Kinetic Evidence of Reaction Diffusion during the Polymerization of Multi(meth)acrylate Monomers

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ABSTRACT: The polymerization behavior and reaction kinetics for a series of multifunctional (meth)acrylate monomers were experimentally characterized and modeled with particular attention focused on the importance of the reaction diffusion mechanism in these polymerizations. In general, reaction diffusion was found to be the primary mechanism for termination beginning as low as 5% double-bond conversion. Termination mechanisms in linear systems have been found to become reaction diffusion controlled, but not until much higher conversions, 40–50%. Evidence of reaction diffusion included a significant plateau in the termination kinetic constant and strict proportionality of k_p and k_t at higher conversion (>10%) for all monomers studied. The ratio of k_t to k_p was found to be a single constant for all multiacrylates, independent of the number of acrylate groups. A model that was previously developed by the authors for predicting cross-linking reaction behavior was tested using this experimental data. The kinetic constants for termination and propagation that were experimentally determined provided a method for quantifying the theoretical model parameters associated with reaction diffusion.

Introduction

Photopolymerization of multifunctional monomers provides a facile method for producing highly cross-linked polymer networks that have a wide variety of applications. The high cross-linking density of these systems enhances the mechanical and thermal stability of the polymer while also reducing the tendency for solvent absorption. The rapid curing and excellent physical properties of these networks have led to an increased demand and new applications for these materials. In particular, highly cross-linked networks are used in dental restorative materials, aspherical lens production, second harmonic generating materials, and abrasion-resistant coatings for eyeglass lenses and optical fibers.[1–5] All of these applications require mechanically and thermally stable materials that are easily processed and resistant to dimensional changes.

Unfortunately, the reactions that produce these networks occur in the high-cross-linking regime where anomalous behavior is often observed. This behavior includes autoacceleration and autodeceleration,[5,6] incomplete functional group conversion,[7,8] trapping of radicals,[9–11] microstructural heterogeneity,[12–14] and delayed volume shrinkage with respect to equilibrium.[5,15,16] All of this behavior occurs because of the extremely low mobility of reacting species in the cross-linked network. In our preliminary work studying the photopolymerizations of various multiacrylates and multimethacrylates,[17,18] we characterized these tendencies using differential scanning calorimetry (DSC), dilatometry, and dynamic mechanical testing.

As polymerization reactions of multifunctional monomers approach their maximum rates (at less than 4% functional group conversion), the termination mechanism becomes reaction diffusion (or residual termination) dominated. Reaction diffusion occurs when relatively immobile radicals propagate through a matrix of unreacted functional groups and monomer until encountering a second radical for termination. This behavior is observed experimentally when the termination kinetic constant plateaus and is proportional to the propagation kinetic constant at higher conversion. Previous studies were conducted over a limited conversion range (less than 6% double-bond conversion), while the current work represents a complete study of the entire conversion regime and emphasizes the characterization and modeling of the reaction diffusion behavior.

Evidence of a dominant reaction diffusion mechanism in the polymerization of difunctional monomers (i.e., monomers with only one double bond) has been observed by several researchers.[9,19–25] It was found that the reaction diffusion termination mechanism became important only after the onset of gelation, typically from 40 to 60% conversion. We postulate that in polymerizations of multifunctional monomers this mechanism will predominate over nearly the entire conversion range because translational and segmental diffusion may be severely hindered even at less than 2% conversion of the functional groups. This study emphasizes the significance and fundamental importance of reaction diffusion during the homopolymerization of multifunctional monomers. Evidence of the importance of reaction diffusion, the conversions after which reaction diffusion dominates, and modeling of the reaction diffusion mechanism are presented for a series of multiacrylates and multimethacrylates.

Background

The concept of reaction diffusion or residual termination was first introduced by Schulz[26] and involves an alternative mechanism for termination in free-radical polymerizations. In general, as translational and segmental diffusion of macroradical chains becomes severely limited, the active radicals on the chain ends may still terminate at a significant rate by propagating through unreacted functional groups until encountering a second radical and terminating.

Experimentally, several researchers have found polymerization reactions to proceed at nonnegligible rates beyond the glass transition region.[18,27,28] This evidence further substantiates the concept of reaction diffusion as a mechanism for termination in free-radical polymerizations since traditional termination mechanisms (translational and segmental diffusion) would clearly predict an exceedingly small value for k_t as the glass transition region is approached. The fact that polymerization proceeds at

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perceptible rates in the glassy region increases the likelihood that radicals will terminate via the propagation mechanism of reaction diffusion. Furthermore, during the polymerization of various monomethacrylate-based monomers, several workers observed a plateau in k_t with respect to double-bond conversion as it becomes proportional to the propagation kinetic constant at higher reaction conversions where reaction diffusion is the primary termination mechanism.[9,21-23]

Gardon[29] was one of the first researchers to refine and quantify the idea of reaction diffusion while studying emulsion polymerizations. He developed a lattice model to predict a minimum value of the ratio of the termination to propagation kinetic constant (k_t/k_p) by assuming that the propagating macroradicals have no diffusive mobility and terminate by reaction diffusion alone. While this ratio represents a theoretical lowest limit to k_t, in general, chain ends have significant mobility, and the actual k_t may be orders of magnitude higher than this lower limit.

Recognizing this limitation, Soh and Sundberg[30] introduced their theory of excess chain end mobility. Here, the polymer chains were considered unable to move translationally, but the chain ends were modeled to move in a restricted manner through a sphere with a characteristic radius and centered at an entanglement. Basing their kinetic expression for the reaction diffusion termination on the volume-swept-out model,[31] Soh and Sundberg arrived at the expression

$$k_{tp} = f_t \pi \sigma^2 a N_{Av} k_p [\mathrm{M}]/(1000 j_c^{1/2}) \tag{1}$$

Here, k_{tp} is the reaction diffusion termination kinetic constant, f_t is an efficiency factor, σ is a radius of termination, a is the average root-mean-square end-to-end distance per square root of the number of monomer units in the chain, N_{Av} is Avogadro's number, k_p is the propagation kinetic constant, [M] is the molar concentration of monomer, and j_c is the entanglement spacing.

While Soh and Sundberg were relatively successful in using their model to predict the polymerization rates and molecular weights of a series of bulk monovinyl polymerizations,[19] certain assumptions inherent in the development of their model should be considered. First, σ is calculated by assuming that the chain end mobility is sufficient to completely sweep out the volume defined by the termination radius between each propagation step and that macroradical diffusion into the sphere is negligible. These assumptions necessitate the introduction of the efficiency factor, f_t, which must be empirically estimated. Also, in the scheme of multifunctional monomer reactions, the high cross-linking density makes the application of this model limited for these systems.

Stickler[20] developed another model for the reaction diffusion termination kinetic constant while characterizing the free-radical polymerization kinetics of methyl methacrylate. Considering the termination mechanism to be completely diffusion controlled and utilizing Smoluchowski's equation,

$$k_t = (4\pi N_{Av} \sigma D)/1000 \tag{2}$$

where D is the reaction diffusion coefficient, D_R, when reaction diffusion dominates the termination mechanism.

$$D_R = (n_s l_0^2 k_p [\mathrm{M}])/6 \tag{3}$$

Here, n_s is the number of monomeric units in an average segment and l_0 is the average segment length. N_{Av}, σ, k_p, and k_t remain as previously defined. While this model predicted the reaction behavior during the bulk polymerization of methyl methacrylate, it too is limited by the estimation of the parameters σ, n_s, and l_0. These parameters become much more difficult to characterize or are without definition in a complex, cross-linked network.

Later, Russell *et al.*[32] reviewed existing theories of reaction diffusion and expanded on Stickler's work with the Smoluchowski expression. By assuming either rigid chains (i.e., on the time scale of propagation and termination) or totally flexible chains, the upper and lower limits on the reaction diffusion termination kinetic constant were determined. The model was compared to experimental data of Ballard *et al.*[33] during the seeded emulsion polymerization of methyl methacrylate. One should note that the previously developed models were used to describe linear polymerization behavior, and no comparisons were drawn to cross-linked systems.

The complexity of the polymerization kinetics of cross-linked systems renders parameters such as entanglement distances and diffusion coefficients extremely difficult to estimate and, in essence, makes them empirical parameters. In an alternative approach, Marten and Hamielec[34] and Bowman and Peppas[15] have developed models based on free volume theory to model the polymerization kinetics of linear and cross-linked systems, respectively. These models are semiempirical in approach and lump all unknown parameters into a single constant. Anseth and Bowman[35] later modified these models to make them more appropriate for predicting the reaction behavior during the homopolymerizations of multifunctional monomers. The termination mechanism was modeled as the resistance to mass transfer in parallel with the reaction diffusion resistance which were then in series with the chemical reaction resistance.

Buback *et al.*[36,37] proposed a similar model that incorporates the mass transfer resistance and chemical reaction resistance in series which is then in parallel with the reaction diffusion resistance. Anseth and Bowman[35] claim that reaction diffusion occurs via propagation of trapped radicals through unreacted functional groups until encountering a second radical for termination (a chemical reaction resistance), and, therefore, they model the reaction diffusion resistance in series with the chemical reaction resistance. The resulting expression for k_t was

$$k_t = k_{t0}\left[1 + \frac{1}{R\left(\frac{k_p}{k_{p0}}\right) + \exp[-A(1/\vartheta_f - 1/\vartheta_{f,ct})]}\right]^{-1} \tag{4}$$

where A is an adjustable parameter that controls the rate of autoacceleration, v_f is the free volume of the system, $v_{f,ct}$ is the critical free volume where termination becomes diffusion controlled, k_{p0} is the propagation kinetic constant at infinite free volume, and R is a proportionality constant that relates the mass transfer coefficient for reaction diffusion to the kinetic rate. Determination of the model parameters and the parameter values are discussed further elsewhere.[15,35] At high conversions, translational and segmental mobilities are negligible, and reaction diffusion is the primary mechanism for termination. Equation 4 then reduces to a proportionality between k_t and k_p where the proportionality constant is Rk_{t0}/k_{p0}. This work compares this model's predictions to experimental measurements of the polymerization kinetic constants of multifunctional monomers and attempts to better characterize the reaction diffusion parameter, R.

Experimental Section

Materials and Procedure. This work focused on studying multifunctional monomers including the following series of

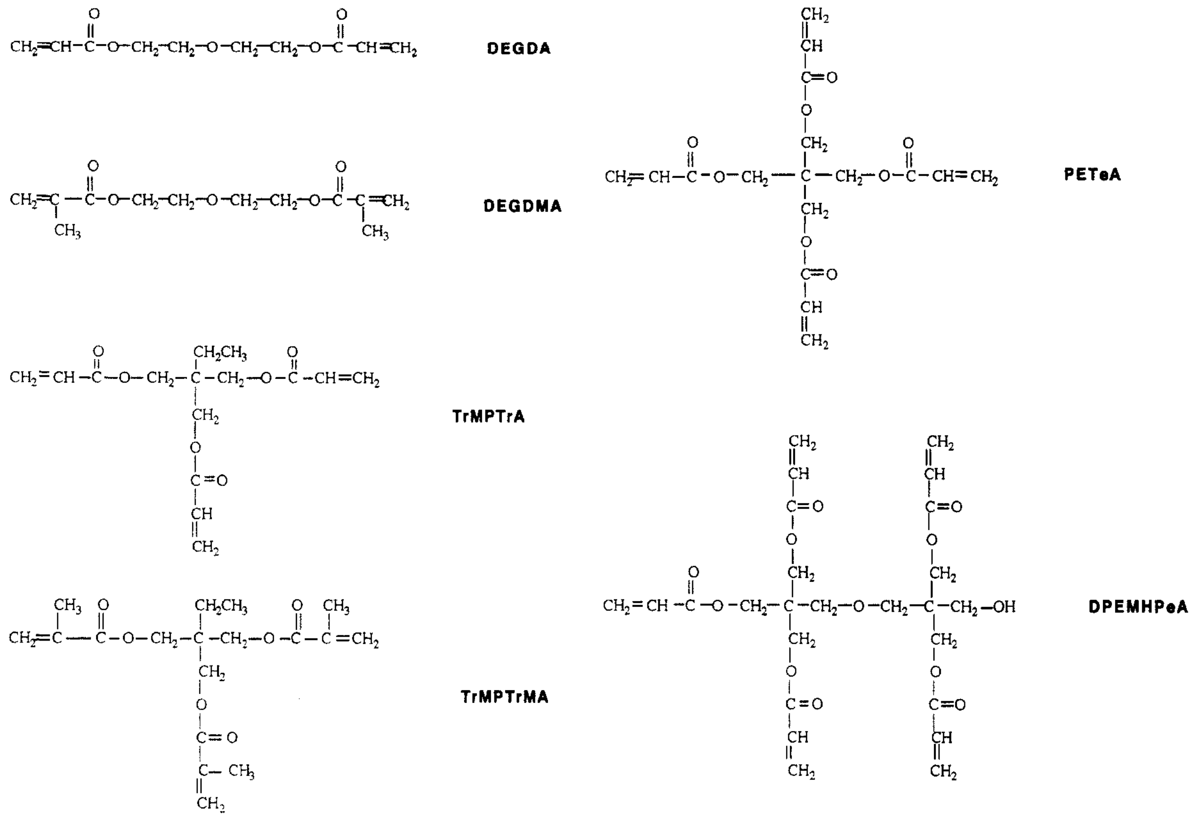

Figure 1. Monomer structures.

acrylate and methacrylate monomers: diethylene glycol dimethacrylate (DEGDMA, Polysciences Inc., Warrington, PA), trimethylolpropane trimethacrylate (TrMPTrMA, Polysciences Inc.), diethylene glycol diacrylate (DEGDA, Polysciences Inc.), trimethylolpropane triacrylate (TrMPTrA, Polysciences Inc.), pentaerythritol tetraacrylate (PETeA, Polysciences Inc.), and dipentaerythritol pentaacrylate (DPEMHPeA, Polysciences Inc.). All monomers were used as received, and Figure 1 illustrates the structure of each monomer molecule. All of the photopolymerizations were initiated with the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorn, NY).

Reaction rates were monitored with a differential scanning calorimeter adapted with a photocalorimetric accessory capable of producing either monochromatic or full-beam ultraviolet light (Perkin-Elmer, DSC-DPA 7, Norwalk, CT). The light intensity was controlled by neutral density filters (Melles Griot, Irvine, CA), and the DSC was cooled with a refrigerated recirculating chiller to enable isothermal reaction studies near room temperature (NESLAB, CFT-25, Newington, NH). To characterize the reaction kinetics better, monochromatic 365-nm ultraviolet light was selected for all of the photopolymerizations.

Samples were prepared by dissolving 0.1 wt % of DMPA in the appropriate monomer. Typically, 3–5 mg of sample, weighed to the nearest 0.1 mg, was placed in uncovered aluminum DSC pans and cured at various reaction temperatures and light intensities. Low sample weights and initiator concentrations were chosen to ensure the applicability of the thin-film approximation for uniform light intensity across the sample. In addition, the DSC cell was continuously flushed with nitrogen, since oxygen is a well-known inhibitor of these reactions. Nitrogen flushing occurred for 10 min prior to exposure of the sample to UV light.

The minimum time for nitrogen flushing was determined by monitoring the reaction rate profiles of samples that were flushed with nitrogen for 1, 3, 5, 10, 15, and 30 min prior to polymerization. Samples that were polymerized in the DSC cell with less than a 10-min nitrogen purge had lower maximum reaction rates and a delay in polymerization from the time the shutter was opened. No noticeable changes in the rate profiles were observed for the 10-, 15-, and 30-min nitrogen purging times. Thus, 10 min was chosen as the optimum time to completely purge the DSC cell before polymerization.

Analysis. The DSC monitors the heat flux as a function of reaction time, and this heat flux is related to the rate of polymerization. Using the heat of reaction per double bond, the conversion as a function of time can be ascertained. For this study, the heats of reaction used were 13.1 kcal/mol for the methacrylate double bond and 20.6 kcal/mol for the acrylate double bond.[38–40]

To determine the individual kinetic constants for propagation and termination, a series of experiments was performed. First, the rate of polymerization was monitored as a function of reaction time to determine the lumped kinetic constant, $k_p/k_t^{1/2}$.

$$\frac{k_p}{k_t^{1/2}} = \frac{R_p}{[M](\phi I_0 \epsilon [A])^{1/2}} \tag{5}$$

Here, R_p is the rate of polymerization, [M] is the molar concentration of monomer, ϕ is the initiator efficiency, I_0 is the incident light intensity in light quanta per area-second, ϵ is the extinction coefficient of the initiator, and [A] is the initiator concentration. Then by stopping the initiation mechanism at various stages in the reaction (i.e., closing the shutter which exposes the sample to the UV light) and following these reaction rates in the dark, the termination and propagation kinetic constants were uncoupled.[13]

$$k_t^{1/2} = \frac{k_p/k_t^{1/2}}{2(t_1 - t_0)}\left[\frac{[M]_{t=t_1}}{R_p|_{t=t_1}} - \frac{[M]_{t=t_0}}{R_p|_{t=t_0}}\right] \tag{6}$$

Here, t_0 is the beginning of the dark period and t_1 is some time later in the dark reaction. Figure 2 shows a series of such experiments to determine the propagation and termination kinetic constants. At various time intervals, the shutter was closed, and the observed decrease in the rate of polymerization was monitored. Figure 2 shows eight dark reactions from which we were able to determine the kinetic constants at eight different reaction times and double-bond conversions. These kinetic constants will be used to provide information about the importance of reaction diffusion.

Results and Discussion

Parts a and b of Figure 3 contain the experimentally determined and simulated values for the propagation and

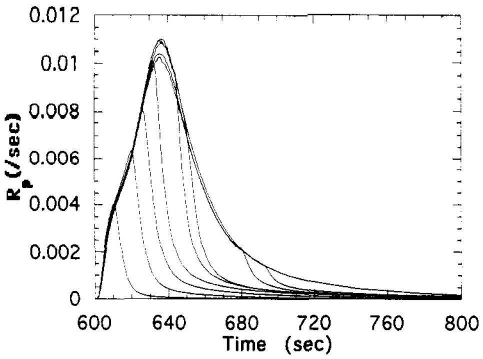

Figure 2. Rate of polymerization as a function of time for eight different dark reactions during the photopolymerization of DEGDMA with 0.1 wt % DMPA at 30 °C and 4.7 mW/cm^2 of 365-cm ultraviolet light.

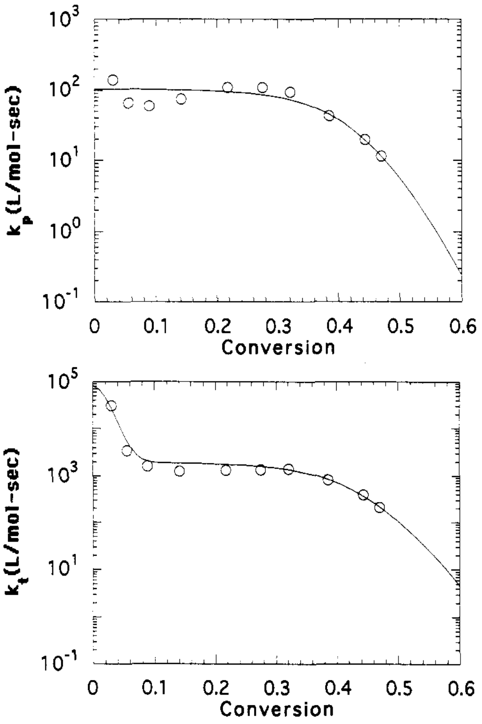

Figure 3. (a) Experimental and simulated values of the propagation kinetic constant versus double-bond conversion of DEGDMA with 0.1 wt % DMPA at 30 °C and 4.7 mW/cm^2 of 365-nm ultraviolet light: (○) experimental; (—) simulated. (b) Experimental and simulated values of the termination kinetic constant versus double-bond conversion of DEGDMA with 0.1 wt % DMPA at 30 °C and 4.7 mW/cm^2 of 365-nm ultraviolet light; (○) experimental; (—) simulated.

termination kinetic constants of diethylene glycol dimethacrylate, respectively. The model of Anseth and Bowman[35] was used to simulate the polymerizations. The polymerization was conducted at 30 °C with an incident light intensity of 4.7 mW/cm^2. The typical shape of k_p as a function of conversion was observed as the propagation kinetic constant remained fairly constant (i.e., chemically controlled) until a higher conversion was reached where diffusion of the monomer was significantly decreased. The curve of k_t versus conversion showed an immediate decrease as the diffusion of the macroradical chains became limited. This decrease in the termination rate while propagation remains unhindered leads to the autoaccelerative behavior of these systems (as seen in Figure 2). As the system approached the gel point and the maximum in its polymerization rate, a transition in the termination mechanism was seen as k_t plateaued. Termination was no longer predominantly controlled by the segmental diffusion of the radicals but rather by reaction diffusion, and k_t was proportional to k_p.

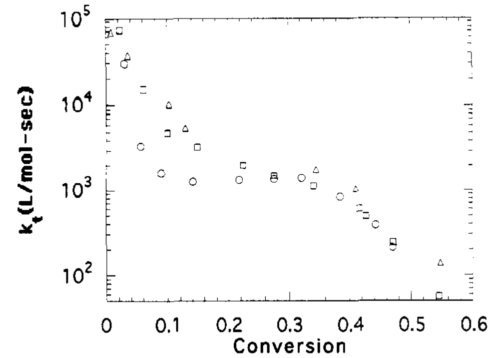

Figure 4. Termination kinetic constants for DEGDMA as a function of double-bond conversion at three different reaction temperatures: (○) 30 °C; (□) 40 °C; (△) 60 °C.

Figure 3b clearly shows the postulated early dominance and importance of reaction diffusion in reactions that produce cross-linked polymers as compared to linear polymerizations. During the polymerization of methyl methacrylate, the plateau in k_t is observed only near the end of the reaction after 40–50% conversion, whereas the cross-linking reactions have a much earlier onset of gelation, and the plateau in k_t is seen as early as 5% conversion.

To better characterize the regions of reaction versus diffusion control, the kinetic constants for DEGDMA were determined at three different temperatures: 30, 40, and 60 °C. Assuming an Arrhenius form for the diffusion coefficients and the kinetic constants, activation energies for chemical reaction are generally higher than activation energies for diffusion. Therefore, in the termination kinetic constant curve, we expected that regions of mass transfer control (i.e., before the plateau where diffusion of the polymer controls and after the plateau where diffusion of the monomer controls) would be least sensitive to temperature increases. The plateau, which represents a region where the chemical reaction barrier to propagation controls the termination rate, should be most sensitive to temperature increases.

Figure 4 contains k_t for DEGDMA as a function of conversion at the three different reaction temperatures. Although somewhat ambiguous from the scatter in the data, a definite trend in a higher value of k_t at the plateau for higher reaction temperatures is seen. In addition, a delay in the plateau until higher conversions for the elevated temperatures is observed. At higher conversions, where diffusion of the monomer was dominating, k_t seemed relatively unaffected by the temperature increase, as was true at very low conversions where segmental diffusion of the polymer dominated. The change in the plateau behavior as a function of temperature can be explained by the enhanced mobility of the segmental diffusion controlled regime at the beginning of the reaction. At higher temperatures, mobility and free volume are increased so reaction diffusion dominance over the segmental diffusion termination mechanism is delayed. Also, the enhanced mobility and increased propagation constant decrease the initial drop in k_t, so that k_t plateaus at a higher value.

From our model[35] when reaction diffusion is the predominant termination mechanism, eq 4 reduces to

$$\frac{k_t}{k_p} = R\frac{k_{t0}}{k_{p0}} \qquad (7)$$

To better characterize the model parameter R, the ratio k_t/k_p for DEGDMA was plotted as a function of conversion

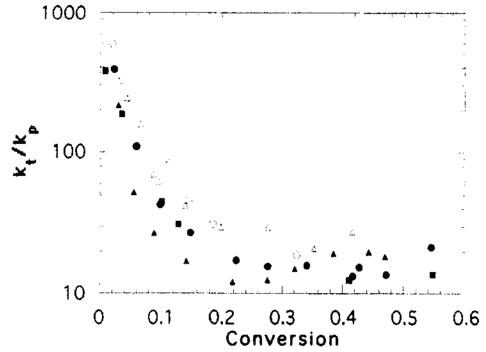

Figure 5. Ratio k_t/k_p for DEGDMA as a function of double-bond conversion for various reaction temperatures and light intensities. I_0 = 0.6 mW/cm^2: (△) 30 °C; (○) 40 °C. I_0 = 4.7 mW/cm^2: (▲) 30 °C; (●) 40 °C; (■) 60 °C.

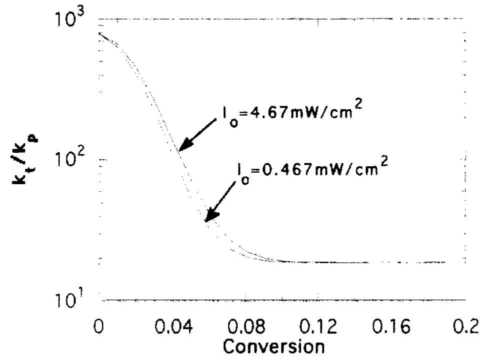

Figure 6. Model predictions of the ratio k_t/k_p as a function of double-bond conversion at two different light intensities.

for various reaction temperatures (30, 40 and 60 °C) and light intensities (4.7 and 0.6 mW/cm^2) in Figure 5. When the termination mechanism became completely reaction diffusion controlled (after ca. 10% conversion), this ratio reduced to a constant which was related to R by the right-hand side of eq 7. The fact that this ratio reduced to a single constant value adds validity to the postulated modeling scheme for reaction diffusion. In other words, the reaction diffusion mechanism implies the proportionality of termination and propagation seen in the kinetic data.

The final value of R appeared to be rather insensitive to the reaction temperature and light intensity as all of the ratios seemed to level off between 15 and 20. Yet the rate and conversion at which the ratio approached this final value was dependent on the curing conditions as expected. Faster rates of polymerization tend to create excess free volume in these systems,[5,15,16] and, therefore, k_t should decrease more slowly. Since k_p remains relatively constant at lower conversions, a slower decrease in the ratio k_t/k_p for higher polymerization rates would be expected. This behavior was predicted by our model in Figure 6 for polymerizations occurring at two different light intensities.

Unfortunately, the data in Figure 5 seem to follow the opposite trend where higher rates of polymerization have lower ratios of k_t to k_p and decrease to the final value of R at a faster rate. One explanation for this anomaly might be the difference in microstructure of the polymer formed at faster rates of polymerization. Faster rates of polymerization create an increase in the number of microgel regions and affect the polymer network heterogeneity.[12-14] The localized concentration of radicals in the microgels might enhance the termination rate in these regions. Also, the assumption of pseudo steady state might introduced more error in the faster polymerization rates at lower conversions.

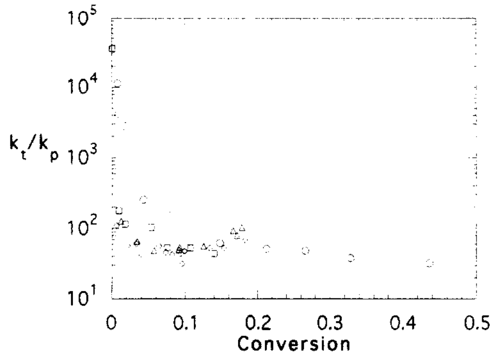

Figure 7. Ratio k_t/k_p for four different acrylates versus double-bond conversion: (○) DEGDA; (□) TrMPTrA; (◇) PETeA; (△) DPEMHPeA.

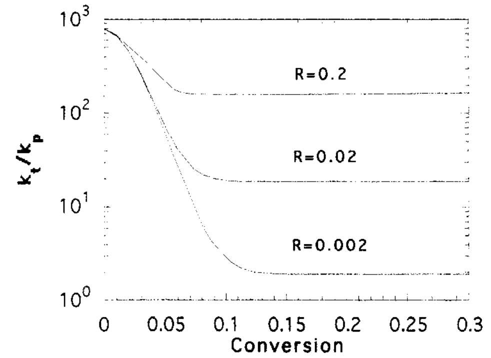

Figure 8. Model predictions of the ratio k_t/k_p as a function of bouble-bond conversion for different values of the reaction diffusion parameter R.

To further characterize the reaction diffusion parameter R, the ratio k_t/k_p was determined as a function of conversion for a series of acrylates: DEGDA, TrMPTrA, PETeA, and DPEMHPeA. All polymerizations were conducted at 30 °C with an incident light intensity of 4.7 mW/cm^2. The results are shown in Figure 7. In general, as the functionality of the monomer was increased, the average cross-linking density of the system was increased. This increased cross-linking led to an earlier dominance of reaction diffusion in these systems. In particular, the penta- and tetraacrylates show reaction diffusion dominating at less than 4% double-bond conversion. Clearly, to understand and model the reaction behavior of multifunctional monomers, reaction diffusion must be considered as it is the dominating termination mechanism for a majority of the polymerization time.

In addition to the trend of reaction diffusion dominance at lower conversions with increasing functionality, the ratios for k_t/k_p appear to level off at nearly the same value of 30–40 for all of the acrylates studied. These data might suggest that a universal value of R may exist for a particular type of monomer functionality. If such a value can be established, determining the high-conversion kinetic constant would appear to become quiet trivial compared to existing techniques. At high conversions where reaction diffusion is the predominant termination mechanism, the relationship between k_p and k_t would be established by the parameter R. By performing the proposed analysis in eq 3 on a polymerizing sample, the ratio $k_p/k_t^{1/2}$ is established as a function of conversion. These two relationships would allow individual calculation of k_p and k_t at the high conversions where reaction diffusion dominates.

Finally, Figure 8 shows the predicted behavior of the ratio k_t/k_p as a function of conversion for varying values of the reaction diffusion parameter R. In general, as R is increased, the relative importance of reaction diffusion is increased. For higher values of R, the trends observed in k_t/k_p were a higher offset and an earlier conversion for complete reaction diffusion dominance. From Figures 5 and 7, the value of R for a methacrylate or acrylate was estimated ($R = 0.02$ for DEGDMA and $R = 0.024$ DEGDA). To clarify, the values for k_{t0} and k_{p0} are predicted values determined at infinite free volume and not at zero conversion.[35]

Conclusions

This work has focused on the importance of the reaction diffusion mechanism for termination during the polymerizations of multifunctional monomers. It was found for both multimethacrylates and multiacrylates that reaction diffusion became the dominant termination mechanism early in the reaction (as early as 5% conversion). This behavior was different from that previously observed for linear polymerizations in which reaction diffusion controlled termination only after 40–50% conversion. Also, the proportionality of k_p and k_t was explored, and it was found that above 15% conversion these kinetic constants were proportional because of the dominance of reaction diffusion termination. Finally, it appears that the proportionality constant for termination and propagation kinetic constants depends only on the type of functional group. This hypothesis was supported by the data which showed that the proportionality constant was nearly identical for a diacrylate, triacrylate, tetraacrylate, and pentaacrylate.

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