction heat released up to time t and $\Delta H_0^\mathrm{theor}$ (−54.85 kJ/mol [28]) is the theoretical enthalpy of methacrylate double bond in the complete conversion. All the measurements were run twice and the parallel DSC runs gave a less than 5% error.

2.4. Gelation characterization

The gelation process was followed by a strain-controlled rheometer (Physica, MCR-301, Anton Paar) with parallel plate geometry (25 mm in diameter) and an environmental chamber. Approximately 1 g reaction mixture, same as the one in the kinetic study, was put into the lower plate. The upper parallel plate was lowered to contact tightly with the sample and the final gap was adjusted to 1.0 mm. A 5 L/min nitrogen flow was maintained as the heating medium and protection atmosphere. After the chamber was quickly heated to the defined temperature, a time sweep was conducted in an oscillatory mode at a constant frequency of 1 Hz and a constant strain of 0.5%. The variation in the reaction medium complex viscosity during the polymerization was recorded and the abrupt acceleration in the increase of the complex viscosity was taken as the onset of macro-gelation (i.e., the macrogel point).

2.5. Determination of gel fraction

The gel fraction was determined using the same procedure as in Ref. [29]. It should also be pointed out that some of the RAFT data reported in Ref. [29] are included in this paper for the comparison purposes, as cited in the figure captions. The glass ampoules filled with the same reaction mixture as in the kinetic study were immersed into an oil bath for parallel experiments. The reaction was stopped at a pre-set interval by immersing the ampoule into an ice-water bath. The resulting product was put into a bottle containing 50-fold THF to extract monomer residues and sol polymers. The solvent was replaced every other day over a period of two weeks until no more extractable polymer was detected. The insoluble portion (gel) was collected in a 600 mesh stainless metal screen with a pore size of 20 μm, and then dried to a constant weight in a vacuum oven at 50 °C. The gel fraction (f_g) was obtained by $f_g = W_g/W_p$, where W_g is the dried gel weight, and W_p is the total sample weight. The moment for gel materials to appear was taken as the onset of micro-gelation (i.e., the microgel point). It should be pointed out that the choice of screen pore size is very important in a gel extraction experiment. Many studies reported in literatures used much bigger pore sizes that could collect only macrogel materials.

3. Results and discussion

3.1. Kinetic features and autoacceleration in rate

As shown in Fig. 1(a)–(c), there existed significant differences in the polymerization rate and vinyl conversion profiles between the FRP, RAFT and ATRP copolymerization of OEGMEMA with four OEGDMA molar fraction levels from 2.56, 5.26, 8.11, to 11.11%. The FRP proceeded much faster than its RAFT and ATRP counterparts. The maximum rates for the three systems with 11.11% OEGDMA were $26.9 \times 10^{-4}\ s^{-1}$ in the FRP, $12.2 \times 10^{-4}\ s^{-1}$ in the RAFT, and $2.32 \times 10^{-4}\ s^{-1}$ in the ATRP, respectively. This difference in the rate could be attributed to the difference in their propagating radical concentrations. In the FRP, the propagating radical concentration is determined by the balance between radical initiation and termination. However, in the ATRP, the radical population is controlled by the activation/deactivation equilibrium between propagating radicals and dormant species [30]. Because the deactivation is much faster than the activation, the equilibrium constant is very small and the radical concentration is much lower than that in the FRP, which resulted in the lower polymerization rate.

The total radical concentration in the RAFT system is also determined by the balance between initiation and termination, following the same manner as in the FRP. The introduction of RAFT agent does not affect the total radical concentration. However, there are two types of radical populations involved in the RAFT process, propagating and intermediate radicals. While the propagating

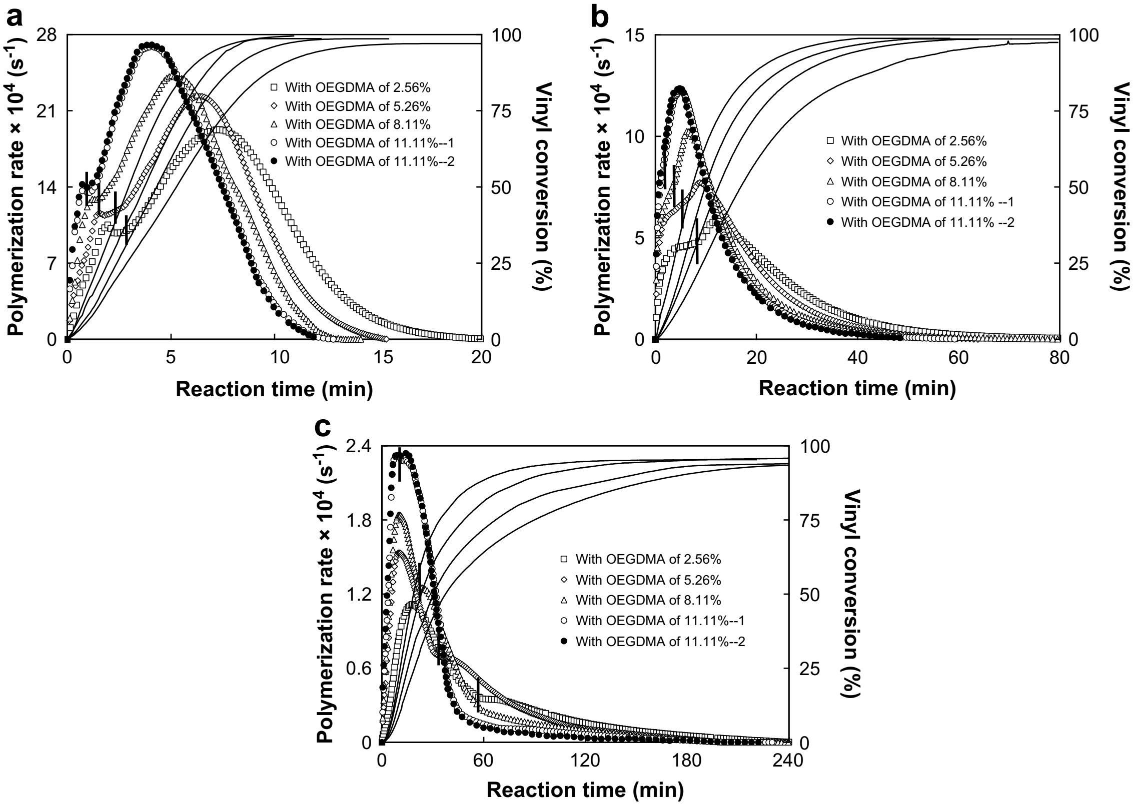

Fig. 1. Polymerization rate and vinyl conversion profiles of the OEGMEMA copolymerization at 80 °C with four OEGDMA molar fraction levels from 2.56, 5.26, 8.11, to 11.11% by (a) FRP, (b) RAFT (Ref. [29]), and (c) ATRP, respectively. In the FRP, [Vinyl]:[AIBN] = 100:0.25; in the RAFT, [vinyl]:[AIBN]:[BDB] = 100:0.25:1; and in the ATRP, [vinyl]:[MBPA]:[CuBr]:[TMEDA] = 100:1:1:1. The points are rate data; the lines are conversion curves; and the bars mark the onset of autoacceleration.

radicals are responsible for chain growth through propagation, the intermediate radicals do not react with monomers or pendant double bonds. The population of propagating radicals depends on the relative magnitude of the addition and fragmentation rates [31]. The intermediate radicals are stabilized through radical delocalization in the aromatic group of dithiobenzoate. The stabilized intermediate radicals have a slow fragmentation rate, which leads to a reduced propagating radical population, and thus lower the polymerization rate [32–35].

It is noteworthy that all the three systems experienced rate autoacceleration (termed as "Trommsdorff effect" or misnomer "gel effect"), evident from the appearance of a shoulder in their rate curves in Fig. 1(a)–(c). This autoacceleration occurred at different vinyl conversions, depending on the OEGDMA molar fraction (see Fig. 2). For example, the autoacceleration occurred at ∼18, 24, and 63% of vinyl conversion in the FRP, RAFT and ATRP systems with 2.56% OEGDMA molar fraction, respectively. This observation suggests different mechanisms for the origin of autoacceleration. It is widely accepted that the autoacceleration in the FRP is caused by a diffusion-controlled radical termination. The radical termination in the FRP involves two macromolecular species at an extremely low concentration and readily becomes diffusion-controlled. In the FRP with crosslinking, highly branched polymers and microgels were formed at a very early stage of polymerization. The branching and microgel structures restricted mobilities of the macromolecular radicals, and the propagating radicals experienced difficulty in bimolecular termination. The reduction in the termination rate resulted in an accumulation of radical population and thus an autoacceleration in the polymerization rate.

On the other hand, the occurrence of autoacceleration in the RAFT was related to the diffusion-controlled addition of propagating radicals to RAFT-capped chains. The addition reaction also involves two polymer chains. In the RAFT system, all primary chains were initiated within a short period of time at the early stage of polymerization. These short chains grew gradually through propagation with monomers and pendant double bonds in activation/deactivation cycles. The chains became long and branched, which restricted the mobilities of propagating radicals and RAFT-capped chains, and eventually resulted in a diffusion-controlled addition reaction. This diffusion-controlled addition influenced the equilibrium between propagating and intermediate radical populations, slowed down the deactivation of propagating radicals, and resulted in an increase in the propagating radical population and thus an increase in the polymerization rate. Because the molecular weight of primary chains in the RAFT was much smaller than that in the FRP, the diffusion-controlled addition in the former occurred later than the diffusion-controlled termination in the latter.

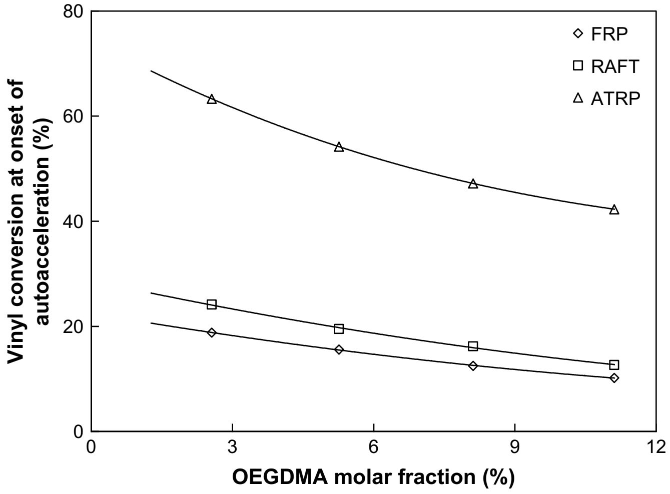

Fig. 2. Relationship between the vinyl conversion at the onset of autoacceleration and the OEGDMA molar fraction in the FRP, RAFT (Ref. [29]), and ATRP systems under the same reaction conditions as in Fig. 1.

The autoacceleration in the ATRP occurred at a high vinyl conversion region, where densely crosslinked network has been formed. This autoacceleration could be ascribed to the diffusion-controlled deactivation of propagating radicals, which is bimolecular in nature involving one macromolecular species (radical) and one small molecule (Cu(II) complex) [9,15]. In the ATRP with crosslinking, the equilibrium of activation/deactivation was influenced by the diffusion rates of catalyst/ligand complexes. Once the Cu(II) complex diffusion was restricted, the equilibrium of activation and deactivation would be interfered with impeding radical deactivation, which led to an increase of radical concentration and then the autoacceleration in the polymerization rate. Because Cu(II) complex was a small molecule, it became diffusion controlled only after a densely crosslinked network was formed. Therefore, the diffusion-controlled deactivation, and then the autoacceleration came much later in the ATRP than in the FRP and RAFT systems.

There are also some commonalities in the kinetic behaviors of the FRP, RAFT and ATRP copolymerization runs of OEGMEMA with the four OEGDMA molar fraction levels: The polymerization rate increased with increasing divinyl concentration, and the autoacceleration appeared earlier at the higher level of OEGDMA molar fraction. The high OEGDMA concentration introduced more pendant groups into polymer chains. The growing chains became branched and gelled at an earlier stage of polymerization in the FRP and RAFT, leading to the earlier autoacceleration. The high OEGDMA concentration also increased the network crosslink density in the ATRP, leading to the diffusion-controlled deactivation, and thus to the earlier autoacceleration.

3.2. Gelation behavior and evolution of network

The onset of gelation (gel point) is an important parameter in understanding reaction mechanism in the network-forming system. In the literatures, some defined the gel point as the moment when the reaction fluid lost its mobility in a tube at an upside-down position for 10 s [8,19,20,23], others determined the gel point as the time that gel materials could be detected by solvent extraction [10,15,16]. In this work, the gelation process was followed by both rheological measurement and solvent extraction. The dynamic rheology test monitored the variation of complex viscosity of the reaction medium during the polymerization. The complex viscosity increased gradually at the beginning of reaction, followed by an abrupt acceleration upon the network formation (see the complex viscosity curves in Fig. 3(a)–(c)). The abrupt acceleration point was taken as the *onset of macro-gelation* (the *macrogel point*) [36]. The solvent extraction collected the gel fractions at various time intervals. The moment that the gel materials started to appear was taken as the *onset of micro-gelation* (the *microgel point*), and the rapid increase of gel fraction with vinyl conversion also marked the occurrence of macro-gelation.

Fig. 4(a)–(c) gives the gel fraction and swelling ratio curves for the FRP, RAFT and ATRP systems. It was observed that in the FRP, the micro-gelation occurred at a very early stage of the polymerization and the macro-gelation appeared much later. Take the 5.26% OEGMA curve in Fig. 4(a) as an example. The microgel materials started to appear at about 10% vinyl conversion (the microgel point). The microgels content increased gradually with increased conversion, however, the increase suddenly accelerated at about 35%, which corresponded to the onset of macro-gelation (the macrogel point). On the other hand, the micro- and macro-gelation

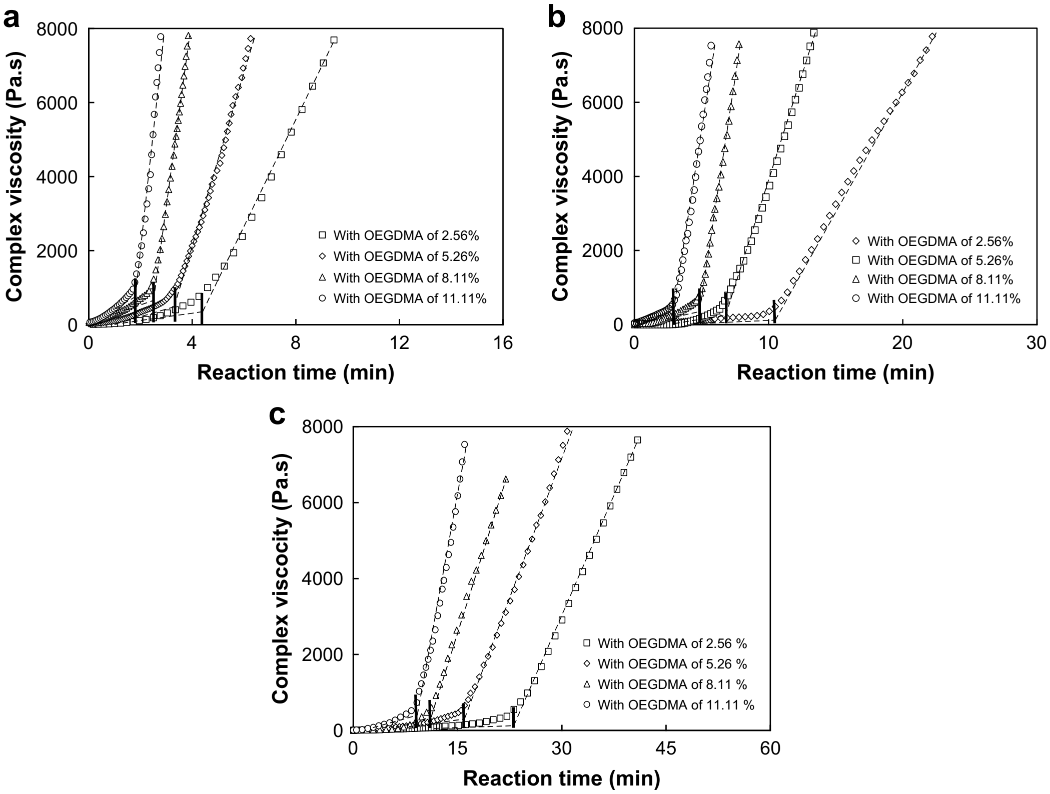

Fig. 3. Variation of the complex viscosity during the copolymerization of OEGMEMA with four OEGDMA molar faction levels by (a) FRP, (b) RAFT (Ref. [29]), and (c) ATRP, under the same reaction conditions as in Fig. 1. The bars mark the onset of macro-gelation.

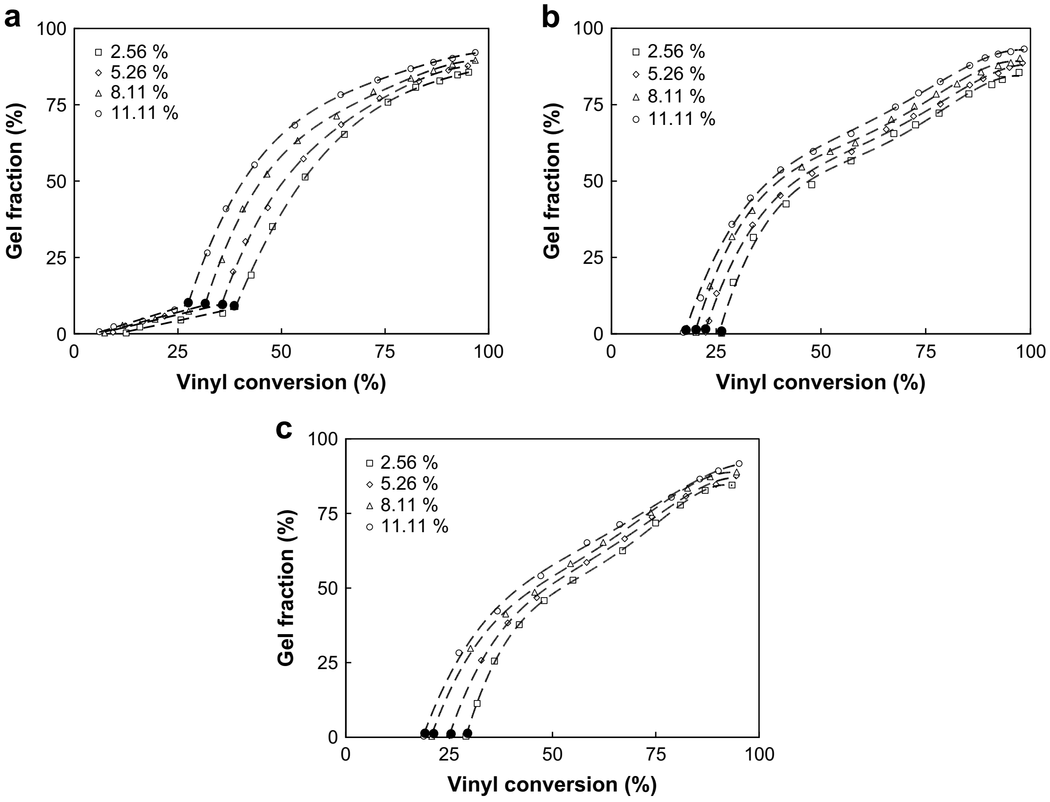

Fig. 4. Gel fraction versus vinyl conversion curves in the OEGMEMA copolymerization with four OEGDMA molar faction levels by (a) FRP, (b) RAFT (Ref. [29]), and (c) ATRP, under the same reaction conditions as in Fig. 1. The black circles mark the onset of macro-gelation.

in the RAFT and ATRP systems occurred at similar conversion regions, indicated by an absence of the sudden change in the gel fraction versus conversion curves in Fig. 4(b) and (c), as in Fig. 4(a). That is, the microgel and macrogel points in the RAFT, as well as in the ATRP, were overlapped with each other. In all the three systems, the vinyl conversions at the onsets of micro- and macro-gelation decreased with the increase of OEGDMA molar fraction.

Fig. 5(a)–(c) summarizes the microgel (measured by solvent extraction) and macrogel (by both rheological measurement and solvent extraction) points observed in the FRP, RAFT and ATRP systems and their dependence on the OEGDMA molar fraction. It can be seen in Fig. 5(a) that the macrogel points in the FRP system determined by the sudden increase in viscosity (Fig. 3(a)) agreed very well with those by the sudden increase in gel fraction (Fig. 4(a)) and that the microgel points came much earlier than the macrogel points at all the studied OEGDMA molar fraction levels. It can also be seen in Fig. 5(b) and (c) that the micro-gelation and macro-gelation in the RAFT and ATRP systems occurred almost simultaneously in terms of vinyl conversion, later than the micro-gelation but earlier than the macro-gelation in the FRP system.

It has been well studied that FRP with crosslinking could lead to gelation [2,5,6,37,38]. An FRP system is characteristic of slow initiation, fast propagation and fast termination. Individual chains grow to full length in seconds. The highly diluted fully grown chains generated at the beginning of polymerization migrate slowly, relative to fast chain propagation. This promotes reactions between radicals and pendant double bonds within the same chains, leading to formation of various intramolecular cycles. As such chains accumulate, some intermolecular reactions between these chains result in formation of densely crosslinked domains (microgels) at an early stage of polymerization [37,38]. Microgels grow quickly through reacting with other chains and become detectable by solvent extraction (microgel point). At a higher conversion, these microgels combine one another through intermolecular crosslinking to form huge networks evident from an abrupt increase in viscosity and/or a loss of mobility of the fluid (macrogel point). The difference in the microgel and macrogel points provides a good indicator for the heterogeneity of the formed networks.

The closer onsets of micro- and macro-gelation in the RAFT and ATRP than in the FRP suggest a different gelation mechanism involved in the CLRP processes. In the CLRP such as RAFT and ATRP, all primary chains are initiated at an approximately same time, and ideally the number of primary chains remains nearly constant throughout the polymerization. The primary chains grow through propagation with vinyl groups in both monomer and crosslinker molecules. Because of the rapid exchange of propagating radical and dormant chain, the chain growth is temporarily and frequently interrupted, leading to a slow (in hours) but simultaneous growth of all the primary chains. The primary chains are relaxed and have adequate time to diffuse around. The micro-gelation and intramolecular cyclization in the early stage are thus significantly limited. In this work, no gel materials were collected from our low conversion samples in the ATRP and RAFT systems. With more and more pendant double bonds participating reactions, the primary chains become highly branched. Branched chains have higher possibilities than linear ones to react with each other because of their high numbers of pendant vinyl groups. Successive intermolecular reactions between highly branched chains eventually yield a polymer network with an "infinitely large" molecular weight (i.e., macrogels).

The macrogel points in the three studied systems followed the order of ATRP ~ RAFT < FRP. According to Flory's mean-field

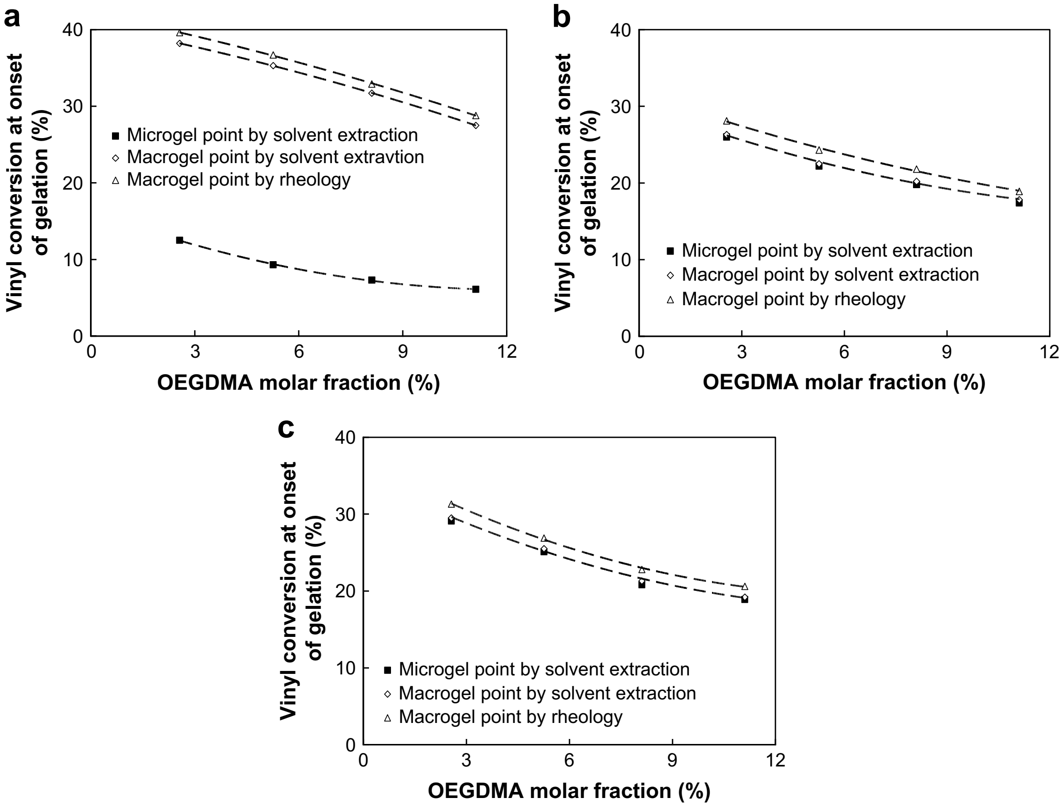

Fig. 5. Dependence of the microgel and macrogel points (vinyl conversion) on the OEGDMA molar fraction in the (a) FRP, (b) RAFT (Ref. [29]), and (c) ATRP systems, under the same reaction conditions as in Fig. 1.

theory [39], the gelation occurs when the number of crosslinking points (note: one crosslinkage consists of two crosslinking/branching points in the H type crosslinking) per primary chain equals unity, provided all vinyl groups have the same reactivity and absence of intramolecular cyclization. However, it has been shown [19,20] that the intramolecular cyclization reactions inevitably occur in the copolymerization of vinyl/divinyl monomers. The competition between intermolecular crosslinking and intramolecular cyclization is the main factor in determining the experimental gel point. As discussed above, the extent of intramolecular cyclization relative to intermolecular crosslinking strongly depends on the polymerization mechanism. The intramolecular cyclization in the early stage of FRP consumed a significant amount of pendant double bonds, and thus postponed the macro-gelation.

In this work, the macro-gelation onset points in ATRP and RAFT were very close to each other, which are different from those reported by Dr. Armes' group [24,25]. They used RAFT technique to copolymerize 2-hydroxyisopropyl acrylate (HPA) with diacrylate crosslinkers and found that the macro-gelation occurred much later than in the ATRP of a similar monomer system. It was attributed to more intramolecular cyclization in the RAFT process, which consumed pendant vinyl groups and delayed gelation. This discrepancy might be caused by the different reaction conditions used in their ATRP and RAFT systems. The HPA concentration in RAFT was ∼2.8 M [25], lower than ∼3.5 M 2-hydroxypropyl methacrylate (HPMA) in ATRP [23]. *tert*-Butanol was used as solvent in the former while methanol used in the latter. It has been found that dilute condition enhances intramolecular cyclization [20]. Polymer chains in a poor solvent also tend to be tightly coiled, and to favor intramolecular cyclization.

4. Conclusion

Based on the experimental investigation and comparison of the reaction kinetics and gelation behaviors of the FRP, RAFT and ATRP copolymerization of OEGMEMA and OEGDMA, the following conclusions can be drawn. First, all the three systems experienced rate autoacceleration but in different vinyl conversion regions due to different mechanisms. In the FRP, the autoacceleration occurred very early and it was resulted from diffusion-controlled radical termination which involves two long chain radical species at a very dilute concentration. In the RAFT, the autoacceleration came slightly later and it was caused by diffusion-controlled addition, which involves two shorter chain species with one propagating radical chain and the other being high concentration RAFT-capped chain. In the ATRP, the autoacceleration appeared at much higher vinyl conversion region where densely crosslinked networks were formed, and it was induced by diffusion-controlled radical deactivation, which involves one radical chain and the other small molecule catalyst complex. The onset conversion of autoacceleration in all the three systems decreased with increased OEGDMA concentration. Second, the micro-gelation occurred much earlier than the macro-gelation in the FRP, however, the microgel and macrogel points of the RAFT and ATRP systems were overlapped. The vinyl conversion onsets of macro-gelation was in the order of ATRP ∼ RAFT < FRP. The postponed macro-gelation in the FRP could be attributed to its significant consumption of pendant double bonds in the intramolecular reactions that caused micro-gelation. The overlap between the microgel and macrogel points in the RAFT and ATRP systems suggested that the intramolecular cyclization and thus micro-gelation were greatly suppressed in the CLRP processes. This was due to slow chain growth that allowed adequate relaxation and diffusion of growing chains and in turn facilitated the formation of more uniform networks.

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