

Communications to the Editor

Real-Time Infrared Characterization of Reaction Diffusion during Multifunctional Monomer Polymerizations

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Introduction. The properties of highly cross-linked polymers (high strength, superb moisture resistance, and rapid curing) have made them desirable for a wide range of applications including clear coatings for integrated circuits and optical fibers, aspherical lenses, and dental restorative materials.¹⁻³ Unfortunately, the polymerization kinetics, which dramatically affect the polymer properties, have not been well characterized. This characterization has been rather difficult for the homopolymerization of multifunctional monomers because anomalous behavior is often in the high cross-linking regime.^{2,4} However, it was recently discovered that reaction diffusion dominated the termination kinetics from low double bond conversions.^{5,6}

Reaction diffusion involves radicals moving by propagating through unreacted double bonds. Figure 1 presents a schematic of the reaction diffusion process. Previously, it had been hypothesized that termination was segmental diffusion controlled throughout the reaction; however, recent data indicate that segmental diffusion controls termination for as little as 5–20% conversion depending on the nature of the monomer. When reaction diffusion dominates the termination reaction, the termination kinetic constant is found to be proportional to the product of the propagation kinetic constant and the double bond concentration.⁷⁻¹² An illustration of the importance of reaction diffusion during the polymerization of diethylene glycol dimethacrylate (DEGDMA) is presented in Figure 2.

Figure 2 plots the ratio $k_t/k_p[M]$ (or the reaction diffusion parameter) and k_t (the termination kinetic constant) as a function of double bond conversion for DEGDMA. Interestingly, the reaction diffusion parameter becomes constant and then does not vary significantly after approximately 10–20% conversion. The influence of reaction diffusion is also observed in the termination kinetic constant as k_t begins to plateau and become proportional to $k_p[M]$ near 20% conversion. The mechanism of segmental diffusion of the macroradicals controls termination for only the first 10–20% conversion. Unfortunately, the differential scanning calorimetry technique that was used to measure these kinetic constants requires the steady-state assumption for

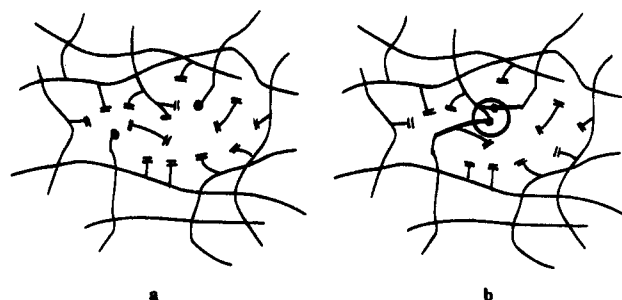


Figure 1. Illustration of the reaction diffusion process in a cross-linked polymer. In part a the radicals are well separated and unable to terminate, while in part b the radicals have moved by propagating through several double bonds to reach each other, enabling termination. Thus, the radical mobility or diffusion via the propagation reaction has facilitated termination of the radicals.

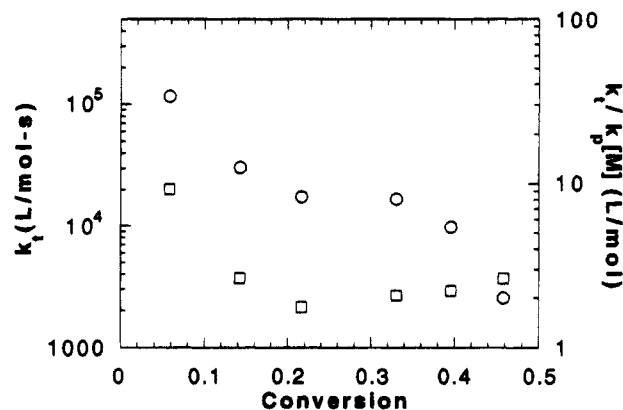


Figure 2. Kinetic constant for termination, k_t (○), and the reaction diffusion parameter, $k_t/k_p[M]$ (□), as a function of double bond conversion for DEGDMA (modified from ref 13). Photopolymerizations were initiated with 0.8 mW/cm² of UV light and 0.1 wt % Irgacure 651.

radicals, assumes the initiator efficiency is constant, and can only be performed on polymerizations which occur slowly.^{5,6} Thus, the information, though extremely valuable, is limited in its scope. Other, similar techniques for characterizing reaction diffusion constants in linear systems have corresponding problems.

In this paper, a real-time infrared (RTIR) technique was used to extend our analysis of reaction diffusion by eliminating all of the previous assumptions and obtaining the reaction diffusion parameter precisely under a much wider range of conditions. This characterization was possible by coupling the fast, precise RTIR developed by Decker *et al.*¹⁴⁻¹⁶ with the procedure and analysis presented below.

Experimental Section and Analysis. To determine the reaction diffusion parameter, ultraviolet (UV) light initiated polymerizations were performed. The reaction diffusion constant was measured as a function of conversion by stopping the initiation at various conversions (by closing the shutter which exposed the sample to the UV light) and monitoring the dark reaction. Thin films of monomer were prepared with

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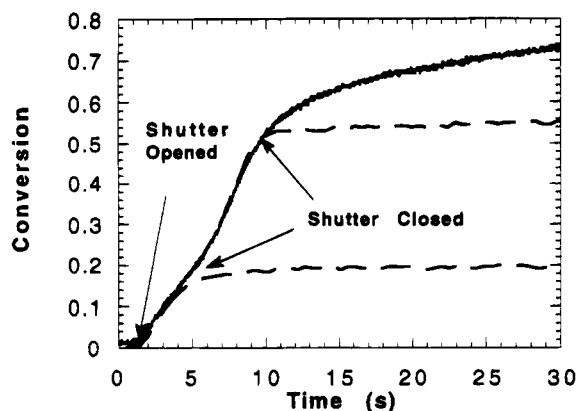


Figure 3. Double bond conversion versus polymerization time for DEGDMA photopolymerized with 110 mW/cm² of UV light and 1.0 wt % Irgacure 651. Full cure (—) and shutter closed after 3.9 and 9.4 s (---).

uniform thickness of approximately 24 μm between polypropylene sheets. The films were subsequently photopolymerized, while changes in the methacrylate double bond absorbance peak at 1647 cm^{-1} were monitored. Thin films were studied for several reasons. First, the attenuation of light in the sample was negligible at the polymerizing wavelengths, so the light intensity was uniform throughout the sample. Second, the initial high concentration of double bonds in the multifunctional monomer required that the films were thin so the infrared absorbance of the double bonds remained in a regime that was quantifiable. Finally, the polymerizations are highly exothermic which can lead to temperature rises during the polymerization which further complicates the kinetic analysis. To reduce the magnitude of the temperature rise during polymerization, the polypropylene sheets were mounted on a KBr salt window which acted as a heat sink during the polymerization. Polymerizations were conducted at room temperature, and the system was kept nearly isothermal (conservative estimates predict less than a 5 $^{\circ}\text{C}$ rise in temperature during polymerization).

In Figure 3, the double bond conversion as a function of polymerization time is shown for DEGDMA photopolymerized with a light intensity of 110 mW/cm² and 1 wt % Irgacure 651. Irgacure 651 (Ciba Geigy, Hawthorn, NY) is the photoinitiator 2,2-dimethoxy-2-phenylacetophenone. The solid curve shows the polymerization behavior during a full cure of DEGDMA. Several features of the polymerization are apparent from the general shape of the curve and include autoacceleration, autodeceleration, and a limiting functional group conversion ($\sim 74\%$). The dashed curves show the same polymerization, but the shutter which exposes the sample to the UV light was closed after 3.9 and 9.4 s. Closing the shutter stops initiation, and the polymerization is monitored in the "dark". In the absence of further radical initiation, a rapid decline in the rate of polymerization is observed along with much smaller and slower changes in the double bond conversion. By monitoring these changes that are occurring in the dark, insight is gained into the reaction diffusion mechanism of radical termination.

In the absence of initiation during polymerization (i.e., $R_i = 0$), the analysis of the polymerization kinetics simplifies to species balances on the radicals and double bonds:

$$\frac{d[\text{M}\cdot]}{dt} = -2k_t[\text{M}\cdot]^2 \quad (1)$$

$$\frac{d[\text{M}]}{dt} = -k_p[\text{M}][\text{M}\cdot] \quad (2)$$

where $[\text{M}\cdot]$ is the radical concentration, $[\text{M}]$ is the double bond concentration, k_p is the propagation kinetic constant, and k_t is the termination kinetic constant. If it is assumed that only small changes in the system occur in the absence of initiation (i.e., that the dark polymerization is followed for only a short period of time in which a small, but measurable, change in conversion occurs), then the kinetic constants and double bond concentration will remain approximately constant. The radical species balance may then be integrated and simplified to find that the radical concentration as a function of time is

$$[\text{M}\cdot] = \frac{[\text{M}\cdot]_0}{2k_t[\text{M}\cdot]_0 t + 1} \quad (3)$$

in which $[\text{M}\cdot]_0$ is the radical concentration at time, t , zero. Time zero may correspond to any point after initiation stops, and it represents the point at which the change in double bond concentration begins to be monitored. The radical concentration is then substituted into the double bond species balance (eq 2), which is integrated to obtain the change in monomer concentration (where $\Delta[\text{M}] \ll [\text{M}]_0$):

$$\Delta[\text{M}] = [\text{M}] - [\text{M}]_0 = \frac{k_p[\text{M}]}{2k_t} \ln(2k_t[\text{M}\cdot]_0 t + 1) \quad (4)$$

Equation 4 further simplifies by incorporating the definition of the reaction diffusion parameter, $R \equiv k_t/k_p[\text{M}]$, and substituting the rate of polymerization at time 0, R_{p0} , which is equal to the product of $k_p[\text{M}][\text{M}\cdot]_0$. Equation 4 then reduces to an expression with only one unknown, the reaction diffusion parameter, R :

$$\Delta[\text{M}] = \frac{1}{2R} \ln(2RR_{p0}t + 1) \quad (5)$$

The initial rate of polymerization, R_{p0} , is determined by differentiating the conversion as a function of time at time zero after initiation has stopped. Then, the reaction diffusion parameter can be determined from a least-squares analysis on double bond conversion (i.e., double bond concentration) as a function of time during the dark reaction.

Results and Discussion. The analysis is shown in parts a and b of Figure 4 for DEGDMA polymerized with 10 mW/cm² of UV light and 1 wt % Irgacure 651. Initiation was stopped at 18% conversion of double bonds, and the dark reaction was monitored for 500 s. In Figure 4a, the entire 500 s of data were used in the least-squares analysis, and R was determined to be 15.2. In comparison, Figure 4b shows the analysis for the first 50 s, and R was found to be 14.1. Thus, the value of R appears to be independent of the length of time the polymerization is monitored in the dark. Likewise, the analysis may start at any point during the dark reaction, but estimates of R_{p0} are more accurate near the instant the shutter is closed.

This analysis was applied to three different dimethacrylate monomers: DEGDMA, poly(ethylene glycol 200) dimethacrylate (PEG200DMA), and poly(ethylene

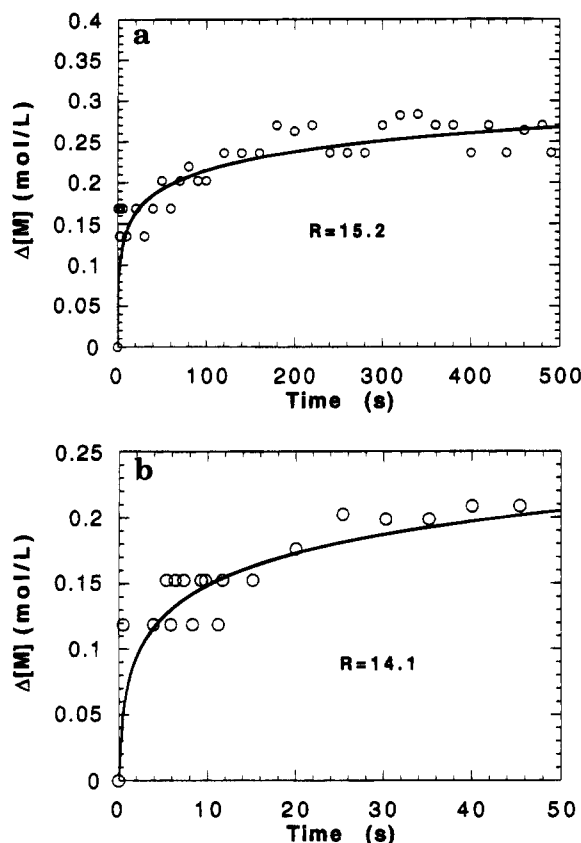


Figure 4. Change in the molar concentration of double bonds, $\Delta[M]$, as a function of time after initiation was stopped during the polymerization of DEGDMA. The polymerization was initiated with 10 mW/cm² of UV light and 1.0 wt % Irgacure 651. The shutter was closed, and initiation was stopped at 18% double bond conversion. Least-squares analysis is presented for (a) 500 s in the dark and (b) the first 50 s in the dark.

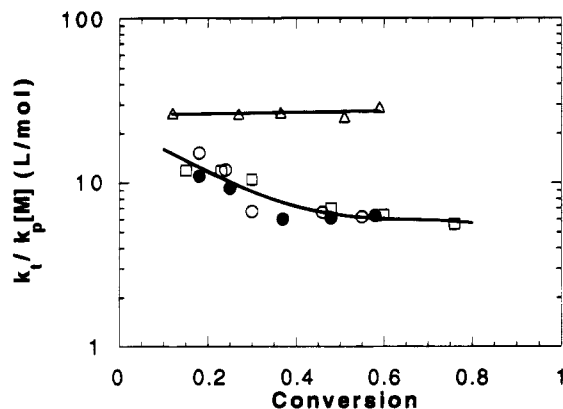


Figure 5. Reaction diffusion parameter, $k_t/k_p[M]$, as a function of double bond conversion for DEGDMA at 10 mW/cm² (○), DEGDMA at 110 mW/cm² (●), PEG200DMA at 10 mW/cm² (□), and PEG600DMA at 10 mW/cm² (△). All polymerizations were initiated with 1.0 wt % Irgacure 651.

glycol 600) dimethacrylate (PEG600DMA). By selecting these monomers, the range of glassy to rubbery polymer networks was spanned. Polymerizations of DEGDMA and PEG200DMA produce glassy polymer networks, while poly(PEG600DMA) is a rubbery network. The results for the reaction diffusion parameter as a function of double bond conversion are presented in Figure 5. All polymerizations were initiated with 1 wt % Irgacure 651 and light intensities of 10 or 110 mW/cm². For DEGDMA and PEG200DMA, R appeared to plateau around 30% double bond conversion at a value of 6. The

calculated value of R was also independent of light intensity as shown in the data for DEGDMA polymerized with 10 or 110 mW/cm² of UV light. This value was slightly higher than that previously determined by DSC (between 2 and 3), but the difference is easily reconciled considering the lumped initiator efficiency and steady-state approximation used in the DSC method. In contrast to DEGDMA and PEG200DMA, the reaction diffusion parameter for PEG600DMA plateaus at a higher value around 25, and reaction diffusion appears to control termination already at 10% conversion.

The differences between the behavior and magnitude of the reaction diffusion parameters in these systems are attributed mainly to differences in the macroscopic properties of the resulting networks (i.e., rubbery versus glassy networks). Therefore, when polymerizing DEGDMA and PEG200DMA, the system mobility and flexibility is reduced and k_p is relatively low. The reduced mobility leads to reaction diffusion controlled termination between 20 and 30% conversion. However, when polymerizing PEG600DMA, the high flexibility and mobility in this rubbery system coupled with a higher value of k_p lead to quite different behavior. Despite the enhanced mobility of the system, which should enhance segmental diffusion, the onset of reaction diffusion controlled termination is earlier in PEG600DMA because of its higher value of k_p . Finally, the differences in magnitude of R arise from physical arguments. In models for R ,^{7,17-19} the diffusion coefficient, capture radius, or collision radius for encounter all depend on monomer parameters that are affected by the size of the monomer molecule and flexibility in the system. Physically, the higher mobility in rubbery PEG600DMA leads to a larger collision radius for reaction and a correspondingly higher k_t . The higher k_t proportionally increases the reaction diffusion constant.

In summary, this paper has presented a method to analyze data from a RTIR technique to characterize reaction diffusion termination during free-radical photopolymerizations. The analytical method combined with the experimental technique provides a direct measure of the parameter associated with reaction diffusion termination while requiring minimal assumptions. In particular, no assumptions regarding the initiator efficiency or steady-state approximation were employed in the analysis. By accurately determining the reaction diffusion parameter and the point at which reaction diffusion begins to dominate termination, progress can be made in several ways. First, analysis of high conversion kinetics (i.e., when reaction diffusion controls termination) can be dramatically simplified when the reaction diffusion parameter has been characterized. When reaction diffusion controls termination, one simple, continuous experiment can be performed to measure the ratio of $k_p/k_t^{0.5}$. Once this ratio and the reaction diffusion parameters are known, the independent kinetic constants, k_p and k_t , can be determined as a function of conversion. Also, this characterization provides a greater fundamental understanding of termination mechanisms in radical polymerization reactions by characterizing the onset of reaction diffusion controlled termination and quantifying the associated reaction diffusion parameter.

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