

Development of networks in atom transfer radical polymerization of dimethacrylates

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Abstract

The development of networks and structural heterogeneity in the atom transfer radical polymerization (ATRP) of dimethacrylates was studied. The structural and kinetic evolutions during the polymerization were followed using differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and extraction/swelling measurement. The reversible activation/deactivation equilibrium between growing radical and dormant species slowed down the polymerization process, giving rise to sufficient chain relaxation and diffusion of reactive species, which favored the formation of homogeneous networks. Compared to the networks prepared by conventional free radical polymerization that favored microgel formation, the ATRP products were more homogeneous, suggested by narrower peak width of the $\tan \delta$ curve. It was also found that crosslinking density and degree of structural heterogeneity of the ATRP products increased with vinyl conversion. The loss of the living feature at high conversions did not further increase the structural heterogeneity. The ATRP of dimethacrylates with longer spacer yielded more homogeneous networks with lower crosslinking density and lower glass transition temperature.

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1. Introduction

Free radical polymerizations of multifunctional monomers produce crosslinked polymer networks. These network materials have a wide range of applications such as dental restorative materials, ophthalmic lenses, and optical fiber coatings [1–4]. It has been recognized, however, that the polymerization with crosslinking exhibits anomalous reaction behaviors [5–21], including prominent autoacceleration and autodeceleration [10,11], unequal functional group reactivity [12,16], reaction-diffusion controlled termination [10,12,16], and limited functional group conversion due to hindered mobility of

vinyl groups [13,15]. In addition, one of the most important characteristics of the polymerization is the formation of massive microgels, which leads to the heterogeneous polymer networks [20,21]. An ideal polymer network consists of a homogeneously crosslinked structure with little variation in molecular weight between the crosslinks. In the high performance applications such as information storage materials, microelectronic devices, and biomedical materials, the structural homogeneity of the networks is required.

Atom transfer radical polymerization (ATRP), as well as other types of controlled/living radical polymerization (CLRP), has advantages over conventional free radical polymerization (FRP) in preparing homogeneous polymer networks. The reversible equilibrium between growing radical and dormant species in ATRP results in a low radical concentration and makes chain growth slower, giving sufficient time for chain relaxation and diffusion of reacting species. This would favor intermolecular crosslinking and suppress

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microgel formation. More homogeneous polymer networks are thus expected. Recently, the syntheses of crosslinked polymers with homogeneous network structure by controlled/living radical polymerization (CLRP) have been reported [22–30].

In our previous studies, the mechanism and kinetics in the ATRP of dimethacrylates have been investigated [27–29]. From an application point of view, a fundamental understanding of the structural evolution of networks during the ATRP with crosslinking and the relationship between polymerization behavior and network structure are essential for the development of specialty materials with tailor-made properties. In this work, we report the experimental results on the structural properties of the networks prepared by the ATRP of dimethacrylates. The structural evolution during polymerization was followed by dynamic mechanical analysis (DMA) and extraction/swelling techniques. The effect of the spacer length between vinyl groups in dimethacrylate on the network structure was also examined. Coupled with the kinetic information, we correlated the evolution of network and structural heterogeneity with the ATRP mechanism and kinetics.

2. Experimental part

2.1. Materials

Three polyethylene glycol dimethacrylates (PEGDMA) with similar chemical structures (see Fig. 1) but different spacer lengths between the methacrylate moieties were used. The number-average molecular weights measured by ^1H NMR were 330, 550 and 787 g/mol, respectively. The three monomers were denoted as PEGDMA-330, PEGDMA-550 and PEGDMA-787. The average numbers of ethylene glycol units were $X = 4, 9,$ and $14,$ respectively. The ATRP system consisted of methyl α -bromophenylacetate (MBPA, 97%) as initiator, copper (I) bromide (CuBr, 98%) as catalyst, and N,N,N',N' -tetraethyldiethylenetriamine (TEDETA, 90%) as ligand. Benzoyl peroxide (BPO) was the initiator for the conventional free radical polymerization (FRP). All the oligomers and chemicals were supplied by Aldrich and were used as received, except for BPO that was used after purification by recrystallization.

2.2. Polymerization recipe

The molar ratio of vinyl group to initiator, catalyst, and ligand was set to 100:1:1:1 for the ATRP of PEGDMA-550 system. In a typical experiment, 2 g of PEGDMA-550 (7.27 mmol of vinyl group), 10.40 mg of CuBr (0.0727 mmol), and 17.40 mg of TEDETA (0.0727 mmol) were added to a dry 5 mL glass ampoule. The concentrations of initiator, catalyst and ligand

were $[\text{MBPA}] = [\text{CuBr}] = [\text{TEDETA}] = 0.04$ mol/L. The ampoule was then sealed with a rubber septum and degassed with ultrahigh-purity nitrogen for 10 min. MBPA of 11.44 μl (0.0727 mmol) was quickly added to the ampoule by a degassed syringe. The ampoule was shaken for 1 min prior to the start of polymerization. For PEGDMA-330 and PEGDMA-787, the concentrations of CuBr, TEDETA, and MBPA were the same as in the PEGDMA-550 system, regardless of the variation in the vinyl concentration. In the FRP system, the molar ratio of vinyl group to BPO was 200:1. BPO of 24.2 mg (0.10 mmol) was dissolved into 5.5 g (20 mmol) of PEGDMA-550 in a 10 mL tube with stirring.

2.3. Polymerization kinetics

The polymerization runs of dimethacrylates were conducted in a differential scanning calorimeter (DSC, Pyris-1, Perkin–Elmer) in an isothermal mode. Approximately 25 mg of reaction mixture was placed in a small aluminum pan. The DSC cell was purged with ultrahigh-purity nitrogen for 5 min before it was equilibrated at the reaction temperature (100 $^{\circ}\text{C}$). During the isothermal DSC operation, a 50 ml/min of nitrogen flow rate was maintained to prevent the intervention from oxygen. The heat flow (dH/dt) evolved from the exothermic reaction was measured as a function of time. Since the heat evolved from consumption of vinyl groups was very large compared to other possible reactions such as activation and deactivation, it was assumed that other reactions would not have a significant effect on the heat released. Therefore, the rate of polymerization (R_p) in a unit of fractional vinyl conversion per second could be calculated by Eq. (1). Integrating the heat flow curve versus time provided the vinyl conversion (x) by Eq. (2).

$$R_p = \frac{dH/dt}{\Delta H_0^{\text{theor}}} \quad (1)$$

$$x = \frac{\int_0^t dH/dt}{\Delta H_0^{\text{theor}}} = \frac{\Delta H_t}{\Delta H_0^{\text{theor}}} \quad (2)$$

where ΔH_t is the reaction heat released up to time t and $\Delta H_0^{\text{theor}}$ (-54.8 kJ/mol [12]) is the theoretical enthalpy of methacrylate double bond in the complete conversion.

2.4. Network characterization

The reaction mixture, same as the one used in the kinetic study, was introduced into a mould made of two glass plates separated by a 1 mm silicone gasket. The mould was then immersed into an oil bath to start the crosslinking polymerization. The reaction was stopped at different time intervals and the resulting products were taken for structure characterization. The dynamical mechanical measurement was performed using a dynamic mechanical analyzer (Rheometrics, MCR-301, Anton Paar) in a torsion model by applying a sinusoidal stress of 1 Hz frequency. The specimen was a thin rectangular

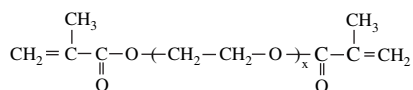


Fig. 1. Chemical structure of poly(ethylene glycol) dimethacrylate (PEGDMA).

sheet of 1 mm thick and 10 mm × 40 mm area. The storage shear modulus, G' , and the loss tangent, $\tan \delta$, were recorded as a function of temperature over a range of -150 to 150 °C with a ramping rate of 5 °C/min.

The remainder of the sample was put into a bottle that contained 50-fold THF to extract monomer residue and sol materials. The solvent was replaced every other day over a period of at least 1 week until no more extractable polymer was detected. The gel materials were dried to a constant weight in a vacuum oven at 50 °C. The gel fraction (f_g) was then 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 swelling experiment was carried out by immersing weighed gel materials into THF at 25 °C for at least 1 week to reach swelling equilibrium. The swollen gel was then weighed to determine the swelling ratio (s_g), which was defined by $s_g = (W_s - W_g)/W_g$, where W_s is the weight of the swollen gel, and W_g is that of the dried gel.

3. Results and discussion

3.1. Comparison of ATRP and FRP networks

To illustrate the advantage of controlled/living radical polymerization (CLRP) with crosslinking in preparing homogeneous networks, the ATRP of PEGDMA-550 with $[MBPA] = [CuBr] = [HMTETA] = 0.04$ mol/L and the FRP of PEGDMA-550 with $[BPO] = 0.02$ mol/L were conducted at 100 °C in DSC and oil bath environment. The rate profiles for the two systems are shown in Fig. 2. The final vinyl conversions were 87.5% in the ATRP and 96.3% in the FRP. After polymerization, the characterization of the network structure was carried out by DMA. Fig. 3 shows the storage modulus and $\tan \delta$ curves.

It is observed from Fig. 3 that the modulus behavior was well captured over a temperature range of 250 °C. The modulus of both network samples decreased from a glassy state

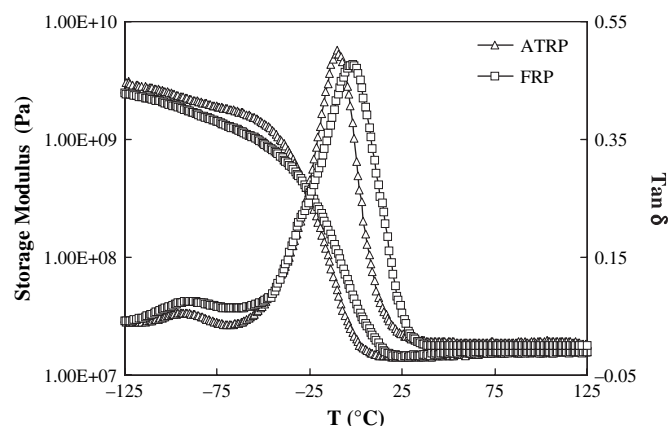


Fig. 3. Storage shear modulus and loss tangent versus temperature of the samples prepared by the ATRP and FRP in Fig. 2.

value $\sim 3 \times 10^9$ Pa to a rubbery state value $\sim 1.5 \times 10^7$ Pa. The storage modulus in the rubbery region is an indication of the crosslinking density of the network. The nearly identical rubbery modulus for the ATRP and FRP networks suggested that the two polymers had similar crosslinking densities. The higher vinyl conversion and similar rubbery modulus of the FRP network sample suggested that more vinyl groups were consumed in cyclization and did not effectively contribute to crosslinking in the FRP system.

An important feature of the DMA measurement is the peak width of the $\tan \delta$ curve. The DMA temperature scan of the FRP network sample exhibited a broader $\tan \delta$ peak than that of the ATRP counterpart (42 °C versus 31 °C). This difference indicated a broader glass transition region of the former. The breadth of transition region was related to the degree of structural heterogeneity [11,20,31–35]. Highly crosslinked polymers formed by the polymerization of multifunctional monomers contain primary and secondary cycles as well as crosslinks. A primary cycle occurs when a growing radical loops back and propagates a pendant double bond on the same chain. A secondary cycle forms when one polymer chain forms more than one crosslinks with another chain. Primary cycles do not contribute to the overall crosslinking density, but facilitate microgel formation [31,33]. Intermolecular crosslinking reactions, which are responsible for the aggregation of microgels, lead to the formation of a network. Microgels are very highly crosslinked domains with extremely restricted segmental mobility, while other parts of the network possess far more mobile microenvironments. Such network evolution causes an inhomogeneous distribution of segmental mobilities, leading to a broad distribution of relaxation times. Therefore, the structural heterogeneity of network could be quantified using the breadth of transition region in DMA.

It is clear that the ATRP network was more homogeneous than the FRP network. The heterogeneous network structure of the FRP polymer could be attributed to the rapid chain growth and slow chain relaxation. As far as the growth of individual primary chains in the FRP and ATRP networks, the time difference was in 3–4 orders of magnitude (seconds for FRP versus hours for ATRP). In the FRP, it took only seconds

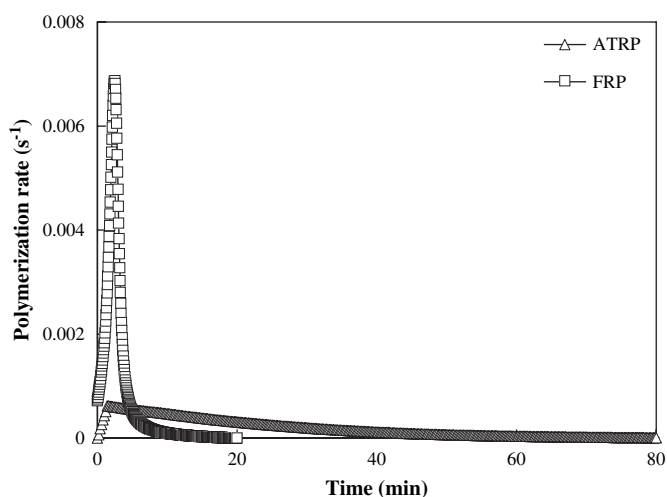


Fig. 2. Polymerization rate profiles of the ATRP of PEGDMA-550 with $[MBPA] = [CuBr] = [TEDETA] = 0.04$ mol/L and the FRP of PEGDMA-550 with $[BPO] = 0.02$ mol/L at 100 °C.

for an individual chain to fully grow so that there was a lack of time for chain relaxation. Due to close proximity of pendant double bonds to the radical and a relatively high local pendant double bond concentration in its vicinity, the rapid reaction between the radical and the pendant double bonds yielded various cycles and microgels (i.e., densely crosslinked domains). The slow chain relaxation relative to chain growth in the FRP system was responsible for the structural heterogeneity.

The improvement of structural homogeneity in polymer network by ATRP is related to its mechanism and kinetic behavior. In the ATRP system, all the primary chains (both radical and dormant) were started in the early stage of polymerization. The reversible activation/deactivation equilibrium between growing radical and dormant species significantly reduced the rate of chain growth. Since the radical was temporarily and frequently deactivated by catalyst, chain growth through propagation was often interrupted. The slow chain growth gave sufficient time for chain relaxation that allowed vinyl groups (pendant and monomeric) uniformly distributed in the network and thus reduced the local double bond concentration at the vicinity of radicals. This favored the intermolecular crosslinking reactions to form homogeneous networks.

3.2. Structural evolution of ATRP networks

During the ATRP of multifunctional monomers, the formation of a three-dimensional network restricts the mobility of chains and other reacting species, which not only influence the reaction mechanism and kinetics, but also affects the structural evolution of the network including structural heterogeneity. To follow the structural evolution of the networks, the polymer samples of PEGDMA-550 prepared under the same condition as in Fig. 2 were subject to extraction and swelling, as well as dynamic mechanical analysis. Fig. 4 shows the vinyl conversion, gel fraction and swelling ratio versus reaction time. Figs. 5 and 6 give the storage modulus and loss tangent versus temperature.

It is observed from Fig. 4 that the vinyl conversion increased gradually with reaction time and finally reached to

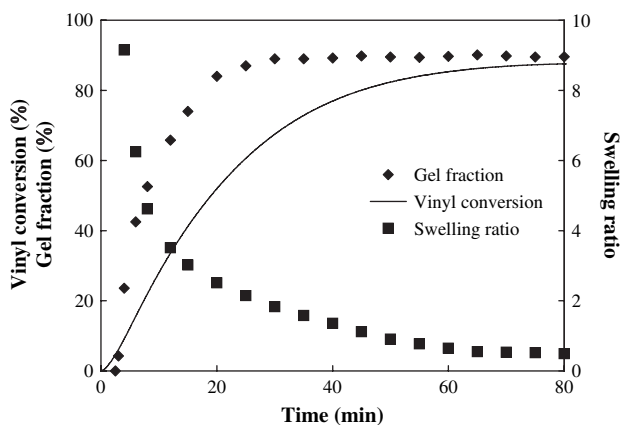


Fig. 4. Evolution of vinyl conversion, gel fraction, and swelling ratio in the ATRP of PEGDMA-550 with $[MBPA] = [CuBr] = [TEDETA] = 0.04 \text{ mol L}^{-1}$ at 100°C .

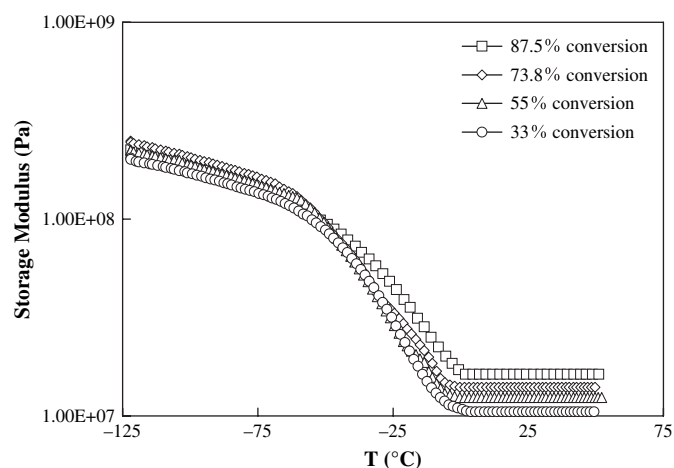


Fig. 5. Storage modulus of the ATRP samples of PEGDMA-550 obtained at different vinyl conversions.

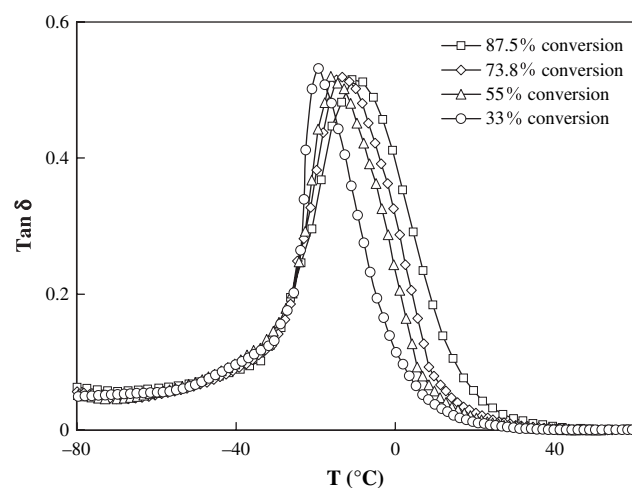


Fig. 6. Loss tangent ($\tan \delta$) curves of the ATRP samples of PEGDMA-550 obtained at different vinyl conversions.

87.5%. The gelation occurred at 4.8% vinyl conversion. After the gel point, the gel fraction increased drastically and leveled off in 30 min, corresponding to 65% vinyl conversion. The final gel fraction was 89%. The swelling ratio continuously decreased. The gel fraction and swelling ratio data suggested that the intermolecular crosslinking and gel radical propagation with monomer dominated in the early stage of polymerization. However, in the late stage, the reactions between pendant double bonds and radicals inside the networks were the major contributors for the further increase of crosslinking density.

The rubbery modulus in Fig. 5 was related to crosslinking density of the network. The rubbery elasticity theory could be used to estimate the crosslinking density from rubbery modulus. However, this procedure would involve an assumption of Gaussian chain distribution, which is not valid in highly crosslinked network systems. Therefore, the rubbery modulus was used as a measure of crosslinking density on a qualitative basis and the actual values were not calculated. Fig. 7 shows the modulus (or crosslinking density) and glass transition temperature as a function of vinyl conversion. The

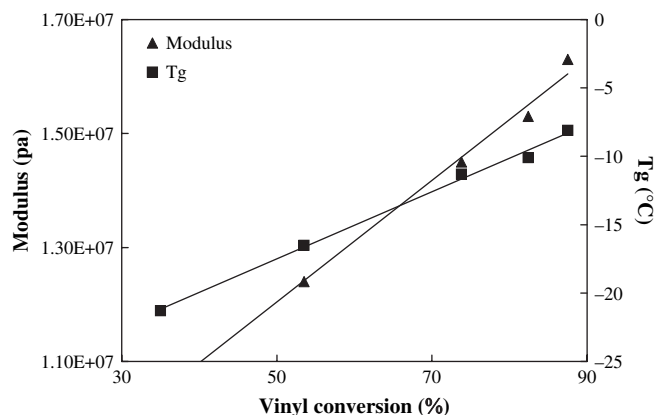


Fig. 7. Crosslinking density and glass transition temperature of the ATRP samples of PEGDMA-550 as a function of vinyl conversion.

glass transition temperature was obtained from the peak maximum of the $\tan \delta$ curves in Fig. 6.

It is observed that the crosslinking density and thus glass transition temperature of the network increased with vinyl conversion. This result is expected because the further conversion of vinyl groups contributed to the increased number of effective crosslinks and then to the denser network. The dense network severely restricted the mobility of chains and thus gave higher glass transition temperature. Similar behavior has been observed by Bowman and others [34,36,37] in the polymerization of dimethacrylates. However, the observed change in T_g with conversion was smaller than that reported in the literature [36,37]. It might be attributed to the different reaction mechanism in our system, which led to the different evolution of the networks.

Fig. 8 plots the peak half-width of $\tan \delta$ curve as a function of vinyl conversion. The data provided further insight into the structural evolution of the ATRP networks. It can be seen that as the vinyl conversion of PEGDMA increased from 33 to 87.5%, the half-width of the $\tan \delta$ peak increased from 18 to 31 °C. This increase in the half-width indicated an increase

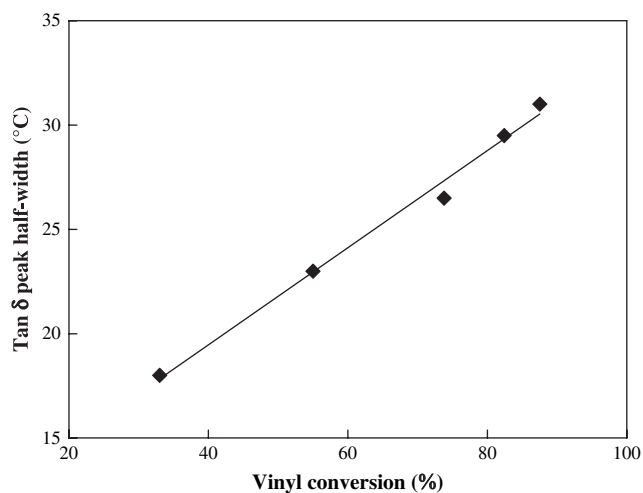


Fig. 8. $\tan \delta$ peak half-width of the ATRP samples of PEGDMA-550 as a function of vinyl conversion.

in the degree of structural heterogeneity. Interestingly, there appeared to be a linear dependence of the half-width on the vinyl conversion. As described in the literature [27], in the ATRP of PEGDMA, when the crosslinking density reached a certain level, the restricted mobility of transition metal complexes would impede the radical deactivation and resulted in an increase of radical concentration. The accumulation of radical population and the lack of protection of radicals by catalyst led to a significant radical termination. The livingness of the polymerization became lost and the reaction behaved like a conventional free radical polymerization (FRP). From Fig. 8, it appears that this change of mechanism from ATRP to FRP in the late stage of the reaction did not contribute further structural heterogeneity of the network.

3.3. Effect of spacer length on structural heterogeneity

The effect of dimethacrylate spacer length on polymerization behavior has been widely studied in FRP and ATRP crosslinking systems [9,10,15,17,18,29]. The network formation occurs with extensive cyclization and crosslinking. The structure and flexibility of monomer dramatically affect the network structure. Three types of PEGDMA monomers were used to investigate the spacer length effect on the evolution of network and structural heterogeneity. The average numbers of ethylene glycol units between methacrylate groups were $X = 4, 9,$ and $14,$ respectively. Fig. 9 shows the storage modulus curves of the ATRP samples with different spacer lengths. Fig. 10 shows the loss tangent versus temperature curves of the same samples. All the samples were polymerized at 100 °C with the same MBPA, CuBr and TEDETA concentrations as in Fig. 2.

Fig. 9 shows the storage moduli in the rubbery region of the three polymers. They were $9.8 \times 10^7,$ 1.5×10^7 and 4.6×10^6 Pa for the PEGDMA-330, PEGDMA-550 and PEGDMA-787 networks, respectively. The difference in the storage modulus was related to the variation in the crosslinking density that was determined by the numbers of reacted vinyl groups in the

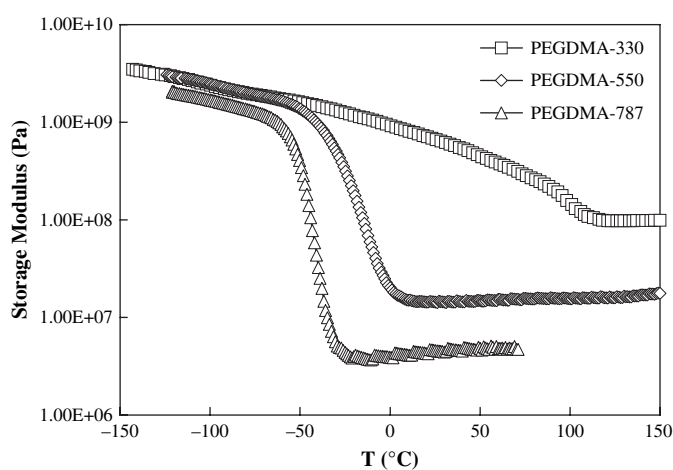


Fig. 9. Storage modulus curves of the ATRP samples of PEGDMA with different spacer lengths.

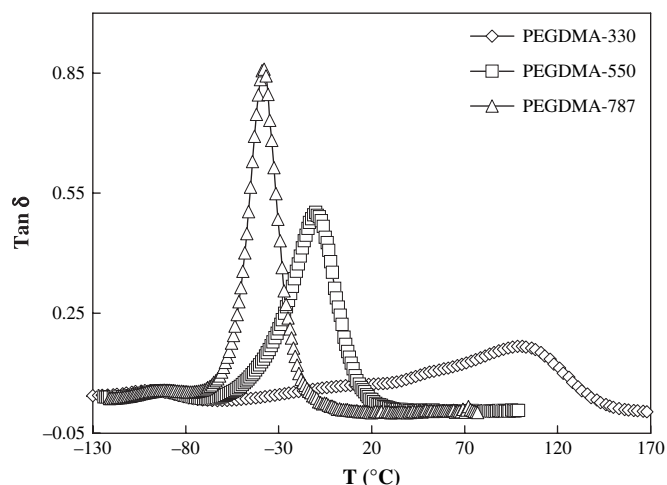


Fig. 10. Loss tangent ($\tan \delta$) of the ATRP samples of PEGDMA with different spacer lengths.

samples. Fig. 10 shows that the glass transition of the three polymers occurred in different temperature regions. The height of the $\tan \delta$ peaks also differed with PEGDMA-787 as the highest and PEGDMA-330 as the lowest. It has been suggested [38] that the height of glass transition peak in a $\tan \delta$ -temperature curve depends on the number of kinetic units adequately mobile to contribute to transition. The breadth depends on the distribution of environments in which these units are located. Our experimental result supported this dependence because the height of the $\tan \delta$ peak increased with the length of spacer.

It is also observed that the half-width of the $\tan \delta$ peak decreased with the number of ethylene glycol units. The half-width values were 126 °C for PEGDMA-330, 31 °C for PEGDMA-550 and 17 °C for PEGDMA-787. This indicated that the network formed by the longer monomer was more homogeneous. This spacer length dependence could be explained from three aspects. First, the tendency of cyclization depends on the distance and flexibility between vinyl groups. In the PEGDMA-330 system, the distance between propagating radical and pendant double bond was relatively short. The local pendant double bond concentration in the close proximity of radical was high. The system was prone to cyclization and microgel formation, resulting in a heterogeneous network. Secondly, the PEGDMA with shorter spacer contributed to a higher level of crosslinking density and possibly a wider distribution of the density. Finally, the ATRP rate of the three monomers followed the order of PEGDMA-330 > PEGDMA-550 > PEGDMA-787 [29]. The fast chain growth and slow chain relaxation in the PEGDMA-330 system also promoted the structural heterogeneity.

4. Conclusion

Based on the experimental investigation on the structure of crosslinked networks prepared by the ATRP of dimethacrylates, the following conclusions can be drawn.

- (1) The polymer networks made by the ATRP of PEGDMA were more homogeneous than the FRP counterparts. The reversible activation/deactivation equilibrium between growing radical and dormant species reduced the chain growth rate. The sufficient chain relaxation allowed the reacting species (radical, vinyl group, and catalyst complex) uniformly distributed in the network. This facilitated intermolecular crosslinking and reduced the microgel formation.
- (2) In the ATRP of PEGDMA, the gel fraction increased rapidly at the early stage of gelation and leveled off at high vinyl conversions. However the crosslinking density increased gradually with further reactions between radicals and pendant double bonds inside the network. The glass transition temperature and the degree of structural heterogeneity of the network increased with vinyl conversion. The loss of living nature of the ATRP did not further contribute to the network heterogeneity.
- (3) The ATRP of PEGDMA with shorter spacer yielded networks with higher crosslinking density, higher glass transition temperature, and higher degree of structural heterogeneity. The local concentration of pendant double bonds at the vicinity of radicals was higher with shorter spacer. Such a system was more likely to form microgels, resulting in a more heterogeneous network.

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