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The effect of kinetic chain length on the mechanical relaxation of crosslinked photopolymers

Lale G. Lovell[1], Christopher N. Bowman*

Department of Chemical Engineering, University of Colorado, ECCH 111, Campus Box 424, Boulder, CO 80309-0424, USA

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Abstract

This work investigates the effect of kinetic chain length on the network structure of multi-functional (meth)acrylates. Two chain transfer agents, dodecanethiol and *m*-toluenethiol, were added to a series of crosslinking free radical polymerizations to decrease the kinetic chain length. Using near-IR spectroscopy and dynamic mechanical analysis, the effect of chain transfer on the polymerization rate and network properties (i.e. T_g and modulus) was investigated. The results suggest that macroradical chain length, which has been shown to play a role in the termination kinetics of crosslinking systems, may also impact the network properties of the formed polymer. With the addition of only 0.5–1 wt% chain transfer agent, differences in the polymerization rate and mechanical properties were observed in the crosslinking methacrylate systems. The polymerization rate was significantly suppressed and the T_g of the cured network was found to decrease by up to 10 °C, depending on the monomer formulation. The largest differences in the mechanical properties occurred in the systems with the lowest crosslinking density and diminished as the crosslink density of the cured polymer increased. Furthermore, the differences were less dramatic in the multi-EGDMA systems, that have some inherent ability to chain transfer, and were not discernable in the transfer dominated diacrylate systems.

Keywords: Dimethacrylates; Chain transfer agents; Chain length dependent termination

1. Introduction

The kinetic chain length is an important parameter in free radical polymerizations. Though the kinetic chain length (ν) is not generally discussed for crosslinked networks, it is defined here as the average number of double bonds that react with a radical prior to any chain breaking reaction such as chain transfer or termination. Under pseudo-steady state conditions, this relationship is calculated by Eq. (1). The average number of double bonds consumed is the polymerization rate (R_p), and the rate of chain breaking reactions is the sum of the termination (R_t) and chain transfer (R_{ct}) rates. Based on this relationship, decreasing the polymerization rate or increasing the rate of chain breaking reactions will decrease the kinetic chain length.

$$\nu = \frac{R_p}{R_t + R_{ct}} \tag{1}$$

It is well documented that the kinetic chain length of a linear polymer directly impacts its polymerization kinetics and the final mechanical properties of the polymer [1,2]. However, research studies are lacking about the effect of kinetic chain length in crosslinking systems. One reason for the lack of interest is the perceived unlikelihood that kinetic chain length is important in the kinetics of crosslinking systems that quickly form gels of infinite molecular weight. During cure, oligomeric chains are rapidly incorporated into the growing network. For instance, in a homogeneous crosslinked system at 10% conversion, the probability that a 10-mer chain is not attached to another polymer chain (and likely the macroscopic gel) is only 35%. As either the conversion or the kinetic chain length increases, this percentage decreases dramatically. Though it may seem counterintuitive, recent research has shown that chain length does have a measurable

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* Corresponding author. Address. Biomaterials Research Center, University of Colorado Health Sciences Center, Denver, CO 80262, USA. Tel.: +1-303-492-3247; fax: +1-303-492-4341/735-0095.

E-mail address: christopher.bowman@colorado.edu (C.N. Bowman).

[1] Present address. Agilent Technologies, Inc., 4380 Ziegler Road, MS 23, Fort Collins, CO 80525-9790, USA.

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effect on the polymerization kinetics of multi-functional methacrylates. In a series of works, our research group has illustrated that chain length dependent termination is important in crosslinking systems.

Adding a chain transfer agent to the system or increasing the initiation rate (i.e. decreasing the kinetic chain length) leads to a more mobile reaction environment and more rapid termination rates [3,4]. Additionally, the presence of a chain transfer agent alters the chemical identity of the radical fragment that begins a polymer chain. In chain transfer dominated systems, the initiator fragments are not responsible for initiating the majority of chains. Rather, the chain transfer agent fragment will reinitiate and begin a new polymer chain. In the presence of small amounts of chain transfer agents, like those used here, it is unlikely that the chemical identity of this beginning fragment has any significant impact on the polymer properties or the network formation. Thus, the effect of chain transfer, even in these systems, is primarily on the kinetic chain length distribution.

As the double bond conversion increases and reaction diffusion controlled termination begins to dominate the kinetics, the effect of kinetic chain length on the polymerization kinetics diminishes. The studies illustrate that the kinetics of multi-functional methacrylate systems are significantly impacted by chain length and the termination environment is dominated by the more mobile radical species present in the system [3,4].

Therefore, based on these results, the effect of kinetic chain length on the network structure of crosslinked methacrylate systems was investigated using dynamic mechanical analysis (DMA). Both mono/divinyl copolymers and divinyl homopolymers cured at identical experimental conditions were studied to yield materials with a wide range of molecular weights between crosslinks ($M_{\mathrm{w,c}}$). Like the kinetic studies, chain transfer agents will be added to decrease the molecular weight of the kinetic chains ($M_{\mathrm{w,v}}$). It is important to note that in these studies the chain transfer agent is used as a means for altering the polymeric network structure. Because the chain transfer agent represents a very small fraction of the materials used and because reinitiation by the chain transfer agent fragment is facile, changes in the kinetics and material properties that are observed are primarily a result of the ensuing changes in the network structure.

Chain transfer agents are often added to polymerizations to control the molecular weight of the final product. For example, mercaptans are used in the industrial polymerization of styrene and butadiene to create SBR rubbers [2]. Due to their extensive use, chain transfer constants for a wide variety of additives have been published [5] and many studies exist regarding the effect of chain transfer agents on the kinetics and molecular weight distribution of linear systems. In one recent example, size exclusion chromatography was used to measure the molecular weight distribution of styrene–methyl methacrylate and butyl acrylate–methyl methacrylate copolymers cured to very low conversion (4–8%) in the presence of dodecanethiol [6]. The smallest dodecanethiol concentration studied (10^{-3} mol/l), led to a dramatic decrease in the molecular weight of the polymer for both systems. Increasing the chain transfer agent concentration led to further reductions in the molecular weight. In a second study, the transfer ability of *n*-dodecyl mercaptan in methyl methacrylate was investigated using pulsed laser polymerizations [7]. The molecular weight distribution shifted lower, the shape of the distribution became more symmetric, and the system became transfer-dominated with the addition of only 1 vol% transfer agent. The researchers also discussed the effect of initiator concentration on the molecular weight distribution. In general, increasing the initiator concentration shifted the molecular weight distribution to lower values. However, the effect was less pronounced in the polymerizations that contained transfer agents since transfer to the mercaptan controlled the molecular weight. These studies illustrate the powerful chain transfer effect thiol derivatives, which possess a weak S–H bond, have on free-radical polymerizations. Due to their high radical transfer rates from methyl methacrylate, thiol derivatives were also employed in the current study.

Since multi-functional monomers form networks of infinite molecular weight, size exclusion chromatography and other techniques which yield molecular weight distributions are inappropriate to discern the effect of the radical generation rate on the polymer structure. However, even with these limitations, several studies have been performed to investigate the effect of initiation rate on the network structure [8–12]. In one, multi-functional anhydride monomers were used to form highly crosslinked degradable networks [9]. The degraded product's molecular weight distribution (linear poly(methacrylic acid)) was measured using matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) spectroscopy. Varying the light intensity an order of magnitude (from 10 to 100 mW/cm^2) altered the radical generation rate, and the results showed that the distribution shifts to lower molecular weights with increased light intensity. This finding is consistent with the effect initiation rate would have on the kinetic chain length (Eq. (1)). In addition, a series of papers have been published which discuss microgel formation during the polymerization of ethylene glycol dimethacrylate (EGDMA) [10,11]. A variety of experimental techniques, such as rheological measurements and dynamic light scattering (DLS), were utilized to determine the morphological changes of the partially crosslinked EGDMA system [10]. The particle size distributions at and before the gel point (as obtained from DLS measurements) were shown to decrease and broaden as initiator concentration increased. On the other hand, reaction temperature (range 55–70 °C) was shown to affect the polymer size distribution only slightly. Though this study is not a direct measure of the kinetic chain lengths, the differences observed as a function of initiator concentration suggest that the network structure at very low conversions may be affected by the radical

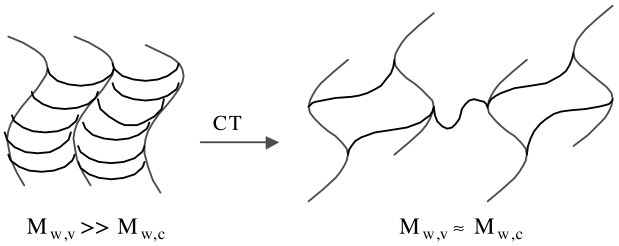

Fig. 1. A possible effect of adding CT agent to a crosslinked network. The CT agent may decrease the kinetic chain length and create a network, where $M_{w,v}$ is comparable to $M_{w,c}$.

generation rate. However, at higher conversions, highly crosslinked methacrylate networks do not show a correlation between initiation rate and network structure. In previous work [12], the mechanical properties of a common dimethacrylate dental resin formulation (75/25 bis-GMA/TEGDMA) were measured using DMA. Even though the copolymers were cured with UV and visible light initiating systems, UV light intensities that varied by four orders of magnitude, and cure temperatures that differed by 60 °C, similar T_g and modulus were measured for specimens cured to the same final double bond conversion.

In this work, chain transfer agents were used to decrease the kinetic chain length. As illustrated in Fig. 1, the molecular weight of the kinetic chains (i.e. the backbone chains with all crosslinks severed) in a crosslinked system is typically much larger than the molecular weight between crosslinks ($M_{w,v} \gg M_{w,c}$). Therefore, subtle changes in the kinetic chain length have little effect on the network structure or mechanical properties. However, if chain transfer agents are added to decrease the kinetic chain length significantly, it may be possible to create networks, where the scale of $M_{w,v}$ approaches $M_{w,c}$. For this particular case, the number of chain ends within the network will increase dramatically and may result in a change in the mechanical properties. Therefore, the goal of this work is to add chain transfer agents to the polymerization of crosslinking monomers to facilitate the creation of networks with decreased $M_{w,v}$ and to determine using DMA whether such changes in kinetic chain length lead to changes in the mechanical properties.

2. Experimental

2.1. Materials

An array of monomers was used for this study. Octyl methacrylate (OcMA), polyethylene glycol-400 dimethacrylate (Peg400DMA), and triethylene glycol dimethacrylate (TEGDMA) were received from Polysciences Inc. (Warrington, PA, USA). Polyethylene glycol-200 dimethacrylate (Peg200DMA), diethylene glycol dimethacrylate (DEGDMA), polyethylene glycol-400 diacrylate (Peg 400DA), and triethylene glycol diacrylate (TEGDA) were obtained from Sartomer (West Chester, PA, USA), and 1,6-hexanediol dimethacrylate (HDDMA) was purchased from Aldrich (Milwaukee, WI, USA). Two chain transfer agents, 1-dodecanethiol (DDT, ACROS, NJ, USA) and *m*-toluenethiol (*m*-TT, Aldrich, Milwaukee, WI, USA), were also used in conjunction with the ultraviolet initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, 0.2 wt%, Ciba Geigy, Hawthorne, NY, USA). The chain transfer agents were added in the following amounts: 0.5 and 1.0 wt% *m*-TT (0.043 and 0.085 mol/l, respectively) and 1.0 wt% DDT (0.052 mol/l). All materials were used as received.

2.2. Polymerization conditions

The monomer mixtures were irradiated by an ultraviolet light source (Ultracure 100SS 100 W Hg short-arc lamp, EFOS, Mississaugua, Ont., Canada) equipped with a liquid light guide. The light intensity was 5 mW/cm^2 at 365 nm for all polymerizations. A temperature control cell (built at the University of Colorado) was used to maintain the reaction temperature at 80 °C [14]. A high reaction temperature was chosen to ensure rapid polymerization and high conversion of the monomers. A rapid polymerization was desired to minimize the decrease of initiator concentration with polymerization time. A dramatic decrease in the initiator concentration leads to a decay in the initiation rate and a non-constant kinetic chain length. One can determine the decrease in initiator concentration ($[A]$) with irradiation time (t) assuming an exponential decay function (Eq. (2)) [2].

$$[A] = [A]_0 \exp(-2\phi\varepsilon I_0 bt) \quad (2)$$

For this calculation, the efficiency of DMPA (ϕ) was assumed to be 0.6, which is in the bounds reported by others [13]. In addition, the light source was approximated as monochromatic (only 365 nm light). Therefore, the molar absorptivity of DMPA (ε) at 365 nm was used (150 l/mol cm)) and the calculated value of the incident light intensity per unit thickness (I_0/b) for 5 mW/cm^2 was 1.5×10^{-8} mol/cm^2 s. Based on these values, the amount of initiator that remained after 400 s (the longest polymerization time for a pure sample in this set of experiments) was estimated to be 0.07 wt%, relative to the 0.2 wt% present initially. However, most of the polymerizations were complete within 100 s (0.15 wt% DMPA remaining). Regardless, the decrease in initiator concentration with time during the cure was accounted for in the kinetic chain length calculations. Similar to previous studies [12], curing the samples at 80 °C and storing them at room temperature kept the final conversion unchanged during DMA testing.

2.3. Near-IR spectroscopy

Near-IR spectroscopy (Magna 750, Series II, Nicolet Instrument, Madison, WI, USA, KBr beamsplitter and DTGS detector) was used to measure the change in double bond conversion as a function of irradiation time for samples in the geometry needed for DMA analysis ($15 \times 4 \times 1$ mm^3). As discussed in previous work [12], the change in absorbance of the methacrylate =C–H peak (6102–6233 cm^{-1} with an absorption maximum at 6164 cm^{-1}) was used to determine the extent of conversion. The samples were cured within the near-IR unit using a horizontal-mounting unit that redirects the near-IR beam vertically and allows the sample to be placed horizontally within the chamber. A detailed description of this novel unit has been published elsewhere [14]. The photopolymerization reaction was monitored by real-time near-IR spectroscopy (series run with eight scans per spectrum and four wavenumber resolution to give an acquisition rate of approximately 25 spectra/min). Spectra, taken immediately before and after irradiation (64 scans per spectrum and four wavenumber resolution), were recorded to verify the final conversion.

2.4. Estimation of ν, $M_{w,v}$, and $M_{w,c}$

As shown in Eq. (1), the kinetic chain length (ν) calculation requires knowledge about the polymerization rate (R_p), initiation rate (R_i) and chain transfer rate (R_{ct}). The rate of polymerization was estimated graphically using the slope of the conversion vs. time curve (obtained from near-IR) and multiplying by the initial concentration of double bonds. The initiation rate (R_i), which is equivalent to the termination rate under pseudo-steady state conditions, was estimated using Eq. (3) [2], where the initiator concentration ($[A]$) was varied according to Eq. (2).

$$R_i = 2\phi\varepsilon I_0 b[A] \tag{3}$$

The rate of chain transfer was also estimated; however, little quantitative information is available for these systems. The chain transfer constants of DDT and *m*-TT to multifunctional methacrylate systems are not readily available, so the values for methyl methacrylate were used instead ($C_{CT} = 1.2$ (DDT) [15] and 4.7 (*m*-TT) [5]). The chain transfer constant, which is the ratio of the transfer rate constant (k_{CT}) to the propagation rate constant (k_p), was transformed into the ratio of the transfer rate (R_{ct}) to the propagation rate (R_p) using the initial concentrations of double bonds and chain transfer agent (i.e. $R_{ct}/R_p = C_{CT}[\mathrm{CT}]/[\mathrm{DB}]$). These assumptions may be reasonable for the systems that were comprised largely of OcMA since other studies have suggested that the chain transfer constants of *n*-dodecyl mercaptan to the methyl methacrylate family (i.e. ethyl, butyl, etc.) are similar [7]. However, multi-ethylene glycol dimethacrylate monomers undergo inherent chain transfer due to the abstractable hydrogens present on the ethylene glycol backbone. Therefore, the rate of chain transfer is likely higher than the values estimated. Because of these estimations, the values of the kinetic chain length are merely shown for comparative purposes and are not meant to be absolute.

The value for the molecular weight of the kinetic chain ($M_{w,v}$) is merely the kinetic chain length (ν) times the molecular weight of the repeat unit (M_r). The value for the molecular weight between crosslinks ($M_{w,c}$) was calculated using Eq. (4)

$$M_{w,c} = \frac{M_r[\mathrm{DB}]_{\mathrm{total}}}{[\mathrm{DB}]_{\mathrm{xlink}}} \tag{4}$$

where M_r is the average molecular weight of the repeat unit and [DB] is the double bond concentration (both total and of the crosslinking agent). Cyclization reactions, which increase the molecular weight between crosslinks, are neglected. Furthermore, if the system is comprised of only a crosslinking agent, then the molecular weight between crosslinks ($M_{w,c}$) is approximated by the molecular weight of the repeat unit (M_r).

2.5. Dynamic mechanical analysis

DMA was performed on a DMA7e dynamic mechanical analyzer (Perkin Elmer, Norwalk, CT, USA). The specimens were of uniform size ($15 \times 4 \times 1$ mm^3). DMA was performed over a temperature range of −60–200 °C with a ramping rate of 5 °C/min using extension mode (sinusoidal stress of 1 Hz frequency). The loss and storage moduli and the loss tangent (tan δ, ratio of loss to storage modulus) were recorded as a function of temperature, and the glass transition temperature (T_g) was taken to be the maximum of the loss tangent versus temperature curve. Two or three samples were tested for each experimental condition. In addition, the chain transfer agents do not appear to have a plasticizing effect on the network. Peg400DMA samples were cured with 1 wt% dodecane, a solvent very similar chemically to dodecanethiol. No differences in polymerization rate or T_g were noted for these samples.

3. Results and discussion

3.1. OcMA/HDDMA copolymerizations

Fig. 2 graphically illustrates the effect of adding a chain transfer agent to the polymerization of 95/5 OcMA/HDDMA (mass ratio). Adding the chain transfer agent depresses the polymerization rate but does not change the final double bond conversion. These results are similar to previous kinetic studies [4] which showed that adding a chain transfer agent led to a more mobile reaction environment. These more mobile radicals are less restricted and are able to terminate more rapidly. Since the termination rate increases, autoacceleration and the maximum polymerization rate are suppressed.

The other OcMA/HDDMA copolymers yielded similar results. However, as the concentration of HDDMA increased, the polymerization occurred on a faster time scale and reached lower final conversions. This type of

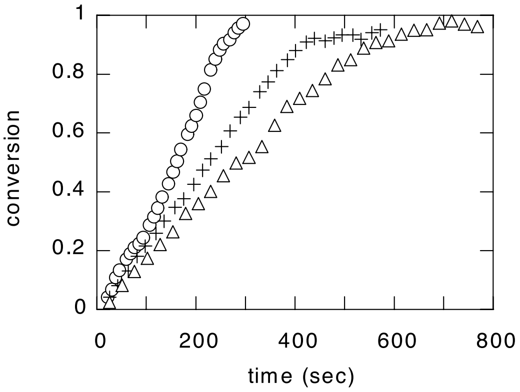

Fig. 2. Conversion as a function of irradiation time for 95/5 OcMA/HDDMA cured with no CT agent (○), 0.5 wt%, *m*-TT (+), and 1.0 wt% *m*-TT (△).

behavior is typical of systems that exhibit reaction diffusion controlled termination [16]. Incorporation of a crosslinking agent decreases the mobility of the reaction environment and leads to a decrease in the termination rate (i.e. enhanced autoacceleration and a higher polymerization rate). However, as the reaction progresses, the mobility decreases further and the polymerization rate drops off before all the reactive double bonds have been consumed. Interestingly, the addition of a chain transfer agent has less of an effect on the polymerization rate of the more crosslinked systems. In systems with a high crosslink density, there is more likelihood that the chains will be bound to the network, so the chain transfer agent is less effective in changing the network structure and creating ‘shorter’, more mobile, macroradicals.

In addition to examining the effect of the chain transfer agent on the polymerization rate, DMA was performed on the resultant polymers. Fig. 3 shows the mechanical behavior of 95/5 OcMA/HDDMA polymers cured with various concentrations of *m*-TT. As the concentration of chain transfer agent increased, the rubbery modulus and glass transition temperature (T_g) decreased. This behavior is evidence in support of the idea that increasing the chain transfer rate in a crosslinked system decreases the kinetic chain length and negatively impacts the mechanical properties by increasing the number of chain ends. According to Table 1, adding 1 wt% *m*-TT decreases the molecular weight of the kinetic chains to the same order of magnitude as the molecular weight between crosslinks. This depression in the kinetic chain length leads to a polymer with a T_g 10 °C lower than that obtained from a polymer formed without any chain transfer agent.

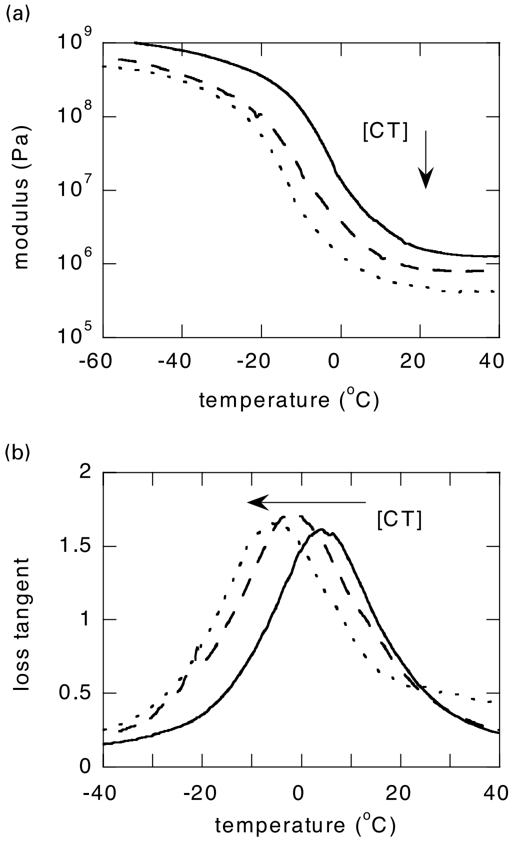

Fig. 3. Modulus (a) and loss tangent (b) of 95/5 OcMA/HDDMA cured with no CT agent (—), 0.5 wt% *m*-TT (- -), and 1.0 wt% *m*-TT (···).

Even though the addition of a chain transfer agent leads to a network with increased chain ends and a lower T_g, the 95/5 OcMA/HDDMA system with *m*-TT is still crosslinked. The modulus as a function of temperature was monitored well into the rubbery region for all of the polymers studied (50–80 °C above the T_g for most cases) and no decay in modulus, which would suggest viscous flow of the material, was observed.

The concentration of the crosslinking agent (HDDMA) was increased to investigate how chain transfer agents affect more highly crosslinked systems. As the data in Table 1 illustrates, increasing the crosslinking agent concentration decreases the molecular weight between crosslinks ($M_{w,c}$).

Table 1
Network properties of OcMA/HDDMA polymers

Composition	$M_{w,c}$	$[(M_{w,v})/(M_{w,c})]$	T_g (°C)	Modulus (Pa) at T (°C)
95/5 OcMA/HDDMA	2400	100	4.8 ± 1.3	2.2×10^6 ± 0.1 (15)
0.5 wt% *m*-TT		2	−4.5 ± 0.1	1.1×10^6 ± 0.1 (15)
1 wt% *m*-TT		1	−5.7 ± 0.4	0.6×10^6 ± 0.1 (15)
75/25 OcMA/HDDMA	540	500–2000	47.0 ± 2.0	3.5×10^7 ± 0.8 (80)
1 wt% *m*-TT		5	31.6 ± 1.4	2.6×10^7 ± 0.1 (80)

Cure conditions: 80 °C, 5 mW/cm^2, and 0.2 wt% DMPA. All samples were fully polymerized ($n = 2$).

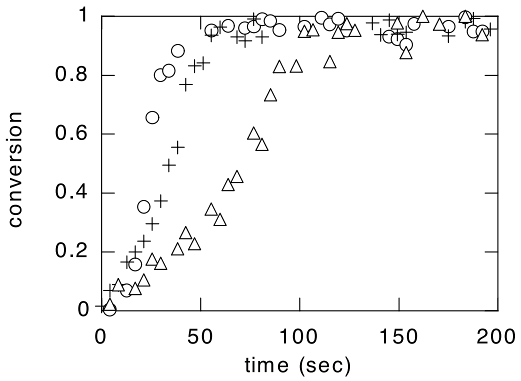

Fig. 4. Conversion as a function of irradiation time for Peg400DMA cured with no CT agent (○), 1.0 wt% DDT (+), and 1.0 wt% *m*-TT (△).

However, the polymerization rate increases with crosslinking agent concentration, due to diffusion limited termination, thus creating polymers with longer kinetic chains (i.e. higher $M_{w,v}$ values). These two effects impact the ratio of $M_{w,v}$ to $M_{w,c}$. However, with the addition a chain transfer agent, the relative rate of chain transfer to propagation (assumed constant at 0.07 for 1 wt% *m*-TT, regardless of the monomer composition) dominates the kinetic chain length calculation and decreases the kinetic chain length to ≈ 13 for all the monomer compositions investigated. Therefore, the increase in the ratio of $M_{w,v}$ to $M_{w,c}$ with crosslinking agent is due to the decrease in $M_{w,c}$.

Using a constant value for the relative chain transfer rate simplifies the calculations, but neglects some of the complexities of methacrylate systems. In one recent work, the polymerization behavior of methyl methacrylate with and without chain transfer agent was discussed [17]. Using both modeling and experimental data, the researchers concluded that chain transfer reactions play an increasingly important role as the conversion increases. Like propagation, transfer reactions involve small molecules for which the reactions do not become diffusion controlled until higher conversions. Therefore, the presence of shorter chains (created by chain transfer) facilitates termination in systems that exhibit low macroradical mobility. Though the discussion focused on a linear system, this same reasoning can be applied to crosslinked systems, where reaction diffusion controlled termination exists [4]. For example, chain transfer was shown to increase the termination rate in a crosslinked network, even at very higher conversions. As the conversion increased, the mobility of the reaction environment decreased, so chain transfer reactions became more important in facilitating termination [4]. Therefore, the relative chain transfer rate, like the polymerization rate, is dependent on the mobility of the reaction environment and may change as a function of crosslinking density or conversion. To gain a better understanding about the effect of chain transfer on the kinetic chain length, experimental methods need to be developed to measure chain transfer constants in crosslinking systems.

In addition to addressing the effect of the chain transfer agent on the ratio of $M_{w,v}$ to $M_{w,c}$, Table 1 also presents data on how the addition of a chain transfer agent impacts the mechanical properties of 25/75 OcMA/HDDMA (mass ratio). As the crosslinking agent concentration and the ratio of $M_{w,v}$ to $M_{w,c}$ increase, the change in the mechanical properties with the addition of a chain transfer agent is still apparent. Though the suppression in the T_g is similar to the more loosely crosslinked network, the result is somewhat surprising since the $M_{w,c}$ value is five times lower than the 95/5 OcMA/HDDMA system.

3.2. Multi-EGDMA homopolymerizations

Since more highly crosslinked networks were affected by the addition of a chain transfer agent, systems that were composed of only divinyl monomers were also investigated. Dimethacrylate monomers with varying numbers of ethylene glycol backbone-units (poly(ethylene glycol=N) dimethacrylates) were chosen for further study since they were readily available and yield fully converted polymers with a wide range of glass transition temperatures (0–150 °C). Fig. 4 depicts the effect of chain transfer on the polymerization rate of Peg400DMA. Instead of variations in the chain transfer agent concentration, two different chain transfer agents, docanethiol (DDT, $C_{CT} = 1.2$) and (*m*-TT, $C_{CT} = 4.7$), are compared. Though all three formulations cured within 100 s, the effect of the chain transfer agents is still evident. As expected, *m*-TT, which has a higher chain transfer constant (to methyl methacrylate), decreased the polymerization rate more dramatically than DDT. Like the OcMA/HDDMA results, all three compositions exhibited similar final conversions.

In addition to decreasing the polymerization rate, the addition of chain transfer agents also affected the modulus and loss tangent of the Peg400DMA polymer (Fig. 5). Similar to the OcMA/HDDMA results, a depression in the mechanical properties is noted. However, the change in T_g is a few degrees less than the 75/25 OcMA/HDDMA system (similar $M_{w,c}$ and $M_{w,v}/M_{w,c}$ values). This result suggests that the properties of the Peg400DMA polymer are less affected by the addition of the chain transfer agent, possibly because the ethylene glycol units in the polymer backbone can undergo chain transfer reactions without additives present. Therefore, the differences reported in the values of the kinetic chain lengths (with and without chain transfer agent, Table 2) may not be as dramatic since the calculations do not account for the inherent chain transfer in the multi-EGDMA systems. Furthermore, one can estimate that the addition of 1 wt% DDT impacts the kinetic chain length in a similar manner to increasing the initiation rate by four orders of magnitude. Therefore, severe changes in the initiation rate would be needed to induce even a 5 °C difference in the measured T_g value. In addition, there is no significant difference between the mechanical behavior of the polymers cured with DDT and *m*-TT. Though the

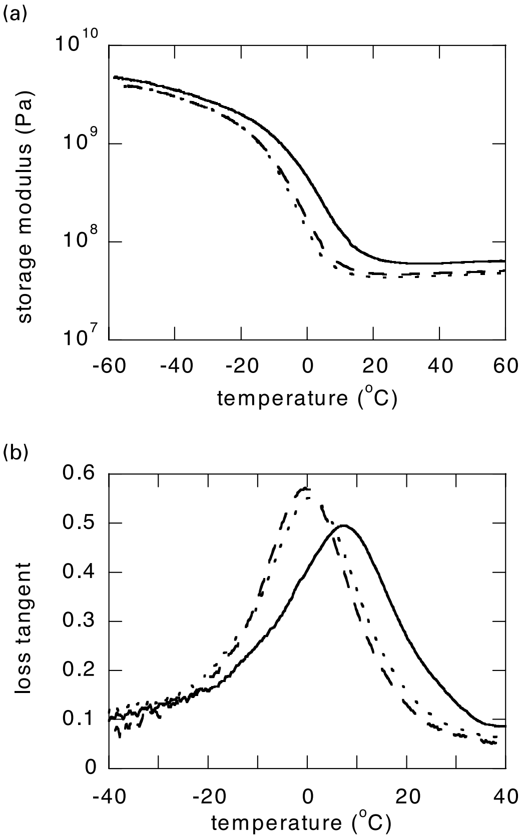

Fig. 5. Modulus (a) and loss tangent (b) of Peg400DMA cured with no CT agent (—), 1.0 wt% DDT (- -), and 1.0 wt% *m*-TT (···).

polymerization rate decreased further with the more reactive chain transfer agent (*m*-TT), the changes in rate do not correlate to significant differences in the material properties. This finding is interesting since other researchers have discussed a shift in the molecular weight distribution of linear polymers with the addition of more powerful chain transfer agents [18].

Another interesting aspect of Fig. 5(b) is the increase and slight narrowing of the loss tangent curves when Peg400DMA was polymerized with chain transfer agents. The width at half max of the loss tangent curve narrows by about 5 °C (from 25 to 20 °C) when compared to the pure homopolymerization. This narrowing of the loss tangent curve is suggestive of the formation of a more homogeneous network. However, the difference is quite small so more sensitive techniques should be used to ascertain whether using chain transfer agents in crosslinked networks could alter the homogeneity of the system. Homogeneous kinetic chain lengths (i.e. more symmetric molecular weight distributions and decreased polydispersity) are quite apparent in linear systems with chain transfer agents [6,7], but the effect seems to be much less obvious in crosslinked systems.

In addition to Peg400DMA, a wide range of multi-ethylene glycol dimethacrylate and diacrylate systems were investigated. As Table 2 illustrates, the polymerization kinetics were a strong function of monomer spacer length. In general, as the length of the ethylene glycol unit in the monomer was reduced (from 8 to 2), the polymerization rate increased and the final double bond conversion decreased. This result is expected since decreasing the molecular weight of the repeat unit decreases the mobility of the system during cure. Decreased mobility enhances autoacceleration, but also leads to lower final conversions. Since the systems are divinyl, the ratio of $M_{w,v}$ to $M_{w,c}$ is equivalent to the kinetic chain length ($M_{w,c} \approx M_r$). Therefore, the enhanced rate directly correlates to larger values of $M_{w,v}/M_{w,c}$. The effect of diffusion controlled kinetics was mitigated by curing all of the samples at 80 °C; however, the polymers

Table 2
Network properties of multi-EGDMA/DA polymers

Composition	$M_{w,c}$	$[(M_{w,v})/(M_{w,c})]$	T_g (°C)	Modulus (Pa) at T (°C)
Peg400DMA	540	8000	7.9 ± 0.1	$6.5 \times 10^7 \pm 0.1$ (70 °C)
1 wt% DDT		80	1.5 ± 0.6	$5.0 \times 10^7 \pm 0.4$ (70 °C)
1 wt% *m*-TT		10	-0.4 ± 0.3	$4.9 \times 10^7 \pm 0.1$ (70 °C)
(90/10) Peg (400/200) DMA	520	9000	13.6 ± 0.8	$7.0 \times 10^7 \pm 0.1$ (90 °C)
1 wt% DDT		80	7 ± 0.1	$5.9 \times 10^7 \pm 0.2$ (90 °C)
(62/38) Peg (400/200) DMA	440	8500	40.2 ± 0.6	$9.0 \times 10^7 \pm 0.1$ (85 °C)
1 wt% DDT		80	36.8 ± 0.3	$8.1 \times 10^7 \pm 0.1$ (85 °C)
Peg200DMA (97% cured)	340	13,000	97.5 ± 2.5	$2.1 \times 10^8 \pm 0.3$ (85 °C)
1 wt% DDT		80	88.8 ± 1.0	$1.7 \times 10^8 \pm 0.1$ (85 °C)
TEGDMA (92% cured)	290	20,000	137.0 ± 1.5	$2.5 \times 10^8 \pm 0.3$ (190 °C)
1 wt% DDT		80	132.0 ± 3.7	$2.6 \times 10^8 \pm 0.1$ (190 °C)
DEGDMA (85% cured)	240	25,000	–	$7.0 \times 10^8 \pm 0.5$ (190 °C)
1 wt% DDT		80	–	$5.3 \times 10^8 \pm 0.6$ (190 °C)
Peg400DA	510	–	-29.5 ± 2.7	$3.7 \times 10^7 \pm 0.1$ (40 °C)
1 wt% DDT		–	-27.9 ± 2.3	$3.6 \times 10^7 \pm 0.1$ (40 °C)
TEGDA (97% cured)	260	–	63.8 ± 1.5	$1.7 \times 10^8 \pm 0.1$ (100 °C)
1 wt% DDT		–	71.4 ± 4.7	$1.4 \times 10^8 \pm 0.2$ (100 °C)

Cure conditions: 80 °C, 5 mW/cm^2, and 0.2 wt% DMPA. All samples fully polymerized except, where noted ($n = 2$ or 3).

with high glass transition temperatures still exhibited incomplete conversion. In addition, all of the dimethacrylates studied showed a reduced rate when DDT was added. Since the relative rate of chain transfer (0.01 for 1 wt% DDT) was kept constant, all of the multi-EGDMA systems with DDT have the same calculated value for the kinetic chain length. Though the rates of polymerization and initiation were slightly different for each monomer, the chain transfer term dominates the kinetic chain length calculation (Eq. (1)). Unfortunately, *m*-TT could only be used with Peg400DMA since the other monomer mixtures polymerized spontaneously upon the addition of the *m*-TT.

In addition to the molecular weight estimations, Table 2 also presents the effect of DDT addition on the mechanical properties of the M-EGD(M)A polymers. The mechanical properties of the multi-EGDMA series were found to be strongly dependent on the monomer molecular weight ($\approx M_{w,c}$) and only slightly affected by the addition of a chain transfer agent. Since increasing the crosslinking density dramatically strengthens the network structure, the relationship between $M_{w,c}$ and T_g is expected. The slight decrease in the mechanical properties with the addition of a chain transfer agent is a novel result. However, the difference is not as dramatic as observed in the OcMA/HDDMA systems. The M-EGDMA systems undergo some inherent chain transfer, thus diminishing the effect of an added chain transfer agent on the polymer network. Nevertheless, the small depression in the mechanical properties is repeatable and suggests that dramatically decreasing the kinetic chain length negatively impacts the polymer properties, even in these relatively highly crosslinked materials. The largest decrease in the T_g and modulus with chain transfer agent occurred in the Peg400DMA system and diminished as crosslinking density increased.

When DDT was added to the acrylate systems (Peg400DA and TEGDA), no discernible differences in the polymerization rates were observed. This result is similar to previous experimental studies that showed acrylate systems to be less affected by chain transfer agents than methacrylate systems [3,4] and modeling studies which found that termination in acrylate systems can be described by a single chain-length independent rate constant [19]. Since acrylate systems readily undergo chain transfer to polymer, adding dodecanethiol to this transfer dominated system has little effect. Values of $M_{w,v}$ for the transfer dominated acrylate polymerizations were not calculated, but one can assume that the values would be far lower than the corresponding methacrylates. In addition, the T_g and modulus of the acrylate systems were found to be nearly unaffected by the addition of a chain transfer agent within the experimental error of the measurement technique. This results supports the theory that acrylate polymerizations exhibit similar network structure regardless of whether chain transfer agents are used or if the initiation rate is changed dramatically.

4. Conclusions

Two chain transfer agents, dodecanethiol and *m*-TT, were added to a series of crosslinking free radical polymerizations to decrease the calculated value of the kinetic chain length. With the addition of only 0.5–1 wt% chain transfer agent, differences in the polymerization rate and mechanical properties were observed in the dimethacrylate systems. The polymerization rate was significantly suppressed and the glass transition temperature of the cured network was found to decrease by up to 10 °C, depending on the monomer formulation. The addition of a chain transfer agent dramatically increases the rate of chain breaking reactions and decreases the kinetic chain length of the growing macroradicals. These reduced macroradical chain lengths promoted more facile termination and created polymer networks with lower mechanical strength (e.g. T_g and rubbery modulus). The largest differences in the mechanical properties occurred in the systems with the lowest crosslinking density and diminished as the crosslinking density of the cured polymer increased. Furthermore, the differences were less dramatic in the multi-EGDMA systems that have some inherent ability to chain transfer, and were not discernable in the transfer dominated diacrylate systems. This study illustrates that macroradical chain length, which has been shown to play a role in the termination kinetics of crosslinking systems, also impacts the network properties of the formed polymer.

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