Reaction Kinetics and Volume Relaxation during Polymerizations of Multiethylene Glycol Dimethacrylates

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ABSTRACT: A series of multiethylene glycol dimethacrylates (MEGDMA) was characterized with respect to the polymerization behavior, kinetics, and mechanisms. By studying a series of MEGDMA's with the number of ethylene glycol units ranging from 2 to 14, the influence of the monomer structure, especially with respect to the system mobility, was determined. For each monomer, the propagation and termination kinetic constants were quantified as a function of conversion to provide insight surrounding the controlling polymerization mechanisms. In particular, the importance of reaction diffusion as a termination mechanism was elucidated. When termination was reaction diffusion controlled, the proportionality constant between the termination kinetic constant and the propagation kinetic constant was found to be the same for all of the MEGDMA's studied and had a value between 2 and 3. The influence of the double bond concentration on the reaction diffusion mechanism was also investigated by polymerizing diethylene glycol dimethacrylate in the presence of an inert solvent. Finally, in addition to characterizing the general reaction behavior, the influence of volume relaxation on the polymerization behavior and kinetics was studied. It was found that in polymerizations of PEG600DMA volume relaxation did not influence the kinetics and the system free volume was nearly independent of rate. However, in DEGDMA, volume relaxation was found to be significant beyond 10% conversion and led to an excess free volume during polymerization performed at higher rates.

Introduction

Polymers produced from polymerizations of multifunctional monomers, especially photopolymerizations, provide excellent materials for coatings and other applications in which thermally stable, strong, solvent-resistant materials are required.[1−3] Often for coating applications and other applications where strength is not as important, multifunctional acrylate coatings are typically produced through photopolymerizations. Typically, when strength and durability are major issues, multimethacrylate polymers will be used. Though they polymerize more slowly, the highly cross-linked methacrylates form a stronger polymer with a higher glass transition temperature when compared to their multiacrylate counterparts. This feature makes them particularly useful for applications such as dental materials in which mechanical strength and durability are primary concerns.[4−6]

Multifunctional monomer polymerizations exhibit many complex features including autoacceleration and autodeceleration,[3,7−10] limiting double bond conversion,[3,7,11−14] polymerization kinetics which are dependent on the rate of the polymerization,[3,15] and a reaction diffusion-controlled termination mechanism.[16−22] Most of this polymerization behavior can be attributed to the mobility of the reacting species in the polymerizing system. For example, limited mobility of the macroradicals leads to autoacceleration and diffusion-limited propagation leads to maximum double bond conversions. Therefore, to gain insight into the polymerization behavior and underlying reaction mechanisms during cross-linking polymerizations, it is desirable to study the effects of monomer structure, especially mobility, on the polymerizing system.

Several researchers[23−30] have studied the effects of increasing dimethacrylate concentration on the cure behavior of methacrylate and dimethacrylate copolymerizing systems. In general, as the concentration of dimethacrylate monomer is increased, macroscopic gelation occurs at lower conversions, severely limiting translational and segmental mobility of the polymer macroradicals. Kopecek and co-workers[23−26] found that increasing the dimethacrylate concentration led to higher double bond conversions for a given polymerization time. These results were interpreted in terms of the effects of mobility in the polymerizing system on the termination kinetics. Hamielec and collaborators[27−29] have also extensively studied the copolymerization of methyl methacrylate with ethylene glycol dimethacrylate. Their results show a decrease in the conversion where autoacceleration occurs with an increase in the dimethacrylate content of the system. A sudden decrease in the conversion rate was also seen at higher conversions and related to the limited mobility of the monomer molecules (diffusion-controlled propagation) and the initiator radicals (increased recombination rate because of the cage effect). Along with these experimental studies, Hamielec and co-workers[31−36] have also modeled the polymerization behavior and kinetics of these copolymerization cross-linking reactions.

In general, these studies were conducted in the low cross-linking regime (<5 wt % cross-linker), but they still show the dramatic effect of gelation and cross-linking density on the system mobility and the resulting polymerization behavior. In the high cross-linking regime such as the homopolymerization of dimethacrylates, autoacceleration is apparent from the beginning of the reaction, and mobility is further restricted upon the onset of gelation. Gelation may even occur at less than 1% conversion of double bonds in many of the multifunctional monomer homopolymerizations. Therefore, to increase the mobility in these systems, the

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flexibility of the monomer can be increased, such that the cross-linking density is decreased. Alternatively, as will be discussed later, increasing the rate of polymerization leads to an excess free volume which also provides additional mobility.

Scranton *et al.*[37] have studied the effects of mobility on the polymerization rate by increasing solvent concentration during the thermal homopolymerization of ethylene glycol dimethacrylate and other mono-/dimethacrylate copolymerizations. As the solvent content was increased, the initial polymerization rate was decreased, the magnitude of the gel effect was reduced, and the onset of the gel effect was delayed. These observations were attributed to the additional mobility of the polymer chains introduced by the solvent. By adding as little as 10 mol % ethylene glycol (solvent), autoacceleration was completely suppressed in the rate profile. The effect of ethylene glycol chain length on the dimethacrylate polymerization rate was also studied for ethylene glycol dimethacrylate (EGDMA), tetraethylene glycol dimethacrylate (TeEGDMA), and poly(ethylene glycol 400) dimethacrylate (PEG400DMA). The maximum rate of polymerization was greatest for TeEGDMA followed by PEG400DMA and then by EGDMA.

Cook[20] also studied homopolymerization rate profiles of ethylene glycol dimethacrylate, diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), tetraethylene glycol dimethacrylate, and nonaethylene glycol dimethacrylate (NEGDMA) during photopolymerizations. The effects of the monomer structure (number of ethylene glycol units), reaction temperature, and light intensity on the polymerization rate were studied. Similar to the results of Scranton *et al.*, Cook found a suppression in the gel effect with increasing length of the ethylene glycol bridge in the monomer. In addition, Cook's results show a dependence of the normalized maximum rate of polymerization on the number of ethylene glycol units in the following order: EGDMA < TeEGDMA < TrEGDMA < DEGDMA < NEGDMA. The normalized rate profile is the rate of polymerization divided by the initial monomer concentration.

Cook[20] also studied the influence of temperature and light intensity on the polymerization rate profiles of EGDMA and TrEGDMA. In general, as the rate of polymerization was increased, the limiting double bond conversion was increased and the maximum rate of polymerization was shifted to higher conversions. These results are a direct indication of the coupling of volume relaxation with the polymerization kinetics. While Cook[20] did not experimentally determine the polymerization kinetic constants, the dependence of the kinetics on volume relaxation can be inferred.

At faster rates of polymerization, the macroscopic rate of volume shrinkage is much slower than the rate at which double bonds are consumed. Polymerization shrinkage is partially explained by a decrease in the van der Waals volume from the conversion of van der Waals bonds into covalent bonds.[38] While this explanation explains some of the shrinkage behavior observed during polymerizations, it severely underestimates the experimentally observed volume shrinkage. Patel *et al.*[39] characterized this volume shrinkage for methacrylate double bonds to be approximately 22.4 cm^3/mol. If the system relaxes much slower than the rate of polymerization (which is often the case for photopolymerizations of multifunctional monomers), an excess free volume is present in the system. This excess free volume results in greater mobility of the reacting species which leads to a higher maximum functional group conversion and a shift in the peak maximum of the rate to higher conversions. Kloosterboer *et al.*[3,14] have also observed this dependence of the polymerization kinetics during the polymerization of several diacrylates. Additionally, Bowman and Peppas[15] modeled this dependence of the rate of polymerization and the polymerization kinetics on the rate of volume relaxation.

This work attempts to characterize further the polymerization behavior and kinetics of a series of multiethylene glycol dimethacrylates (MEGDMA's) ranging from 2 to 14 ethylene glycol units. While previous works have focused on studying the polymerization rates and double bond conversions, this work provides an experimental investigation and quantification of the polymerization kinetics. As the number of ethylene glycol units in the monomer is increased, the effect of mobility on the polymerization propagation and termination kinetics, as well as the reaction mechanisms, can be determined.

Recently, it was shown that polymerizations of multifunctional acrylate monomers are typically dominated by reaction diffusion-controlled termination kinetics.[22] Reaction diffusion occurs when radicals move together by propagating through unreacted double bonds rather than through segmental or other types of diffusion. Because of the highly cross-linked structure that arises during polymerizations of multifunctional monomers, mobility through reaction diffusion becomes more facile than all other forms of mobility for the radical. Thus, when reaction diffusion dominates the termination reaction, the kinetic constant for termination and the rate of propagation will be related through a proportionality constant and the concentration of double bonds.

In our previous work on multifunctional acrylates,[22,40] the functionality of the monomer was increased while the molar concentration of double bonds remained approximately constant. By studying the MEGDMA series, the effects of double bond concentration and pendant functional group mobility on the reaction diffusion termination mechanism can be determined. Finally, the effects of volume relaxation on the polymerization kinetics will be further characterized by comparing two systems of drastically differing mobility, poly(DEGDMA) to poly(PEG600DMA). Poly(DEGDMA) is a glassy polymer network with very large relaxation times upon completion of cure, whereas poly(PEG600DMA) remains rubbery and relaxes very quickly. The differences in relaxation times of these systems vary by orders of magnitude. Thus, by comparing these monomers, we are able to see volume relaxation effects on the polymerizations.

Experimental Section

Materials and Procedure. The multifunctional monomers chosen for study were the following series of commercially available multiethylene glycol dimethacrylates: diethylene glycol dimethacrylate (DEGDMA), triethylene glycol dimethacrylate (TrEGDMA), poly(ethylene glycol 200) dimethacrylate (PEG200DMA), and poly(ethylene glycol 600) dimethacrylate (PEG600DMA) (Polysciences Inc., Warrington, PA). All monomers were used as received. The purity of these compounds (as stated by Polysciences) is that they are 98+% reactive esters, with at least 95% of the reactive esters being the desired dimethacrylate compound. In addition, poly(ethylene glycol 400) (PEG400; Aldrich, Milwaukee, WI) was used as a diluent for some of the polymerization studies. Some of the studies on the effects of the rate of polymerization on the network microstructure and system mobility also used the

photochromic probe azobenzene (AB; Aldrich, Milwaukee, WI). The photopolymerizations were initiated with 2,2-dimethoxy-2-phenylacetophenone (DMPA; Ciba Geigy, Hawthorn, NY).

Reaction rate profiles were monitored with a differential scanning calorimeter equipped with a dual beam photocalorimetric accessory (DSC-DPA 7; Perkin-Elmer, Norwalk, CT). The photocalorimetric accessory included transfer optics to produce full beam ultraviolet–visible light of varying intensity and a monochromator to produce light of a given wavelength. For the kinetic studies, monochromatic light of 365 nm was selected and the intensity was controlled by neutral density filters (Melles Griot, Irvine, CA). The DSC cell was attached to a refrigerated recirculating chiller (CFT-25; NESLAB, Newington, NH) to keep the cell cool and isothermal when reactions were performed near room temperature.

In the kinetic studies, 0.1 wt % of DMPA was used to initiate the polymerizations and the light intensity was varied. Samples of 3–5 mg were weighed in aluminum DSC pans, and the samples were left uncovered during the photopolymerizations. Small sample sizes were used to ensure the applicability of the thin film approximation and uniform light intensity across the sample. The DSC cell was flushed with nitrogen 10 min prior to the polymerization and continuously during the polymerization since oxygen is a well-known inhibitor of these reactions.[3,41–43]

For the photochromic studies, 0.1 wt % of AB was dissolved in a solution of monomer and 1 wt % DMPA. Thin films of these samples were cured using a 365-nm 6-W ultraviolet light source (Cole-Parmer, Chicago, IL). This light served to induce the trans to cis conformational changes in the photochromic probe as well as initiate the polymerization. The trans to cis conformational isomerization is a direct measure of the system free volume. During the polymerization, the absorbance changes in the sample were monitored with an HP8452 UV–vis spectrophotometer (Hewlett Packard, Fort Collins, CO). A complete experimental description and analysis has previously been reported.[44]

Analysis. The rate of polymerization as a function of polymerization time was determined from the heat flux measured by the DSC. By subsequent integration of this curve and knowledge of the heat of reaction per double bond, the conversion was also determined as a function of the polymerization time. For the methacrylate monomers studies, 13.1 kcal/mol was used as the theoretical heat evolved per methacrylate double bond reacted.[8,45,46] As described previously, the propagation and termination kinetic constants were determined from a series of experiments. First, a complete polymerization was performed to measure the lumped kinetic constant, $k_p/k_t^{1/2}$, as a function of the reaction time. Then, by stopping the initiation of radicals at various stages in the polymerization (i.e., closing the shutter which exposes the sample to the UV light) and monitoring the dark reaction, the termination and propagation kinetic constants were uncoupled. The complete method for analysis of the DSC results and the methods for converting these results into kinetic constants can be found elsewhere.[22,40,47]

The photochromic probe experiments require monitoring the absorbance changes in two different systems. The first is a monomer system where the probe is dissolved in the monomer, but no photoinitiator is added. The second is a polymerizing system where probe and photoinitiator are dissolved in the monomer. Both systems are exposed to UV light which induces the trans to cis isomerization of the probe, but in the monomer system (as in contrast to the polymerizing system), polymerization does not occur in parallel with the probe isomerization. Therefore, all of the probe molecules in a monomer system are surrounded by enough free volume to allow the molecules to isomerize, and these probes are mobile in their local environment. In contrast, in a polymerizing system, some of the probe molecules will reside in regions of restricted mobility caused by a lower free volume with an increasing polymer fraction in the system. As polymerization continues, the fraction of probe molecules that are unable to isomerize because of their restricted mobility increases. By monitoring the absorbance changes as a function of UV exposure time in both the monomer and polymerizing system, the fraction of probe molecules that are surrounded by sufficient free volume to isomerize and remain mobile can be determined. The complete details of this analysis have been discussed elsewhere.[44]

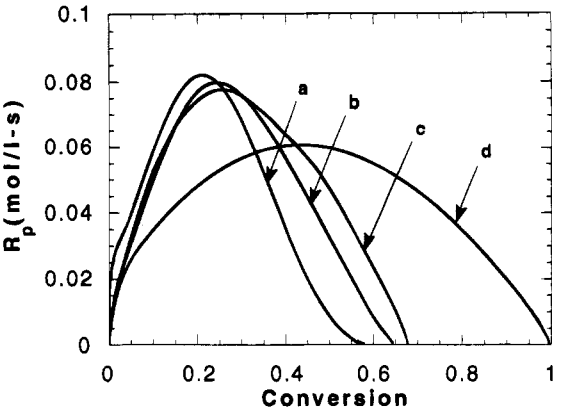

Figure 1. Rate of polymerization as a function of conversion for (a) DEGDMA, (b) TrEGDMA, (c) PEG200DMA, and (d) PEG600DMA. Photopolymerizations were initiated with 0.1 wt % DMPA and $I_0 = 0.8$ mW/cm^2.

Results and Discussion

During the polymerization of multifunctional monomers, several features are characteristic of the polymerization behavior as seen in Figure 1. Figure 1 contains the rate of polymerization as a function of double bond conversion for DEGDMA, TrEGDMA, PEG200DMA, and PEG600DMA. From the general shape of the curves, one observes the immediate onset of autoacceleration caused by the restricted mobility of the terminating radicals in these cross-linking systems. As has been shown elsewhere,[16–22] at some point in this autoaccelerating regime, the termination mechanism becomes reaction diffusion controlled. Instead of termination occurring by translational and/or segmental diffusion of the macroradicals (improbable mechanisms past macrogelation in highly cross-linked systems), the radicals are mobile primarily by propagating through the unreacted double bonds in the system. This behavior is more clearly observed in the termination kinetic constant as will be discussed later. Shortly after the polymerization reaches its maximum rate, autodeceleration occurs and the polymerization eventually stops when vitrification/cross-linking suppresses the propagation reaction.

When comparing the cure profiles of the different monomers, several trends are apparent. As the number of ethylene glycol units in the monomer is increased, the maximum rate of polymerization decreases, the conversion at the maximum rate of polymerization increases, and the maximum double bond conversion increases. Most of this behavior can be attributed to the enhanced mobility of the system introduced by increasing the number of ethylene glycol units in the monomer, thereby decreasing the concentration of double bonds and decreasing the cross-linking density of the system. For example, the enhanced mobility of PEG600DMA leads to nearly 100% conversion of the double bonds. As the number of ethylene glycol units in the monomer is further decreased from 4.5 (PEG200DMA) to 3 (TEGDMA) to 2 (DEGDMA), the limiting conversions are correspondingly lowered from 0.68 to 0.64 to 0.57, respectively. This limiting double bond conversion results from the reduced mobility in the system which leads to diffusion-controlled propaga-

tion and autodeceleration. Eventually, the reduction in mobility of the system with further reaction and cross-linking limits further polymerization, and a maximum double bond conversion is reached.

The general decrease in the maximum rate of polymerization from DEGDMA to PEG600DMA is attributed mainly to the lower concentration of double bonds in systems with a greater number of ethylene glycol units. All else being equal, the rate of polymerization should be correspondingly lower for the system with the lowest concentration of double bonds. Of further interest, as the mobility in the system is increased from DEGDMA to PEG600DMA, the gel effect or autoacceleration is delayed and somewhat suppressed. Autoacceleration causes a buildup in the active radical concentration (from diffusion-controlled termination) which increases the rate of polymerization. Relative to the other polymerizing systems, the magnitude of the gel effect or autoaccelerating regime is highest in DEGDMA, but the higher cross-linking density also leads to an earlier onset of diffusion-controlled propagation. In PEG600DMA, the magnitude of the gel effect is comparatively suppressed, but it occurs over an extended conversion range. Eventually, the rate of polymerization of PEG600DMA even exceeds that of DEGDMA which beings to autodecelerate at a much lower conversion.

Finally, the conversion at which the maximum rate of polymerization occurs increases as the number of ethylene glycol units in the monomer is increased. The maximum in the rate of polymerization results primarily from a balance between diffusion-controlled propagation (which decreases the rate of polymerization) and diffusion-controlled termination (which increases the rate of polymerization). Increasing the number of ethylene glycol units in the system delays diffusion-controlled propagation and autodeceleration until higher conversions. The result is a shift in the conversion at the maximum rate of polymerization from 0.20 for DEGDMA to 0.46 to PEG600DMA. These results are further supported by the polymerization kinetic data which will be presented in figures that follow.

Interestingly, the rates of polymerization presented in Figure 1 all have similar shapes with consistent trends as the number of ethylene glycol units is increased. This led us to examine whether this rate information could be reduced to a single curve which somehow factored in the number of ethylene glycol groups and/or the monomer concentration. Figure 2 presents the results of that exploration, in which it was found that the normalized rate of polymerization (normalized by the pure monomer concentration of each monomer) divided by the number of ethylene glycol groups raised to the 0.35 power scaled with the double bond conversion divided by the same factor. When the data are examined in this manner, it appears that the scaled plot indicates that rates of polymerization can be predicted to within 15%. The advantage of this scaling is that a single polymerization can be performed with one of the ethylene glycol dimethacrylates, and a good estimate of the rate as a function of conversion can be obtained. Additionally, the maximum attainable double bond conversion, which dramatically affects the mechanical properties, can also be reasonably predicted. If this type of behavior also held for copolymerizations, then the rate behavior and maximum conversion could be predicted for various comonomer compositions without performing those experiments.

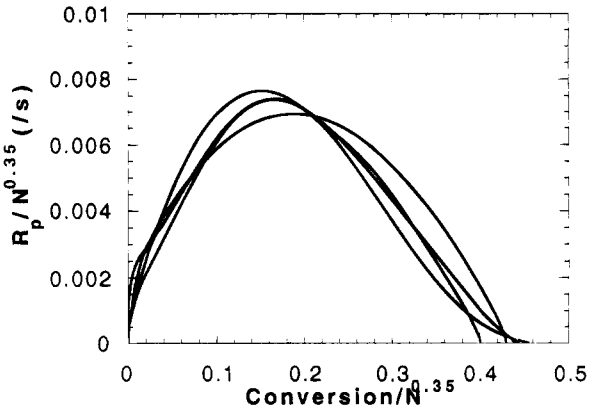

Figure 2. Normalized rate of polymerization divided by the number of ethylene glycol units in the monomer raised to the 0.35 power versus the conversion divided by the same scaling factor for DEGDMA, TrEGDMA, PEG200DMA, and PEG600DMA. Photopolymerizations were initiated with 0.1 wt % DMPA and $I_0 = 0.8$ mW/cm^2.

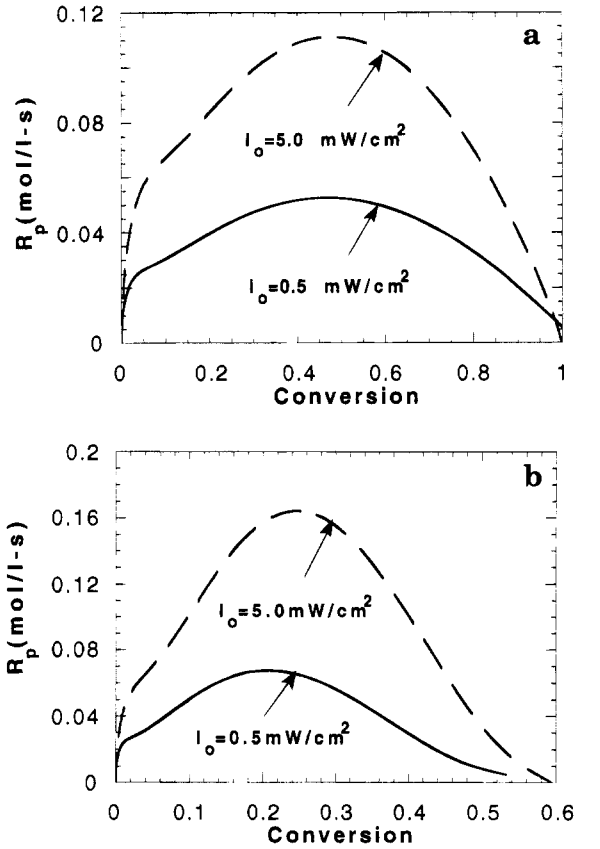

Figure 3. Rate of polymerization as a function of conversion for (a) PEG600DMA and (b) DEGDMA at two different light intensities: (– –) 5.0 mW/cm^2; (—) 0.5 mW/cm^2.

In examining the polymerization behavior of multifunctional monomers, it has often been hypothesized that volume relaxation is strongly coupled to the polymerization kinetics. When the polymerization proceeds more rapidly than the volume relaxation, excess free volume is generated such that mobilities and kinetic constants will depend strongly on both the double bond conversion and the rate at which that conversion was reached. To explore this effect, polymerizations of PEG600DMA and DEGDMA were studied at different light intensities. These data are presented in parts a and b of Figure 3, respectively. In Figure 3a it is apparent that the PEG600DMA curves at two different light intensities appear to have similar shapes as a

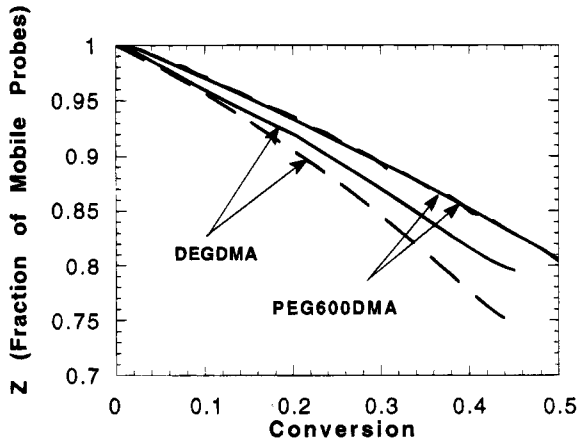

Figure 4. Fraction of mobile azobenzene probes as a function of conversion for PEG600DMA and DEGDMA at two different light intensities: (– –) 0.2 mW/cm^2; (—) 2.0 mW/cm^2.

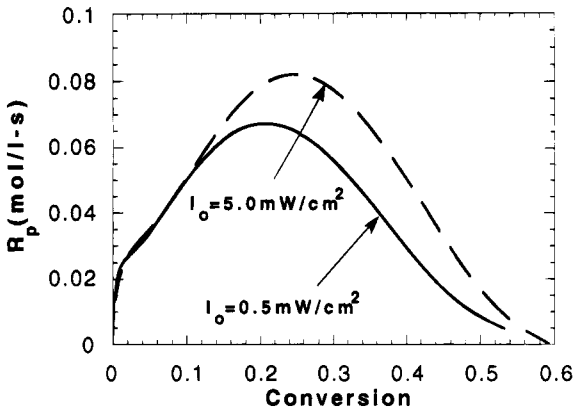

Figure 5. Rate of polymerization versus conversion for DEGDMA at two different light intensities: (– –) 5.0 mW/cm^2; (—) 0.5 mW/cm^2. The polymerization at the higher light intensity was scaled by the increase in the light intensity, 10, to the 0.3 power.

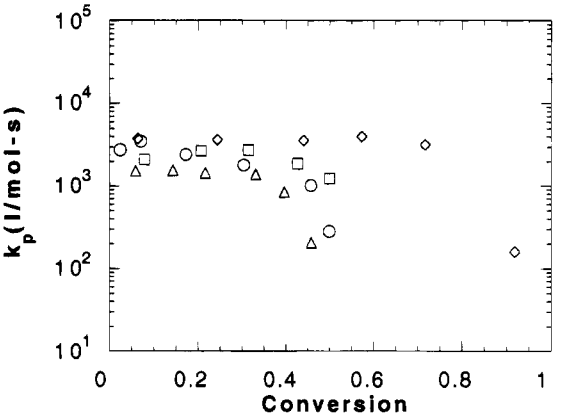

Figure 6. Propagation kinetic constant, k_p, as a function of conversion for DEGDMA (△), TrEGDMA (○), PEG200DMA (□), and PEG600DMA (◇). Photopolymerizations were initiated with 0.1 wt % DMPA and I_0 = 0.8 mW/cm^2.

function of conversion, while Figure 3b indicates that the shape of the rate curves shift to higher conversions as the light intensity is increased. This shifting in DEGDMA is most easily observed by determining the conversion at which the rate reaches its maximum (0.21 to 0.26) and the maximum attainable conversion (0.56 to 0.59).

For polymerizations in which the kinetic constants depend only on the double bond conversion, the rate as a function of conversion will maintain the same shape as the light intensity is increased. In PEG600DMA this shape similarity is exactly observed. Because PEG600DMA has a much lower cross-linking density and a greater degree of flexibility, volume relaxation occurs much more quickly than polymerization. Thus, there is no excess free volume, and the kinetic constants depend only on conversion. In DEGDMA, however, the volume relaxation should be significantly slower and should allow for the generation of excess free volume. Indeed, the shifting in the polymerization rates for DEGDMA is evidence of this excess free volume. As the polymerization rate increases, the excess free volume increases, and the conversion is higher when autodeceleration begins to control.

As further evidence of the different volume relaxation effects in polymerizations of DEGDMA and PEG600DMA, Figure 4 presents results of photochromic experiments which are sensitive to the free volume of the system. In Figure 4, the fraction of azobenzene probes which are mobile as a function of conversion is presented for polymerizations of DEGDMA and PEG600DMA at two different light intensities. As described elsewhere[44] the fraction of azobenzene probes which are mobile is a measure of the free volume in the system. In Figure 4 it is apparent that the fraction of azobenzene probes which are mobile, and thus the free volume, in PEG600DMA does not depend on the polymerization rate. However, the free volume in the DEGDMA polymerizing system depends strongly on the rate, particularly above 8–12% double bond conversion, beyond which the two curves separate dramatically.

Before the conversion reaches approximately 10%, the DEGDMA polymerizing system is relatively nonviscous and relaxes faster than the polymerization proceeds. As the polymerization continues, the relaxation time increases dramatically and leads to the differences between the free volumes at the different light intensities. To further support this conclusion, the rate data for polymerizations of DEGDMA from Figure 3b can be reexamined. In Figure 5, the rate of polymerization divided by the light intensity to the 0.3 power is plotted as a function of conversion.

The exponent 0.3 was used as it was the exponent found to be the scaling exponent for PEG600DMA (data from Figure 3a) and also the scaling exponent for the initial portion of the DEGDMA polymerization. The 0.3 exponent found in this work as the dependence of rate on light intensity is quite surprising, as the theoretical value for bimolecular termination is 0.5 and that for unimolecular termination 1.0. Typically, in multiacrylate polymerizations, values between 0.5 and 1.0 have been found.[48,49]

In Figure 5 it is clear that the rate curves exactly scale until the conversion reaches 10–12%. At this point the slower polymerization begins to autodecelerate, while the more rapid polymerization begins to create excess free volume that leads to more mobility and a delayed onset of autodeceleration. Thus, the data from the photochromic technique and the rates of polymerization appear to be in agreement in predicting that volume relaxation effects become significant around 10% double bond conversion.

In Figures 6 and 7, the propagation and termination kinetic constants are plotted versus double bond conversion for each of the multiethylene glycol dimethacrylates studied. The kinetic constants were determined by monitoring a series of dark reactions in each polymerizing system with a DSC.[22,40,47] No attempts were made

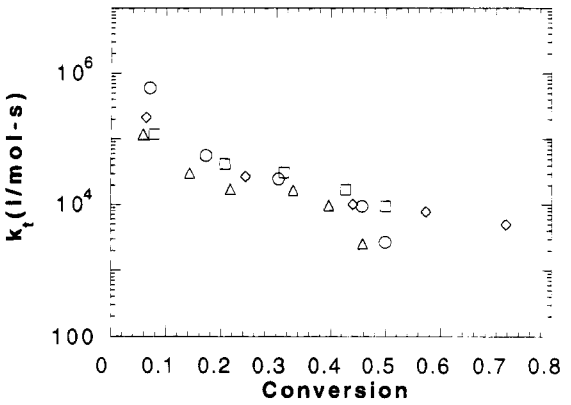

Figure 7. Termination kinetic constant, k_t, as a function of conversion for DEGDMA (△), TrEGDMA (○), PEG200DMA (□), and PEG600DMA (◇). Photopolymerizations were initiated with 0.1 wt % DMPA and $I_0 = 0.8$ mW/cm^2.

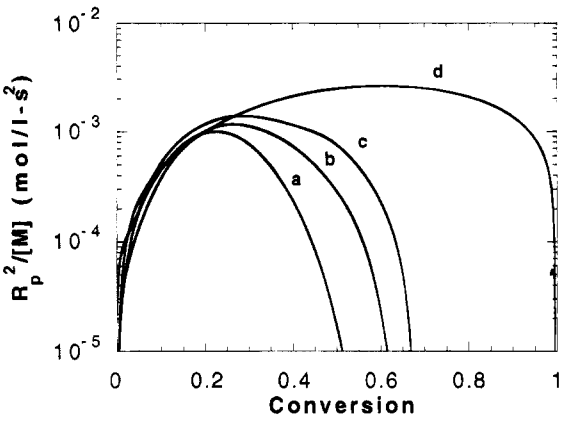

Figure 8. Rate of polymerization squared divided by the double bond concentration, R_p^2/[M], versus conversion for (a) DEGDMA, (b) TrEGDMA, (c) PEG200DMA, and (d) PEG600DMA. Photopolymerizations were initiated with 0.1 wt % DMPA and $I_0 = 0.8$ mW/cm^2.

to measure the initiator efficiency independently, so the propagation kinetic constant, k_p, reported is lumped together with the efficiency. Thus, k_p in the following discussions is actually $f^{1/2}k_p$.

The kinetic data were used to provide some evidence as to the controlling mechanism for propagation and termination. For example, in Figure 6, the propagation kinetic constant remains relatively unchanged at low conversion where chemical reaction is controlling the propagation mechanism, but the beginning of diffusion-controlled propagation is clearly observed as k_p begins to decrease at higher conversions. From the data shown, diffusion-controlled propagation occurs first in DEGDMA followed by TrEGDMA, PEG200DMA, and PEG600DMA, indicating the effects of lower mobility and higher cross-linking as the ethylene glycol bridge in the monomer is decreased. Also, in comparing the value of k_p during the chemical reaction controlled regime for each monomer, a slight increase in the reactivity of the double bond is seen with increasing ethylene glycol units in the monomer. In DEGDMA the initial value of k_p is around 1500 L/mol·s, whereas in PEG600DMA it is closer to 4000 L/mol·s.

The behavior observed in the termination kinetic constant, k_t, is slightly more complex. In the cross-linking reactions of MEGDMA's, radical termination is always diffusion controlled and occurs by one of two mechanisms. The first mechanism involves reorientation of polymer segments to bring two macroradicals together to react. The process is related to diffusion of the polymer segments which is continually decreasing with increasing conversion in the system. The second mechanism has been called reaction diffusion or residual termination and occurs as immobile radicals on the network react through unreacted double bonds in their vicinity to move and encounter a second radical for termination. By the nature of this mechanism, k_t becomes proportional to the product of k_p and the concentration of double bonds in the system when reaction diffusion is controlling.

In Figure 7, k_t is initially decreasing which indicates that termination is occurring primarily through segmental diffusion. Around 20% conversion, the mobility of the radicals through segmental diffusion becomes extremely limited, and the dominance of reaction diffusion as the termination mechanism becomes evident. When the termination mechanism is reaction diffusion controlled, k_t becomes proportional to k_p[M] where [M] is the molar concentration of double bonds. Around 20% conversion, where reaction diffusion begins to control radical termination, k_p is still nearly constant as observed in Figure 6. Therefore, the initial sharp decrease in k_t begins to slow, and k_t now only slowly decreases proportionally to the consumption of double bonds. As still higher conversions are reached, k_p becomes diffusion controlled and begins to decrease markedly. From this point onward, k_t also decreases much faster, indicative of its dependence on k_p in the reaction diffusion-controlled termination regime.

Complementary to the kinetic data, the rate of polymerization can also be used to identify and define more clearly the regions of diffusion-controlled propagation and reaction diffusion-controlled termination. From standard free-radical polymerization kinetics,

$$R_p = \frac{k_p}{k_t^{1/2}}[M]\left(\frac{R_i}{2}\right)^{1/2} \quad (1)$$

where R_p is the rate of polymerization and R_i is the rate of initiation. If the termination mechanism is reaction diffusion controlled, then

$$k_t = Rk_p[M] \quad (2)$$

Here, R represents the reaction diffusion proportionality constant. Substituting for k_t in eq 1 and simplifying

$$R_p = \left(\frac{k_p}{R}\right)^{1/2}[M]^{1/2}\left(\frac{R_i}{2}\right)^{1/2} \quad (3)$$

Hence, when termination is reaction diffusion controlled, R_p^2/[M] will be proportional to the propagation kinetic constant. This proportionality relationship assumes the initiation rate to be approximately constant which is reasonable since the initiator concentration changes by less than 3% during the time of the polymerization at these conditions.

Figure 8 plots R_p^2/[M] as a function of double bond conversion for each of the dimethacrylates studied. When the curve begins to flatten at its maximum value, this behavior indicates that termination is reaction diffusion controlled. The curve then remains flat or decreases depending on the behavior of the propagation kinetic constant. If propagation is reaction controlled, the plateau in R_p^2/[M] is extended over a larger conversion range until k_p becomes diffusion controlled and decreases. Then, R_p^2/[M] decreases proportionally to k_p. From Figure 7, one can observe an earlier dominance

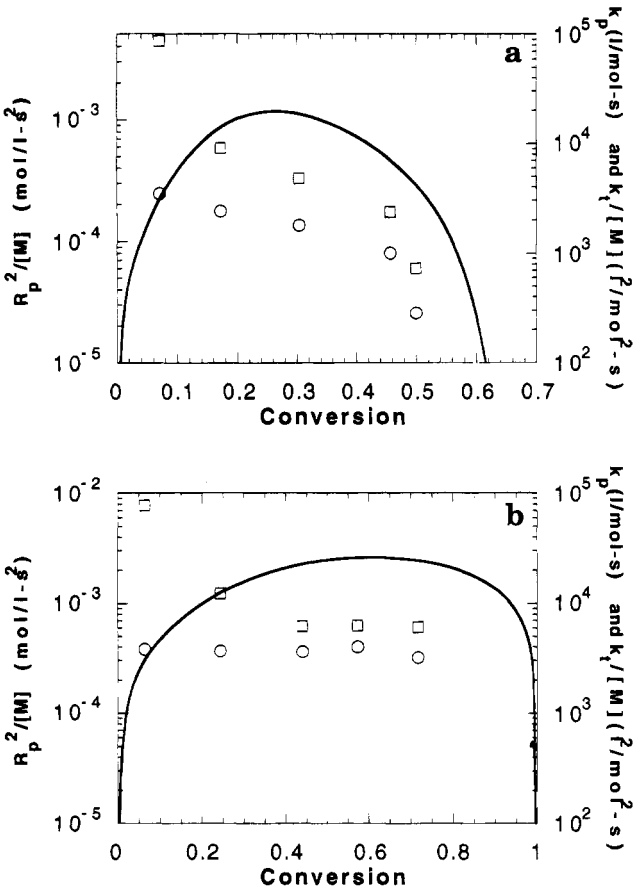

Figure 9. Rate of polymerization squared divided by the double bond concentration (R_p^2/[M]), the propagation kinetic constant (k_0, ○), and the termination kinetic constant divided by the double bond concentration (k_t/[M], □) as a function of conversion for (a) TrEGDMA and (b) PEG600DMA. Photopolymerizations were initiated with 0.1 wt % DMPA and I_0 = 0.8 mW/cm^2.

of reaction diffusion in the more highly cross-linked systems as evidenced by the occurrence of the plateau at lower conversions. Also, the region of diffusion-controlled propagation can also be identified by noting the conversion at which R_p^2/[M] begins to decrease. Again, the higher mobility and lower cross-linking density introduced by increasing the number of ethylene glycol units delays the diffusion limitations on propagation.

Furthermore, parts a and b of Figure 9 compare the kinetic data and the rate data for TrEGDMA and PEG600DMA to support further the identification of the controlling regions of reaction diffusion and diffusion-controlled propagation. In parts a and b of Figure 9, R_p^2/[M], k_p, and k_t/[M] are plotted versus double bond conversion for both TrEGDMA and PEG600DMA. In both systems, the conversion at which k_t/[M] begins to plateau corresponds well with the conversion at which R_p^2/[M] levels. Thus, both the rate and the kinetics predict approximately the same conversion at which termination becomes reaction diffusion controlled. Additionally, R_p^2/[M] remains relatively constant and proportional to k_p when reaction diffusion is controlling. Both results indicate nearly the same regions of reaction-controlled propagation and diffusion-controlled propagation.

Of further interest is the implication these results present for determining kinetics of various systems. If k_p is reaction controlled and its value known when

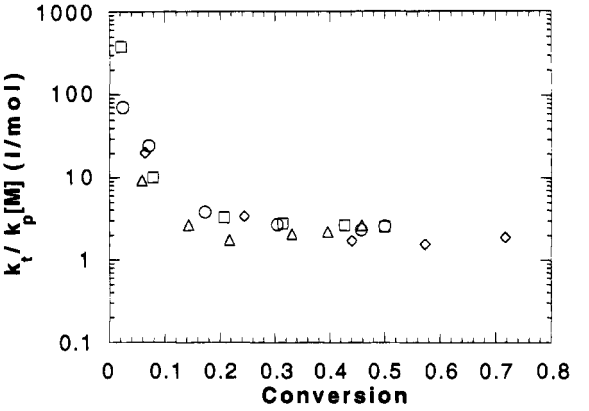

Figure 10. Ratio of $k_t/(k_p[M])$ as a function of conversion for DEGDMA (△), TrEGDMA (○), PEG200DMA (□), and PEG600DMA (◇). Photopolymerizations were initiated with 0.1 wt % DMPA and I_0 = 0.8 mW/cm^2.

reaction diffusion becomes controlling, then the reaction diffusion proportionality constant can be calculated from the value of R_p^2/[M] at its plateau. Since R is a constant, then k_p can be calculated at any conversion beyond the conversion at which reaction diffusion controls termination. Once k_p and R are determined, then k_t can also be calculated from eq 2. Obviously limitations exist with such a method, since it is highly dependent on the value of k_p when the system becomes reaction diffusion controlled. However, it does provide a method to estimate reasonably the high conversion kinetics from a single DSC experiment.

To characterize further the reaction diffusion proportionality constant, the ratio of $k_t/(k_p[M])$ was plotted as a function of conversion for each of the monomers studied in Figure 10. When reaction diffusion is controlling termination, $k_t/(k_p[M])$ should reduce to a constant value, R, as defined in eq 2. For all of the MEGDMA's studied and plotted in Figure 10, the proportionality constant appeared to be approximately the same in each system with a value between 2 and 3. Similar results were obtained for a series of acrylate monomers where the functionality of the monomer was increased from a diacrylate to a pentaacrylate.[22] The value of the reaction diffusion parameter was between 3 and 7 in these acrylate systems. Buback *et al.*[50] have also recently investigated the reaction diffusion parameter for several linear polymer systems. In particular, they report values for R between 9 and 10 for methyl methacrylate. Theoretical estimates of the reaction diffusion parameter were also presented based on the Smoluchowski equation used by Schulz[51] and Russell *et al.*[52] and on the "volume swept out" model used by Soh and Sundberg[16] and Buback and Schweer.[53] For methyl methacrylate, the Smoluchowski model predicts a value of 5.7 for R, while the volume swept out model predicts a higher value of 29.

To define further the mechanism by which reaction diffusion is occurring, Figure 11 presents the kinetic results for the homopolymerization of DEGDMA along with a 50/50 and 10/90 wt % solution polymerization of DEGDMA in PEG400. The results illustrate the importance of the double bond concentration in the reaction diffusion termination mechanism. In many of the cross-linking systems studied, limiting functional group conversions are reached.

For example, in Figure 7, termination in DEGDMA appears to become reaction diffusion controlled around 20% conversion and the last kinetic point was deter-

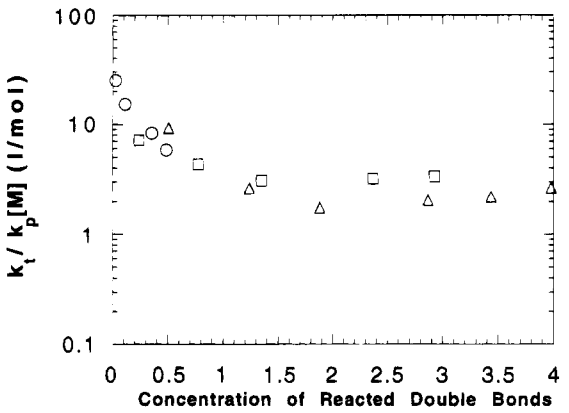

Figure 11. Ratio of $k_t/(k_p[M])$ as a function of concentration of double bonds that have reacted for the homopolymerization of DEGDMA (△) and the solution polymerizations of 50/50 DEGDMA/PEG400 (□) and 10/90 DEGDMA/PEG400 (○). Photopolymerizations were initiated with 0.1 wt % DMPA and $I_0 = 0.8$ mW/cm^2.

mined at 46%. If the change in the monomer concentration is neglected, then the value for R will vary less than 40%, which is on the order of the range reported for the experimental determination of R (between 2 and 3). Therefore, to illustrate the importance of the double bond concentration on the reaction diffusion mechanism, solution polymerizations were conducted where the initial double bond concentration was diluted by 50% and 90%.

The results in Figure 11 show $k_t/(k_p[M])$ as a function of the concentration of double bonds that have reacted for the homopolymerization and the solution polymerizations of DEGDMA. The general shape of the curve is the same as that in Figure 10, and the curve appears to plateau for the 50/50 solution polymerization near the same 2−3 range for R in the homopolymerizations. In the 10/90 solution polymerization, nearly all of the double bonds reacted during the polymerization because of the additional mobility introduced by the solvent, but 100% double bond conversion corresponded to only 0.87 mol/L of double bonds reacted. For DEGDMA, reaction diffusion does not control the termination mechanism until nearly 1.5 mol/L of double bonds have reacted. Therefore, in the 10/90 solution polymerization, the ratio of $k_t/(k_p[M])$ did not plateau since reaction diffusion was not controlling. However, the data points for the 10/90 solution polymerization fit in well with the overall curve, suggesting that the controlling mechanisms in the kinetics of these systems are very similar as a function of reacted double bond concentration.

Conclusions

The polymerization kinetics and mechanisms of a series of multiethylene glycol dimethacrylates were characterized with differential scanning calorimetry. In addition to characterizing the general reaction behavior, the influence of volume reaction on the polymerization kinetics was determined by studying the effects of polymerization rate on DEGDMA and PEG600DMA. The high cross-linking density and low mobility in DEGDMA led to a dependence of the polymerization kinetics on the rate of polymerization. This dependence was not seen in the more mobile and faster relaxing PEG600DMA system. The propagation and termination kinetic constants were also quantified for each of the MEGDMA's studied and provided insight as to the controlling mechanisms. In particular, the importance of reaction diffusion as a termination mechanism in these cross-linking polymerizations was elucidated. By varying the number of ethylene glycol units in the monomer from 2 to 14, the influence of the monomer structure, especially with respect to the system mobility, was determined. As the number of ethylene glycol units in the monomer was increased, diffusion-controlled propagation and reaction diffusion-controlled termination were shifted to higher conversions. The mechanism of reaction diffusion was further characterized by investigating the proportionality between the termination kinetic constant and the product of the propagation kinetic constant and the double bond concentration. The proportionality constant was found to be the same for all of the MEGDMA's studied and had a value between 2 and 3. Additionally, the influence of the double bond concentration on the reaction diffusion mechanism was investigated by polymerizing DEGDMA in the presence of an inert solvent.

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