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Effect of Primary Cyclization on Free Radical Polymerization Kinetics: Modeling Approach

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ABSTRACT: A modified kinetic model is developed which captures how the cross-linked network structure and its evolution in loosely cross-linked polymers affects the polymerization kinetics. In our previous work, diffusion-controlled kinetics has been modeled through the change in free volume of the system as monomer converts to polymer.[1,2] Here, the additional effect of the resistance caused by the need to diffuse through the cross-linked network is incorporated into a model of the polymerization kinetics. With this model, the effects of cross-linking and cyclization observed in experimental systems are predicted. The model quantitatively predicts experimental results for varying concentrations of 1,4-cyclohexanediol dimethacrylate and 1,2-cyclohexanediol dimethacrylate copolymerized with methoxy ethyl methacrylate.

Introduction

Predicting the kinetics of free radical polymerizations of multifunctional polymers has been extensively studied yet still remains a topic of current research. In these free radical polymerizations multifunctional monomers are linked together to produce densely cross-linked networks. Because of the transformation from liquid monomer to a solid, cross-linked polymer network, these polymerizations exhibit abnormal kinetic behavior, including autoacceleration, autodeceleration, reaction diffusion-controlled termination, limiting functional group conversion, and anomalous pendant reactivity.[3−8] Autoacceleration, which is marked by a sharp increase in the polymerization rate, occurs when the termination rate becomes diffusion-limited. The propagating radicals are not able to terminate as easily, and the radical concentration and polymerization rate increase. In contrast, 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 more slowly through the growing polymer network prior to reacting with propagating radicals. A complete model of free radical polymerizations of cross-linked polymers would be able to predict all of these effects.

Many researchers have reported how molecular diffusion through a polymer is reduced with increasing polymer cross-link density,[9−12] and in free radical polymerizations, the polymerization rate is strongly diffusion-controlled. Because cyclization contributes negligibly to the overall network structure, it will hinder diffusion through the system less than cross-linking reactions. By altering the diffusion through the network, the degree of primary cyclization and cross-linking must influence the polymerization kinetics. This effect has been observed in several experimental studies.[13,14] Research comparing divinyl and trivinyl copolymerizations shows that the reduced cross-linking efficiency in the divinyl copolymers corresponds with reduced autoacceleration and maximum polymerization rate.[8,15] Further, in studies of pseudocrown ether formation where the formation of cyclic structures is the goal, dramatic changes in polymerization kinetics with cross-link density are observed. When the divinyl monomer is templated with metal salts, causing the primary cyclization rate to increase, reduced autoacceleration is observed.[13] Recent experimental work has been conducted to control systemically the extent of cross-linking and cyclization to investigate how their balance influences the polymerization kinetics. For these experiments, two cross-linking agents, 1,4-cyclohexanediol dimethacrylate (1,4-CHDDDMA) and 1,2 cyclohexanediol dimethacrylate (1,2-CHDDMA) were utilized that have different propensities to cycle because of the relative position of their two methacrylate double bonds. Measurement of mechanical properties of copolymerizations of these cross-linking agents verified that 1,4-CHDDMA undergoes less cyclization than 1,2-CHDDMA. Kinetic studies showed that the 1,2-CHDDMA copolymers exhibit delayed autoacceleration and confirm that the effect of cross-linking on the diffusion limitations during polymerization is important. In this work, the impact of the network structural evolution is incorporated into the kinetic model.

Background

Many researchers have developed models to predict the kinetics of free radical polymerizations, and these models generally focus on predicting the polymerization kinetics in linear systems. Marten and Hamielec used free volume based kinetic equations to predict diffusion-controlled termination and propagation successfully for linear methyl methacrylate and styrene systems.[16,17] In this approach they fit a critical conversion and molecular weight for termination and propagation to become diffusion-controlled. After the critical conversion was reached, the kinetic constants were proportional to the diffusion of the monomer for propagation and polymer for termination, as predicted by Smoluchowski.[18] The change in diffusion with free volume was then predicted

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by the Doolittle expression from Bueche,[19] and this approach was built upon by numerous other researchers.[20−24] Soh and Sundberg modeled autoacceleration- and diffusion-controlled kinetics that accounted for chain-length-dependent termination in linear systems and were successful in predicting higher molecular weight averages.[25] Other researchers continue to included chain-length-dependent termination in linear polymers,[26−31] while Zhu and Hamielec used an average method to determine the termination kinetic constant to account for all chain-length-dependent effects.[30]

Models continued to be expanded to include more features like volume shrinkage and physical aging that occur in cross-linked systems.[32] The Anseth and Bowman model applied Marten−Hamielec-type free volume equations to cross-linked systems, incorporating reaction diffusion control and volume relaxation.[3] The major advance in this work was that it allowed for a smooth transition between reaction- and diffusion-controlled regions by expressing kinetic constants in terms of resistances to reaction. It altered the model by Buback to have chemical reaction in series with both diffusional resistances.[22,33] Most recent work in modeling cross-linked systems specifically includes modeling that incorporates radical trapping.[34] This work was able to predict partially the effect of light intensity on the final conversion, without including volume relaxation.

The models discussed thus far have utilized the semiempirical free volume based kinetic expression used by Marten and Hamielec to predict diffusion-controlled kinetics. Other methods have been tried, some very mechanistic, others completely empirical. These alternatives include the pioneering work of Cardenas and O'Driscoll for polymerization of methyl methacrylate at high conversion.[26] In this model, the termination rate constant for entangled chains is inversely proportional to the entanglement density. Similarly, in the work by Mikos et al. on cross-linked polymers a mobility factor based on the cross-link density was incorporated to capture diffusion limitations after the gel point.[35] Li et al.[36] modeled the polymerization of methyl methacrylate cross-linked with ethylene glycol dimethacrylate using Tobita's pseudo kinetic approach.[37] The diffusional limitations of the number-average k_t value were described by an empirical equation fit to their data. Finally, Batch and Macosko modeled diffusion-controlled termination in cross-linked polymers through the decay of the active radical fraction and initiator efficiency after a critical conversion.[38] The model was able to predict polymerization behavior of divinylbenzene and a commercial vinyl ester resin.

Kinetic modeling has advanced considerably in the last 20 years and is able to represent polymerization behavior more accurately as additional kinetic features are incorporated into the models. As of yet, no model has included how the balance between primary cyclization and cross-linking influences polymerization kinetics. Inclusion of this feature will add additional capabilities to models predicting the polymerization kinetics.

Experimental Methods

This modeling work is based on an experimental study of polymerization kinetics. The monomers used 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), and 1,2 cyclohexanediol dimethacrylate (1,2-CHDDMA). 1,2-CHDDMA contains a mixture of cis and trans isomers. The cross-linking agents chosen are specifically designed to either form cycles or cross-links. 1,4-CHDDDMA with its two methacrylate groups on opposite sides of the ring is expected to undergo significantly greater degrees of cross-linking than 1,2-CHDDDMA with the two methacrylate groups held close to each other by the cyclohexane ring. To ensure the formation of a more ideal, less densely cross-linked network, the cross-linking agent was polymerized with 90 mol % or greater 2-methoxyethyl methacrylate. In this manner, the majority of the double bonds in the system are always the same monovinyl monomer. 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 the total monomer weight.

The polymerization kinetics were measured using real-time infrared (IR) spectroscopy (Magna 750, Series II, Nicolet Instrument, Madison, WI) initiated by a UV-light source (Ultracure 100SS Watt Hg sort-arc lamp, EFOS, Missississaugua, Ontario, Canada) at a light intensity of 1 mW/cm^2.[39,40] A dynamic mechanical analyzer (DMA7e, Perkin-Elmer, Norwalk, CT) was used to obtain the mechanical properties[41] and ascertain differences in cross-linking between samples. Dynamic mechanical analysis (DMA) experiments were performed to determine the glass transition temperature (T_g) and molecular weight between cross-links ($\overline{M}_c$) of the copolymers. The details of the experimental synthetic methods have been described elsewhere and will not be discussed further here.[14]

Kinetic Modeling

In previous work, we have a developed a kinetic based model to predict the network evolution during polymerization of multifunctional monomers.[15,42,43] This network formation model is the foundation of the model developed to predict how primary cyclization influences kinetics. The model currently incorporates mobility effects through expressions for k_p and k_t as functions of free volume, which is then a function of conversion.[1,2] All conversion is not equal, however, when it comes to how it contributes to the mobility reduction. Cross-linking hastens diffusion-limited kinetics more than cyclization. The current model already predicts cyclization and cross-linking rates as a function of conversion. Cyclization is predicted by the proximity of the pendant double bond to the propagating radical and calculation of a local radical concentration. By combining information from the network formation model on the extent of primary cyclization with how cyclization affects the diffusion limitations, the polymerization kinetics of this system are better predicted.

Incorporation of the Effect of Primary Cyclization. Currently, diffusion-controlled kinetics are modeled based on how the free volume changes with conversion. The kinetic constants for propagation and termination are assumed proportional to the diffusion coefficient for the monomer and radical, respectively. The diffusion coefficients are then determined as a function of free volume using the Doolittle type equation developed by Bueche.[19] The addition of cross-links does not reduce the free volume of the system significantly more than does the addition of a cycle, but it does strongly alter the ability of the polymer chains to slide past each other as they diffuse. Thus, with a cross-linked system there are actually two contributions to the diffusional limitations: (i) the ability of the diffusing species to find sufficient free volume to diffuse and (ii) the ability of the species to diffuse through the cross-linked mesh.[10] The first effect is included in the current model and predicted by Bueche's equation. In this work, the second contribution is added by including the probability for a solute to move through a gel in a manner similar to the work by Lustig and Peppas.[10] This probability (P) represents the sieving mechanism of the species diffusing through a cross-linked polymer, and it is a function of the average network mesh size (ξ) and the size of the diffusing species (B).

$$P = \exp\left(\frac{-B}{\xi}\right) \qquad (1)$$

The exponential function was utilized for this work because it captures the transition as the value ξ approaches and eventually falls below the value of B. There are also several other models available to describe how diffusion depends on polymer structure.[12,43,44] The exponential variation of the Lustig and Peppas expression was chosen because it introduces a minimum number of new parameters and has physically definable variables. The value of ξ is calculated from the average molecular weight between cross-links, $\overline{M}_c$, and the molecular weight of a repeat unit, M_r, assuming an unperturbed (solvent free) state as shown in eq 2.

$$\xi = {C_n}^{1/2}\left(2\frac{\overline{M}_c}{M_r}\right)^{1/2} l \qquad (2)$$

Thus, with the addition of eq 1, the kinetic parameters, when diffusion-controlled (k), are proportional to the diffusion coefficient as a function of fractional free volume (f)[19] times the probability of diffusing through the mesh.

$$k = C\exp\left(\frac{-A}{f}\right)\exp\left(\frac{-B}{\xi}\right) \qquad (3)$$

In eq 3, A, B, and C are constants. This form of the diffusion limitation is incorporated into the expression for k_p and k_t analogously to the derivation by Anseth–Bowman (eqs 4 and 5).[3] Propagation kinetics are controlled by either the chemical reaction or by diffusion depending on the double bond mobility in the polymerizing mixture. For termination, k_t is a function of the chemical reaction resistance and the resistances associated with both diffusion mechanisms: segmental diffusion from eq 3 and reaction diffusion. The value of C is chosen so that when the free volume is equal to a critical free volume (f_c) and the mesh size is equal to the critical mesh size (ξ_c), the contribution to reaction by the chemical reaction term and diffusion term are equal. Hence,

$$k_p = \frac{k_{po}\exp\left(-B_p\left(\frac{1}{\xi}-\frac{1}{\xi_{ct}}\right)\right)}{1+\exp\left(A_p\left(\frac{1}{f}-\frac{1}{f_{cp}}\right)\right)} \approx \frac{k_{po}}{1+\exp\left(A_p\left(\frac{1}{f}-\frac{1}{f_{cp}}\right)\right)} \qquad (4)$$

$$k_t = k_{to}\left\{\frac{1}{\frac{Rk_p[\mathrm{DB}]}{k_{to}}+\exp\left(-A_t\left(\frac{1}{f}-\frac{1}{f_{ct}}\right)\right)\exp\left(-B_t\frac{1}{\xi}-\frac{1}{\xi_{ct}}\right)}+1\right\}^{-1} \qquad (5)$$

k_{po} and k_{to} are the preexponential factors or the initial value of kinetic constants in the absence of diffusional limitions. The critical fractional free volumes at which propagation and termination become diffusion-limited are f_{cp} and f_{ct}. The factors A_p and A_t control how rapidly the rate decreases during the diffusion-controlled regions. R is the reaction diffusion parameter, [DB] is the double bond concentration, and B_p and B_t are related to the size of the diffusing propagating and terminating species, respectively. The critical mesh size for termination, ξ_{ct}, is the cross-link density at which the reaction begins to autoaccelerate and is derived from experimental data as shown in the next section. For propagation, the effect of the critical mesh size is neglected in these copolymerizations because the size of the monomer is much smaller than the mesh size of the polymer network created, and monomer diffusion is not significantly impacted by the cross-link density.

The change in fractional free volume, f, with reaction is calculated by eq 6 and includes contributions from monomer, polymer, and solvent (if present) to the free volume.[46]

$$f = 0.025 + \alpha_m(T - T_{gm})\phi_m + \alpha_p(T - T_{gp})\phi_p + \alpha_s(T - T_{gs})\phi_s \qquad (6)$$

T_{gm}, T_{gp}, and T_{gs} are the glass transition temperatures of the monomer, polymer, and solvent, respectively, and T is the reaction temperature. ϕ_m, ϕ_p, and ϕ_s are the volume fractions of monomer, polymer, and solvent, respectively. The volume fractions are calculated as a function of conversion with appropriate densities. α_m, α_p, and α_s are related to the coefficient of thermal expansion for the monomer, polymer, and solvent, respectively. Each α is defined as the expansion coefficient for the liquid-state minus the expansion coefficient for the glassy state.[46] Utilizing eqs 4, 5, and 6 in the model allows for the prediction of how cross-linking influences the polymerization kinetics.

Model Parameters. Several parameters are required by the model to specify the system. A complete list of values utilized in the simulations is included in Table 1. Since all samples are copolymers consisting of mainly MEMA, the kinetic parameters (k_{po}, k_{to}, f_{cp}, f_{ct}, A_p, A_t, R, and B_t) should be the same for all compositions. The initial value of each kinetic constant, k_{po}, for propagation and for termination, k_{to}, were determined from the conversion vs time data from all four experiments (2% and 5% of 1,4-CHDDMA or 1,2-CHDDMA) utilizing the methods previously described in the literature.[47] The ratio of the kinetic constants was determined from the initial slope of the conversion vs time curves before autoacceleration. The values of k_{po} and k_{to} were individually determined using data from the reaction–diffusion-controlled termination region where propagation is not diffusion limited. In this region the termination kinetic constant (k_{to}) can be represented by the reaction–diffusion constant (R) times the propagation kinetic constant (k_{po}) times the total double bond concentration.[47] The choice of k_{po} = 150 L/(mol s) and k_{to} = 1 000 000 L/(mol s) is validated by good fits to experimental data in both conversion vs time plots and polymerization rate vs conversion plots.

The values of f_{cp}, f_{ct}, A_p, and A_t were also determined from experimental data. The critical free volume for the onset of diffusion-controlled termination (f_{ct}) was determined from the calculated fractional free volume at the conversion where the earliest onset of diffusion control is exhibited. This point is identified as the conversion where the conversion vs time curves begin to diverge

Table 1. Model Parameters Used for Kinetic Simulations

parameter	2% copolymerization	5% copolymerization
propagation kinetic parameter, k_{po}	150 L/(mol s)[a]	150 L/(mol s)[a]
termination kinetic parameter, k_{to}	1 000 000 L/(mol s)[a]	1 000 000 L/(mol s)[a]
reaction−diffusion parameter, R	2[b]	2[b]
exponential constant that controls autoacceleration, A_p	0.3 ± 0.05[c]	0.3 ± 0.05[c]
exponential constant that controls autodeceleration, A_t	0.4 ± 0.05[c]	0.4 ± 0.05[c]
propagation critical free vol, f_{cp}	0.031 ± 0.001[c]	0.031 ± 0.001[c]
termination critical free vol, f_{ct}	0.0625 ± 0.0075[c]	0.0625 ± 0.0075[c]
glass transition temp of monomer, T_{gm}	−60 °C[d]	−60 °C[d]
glass transition temp of polymer with 1,4-CHDDMA, T_{gp}	78 ± 2 °C[e]	82 ± 2 °C[e]
glass transition temp of polymer with 1,2-CHDDMA, T_{gp}	71 ± 2 °C[e]	92 ± 2 °C[e]
density of monomer, ρ_m	1.082 g/cm^3 [f]	1.082 g/cm^3 [f]
density of polymer, ρ_p	1.12 g/cm^3 [f]	1.12 g/cm^3 [f]
difference in thermal expansion coeffs for liquid and glassy states of monomer, α_m	0.0005 1/°C[g]	0.0005 1/°C[g]
difference in thermal expansion coeffs for liquid and glassy states of polymer, α_p	0.000075 1/°C[g]	0.000075 1/°C[g]
difference in thermal expansion coeffs for liquid and glassy states of polymer, α_s	0.0005 1/°C[g]	0.0005 1/°C[g]
B_t, size of diffusion radical chain	$(4.0 \pm 1.0) \times 10^{-6}$ cm[c]	$(4.0 \pm 1.0) \times 10^{-6}$ cm[c]
effective monomer length times characteristic ratio, r_oC_n, for 1,4-CHDDMA	$(3.5 \pm 0.3) \times 10^{-7}$ cm[h]	$(3.5 \pm 0.3) \times 10^{-7}$ cm[h]
effective monomer length times characteristic ratio, r_oC_n, for 1,2-CHDDMA	$(2.1 \pm 0.1) \times 10^{-7}$ cm[h]	$(2.1 \pm 0.1) \times 10^{-7}$ cm[h]
initial double bond concentration	6.94 M[i]	7.02 M[i]
rate of initiation, R_i	2.45×10^{-5} mol/(L s)[i]	2.45×10^{-5} mol/(L s)[i]
temp, T	25 °C[i]	25 °C[i]

[a] Determined from kinetic data using method described by Goodner and Bowman.[47] [b] Typical value for methacrylate polymerization.[48] [c] Fit to experimental data as described in text. [d] From Anseth.[47] [e] Measured using DMA.[14] [f] From Aldrich catalog. [g] From Bueche.[19] [h] Calculated using eq 9 and average cyclization fraction, $\bar{\psi}$, determined from DMA. [i] Reaction conditions of polymerization.

from each other, approximately 11% conversion. For each copolymer experiment, the values of the fractional free volume at 11% conversion were calculated using eq 6. These values were averaged to yield a f_{ct} of 0.0625 ± 0.0075. The critical free volume for propagation (f_{cp}) is similarly determined from the conversion where the maximum polymerization occurs, which is when propagation becomes diffusion-controlled. In the least cross-linked system (2% 1,2-CHDDMA), which should most represent the inherent behavior of MEMA, the maximum rate occurred at approximately 79%. For each copolymer experiment, the values of the fractional free volume at 79% conversion were calculated using eq 6. These values were averaged to yield a f_{cp} of 0.031 ± 0.001. Values of A_p and A_t were chosen that had the best fit to the data for all four copolymers once the other parameters had been established. The least-squares fit yielded values of 0.3 and 0.4 for A_p and A_t, respectively. Error on these fits is approximately ±0.05.

A value of 2 L/mol was used for the reaction diffusion parameter, R, as a reasonable value for methacrylate polymerizations.[48] Using values from 1.5 to 2.5 for R yield a reasonably good fit. The size of the terminating species or radical chain, B_t, cannot be predicted by a straightforward manner. Thus, for simplicity B_t was held constant and fit to the experimental data by least-squares regression. The effective size of the terminating radical species, B_t, utilized in the simulation is 4.0×10^{-6} cm, which is approximately the mesh size at 2% conversion of the 2% cross-linking agent polymerization. With larger or smaller values of B_t, the effect of cyclization on radical species diffusion limitations is more or less pronounced, respectively. Values of B_t of $4.0 \times 10^{-6} \pm 1.0 \times 10^{-6}$ cm capture the experimental behavior fairly well. The glass transition temperature of the polymer, T_{gp}, is measured using DMA for each copolymerization.

The critical mesh size, ξ_{ct}, was derived directly from experimental data for each composition. Using the conversion vs time data, the critical conversion at which autoacceleration begins was determined by the intersection of the lines tangent to the conversion vs time curves before and after autoacceleration as shown in Figure 1. The critical conversion at which autoacceleration commences is a function of the cross-link density of the polymerization, further illustrating how the diffusion-controlled kinetics are related to the degree of cross-linking. Figure 2 shows the critical conversion as a function of the total concentration of cross-links at 100% conversion for all copolymerization data. Using the model to determine the mesh size as a function of conversion, the critical mesh size that corresponds to the critical conversion was determined (Figure 3). In this way the critical mesh size was derived for each copolymerization.

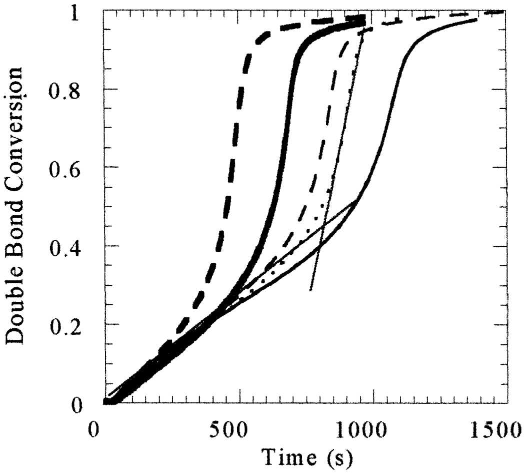

Figure 1. Conversion vs time for 5% 1,4-CHDDMA (thick - -), 5% 1,2-CHDDMA (thick −), 2% 1,4-CHDDMA (- -), 2% 1,3-CHDDMA (· · ·), and 2% 1,2-CHDDMA (−) with MEMA. Tangent lines where intersection is critical conversion (−).

The model predicts the degree of cyclization and cross-linking based on two parameters: the size of the cross-linking molecules, r_o, and the characteristic ratio, C_n, which is a measure of how extended the polymer chains are during polymerization. The experimental value of the $\overline{M_c}$, measured at 100% conversion, is used to determine the lumped parameter of r_oC_n. The concen-

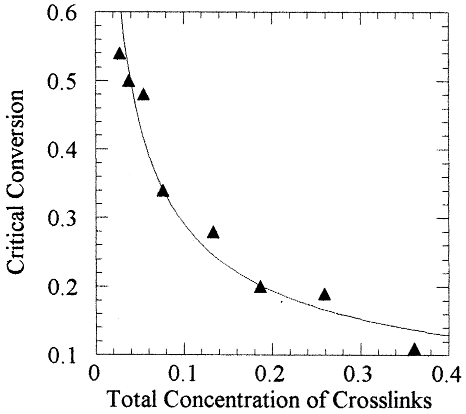

Figure 2. Critical conversion for autoacceleration as a function of cross-link density at 100% conversion: (▲) experimental data; (−) power law fit.

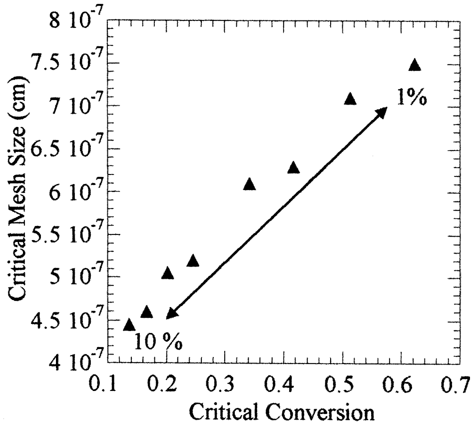

Figure 3. Critical mesh size as a function of the critical conversion conversion for autoacceleration for copolymers with 1% to 10% cross-linking agent.

tration of pendants that have cross-linked [Pen$_{xl}$] at 100% conversion is determined by eq 7 where [DB$_o$] is the initial double bond concentration.[15]

$$[\mathrm{Pen}_{\mathrm{xl}}] = \frac{M_{\mathrm{r}}[\mathrm{DB}_{\mathrm{o}}]}{2\overline{M_{\mathrm{c}}}} \tag{7}$$

Additionally, the concentration of pendants that have cross-linked can be calculated by integrating the fraction of pendants which have not cycled (1-ψ) over the total concentration of cross-linking monomeric double bonds-([M$_{xl}$]).

$$[\mathrm{Pen}_{\mathrm{xl}}] = \int_{[\mathrm{M}_{\mathrm{xl}}]_{\mathrm{o}}}^{0} (1 - \psi)\, \mathrm{d}[\mathrm{M}_{\mathrm{xl}}] \tag{8}$$

ψ is computed analytically as has been shown previously,[42] where Na is Avogadro's number and l is the length of a carbon-carbon bond.

$$\psi = 1 - \exp\left(\frac{-3}{8\pi NA[\mathrm{DB}]r_{\mathrm{o}}C_n l^2}\right) \tag{9}$$

Solving for [Pen$_{xl}$] in 7, the lumped value of r_oC_n is determined numerically by using eqs 8 and 9. The value of r_oC_n depends only on which cross-linking agent is used for all copolymers used here. r_o is a measure of the distance between the double bonds of the cross-linking agent and C_n depends primarily on how extended the polymer chain is during polymerization and will be mainly a property of MEMA, the monovinyl comonomer. Thus, r_oC_n is the same for all copolymers made with 1,4-CHDDDMA and the same for all polymerizations with the 1,2-CHDDMA cross-linking agent. Because calculation of $\overline{M_c}$ from the rubbery modulus is most accurate at low cross-linking density, the $\overline{M_c}$ data at 1% and 2% cross-linking agent were averaged to determine the value of r_oC_n. The average fraction of pendants that cycle over the polymerization, $\bar{\psi}$, is 0.44 ± 0.03 and 0.60 ± 0.02 for 1,4-CHDDMA and 1,2-CHDDMA copolymerizations, respectively.

Although it may appear that the model uses a large number of parameters to fit the data, it is important to note that the same values of k_{po}, k_{to}, f_{cp}, f_{ct}, A_p, A_t, R, and B_t are utilized for all four copolymer samples. The inherent chemical kinetic behavior of these systems should be the same, as the samples are at least 95% MEMA. Because the same values for k_{po}, k_{to}, f_{cp}, f_{ct}, A_p, A_t, and B_t were used for all simulations, these parameters are constants for the experimental systems examined. The variation in the rate data observed experimentally is captured solely through the monomer concentration, polymer glass transition temperature, and two kinetic parameters: the critical mesh size, ξ_{ct} and lumped parameter of r_oC_n. T_{gp}'s and the lumped r_oC_n parameters are determined by DMA from the experimental $\overline{M_c}$. The critical mesh size, ξ_{ct}, is calculated from the experimental kinetic data. The uncertainties on these important parameters are well-defined. Further, correct trends are predicted when ξ_{ct}'s and r_oC_n's are chosen that make physical sense. Specifically, with increasing cross-linking agent concentration the critical mesh size when diffusion-controlled termination occurs should decrease and hasten the onset of autoacceleration. The effective monomer length times characteristics ratio, r_oC_n, is related to the distance between the double bonds and should increase for larger cross-linking agents. In this work 1,4-CHDDMA should have a larger r_oC_n than 1,2-CHDDMA because of the geometry of the molecules. Errors in the assignment of the other kinetic parameters are not critical to predict how cyclization affects kinetic, as they are held constant for all simulations.

Results and Discussion

This kinetic model is able to predict experimental data related to the effects of cyclization on polymerization kinetics. Kinetic experiments conducted using two cross-linking agents, 1,4-CHDDMA and 1,2-CHDDMA, had differing rates of cyclization and cross-linking. Mechanical measurements of the $\overline{M_c}$ confirm that the 1,4-CHDDMA is more cross-linked than the 1,2-CHDDMA copolymer at 100% conversion, although the potential cross-link density was equivalent. Using the measured $\overline{M_c}$ at 100% conversion to fit the lumped r_oC_n parameter by the method described, the model predicts the degree of cross-linking as a function of conversion. Figure 4 shows the predicted results for $\overline{M_c}$ as a function of conversion for copolymerization with 2% cross-linking agent. Results show that the 1,4-CHDDMA has a smaller $\overline{M_c}$ throughout the polymerizations because of reduced primary cyclization.

Figure 5 presents the normalized polymerization rates for polymerizations containing 2% and 5% cross-linking agent. The normalized polymerization rates for the experimental data were calculated by differentiation of

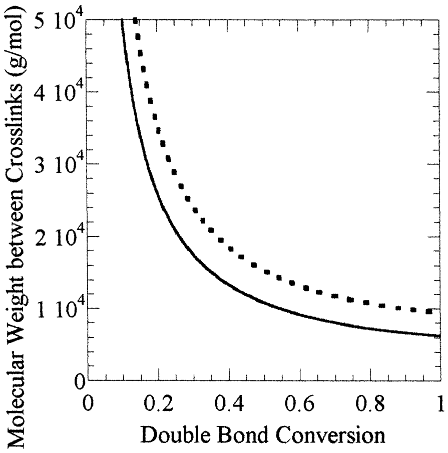

Figure 4. Simulated molecular weight between cross-links as a function of conversion for 2% 1,4-CHDDMA (−) and 2% 1,2-CHDDMA (- -), copolymerized with 98% MEMA.

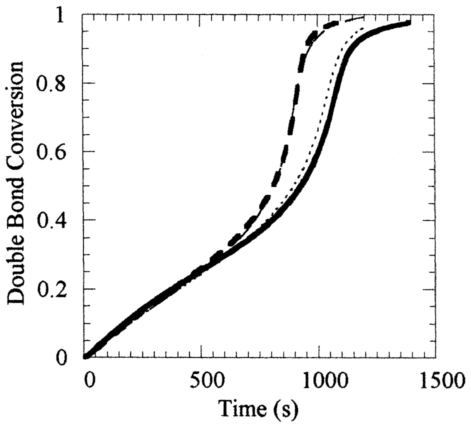

Figure 6. Double bond conversion vs time for 2/98 copolymer from experiments for 1,4-CHDDMA (- -) and 1,2-CHDDMA (−) and from simulations for 1,4-CHDDMA (− −) and 1,2-CHDDMA (· · ·).

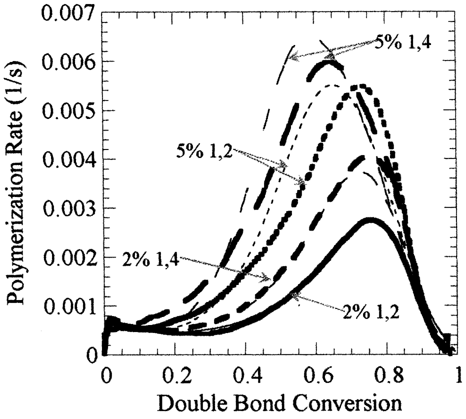

Figure 5. Normalized polymerization rate (1/s) vs conversion from experimental results for 5% 1,4-CHDDMA (thick − −), 5% 1,2-CHDDMA (• • •), 2% 1,4-CHDDMA (- -), and 2% 1,2-CHDDMA thick −). Rate vs conversion from simulations 5% 1,4-CHDDMA (− −), 5% 1,2-CHDDMA (· · ·) 2% 1,4-CHDDMA (- -), and 2% 1,2-CHDDMA (−).

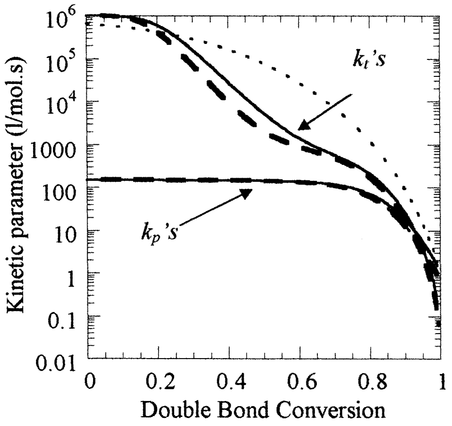

Figure 7. Kinetic parameters as a function of conversion for 5% 1,4-CHDDMA (− −), 5% 1,2-CHDDMA (−), and 5% cross-linking agent assuming no effect of cross-link density on conversion (- -).

the conversion vs time data measured using FTIR. The results show that autoacceleration occurs earlier with increasing cross-linking agent concentration. Additionally, the 1,4-CHDDMA copolymerizations exhibited earlier autoacceleration than the 1,2-CHDDMA copolymerizations at the same cross-linking agent concentration. Also shown in Figure 5 are the simulated data using the kinetic model. The model predicts the correct qualitative trend by calculating the network evolution and degree of primary cyclization and then using that information to determine how the kinetic constants change as a function of conversion.

Figure 6 shows the experimental and simulation data for the double bond conversion as a function of time for the 2% cross-linking agent samples. The kinetic model predicts the rate vs conversion and conversion vs time behavior correctly. The ability of the model to predict the experimental data quantitatively using the same kinetic parameters points to the success of the underlying assumptions. The differences in observed polymerization rates occur because the values of the kinetic parameters are changing differently with conversion. Figure 7 shows the kinetic parameters for 5% 1,4-CHDDMA and 1,2-CHDDMA as a function of conversion. Also shown on the plot are the predicted k_p and k_t if the effects of mesh size were neglected. The value of k_p does not change appreciably with the inclusion of the mesh size effect on diffusion control. This result is expected since propagation is controlled by diffusion of small monomeric molecules, whose size is much less than the mesh size. The value of k_t does, however, change in each case. k_t falls off more rapidly for the 1,4-CHDDMA than 1,2-CHDDMA copolymerization because the 1,4-CHDDMA forms a more cross-linked network. When the effect of the mesh size on diffusion of terminating species is neglected, k_t decays at the slowest rate.

Conclusions

The kinetic model is able to describe how shifting the balance of cross-linking and cyclization alters the polymerization kinetics in loosely cross-linked systems. Experimental results demonstrated that cyclization contributes negligibly to the overall network structure and decreases the mobility of the system less than cross-linking, resulting in a delayed onset of autoacceleration. With this information, the kinetic based network formation model developed previously is expanded to capture the impact of the network structure on the polymerization kinetics. The expressions for species diffusion which determine the diffusion-controlled nature of k_p and k_t are modified to include the effect of the cross-link density. In essence, diffusion in a cross-linked polymer is controlled by the availability of sufficient free volume and the ability of the species to diffuse through the cross-linked mesh. Since the model already calculates the extent of primary cyclization and cross-linking as a function of conversion, the mesh size of the cross-linked polymer is readily calculated as a function of conversion. This method is able to predict the experimental data well by fitting the critical size of the diffusing terminating species.

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