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Effect of Polymerization Temperature and Cross-Linker Concentration on Reaction Diffusion Controlled Termination

Jennifer S. Young[†] **and Christopher N. Bowman***

Department of Chemical Engineering, University of Colorado, Boulder, Colorado 80309

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ABSTRACT: The effects of temperature and cross-linking agent concentration on reaction diffusion controlled termination have been determined for several loosely cross-linked acrylate and methacrylate systems. The systems studied were 10/90 DEGDA/sBA (10 mol % diethylene glycol diacrylate, 90 mol % *sec*-butyl acrylate), 1/99/40 DEGDMA/HEMA/PEG400 (1 wt % diethylene glycol dimethacrylate, 99 wt % 2-hydroxyethyl methacrylate diluted with poly(ethylene glycol) 400 to 40 wt %), and 10/90 DEGDMA/OcMA (10 wt % DEGDMA, 90 wt % *n*-octyl methacrylate.) The effect of increased cross-linking agent concentration is to decrease the reaction diffusion parameter (R), defined as k_t/k_p[M], until a plateau is reached. The reaction diffusion parameter was found to increase as the polymerization temperature is increased above T_g for the methacrylate systems. However, as the temperature is decreased below the T_g for loosely cross-linked systems, R was found to also increase. This phenomenon is not readily predicted using current theory, and thus it is proposed that chain transfer to monomer becomes an important means of radical mobility in loosely cross-linked systems below the T_g. These results enhance the current understanding of reaction diffusion controlled termination, particularly in cross-linked systems.

Introduction

Polymerization reactions consist of initiation, propagation, and termination reactions. The relative rates of these reactions determine the overall rate of polymerization. For cross-linked networks, these relative rates also control the development of the network structure and ultimately the material properties of the final polymer. Consequently, a clear understanding of each of the mechanisms of initiation, propagation, and termination would facilitate modeling and design of new comonomer systems to achieve specific physical, chemical, and mechanical properties.

Of these three reactions, termination is perhaps the least well understood and, therefore, the most difficult to model. In cross-linking polymerizations, termination is diffusion controlled immediately from the beginning of the reaction due to rapid increases in system viscosity. As the large polymer chains become entangled or cross-linked in the network, center-of-mass diffusion is dramatically suppressed. Polymer radicals can still approach each other through segmental diffusion or by reacting through unreacted double bonds. As conversion increases, movement of the radical via propagation through unreacted double bonds becomes much faster compared to segmental diffusion; consequently, reaction diffusion controlled termination dominates the termination mechanism.

Several investigators have proposed various methods for predicting the termination kinetic constant as a function of conversion,[1−12] with various degrees of success. Typical problems with these efforts are applicability over the whole range of conversion, the number of parameters required to fit the data, and the quality of experimental data. Significant scatter in published experimental data confounds the underlying mechanisms of the reactions. Ironically, many of the models, based on different assumptions, fit the experimental data well, which belies the identification of the true underlying processes.

Previous studies by others have focused on the kinetics of multifunctional meth(acrylates) and linear systems. While these previous studies have provided a great deal of information about termination mechanisms, there is still a need for further elucidation of the process. The study of loosely cross-linked systems provides further insight. Loosely cross-linked systems can be polymerized above their T_g, unlike highly cross-linked systems (which would degrade), facilitating the determination of the effect of system mobility on reaction diffusion controlled termination in cross-linked systems.

This work examined the effect of cross-linking density and polymerization temperature on reaction diffusion controlled termination. The reaction diffusion parameter, R, was measured for loosely cross-linked systems polymerized both above and below the T_g. Additionally, this work examined the effect of cross-linking density at a constant polymerization temperature on the reaction diffusion parameter. Through these studies we can probe the validity of the predictions for the reaction diffusion controlled termination kinetic constant and increase the understanding of the termination mechanism.

Background

The notion of reaction diffusion controlled termination was first proposed by Schulz in 1956[13] (Figure 1). Several investigators have shown experimentally that when reaction diffusion is controlling the termination mechanism, the termination kinetic constant becomes proportional to the propagation frequency as shown below:[8,14−16]

$$k_t = R k_p[\mathrm{M}] \tag{1}$$

where k_t is the termination kinetic constant, R is the reaction diffusion parameter, k_p is the propagation

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* To whom correspondence should be addressed.

[†] Current address: Los Alamos National Laboratory, MS-E544, Los Alamos, NM 87545.

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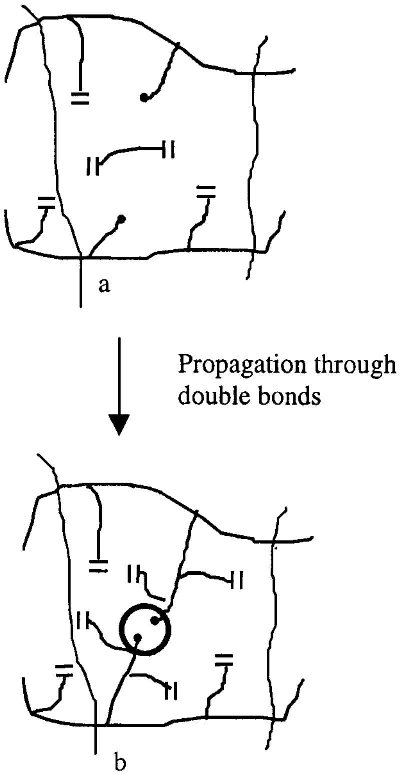

Figure 1. Illustration of reaction diffusion controlled termination. In (a), the radicals are physically separated in space and are unable to terminate. In (b), the radicals have moved closer together by propagating through monomeric or pendent double bonds. The propagation reaction is a means for physical movement of the radical.

kinetic constant, and [M] is the concentration of double bonds. Another possible termination mechanism is unimolecular trapping of radicals which has been demonstrated[17,18] using electron spin resonance spectroscopy (ESR). Anseth and Bowman[17] have shown that bimolecular termination through reaction diffusion is generally the dominant mechanism even in highly cross-linked methacrylates.

A model proposed by Russell et al.[9,19] for linear polymerizations suggests the following equations for predicting the termination kinetic constant when reaction diffusion is the dominant termination mechanism:

$$k_t(\mathrm{res}) = \frac{4\pi}{3} p k_p[\mathrm{M}] a^2 r_a \tag{2}$$

where k_t(res) is the residual termination constant (reaction diffusion controlled termination constant), p is the probability of reaction when two radicals come within the capture distance of each other, a is the root-mean-square end-to-end distance per square root of the number of monomer units, and r_a is the radius of interaction. The parameter p has values between 0 and 1 due to the effects of spin multiplicity and steric hindrance.[19,20] It is thought that p is one at high conversions and 0.25 at low conversions or even 0 in systems that are sterically hindered.[19,20] The equation for k_t(res) was derived from Smoluchowski's equation for the prediction of diffusion controlled bimolecular rate coefficients[10] and Einstein's relation between the diffusion coefficient and the frequency of propagation.[9,21]

To complete the derivation, the radius of interaction must be specified. Russell et al.[9] defined two extremes, the rigid and flexible limits. In the rigid limit, the chain end cannot move on the time scale of propagation, and thus, the radius of interaction is represented by half the Lennard-Jones diameter of the monomer, ($\sigma/2$). In the flexible limit, the chain can sample the entire volume around its last entanglement point. Thus, its radius of interaction is approximated as $a\sqrt{j_c}$[22] where j_c is the distance between entanglements. Consequently, two limiting equations are derived for the reaction diffusion controlled termination constant[9] which can be rearranged to predict minimum and maximum reaction diffusion parameters:

$$R_{\min} = \frac{k_t(\mathrm{res,min})}{k_p[\mathrm{M}]} = \frac{2\pi}{3} p a^2 \sigma \tag{3}$$

$$R_{\max} = \frac{k_t(\mathrm{res,max})}{k_p[\mathrm{M}]} = \frac{4\pi}{3} p a^3 j_c^{1/2} \tag{4}$$

Reaction diffusion parameters have been measured by others for highly cross-linked acrylate and methacrylate systems and were remarkably consistent among systems. For methacrylates R is on the order of 2 L/mol,[14] and for acrylates R is 3−5 L/mol.[23] The equation for $R_{\min}$ (eq 3) can fit these results with reasonable values of the model parameters. The constancy of R for highly cross-linked systems is not too surprising if we examine the ratio of $R_{\max}/R_{\min}$. This ratio is $2aj_c^{1/2}/\sigma$. Since the ratio (a/σ) is order 1 and the parameter j_c approaches 1 as the cross-linking density increases, the ratio $R_{\max}/R_{\min}$ approaches 2 for a highly cross-linked system.

For a loosely cross-linked network, polymerized above the glass transition temperature, R should approach the flexible limit, i.e., $R_{\max}$, because the distance from the last attachment to the network is significantly larger, and the overall mobility of the system is increased by polymerizing above the T_g. As the polymerization temperature is lowered below T_g, the distance back to the last network attachment point (or entanglement) becomes less important, and the mobility of the radical chain end is reduced to the point where it is virtually immobile on the time scale of propagation. In this case, the rigid limit should be applicable, and R should approach $R_{\min}$, just as it would for a highly cross-linked network.

Experimental Section

Materials. The reagents used in these experiments were diethylene glycol diacrylate (DEGDA; Aldrich Chemical Co. Inc., Milwaukee, WI), diethylene glycol dimethacrylate (DEGDMA; Aldrich Chemical Co. Inc, Milwaukee, WI), *sec*-butyl acrylate (sBA; Aldrich Chemical Co. Inc., Milwaukee, WI), 2-hydroxyethyl methacrylate (HEMA; Aldrich Chemical Co. Inc., Milwaukee, WI), poly(ethylene glycol) 400 (PEG400; Polysciences Inc., Warrington, PA), and *n*-octyl methacrylate (OcMA; Polysciences Inc., Warrington, PA). Polymerizations were performed using 1 wt % of the ultraviolet sensitive initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA; Ciba Geigy, Hawthorne, NY). All materials were used as received.

DSC. Differential scanning calorimetry (DSC7; Perkin-Elmer, Norwalk, CT) combined with a monochromatic photo-accessory was used to study the DEGDMA, DEGDMA/HEMA/PEG400, and DEGDMA/OcMA systems. This method was also used extensively to obtain reaction diffusion parameters for highly cross-linked methacrylate systems.[14,23] Small drops of the samples (about 0.5−1 mg) were placed in the center of an aluminum pan or lid (Perkin-Elmer, Norwalk, CT). Samples were polymerized using 365 nm UV light with an intensity between 2 and 4 mW/cm^2. Care was taken to ensure that both the reference and sample pans were exposed to the same light intensity.

The data obtained from DSC experiments is heat evolution versus time. These data can be converted to polymerization rate given the enthalpy of converting a carbon−carbon double bond to a single bond. The heat released is approximately 13.1 kcal/mol for methacrylates.[24−26]

Reaction diffusion parameters are determined from unsteady-state experiments. When irradiation is halted, initiation no longer occurs. The reaction diffusion parameter is determined by plotting the inverse rate of polymerization versus time after initiation is stopped. Assuming bimolecular termination and no significant change in the kinetic constants, then the slope of the resulting line is[27]

$$\text{slope} = \frac{2k_t}{k_p[M]} = 2R \tag{5}$$

If termination were unimolecular, then a plot of polymerization rate versus time would be an exponential function. A final point is that the value of R decreases with increasing conversion until a steady value is reached, after which no further decrease is observed. It is this plateau value that is reported here.

RTIR. Real-time infrared (RTIR) spectroscopy (model 1430, Perkin-Elmer, Norwalk, CT) was used to study the DEGDA/sBA system. The method of RTIR for monitoring polymerization reactions was pioneered by Decker.[28−30] This method has been used extensively to obtain reaction diffusion parameters for highly cross-linked methacrylate systems, and the results are comparable to those obtained using differential scanning calorimetry (DSC).[31] RTIR was chosen over DSC for the acrylate polymerizations because of the volatility of the sample and the rapid rate of polymerization. RTIR can monitor the polymerization much more rapidly than DSC. Additionally, the sample preparation for RTIR minimizes sample loss during polymerization.

Samples were prepared by spin-coating between two sheets of poly(ethylene) (Saran-Wrap) (sample thickness of 15−20 μm). Samples were placed between two sodium chloride salt crystals (Graesby-Specac, Smyrna, GA) in a temperature controller (Boulder Non-Linear Systems, Boulder, CO). Rapid scans (50 ms/data point) of the carbon−carbon double bond peak, typically 811 cm^{-1} for acrylates, were performed. The sample was polymerized using 365 nm UV light (EFOS; Mississauga, Ontario, Canada) with an intensity of 10 mW/cm^2.

Reaction diffusion parameters are also determined from unsteady-state RTIR experiments. The data from RTIR experiments are conversion versus time. One could convert the data to polymerization rate versus time by taking the derivative. However, the noise in the data obscures the polymerization rate, and thus an alternative method of analyzing the data was used. Again, assuming that termination is bimolecular and that the kinetic constants do not change significantly once irradiation is stopped, then the relationship between the change in double-bond concentration and the reaction diffusion parameter is as follows:[31]

$$\Delta[M] = \frac{1}{2R}\ln(2RR_{p0}t + 1) \tag{6}$$

where R_{p0} is the rate of polymerization at the time the monitoring of double bonds begins (i.e., when $t = 0$), $\Delta[M]$ is the change in double-bond concentration, and time t is the duration for which the change in double-bond concentration is monitored after initiation is stopped.

DMA. Dynamic mechanical analysis (DMA7e; Perkin-Elmer, Norwalk, CT) was performed to determine the glass transition temperature for each system. Temperature scans were performed at a frequency of 1 Hz. The glass transition temperatures were determined from the peak of the tan δ versus temperature curve.

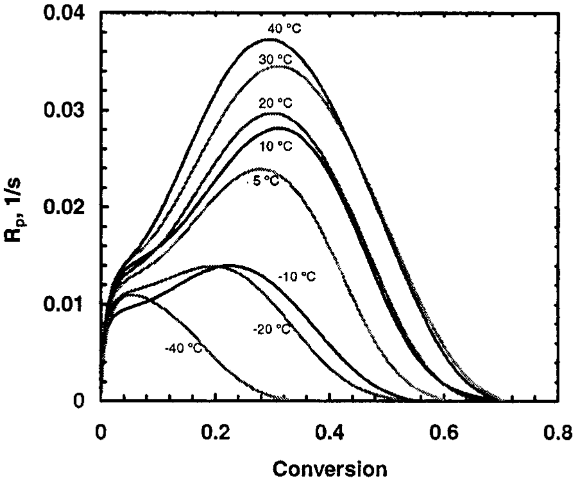

Figure 2. Illustration of the effect of temperature on the rate of polymerization versus fractional conversion for pure DEGDMA with 1 wt % DMPA polymerized with UV light at 2−4 mW/cm^2.

Results and Discussion

Temperature Dependence of *R* for a Highly Cross-Linked Polymer. As a base case, reaction diffusion parameters were determined for pure DEGDMA at temperatures ranging from −40 to 40 °C. DEGDMA forms a highly cross-linked network with a glass transition temperature of 170 °C at a conversion of 80%.[32] Room temperature polymerizations of DEGDMA have been well studied and typically have reaction diffusion parameters between 3 and 5 L/mol.[14] R was not expected to vary in the temperature range of −40 to 40 °C because these temperatures are significantly below the glass transition temperature of the fully cured, highly cross-linked polymer. Thus, there is no significant loss in mobility of the system as the temperature is lowered further.

The rates of polymerization versus conversion data for pure DEGDMA as a function of temperature are shown in Figure 2. These curves exhibit the features that are characteristic of cross-linking polymerizations. If we use the 40 °C curve as an example, we see autoacceleration of the rate at about 5% conversion due to an increase in polymer radical concentration. The polymer radical concentration increases as the frequency of bimolecular termination decreases. An increase in the system viscosity as monomer is converted to polymer causes a decrease in the frequency of bimolecular termination by impairing the ability of the large polymer radicals to diffuse toward each other. As conversion continues to increase, the polymer radicals become more mobile by reacting through double bonds than through diffusion. It is at this point in the reaction that termination is reaction diffusion controlled. This point in the reaction occurs after the peak in the rate of polymerization curve. Propagation may also become diffusion controlled at higher conversions, resulting in autodeceleration of the rate.

Additional characteristics of DEGDMA polymerizations are that as temperature decreases, the maximum rate of polymerization, conversion where the maximum rate occurs, and ultimate conversion are decreased. The maximum rate is reached by 25% conversion for the −10 and −20 °C runs and by about 35% conversion for the

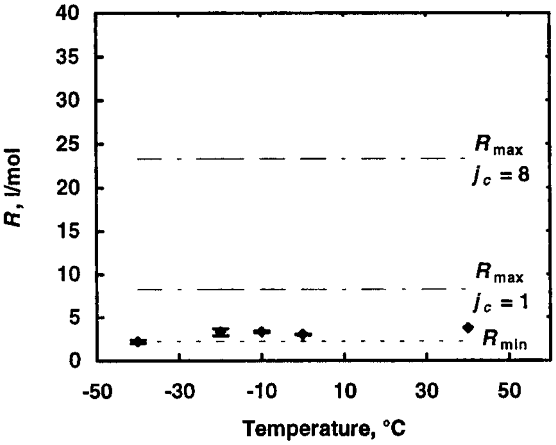

Figure 3. Reaction diffusion parameter versus temperature for DEGDMA with 1 wt % DMPA and 2−4 mW/cm^2 UV light (365 nM). Symbols are averages, and error bars represent the range of values. Parameter values for predicting R_{min} and R_{max} were a = 1.5 nm, σ = 0.79 nm, and p = 1, and j_c was as indicated.

5−40 °C runs. This shift in the conversion at which the maximum rate occurs is due to decreased mobility of the system at lower temperatures; therefore, propagation becomes diffusion-limited at lower conversions. The −40 °C experiment does not exhibit any clear autoacceleration region because termination is reaction diffusion controlled from the beginning of the reaction.

The reaction diffusion parameter for pure DEGDMA behaved as expected (Figure 3). At all temperatures, R reached a plateau between 2 and 5 L/mol. This result indicates that R is independent of temperature for the highly cross-linked network of DEGDMA. Also included in Figure 3 are the predicted R_{max} and R_{min} using eqs 3 and 4. This prediction was generated assuming that the Lennard-Jones parameter, σ, was 0.79 nm[33,34] and p was 1. The parameter a was calculated by fitting R_{min} to the experimental value of R at −40 °C, which resulted in a value for a of 1.5 nm. Reported experimental values of a for linear polymers range from 0.62 nm at 50 °C for poly(butyl methacrylate)[9] to 1.03 nm at 60 °C for *trans*-1,4-polyisoprene.[35] The theoretical minimum limit of parameter a is given by the value obtained for a freely rotating chain, which is about 0.3 nm[22] for a tetrahedrally bonded backbone with a bond length of 0.154 nm. Since a was the parameter used to fit the data, it encompasses all of the uncertainty. Parameter a is larger than expected on the basis of data in the literature.

Two curves are shown in Figure 3 for R_{max}. One curve is based on a value of 8 for j_c, and the other is based on j_c equal to one. A value of 8 was calculated assuming 50% of the pendent double bonds react, and 25% of those reactions form effective entanglements such as cross-links or secondary cycles.[36] No conclusions can be drawn as to the real value of j_c in this case, because the values obtained for R should be close to the minimum limit for this system. It is reasonable to state that the relationship between k_t and k_p[M] for a highly cross-linked methacrylate system is well described by eq 3. A more challenging case is that of loosely cross-linked systems.

Temperature Dependence of *R* for a Loosely Cross-Linked Acrylate. The first loosely cross-linked system studied was 10/90 mol % DEGDA/sBA which had a T_g of −3 °C. An acrylate system was chosen because acrylates in general have lower glass transition temperatures and higher reactivity than methacrylates. Therefore, a loosely cross-linked acrylate system with a room temperature T_g and reasonable rates of polymerization could be identified. It was necessary to find a system with a room temperature T_g to facilitate studies above and below the T_g. These studies were performed using RTIR due to the volatility of the sBA and the rapid rate of acrylate polymerization. As for DEGDMA, there is an increase in conversion as temperature is increased (Figure 4). There is not as dramatic an increase in conversion with increases in temperature as for DEGDMA, because this system is not highly cross-linked and the temperature at which polymerization occurs is not significantly below the T_g. Additionally, as the temperature increases, the rate of polymerization increases, which can be seen from the slope of the conversion versus time curves.

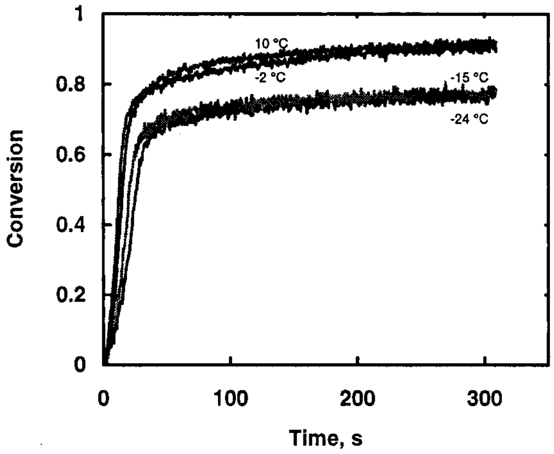

Figure 4. Fractional conversion versus time at various temperatures for 10/90 mol % DEGDA/sBA with 1 wt % DMPA. Data were obtained using RTIR.

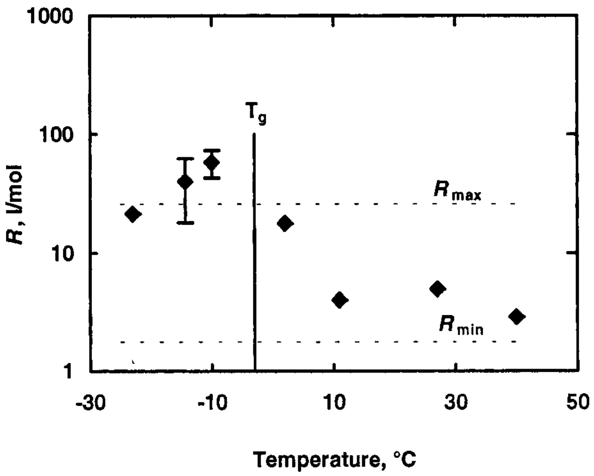

Figure 5. Reaction diffusion parameter versus temperature for 10/90 mol % DEGDA/sBA. Polymerizations were performed using 1 wt % DMPA with UV light intensities of 2−4 mW/cm^2. The dashed lines represent predictions based on eqs 3 and 4. Parameter values were a = 1.5 nm, σ = 0.64 nm (molar average for sBA (0.63 nm) and DEGDA (0.74 nm)), p = 1, and j_c = 10. The T_g of this system was −3 °C.

The value of the reaction diffusion parameter versus temperature for this system is illustrated in Figure 5. Also shown in Figure 5 are R_{max} and R_{min} using eqs 3 and 4. For these calculations, σ was 0.64 nm[33,34] (a molar average for sBA and DEGDA), p was 1, j_c was 10, and a was 1.5 nm. The behavior of the reaction diffusion parameter as a function of temperature is quite interesting. As temperature decreases, an apparent transition from a rigid system to a flexible system takes place. While this may seem counterintuitive, if the reaction diffusion parameter is visualized as a measure of the mobility of the radical between propagation events, then other means of radical movement may become important as temperature decreases.

Another means of radical movement, especially in acrylates, is through chain transfer. As segmental diffusion and propagation frequency decrease with decreasing temperature, the effect of chain transfer may increase. The most likely chain transfer processes are to polymer or monomer. Chain transfer to polymer increases with the concentration of polymer.[37,38] As temperature decreases, transfer to polymer is facilitated by closer packing of the radicals and polymer chains. However, chain transfer to polymer would be expected to increase the degree of cross-linking, which would serve to immobilize the radicals further.

Alternatively, chain transfer to monomer may be a plausible explanation. A major difference between a highly cross-linked network and a loosely cross-linked network is the concentration of free monomer at any given conversion. For example, at 50% conversion, a system of purely divinyl monomer will have only 25% free monomer (assuming equal reactivity). A linear network of monovinyl monomer will have 50% free monomer. A loosely cross-linked network will contain free monomer between these two levels. Thus, chain transfer to monomer could create small, mobile radicals that then terminate with the larger immobile radicals. It is typically unusual for a radical to remain small and unentangled for any length of time. However, if propagation is sufficiently suppressed, then perhaps the persistence of the smaller radicals is long enough to enhance termination relative to propagation.

If chain transfer is a significant mobility mechanism that leads to termination, then the following would hold:

$$k_t \propto k_p[M] + R_{CT} \tag{7}$$

where R_{CT} is proportional to the frequency of chain transfer per radical. Thus, R would become

$$R \propto \frac{k_t}{k_p[M] + R_{CT}} \tag{8}$$

However, the unsteady-state measurements that are performed to measure R would not be able to separate out the kinetics of chain transfer. Thus, the measured value of R would increase because it represents only $k_t/k_p[M]$.

Another interesting aspect of these data is that the reaction diffusion parameter plateaus around 3 L/mol above T_g. Russell et al. found that poly(butyl acrylate) polymerized at 50 °C was described by the rigid limit.[9] A possible explanation is that propagation is so rapid above T_g that the radical chain end is inflexible on the time scale of propagation. In other experiments using only 1 mol % cross-linker, the acrylate system had an R of 3 L/mol above T_g.

Temperature Dependence of R for a Loosely Cross-Linked Methacrylate System. *System Identification.* To determine whether there was any difference in the behavior of acrylates and methacrylates as a function of temperature, a loosely cross-linked methacrylate system (1/99/40 DEGDMA/HEMA/PEG400) was identified that had a glass transition temperature of 20 °C. The addition of PEG400, an unreactive plasticizing agent, was required to reduce the glass transition temperature of the DEGDMA/HEMA system to room temperature.

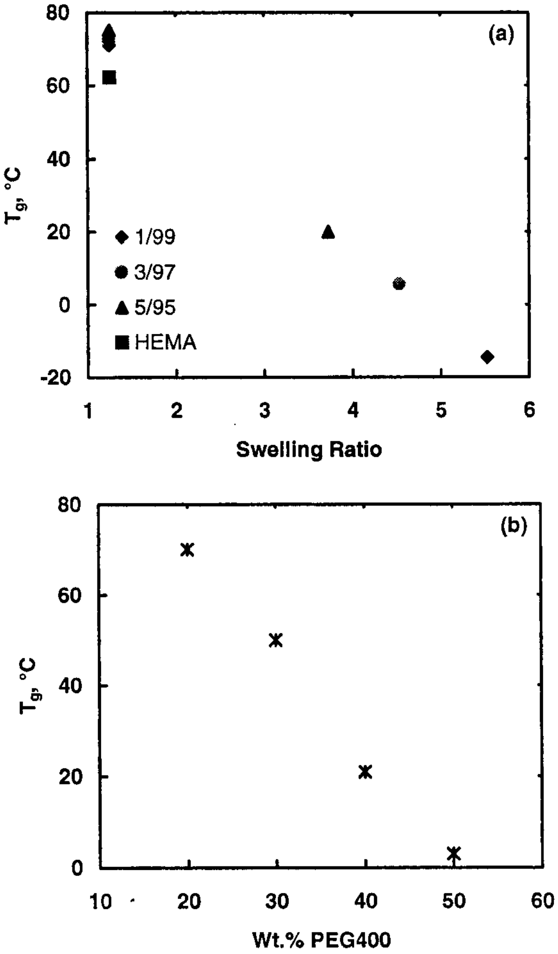

Figure 6. (a) Effect of swelling ratio on the T_g as a function of weight percent cross-linker concentration in DEGDMA/HEMA systems. Samples were polymerized with 20 wt % PEG400 in the monomer solution and then allowed to swell in PEG400. (b) Effect on T_g of increasing the concentration of PEG400 in the monomer solution before polymerization.

The system was identified by using DMA to determine the effect of the concentration of the cross-linker DEGDMA on the T_g of the system. For 1−5 wt % DEGDMA (0.5−2.7 mol %), the T_g ranged from 72 to 75 °C. DMA analysis of swollen samples indicated that there is little difference in the T_g's when the samples are swollen to the same extent (Figure 6a). Thus, a system with 1 part DEGDMA to 99 parts HEMA was chosen as a basis. Subsequently, the effect of the solvent, PEG400, on T_g was determined by polymerizing the 1/99 DEGDMA/HEMA comonomer with 10, 20, 30, 40, and 50 wt % solvent. Figure 6b summarizes the DMA results for the copolymerizations with PEG400. There is a nice linear relationship between the T_g and the weight percent solvent.

In addition to obtaining the desired T_g, it was important to ensure that the addition of solvent did not completely suppress autoacceleration. Figure 7a illustrates how the addition of cross-linker and solvent affect the polymerization kinetics of HEMA. As 1 wt % DEGDMA is added to HEMA, the maximum rate of polymerization increases and occurs at slightly higher

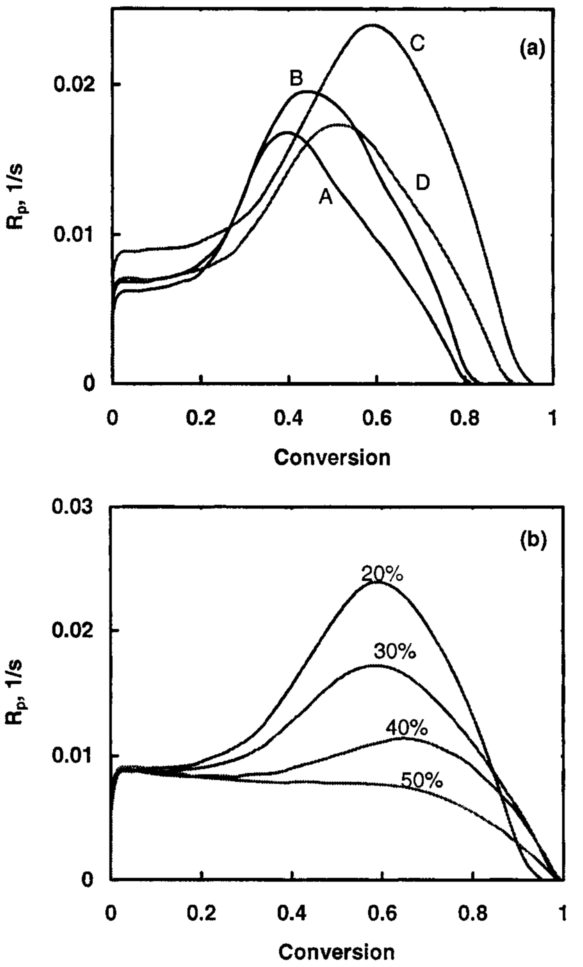

Figure 7. Effect of addition of cross-linking agent and solvent on HEMA rates of polymerization versus fractional conversion (a). Curve A is pure HEMA, curve B is 1/99 wt % DEGDMA/HEMA, curve C is 1/99/20 DEGDMA/HEMA/PEG400, and curve D is 100/20 HEMA/PEG400. (b) Effect of PEG400 concentration on the rates of polymerization of 1/99/X DEGDMA/HEMA/PEG400 at 25 °C versus fractional conversion.

conversions (curves A and B). The overall conversion is essentially the same at 80%. Next, as 20 wt % solvent is added (curve C), the maximum rate increases even further, and conversion is increased to about 95%. If solvent is added to pure HEMA without cross-linker (curve D), the conversion at which the maximum rate occurs is higher, and the final double-bond conversion is increased to 90%.

Figure 7b illustrates the effect of solvent addition to a 1/99 DEGDMA/HEMA system. As solvent content increases above 20 wt %, the maximum rate decreases, and the conversion at which the maximum rate occurs moves further toward 100%. When the solvent reaches 50 wt %, the autoacceleration peak virtually disappears because the polymer radicals are highly mobile and terminate with nearly the same efficiency throughout the entire polymerization. The system that was finally chosen had a T_g of 20 °C and still exhibited autoacceleration during polymerization. The sample was prepared by making a 1/99 wt % DEGDMA/HEMA mixture and then adding PEG400 until it was 40 wt % of the total sample.

Determination of Reaction Diffusion Parameters. Unsteady-state experiments were performed at temperatures ranging from −20 to 40 °C. These temperatures represent the range for which accurate values of the

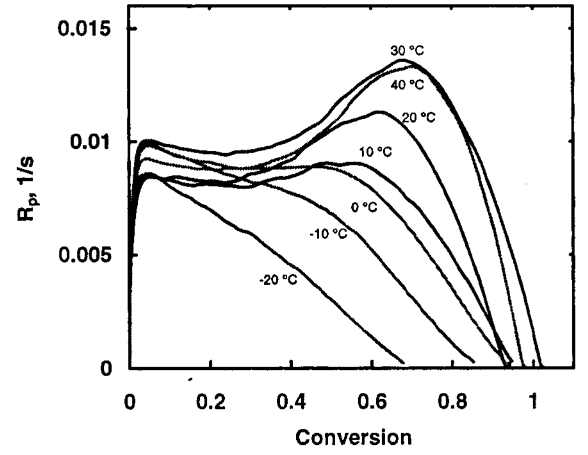

Figure 8. Rates of polymerization versus fractional conversion as a function of temperature for copolymerizations of 1/99/40 DEGDMA/HEMA/PEG400 with 1 wt % DMPA. UV light intensities were between 2 and 4 mW/cm^2.

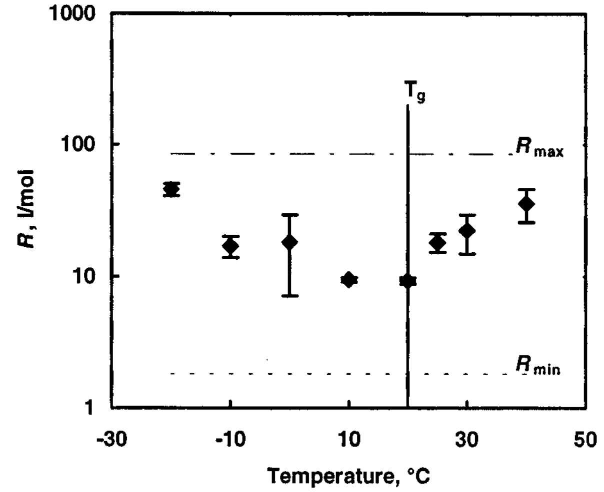

Figure 9. Reaction diffusion parameters versus temperature for 1/99/40 DEGDMA/HEMA/PEG400. The T_g of this system was 20 °C. The symbols are averages, and the bars represent the range of data. R_{min} and R_{max} were predicted using eqs 3 and 4. The values of the parameters were a =1.5 nm, $\sigma = 0.64$ nm, $p = 1$, and $j_c = 100$.

reaction diffusion parameter could be obtained. The rate of polymerization versus conversion for 1/99/40 DEGDMA/HEMA/PEG400 as a function of temperature is shown in Figure 8. As for pure DEGDMA, conversion and maximum rate increase with increasing temperature. The autoacceleration peak disappeared for runs at 0 °C and lower. The maximum conversion also decreases to about 70% for runs performed at −20 °C.

The effect of temperature on the reaction diffusion parameter is shown in Figure 9 along with a prediction of R_{min} and R_{max} using eqs 3 and 4. As for the acrylate system, R increases below T_g, indicating a shift from a rigid to a flexible system. However, in contrast to the acrylate system, an increase in R as the polymerization temperature was increased above the glass transition temperature was observed. Thus, at least for this particular methacrylate system, the flexible limit is approached as temperature is increased above T_g. We theorized previously that below T_g chain transfer to monomer is responsible for the increase in R. Above T_g, the increase in R is probably due to increased mobility of the polymer segments attached to the network. Another way to examine mobility of the polymer seg-

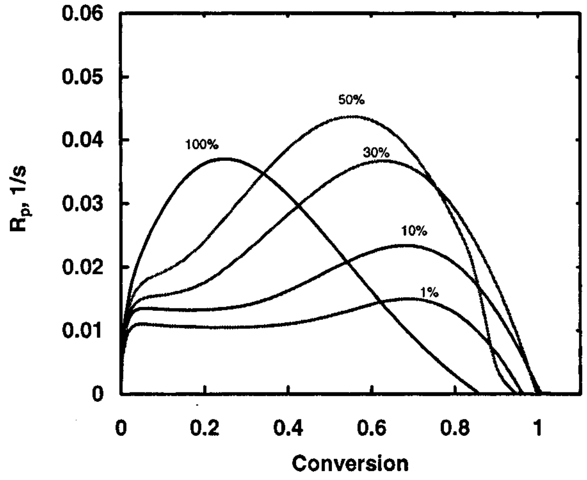

Figure 10. Effect of cross-linker concentration on the rate of polymerization versus fractional conversion for DEGDMA/HEMA/PEG400 with PEG400 concentration constant at 40 wt %.

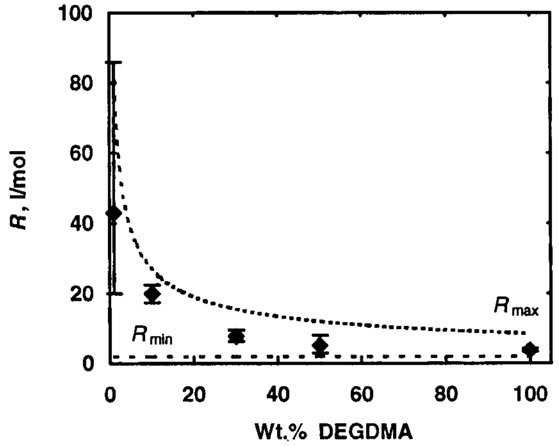

Figure 11. Effect of cross-linker concentration on the reaction diffusion parameter for DEGDMA/HEMA/PEG400 and R_{max} based on eqs 3 and 4. The parameter j_c was inversely proportional to the concentration of DEGDMA on a molar basis. This is a clear example of a transition from R_{min} to R_{max} as a function of the flexibility of the polymer radical on the time scale of propagation.

ments is to change the length by changing the cross-linker concentration.

Figure 10 shows the rates of polymerization versus conversion for DEGDMA/HEMA/PEG400 systems with varying percentages of cross-linker added. The concentration of PEG400 was constant at 40 wt %. The maximum rate of polymerization increases as cross-linker is added until the system becomes sufficiently cross-linked that propagation is diffusion limited, resulting in a decline of the maximum rate. The adverse effect of increasing cross-linking agent on the final conversion is also clearly demonstrated.

These experiments also showed (Figure 11) that as the amount of cross-linking agent is increased, the reaction diffusion parameter decreases and plateaus at a value around 3 for 50 wt % DEGDMA. Further increases in DEGDMA do not significantly affect *R*. The reaction diffusion parameter for DEGDMA polymerized in 40 wt % PEG400 is similar to the value when polymerized with no solvent. No phase separation was observed in any sample. The prediction of R_{max} shown in Figure 11 is based on eq 4 and was generated by decreasing the number of units between cross-links, j_c.

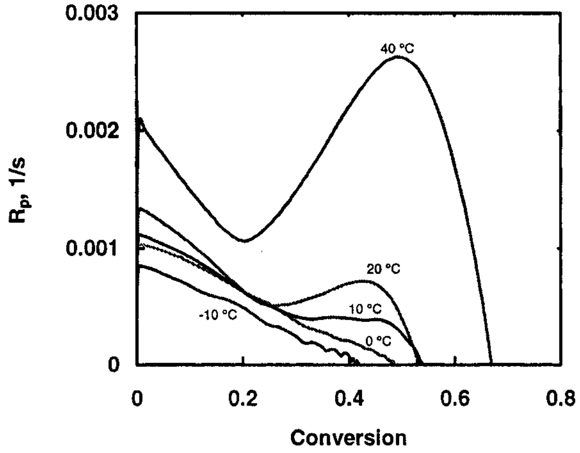

Figure 12. Rates of polymerization versus fractional conversion as a function of temperature for copolymerizations of 10/90 wt % DEGDMA in OcMA with 1 wt % DMPA. The UV light intensity was 2–4 mW/cm^2.

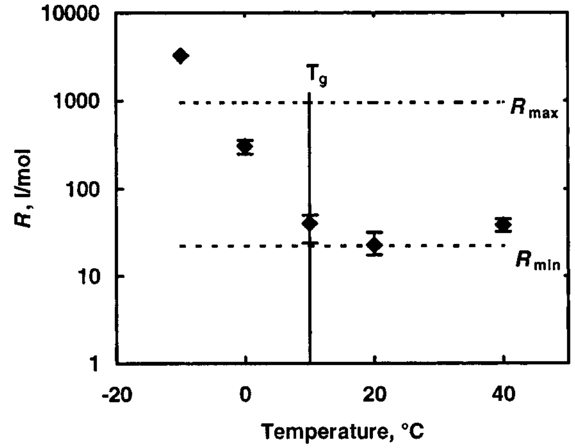

Figure 13. Reaction diffusion parameters for 10/90 wt % (8/92 mol %) DEGDMA/OcMA. Solid symbols are averages, and bars represent the range of values. R_{min} and R_{max} were predicted using eqs 3 and 4. The parameters were $a = 4.8$ nm, $\sigma = 0.77$ nm, $p = 1$, and $j_c = 12$. The T_g of this system was 10 °C.

The parameter j_c in these predictions is inversely proportional to the concentration of DEGDMA on a molar basis. This result is a nice example of a transition from R_{min} to R_{max} as a function of the flexibility of the polymer radical on the time scale of propagation.

Temperature Dependence of *R* for a Solventless Loosely Cross-Linked Methacrylate System. To rule out any anomalous behavior caused by the presence of a solvent, a second methacrylate system was studied. A system of 10 wt % DEGDMA in OcMA (8/92 mol %) has a T_g of 10 °C. The plots of the rates of polymerization versus conversion as a function of temperature are shown in Figure 12. The rates of polymerization are much lower than for the other two systems, and the autoacceleration peak is completely gone at temperatures at or below 0 °C. The measured *R* values from unsteady-state DSC experiments (Figure 13) were much higher for this system than for the other two systems, yet they have the same trends as the DEGDMA/HEMA/PEG400 system. The predicted values of R_{min} and R_{max} are also shown in Figure 13. Using 1.5 nm for the value of *a* resulted in values for R_{min} and R_{max} that were low in comparison to the experimental values. To fit the data at 20 °C using eq 3, a value of 4.8 nm for *a* was required.

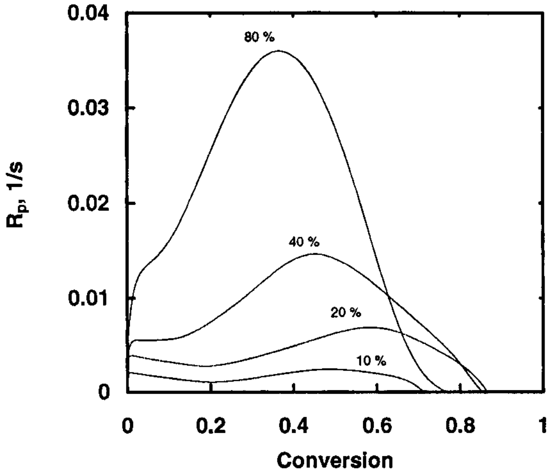

Figure 14. Rates of polymerization versus fractional conversion as a function of weight percent DEGDMA for copolymerizations of DEGDMA and OcMA at 40 °C and 1 wt % DMPA. The UV light intensity was 2−4 mW/cm^2.

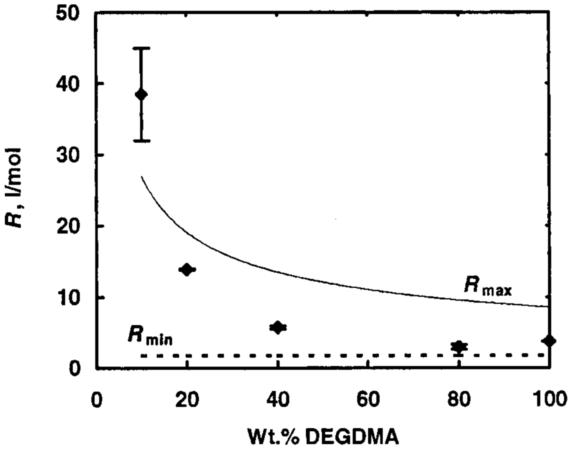

Figure 15. Reaction diffusion parameter versus weight percent DEGDMA for copolymerizations of DEGDMA and OcMA at 40 °C and 1 wt % DMPA. The UV light intensity was 2−4 mW/cm^2. R_{min} and R_{max} were generated using eqs 3 and 4. Parameter j_c was varied inversely with DEGDMA concentration.

This result again makes the point that values for *a* are not readily available or predictable from the literature.

The effect of cross-linker concentration on the reaction diffusion parameter was also studied for this system at 40 °C. Figure 14 shows the rates of polymerization versus conversion as a function of cross-linker concentration. Figure 15 illustrates these results along with predicted values for R_{min} and R_{max}. The parameter j_c was also allowed to vary with DEGDMA concentration as before.

Conclusions

The behavior of the reaction diffusion parameter for loosely cross-linked networks polymerized above and below the glass transition temperature has been characterized for one acrylate system and two methacrylate systems. For both the methacrylates and the acrylate, *R* increases below the glass transition temperature. Additionally, the methacrylates exhibit increases in *R* above the glass transition temperature. However, *R* values for the acrylate system do not increase above T_g. This difference in behavior above T_g between the acrylate system and the methacrylates is a function of their relative flexibility between propagation events. While acrylates form more flexible polymers on a macroscopic level than their methacrylate counterparts, they may be less flexible on the time scale of propagation.

Clearly, there is still more work required to understand the effect of network cross-linking density and polymerization temperature on the reaction diffusion controlled termination mechanism. While the theory of Russell et al. is an excellent approach, experimentally determined values of the model parameters for cross-linked networks are not readily available. As such, the models may be used to fit experimental data effectively but are unable to predict reaction diffusion controlled termination kinetic constants.

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