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The effect of primary cyclization on free radical polymerization kinetics: experimental characterization

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Abstract

Free radical polymerization kinetics are influenced by many factors including solvent concentration during polymerization, monomer structure, and comonomer composition. This study isolates the effects of the balance between primary cyclization and crosslinking on the polymerization kinetics. Isomeric crosslinking agents, 1,2-cyclohexanediol dimethacrylate (1,2-CHDDMA), 1,3-cyclohexanediol dimethacrylate (1,3-CHDDMA), and 1,4-cyclohexanediol dimethacrylate (1,4-CHDDMA), were utilized for the study because they have differing cyclization rates due to the conformation of the two methacrylate groups in the monomer, but they are otherwise similar. In copolymerizations of 1, 2, 5, and 10% crosslinking agents with 2-methoxyethyl methacrylate (MEMA), the 1,4-CHDDMA samples were always found to have an earlier onset of autoacceleration than 1,2-CHHDMA samples. 1,3-CHDDMA copolymerized with MEMA had a polymerization rate between the 1,2-CHDDMA and 1,4-CHDDMA, as expected. Mechanical property data showed that copolymer samples made with the 1,4-CHDDMA crosslinking agent exhibited a lower $\overline{M}_c$ and higher T_g than the analogous 1,2-CHDDMA copolymers. It is concluded that reduced mobility from greater crosslinking than cyclization causes the earlier onset of autoacceleration in the 1,4-CHDDMA copolymers.

Keywords: Kinetics; Cyclization; Autoacceleration

1. Introduction

Free radical polymerization of multifunctional monomers is used to form crosslinked polymers for a wide variety of applications such as fiber optic coatings, photolithography, dental restorative materials, contact lenses, and other biomaterials [1–5]. The polymerization kinetics of these crosslinked polymers have been investigated by many researchers in the last decades [6–13], and several prominent kinetic features have been observed, including autoacceleration, autodeceleration, and reaction–diffusion controlled termination [2,6,14,15]. Autoacceleration, which is marked by a sharp increase in the polymerization rate, occurs when the radical termination rate becomes diffusion limited. The propagating radicals are not able to terminate as easily, and the radical concentration increases. Subsequently, autodeceleration commences when the propagation reaction also becomes diffusion limited and is manifest by diminishing polymerization rate. At this point, the unreacted monomers or double bonds diffuse slowly through the growing polymer network prior to reacting with propagating radicals. Previous research has focused on how the concentration of crosslinking agent, the monomer structure, and the solvent concentration influence the kinetics [11–13,16–18]. This work will focus on the effect of crosslinking versus cyclization on autoacceleration behavior.

Kloosterboer pointed out that autoacceleration occurs at low conversion in crosslinked polymerizations because the formation of a crosslinked network limits the mobility of the system to an extent much greater than observed in linear systems [2]. Previous work shows that increasing the concentration of crosslinking agent in the polymerization increases the extent of autoacceleration and the maximum rate, although it decreases the final conversion [18]. This work focuses on how the polymerization kinetics is changed when primary cyclization occurs instead of crosslinking.

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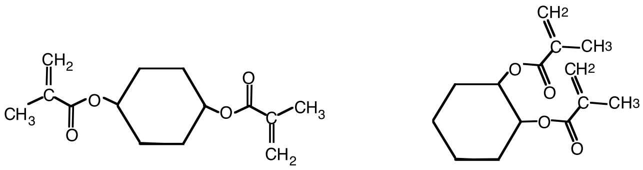

Fig. 1. Molecular structures of 1,4-cyclohexanediol dimethacrylate (1a) and 1,2-cyclohexanediol dimethacrylate (1b).

Primary cyclization occurs when a pendant double bond of a multifunctional monomer reacts intramolecularly with the propagating radical on the same chain, forming a cycle or a loop. The presence of extensive cyclization creates an entirely different network structure as compared to the ideal crosslinked network. It is expected that this will alter the polymerization kinetics as they are closely tied to the structure and mobility of radicals and monomer in the network.

To attribute the differences in kinetics to changes in cyclization, the comonomer system was carefully selected. To alter the degree of crosslinking versus cyclization, two different crosslinking agents are required; one that cycles at a higher rate than the other. The differences in the crosslinking agents must not, however, affect the kinetics in any other manner. To develop this comonomer system, isomers were selected as the crosslinking agents, and thus the total double bond concentration is identical in both copolymerizations. The crosslinking agents utilized in the study are *trans*-1,4-cyclohexanediol dimethacrylate (1,4-CHDDDMA), 1,3 cyclohexanediol dimethacrylate (1,3-CHDDDMA) and 1,2 cyclohexanediol dimethacrylate (1,2-CHDDDMA). To ensure the formation of a more ideal, less densely crosslinked network, the crosslinking agent was polymerized with 90 mol% or greater 2-methoxyethyl methacrylate (MEMA). In this manner, the majority of the double bonds in the system are always the same monovinyl monomer. Also, because the system is largely composed of monovinyl monomer, autoacceleration will not occur until late in the reaction. Using this combination, significant differences in polymerization kinetics due to the extent of cyclization or crosslinking are isolated. Polymerization kinetics were measured using Fourier transform infrared spectroscopy (FTIR), and dynamic mechanical analysis (DMA) was performed to measure the glass transition temperature and molecular weight between crosslinks to confirm that changes in the kinetics are indeed caused by the extent of cyclization.

2. Experimental

2.1. Materials

The monomers for the experimental studies are 2-methoxyethyl methacrylate (MEMA; Aldrich, Milwaukee, WI), diethylene glycol dimethacrylate (DEGDMA: Sartomer, West Chester, PA), *trans*-1,4-cyclohexanediol dimethacrylate (1,4-CHDDDMA: Polysciences Inc., Warrington, PA), 1,3 cyclohexanediol dimethacrylate (1,3-CHDDMA) and 1,2 cyclohexanediol dimethacrylate (1,2-CHDDMA). The crosslinking agents, chosen are specifically designed to cycle or crosslink more. 1,4-CHDDDMA with its two methacrylate groups on opposite sides of the ring is expected to undergo significantly greater degrees of crosslinking than 1,2-CHDDDMA with the two methacrylate groups held close to each other by the cyclohexane ring. (Fig. 1) Further, 1,3-CHDDDMA was additionally used as an intermediate case for comparison [19].

1,2-CHDDDMA was synthesized in our laboratories for these experiments by the following procedure. Ten grams of 1,2-cyclohexanediol, 25 ml of triethylamine and 50 ml of ethyl acetate were added to a three-necked flask, equipped with magnetic stirrer, reflux condenser, nitrogen gas purge, and ice bath. Then, 17 ml of methacryloyl chloride were added dropwise to the solution, carefully keeping the temperature under 5 °C. After all, the methacryloyl chloride was added, the temperature was elevated to ambient conditions and allowed to react for 6 h. Finally, the temperature was further increased to 60 °C for 6 h to complete the reaction. The mixture was filtered (to remove the $N(CH_2CH_3)_3HCl$) and the liquid was washed with 1 wt% NaOH three times, 2 wt% HCl three times, and $NaCl/H_2O$ saturate solution three times. It was dried overnight with Na_2SO_4. After rotovaporation to remove the solvent, the product was chromatographed on silica gel with hexane/ethyl acetate to isolate the 1,2-CHDDMA. 1,3-CHDDMA was synthesized analogously using 1,3-cyclohexanediol as a starting reagent.

All commercially purchased monomers were used as received without further purification. Polymer samples were made with 1, 2, 3, and 5% DEGDMA copolymerized with MEMA to observe the effect of crosslinking agent concentration on autoacceleration. MEMA was used as the monovinyl copolymer because it achieves nearly 100% conversion, and it does not readily dimerize to form a dimethacrylate (like the more commonly used hydroxy ethyl methacrylate). Poly(MEMA) was observed to flow at 150 °C, demonstrating that it forms a non-crosslinked polymer when non divinyl is added. All free radical polymerizations were initiated with 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY), which was added at a concentration of 0.5 wt% based on total monomer weight.

2.2. Methods

The polymerization kinetics were measured using real-time infrared (IR) spectroscopy (Magna 750, Series II, Nicolet Instrument, Madison, WI) with a UV-light source (Ultracure 100SS Watt Hg sort-arc lamp, EFOS, Mississsaugua, Ont., Canada) at a light intensity of 1 mW/cm^2. A thin layer of monomer was placed between two NaCl salt crystals and the C=C (stretch) peak at 1637 cm^{-1} was monitored to

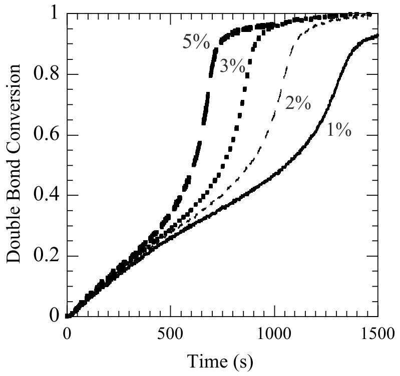

Fig. 2. Conversion versus time plot for 1, 2, 3, and 5% DEGDMA copolymerized with MEMA.

determine the conversion as a function of time for each polymerization reaction [19,20].

A dynamic mechanical analyzer (DMA7e, Perkin–Elmer, Norwalk, CT) was used to obtain the mechanical properties [21] and ascertain differences in crosslinking between samples. DMA experiments were performed to determine the glass transition temperature (T_g) and molecular weight between crosslinks ($\overline{M}_c$) of the copolymers. DMA samples were prepared in a Teflon mold with wells the size of 4 mm × 20 mm × 1 mm. The top was covered with a piece of cellulose acetate and then sealed with high vacuum silicone grease. Teflon and cellulose acetate were used to minimize problems with adhesion to the mold. The polymerization was initiated with an ultraviolet light source (Black Ray) which operated at approximately 1 $\mathrm{mW/cm^2}$ for 1 h. Near-complete double bond conversion for all samples was confirmed using Fourier transform near infrared (near-IR) spectroscopy (Magna-IR 750, Nicolet, Madison, WI) to measure the vinyl CH_2 peak at 6160 $\mathrm{cm^{-1}}$ [22].

To measure the storage modulus (E') and loss tangent as a function of temperature, time–temperature scans were performed with the DMA. A sinusoidal tensile force with a frequency of 1 Hz was applied to the sample while raising the temperature 5 °C/min. The glass transition temperature (T_g) was determined as the maximum value of the loss tangent. The storage modulus of the polymer in the rubbery region was used to calculate the average molecular weight between crosslinks, $\overline{M}_c$, from the following equation:

$$\overline{M}_c = \frac{3\rho RT}{E} \tag{1}$$

In the above equation, ρ is the density of the polymer system, R is the gas constant, T is the absolute temperature, where the modulus was obtained, and E is the storage modulus of the polymer in the rubbery region. This equation is valid assuming the material behaves as an ideal rubber, chain ends can be neglected, i.e. the kinetic chain length is much greater than the distance between crosslinks, chains between crosslinks behave as Gaussian chains, and the storage modulus is much greater than the loss modulus. All of the assumptions should be valid for the systems studied except for the 10% crosslinking agent samples, which are not likely to have a sufficient distance between crosslinks so that non-Gaussian behavior is observed between crosslinks.

3. Results and discussion

To establish how changes in crosslink density influence the polymerization rate, the polymerization kinetics of mixtures containing various amounts of crosslinking agent were monitored with FTIR. In Fig. 2, the conversion as a function of time curve is shown for the copolymerization of 1, 2, 3, and 5 mol% DEGDMA with MEMA. The results confirm what other researchers have observed that increasing the concentration of crosslinking agent affects the onset, duration, and magnitude of autoacceleration. Autoacceleration begins at approximately 50, 40, 35, and 30% double bond conversion for 1, 2, 3, and 5% DEGDMA, respectively. The maximum rate is also influenced, ranging from $1.9 \times 10^{-3}\ \mathrm{s^{-1}}$ for 1% DEGDMA to $4.8 \times 10^{-3}\ \mathrm{s^{-1}}$ to 5% DEGDMA. Notably, a small increase in crosslinking double bonds compared to the total double bond concentration in the system has a significant impact on the inception and magnitude of the autoacceleration.

Controlling the concentration of crosslinking agent is not the only way to modify the crosslink density. Not all double bonds on a particular crosslinking agent will form elastically active crosslinks. Some will form primary cycles that add negligibly to the network structure. A crosslinking agent that forms a primary cycle will not reduce the mobility significantly. Thus, it is expected that the presence of high cyclization rates will change the kinetics similarly to reducing the crosslinking agent concentration. In analyzing how cyclization influences the kinetics, the selection of appropriate crosslinking agents for comparison was critical. As discussed in Section 1, the chosen crosslinking agents are a series of isomers with systematic variation in the relative positions of the two methacrylate groups.

The polymerization kinetics of each crosslinking agent copolymerized with MEMA were monitored by real time FTIR. Figs. 3–5 show the double bond conversion as a function of time for copolymerization with 1, 2, and 5% of each crosslinking agent. All copolymer samples show that the autoacceleration occurs at a lower conversion with the 1,4-CHDDMA than the 1,2-CHDDMA. Fig. 4 shows the comparison of all three crosslinking molecules: 1,2-CHDDMA, 1,3-CHDDMA, and 1,4-CHDDMA. As expected the 1,3-CHDDMA lies between the other two. The differences in polymerization rate are observed in spite of the fact that in each copolymer system the same total double bond concentration and same concentration of potential crosslinking double bonds are present. If all double bonds reacted equivalently, the polymerization rate in each case would be identical. Instead, large variations in the kinetics are observed between the 1,2-CHDDMA and

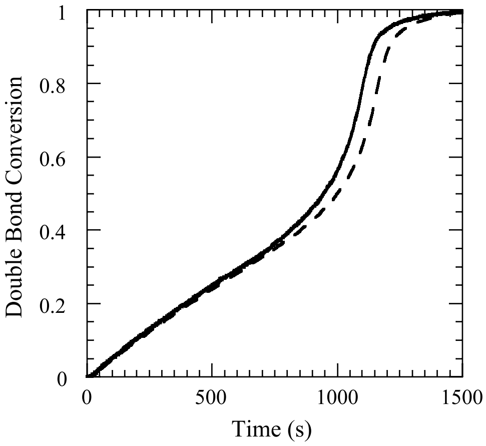

Fig. 3. Conversion versus time for 1% 1,4-CHDDMA, (- - -), and 1% 1,2-CHDDMA, (—), with 99% MEMA.

1,4-CHDDMA with the differences becoming more pronounced in the samples with the higher concentrations of crosslinking agent. Fig. 6 shows the normalized polymerization rate versus conversion for compositions containing 10% crosslinking agent. The normalized polymerization rate was determined by taking the derivative of the conversion versus time curve. The rate curves further illustrate the difference in kinetics in two systems, which have the same crosslinking potential.

Theoretically, in ideal network formation the kinetics and network structure of samples with the same concentration of crosslinking agent and same monovinyl should be the same or at least very similar. The initial polymerization kinetics are, in fact, nearly identical until autoacceleration begins, as shown clearly in Fig. 4. The copolymerization with 2% DEGDMA (Fig. 2) also has this same initial rate, further emphasizing the similarity in the initial network formation. Prior to autoacceleration, the conversion as a function of time is independent of the amount and type of crosslinking agent. As shown in Fig. 4 because the reaction is slow to autoaccelerate, the kinetics are identical until about 25% conversion, when the crosslink density of the

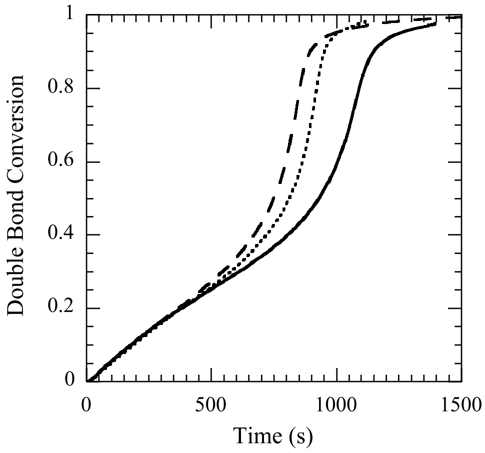

Fig. 4. Conversion versus time for 2% 1,4-CHDDMA, (- - -), 2% 1,3-CHDDMA, (· · ·), 2% 1,2-CHDDMA, (—), with 98% MEMA.

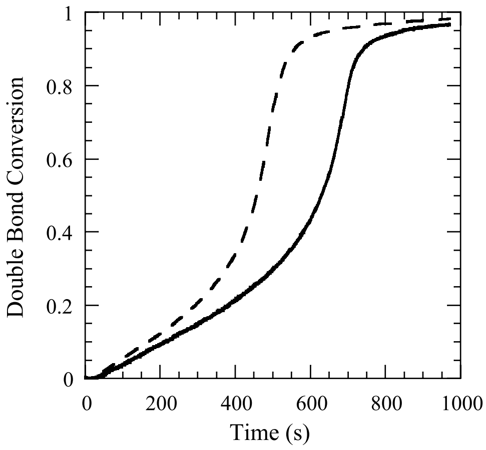

Fig. 5. Conversion versus time for 5% 1,4-CHDDMA, (- - -), and 5% 1,2-CHDDMA, (—), with 95% MEMA.

1,4-CHDDMA copolymer reaches a critical threshold for radical termination to be diffusion controlled. The variation in when the samples autoaccelerate demonstrates the crosslink density does not develop equivalently as a function of conversion. The comparison of the 2 and 1% crosslinking systems shows that 2% of the more highly cycling 1,2-CHDDMA has a rate very similar to 1% of the 1,4-CHDDMA. This result indicates that 1,4-CHDDMA is approximately twice as effective at crosslinking as 1,2-CHDDMA. The mechanical property measurements confirm a similar relationship.

The observed delay in autoacceleration in the sample made with 1,2-CHDDMA compared to 1,4-CHDDMA can be explained in terms of the mobility of the network. The highly crosslinked network has more significantly reduced chain mobility than the highly cyclized network. Differences in the chain mobility affect the ability of radical species to terminate. This effect has been observed previously in the reduced autoacceleration exhibited when poly(ethylene glycol 200) dimethacrylate monomer is templated with metal salts in the formation of pseudocrown

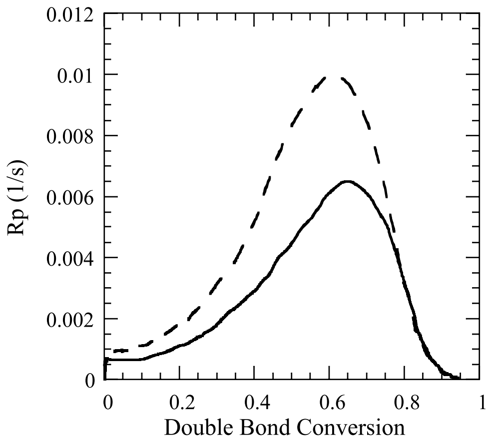

Fig. 6. Normalized rate versus conversion for 10% 1,4-CHDDMA, (- - -), and 10% 1,2-CHDDMA, (—), with 90% MEMA.

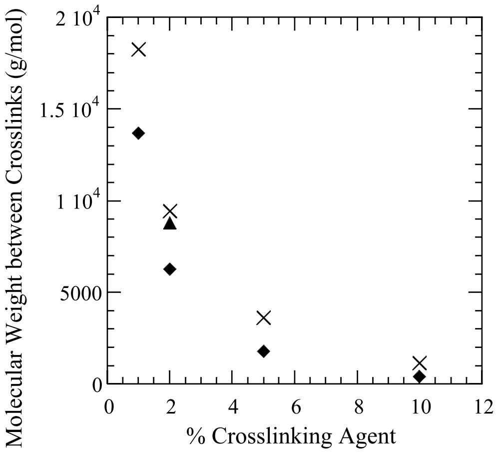

Fig. 7. Average molecular weight between crosslinks for 1,4-CHDDMA, (◆), 1,3-CHHDMA, (σ), and 1,2-CHDDMA, (×).

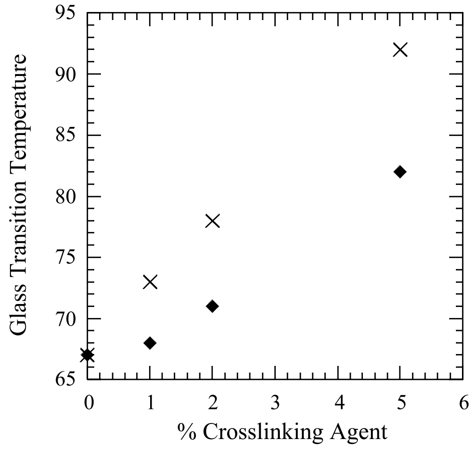

Fig. 9. Glass transition temperature for 100% MEMA and 1, 2, and 5% 1,4-CHDDMA, (×), and 1,2-CHDDMA, (◆).

ethers [23]. The templating metal causes the cyclization rate to increase and delays autoacceleration.

Differences in pendant reactivity could also affect the kinetics. Previous work in the literature with 1,3-divinyl benzene and 1,4-divinyl benzene found the crosslinking reactivity of pendant vinyl groups in the *para* position is much higher than in the *meta* position [24]. To confirm that the differences in rate found in this study are directly attributable to variations in crosslinking, the $\overline{M}_c$ and T_g were measured for all systems. Fig. 7 shows the $\overline{M}_c$ for all comonomer ratios of 1,4-CHDDMA and 1,2-CHDDMA with MEMA. As expected, the $\overline{M}_c$ obtained when 2% crosslinking agent is added is approximately half the $\overline{M}_c$ measured for samples containing 1% crosslinking agent. At each concentration of crosslinking agent, the $\overline{M}_c$ of samples containing 1,4-CHDDMA is less than the $\overline{M}_c$ of polymers containing 1,2-CHDDMA. This result is consistent with what was observed in the polymerization rate and shows that the 1,4-CHDDMA is indeed acting as a more effective crosslinking agent. The $\overline{M}_c$ of 1,3-CHDDMA for 2% crosslinking agent copolymer samples was 8800 g/mol, which is between the $\overline{M}_c$ of 1,2-CHDDMA and 1,4-CHDDMA. Like the kinetic results, the 2% 1,3-CHDDMA copolymer's $\overline{M}_c$ is closer to the 1,4-CHDDMA at 9450 g/mol than 1,2-CHDDMA at 6250 g/mol. This trend shows qualitatively how the magnitude of the shift in autoacceleration correlates with the difference in crosslink density. In fact, the relationship between the conversion at which autoacceleration begins and the final $\overline{M}_c$ is shown in Fig. 8. The autoacceleration conversion was defined by the intersection of the lines tangent to the conversion versus time curves before and after autoacceleration. These results show a direct relationship between the commencement of autoacceleration and the achieved crosslink density, rather than the concentration of crosslinking agent. Further, comparisons of the 1 and 2% $\overline{M}_c$ show that 1% 1,4-CHDDMA provides a level of crosslinking between 1 and 2% 1,2-CHDDMA as the rate curves suggested.

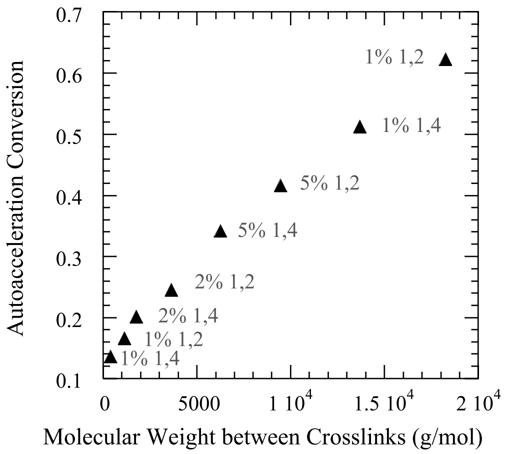

Fig. 8. Autoacceleration conversion as a function of final molecular weight between crosslinks (1,4 = 1,4-CHDDMA and 1,2 = 1,2-CHDDMA).

Although primary cyclization cannot be isolated from secondary cyclization (or multiple crosslinking) by DMA, it is expected that both secondary cycles and crosslinks will increase the storage modulus, and thus decrease the $\overline{M}_c$. Primary cyclization should have minimal affect on the measured storage modulus. For this reason, differences in $\overline{M}_c$ calculated from the storage modulus are attributed mainly to increased primary cyclization.

In addition to measuring the $\overline{M}_c$, the glass transition temperature was measured and taken as the maximum in the tan delta peak. Fig. 9 shows the glass transition temperature (T_g) as a function of crosslinking agent concentration for both crosslinking agents. The T_g of 100% MEMA was also measured for a baseline point. The T_g results in Fig. 8 show a linear trend with the concentration of crosslinking agent. It is expected that increases in crosslink density will increase the T_g because more thermal energy will be needed for the system to become rubbery. Just as increasing the concentration of crosslinking agent raised the T_g, changing from the 1,2-CHDDMA to 1,4-CHDDMA increased the T_g. This data confirms that using the two different crosslinking agents creates a different network structure. 1,4-CHDDMA is in fact a more effective crosslinking agent.

4. Conclusions

The relative effects of crosslinking and primary cyclization on polymerization kinetics in loosely crosslinked polymers were studied by systematically changing crosslinking agent structure. Polymerization of 1, 2, 3, and 5% DEGDMA with MEMA illustrated how increasing degree of crosslinking increases the polymerization rate by leading to autoaccleration earlier in the polymerization. To determine how primary cyclization rates influence the polymerization kinetics, isomeric crosslinking agents, 1,2-CHDDMA, 1,3-CHDDMA, and 1,4-CHDDMA, were utilized. These crosslinking agents were chosen because they are similar, yet exhibit differing cyclization rates due to the conformation of the methacrylate groups in the monomer. FTIR experiments showed the 1,4-HDDMA copolymers exhibited earlier autoacceleration than equivalent 1,2-CHDDMA copolymers. This effect is observed in copolymer samples made with 1, 2, 5, and 10% crosslinking agent, with the effect being more pronounced when greater concentrations of crosslinking agent are used. Mechanical property data confirmed that reduced mobility due to greater crosslinking than cyclization caused the earlier onset of autoacceleration in the 1,4-CHDDMA copolymer. All copolymer samples made with 1,4-CHDDMA crosslinking agent exhibited a lower $\overline{M}_c$ and higher T_g than the analogous 1,2-CHDDMA copolymers.

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