Reaction behaviour and kinetic constants for photopolymerizations of multi(meth)acrylate monomers

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The polymerization behaviour of a series of multifunctional methacrylate and acrylate monomers was studied using differential scanning calorimetry to characterize the reaction rate profiles. The polymerization rates, double-bond conversion and kinetic constants were determined for each of the monomers, as well as the effects of monomer type, functionality and rates of polymerization on the reaction behaviour. In particular, by quantifying the kinetic constants for termination and propagation, the controlling mechanism for each of these processes was determined as a function of conversion. In contrast to linear polymerizations, the termination mechanism for these reactions proceeded primarily through reaction diffusion. This behaviour was seen as the termination kinetic constant became proportional to the propagation kinetic constant at very low double-bond conversions. In comparing the acrylates to the methacrylates, the increased reactivity of the acrylates was apparent in the greater values (by three orders of magnitude) of both the termination and propagation kinetic constants. Also, as the number of acrylate or methacrylate groups in the monomer was increased, the kinetic constants correspondingly decreased. This decrease resulted mainly from the greater viscosity of the higher-functionality monomers, attributed to their large molecular weights. Finally, with the exception of the trimethacrylate and triacrylate, the average number of double bonds reacted per monomer at the maximum conversion was near unity, independent of the monomer type or functionality.

(Keywords: methacrylates; acrylates; photopolymerization)

INTRODUCTION

Homopolymerization of multifunctional monomers provides a simple method for the production of highly crosslinked polymers. The high mechanical strength and excellent resistance to solvent penetration of densely crosslinked polymers have led to applications of these materials as dental materials, aspherical lenses, non-linear optical materials and coatings[1-5]. The materials are especially valuable as coatings because the monomers usually have low viscosity and rapidly polymerize under atmospheric conditions. Homopolymerization of multifunctional monomers can be carried out under a wide range of conditions, including varying monomer structure, number of reactive functional groups, type of functional groups, temperature and initiation rate. For all of these conditions, it is desirable to understand the kinetic behaviour of the polymerization, especially in terms of kinetic constants. This work characterizes the polymerization reactions of a number of multiacrylates (having two to five acrylate groups per monomer) and multimethacrylates (having either two or three methacrylate groups per monomer) in terms of the kinetic constants for propagation and termination as well as rates of polymerization.

In general, polymerization reactions of multifunctional monomers exhibit anomalous behaviour, especially with respect to reaction kinetics. This behaviour includes autoacceleration and autodeceleration[5-9], structural heterogeneity[10-15], unequal functional-group reactivity[16-18] and a delay in volume shrinkage with respect to equilibrium[5,19,20]. Autoacceleration is nearly always observed in these systems because of the extremely restricted diffusion of radicals in the highly crosslinked polymer. In these polymers, bulk mobility of the radicals is severely hindered, leading to a diffusion-limited termination mechanism. Then, as the radical diffusivity continues to decrease, termination is reduced and the radical concentration increases, sometimes by several orders of magnitude[21-23]. The increased radical concentration leads to higher rates of polymerization, hence autoacceleration. Autodeceleration of the polymerization kinetics has also been frequently observed during polymerizations of this type, especially during polymerizations of small, high-functionality monomers. Autodeceleration occurs because the propagation reaction eventually becomes diffusion-controlled along with the termination reaction. As the mobility of the reactive functional groups is further reduced, the functional groups become less and less reactive until the reaction stops due to vitrification. During photopolymerizations, these rates of autoacceleration and autodeceleration can be controlled by the initiator concentration, incident light intensity and reaction temperature.

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Another unique attribute during polymerizations of multifunctional monomers is the dominance of reaction diffusion as a termination mechanism[24–28]. Reaction diffusion involves the diffusion of radicals by propagation through unreacted functional groups. At very early functional-group conversions (as compared to linear polymerizations), the mobility of radicals through segmental diffusion falls well below their mobility through reaction diffusion. From this point in the reaction, the termination and propagation kinetic constants are found to be proportional, and the termination kinetic constant as a function of conversion may actually exhibit a plateau region.

In addition to the kinetic behaviour, the high crosslink density of these systems leads to unique structural behaviour as well. Unlike linear polymerizations, crosslinking polymerizations produce networks with physical structures that are highly dependent on the curing conditions and essentially unalterable after the polymerization is complete because of the network insolubility. For example, most of the applications for these materials require polymerization in a mould or on-line curing of a coating, which renders the polymer in a form suitable for the application directly after polymerization. In contrast, linear polymers are soluble and can be cast and moulded to the desired shape, and the material properties correspondingly altered. Since the final structure of the crosslinked network is strongly dependent on the reaction conditions, the effects of unequal functional-group reactivity, heterogeneity and volume shrinkage on the reaction behaviour and network structure must be addressed.

When polymerizing multifunctional monomers, two different species of reactive functional groups exist, the monomeric double bond and the pendent double bond(s). At low functional-group conversions, the reactivity of the pendent double bond can be up to 50 times greater than the reactivity of the monomeric double bond[29,30]. This enhanced reactivity of the pendent double bond is mainly due to the close proximity of the pendent group to the active radical. As the pendent double bonds react, microgel regions are formed in the polymer and lead to structural heterogeneity. As the reaction proceeds, the pendent double bonds eventually become shielded in the microgel regions, and the reactivity of the monomeric double bond approaches, and in some cases surpasses, that of the pendent double bond.

Several researchers have explored the structural heterogeneity that arises from the unequal reactivity of functional groups using kinetic gelation models[15,29–32]. Recent improvements in kinetic gelation models have allowed a more realistic picture of free-radical polymerizations by incorporating species mobility, realistic initiator decay mechanisms and varying species sizes[29,30]. Then, by studying the reaction behaviour under various reaction conditions and closely simulating these conditions in the kinetic gelation model, the effects of the reaction behaviour on the network structure can be studied. This work focuses on experimentally characterizing the polymerization behaviour under different reaction conditions, while the importance of these effects on network microstructure and material properties is discussed elsewhere[30].

In addition to the complex reaction characteristics of multifunctional monomers, the physical effects of volume shrinkage/physical ageing can influence the kinetics and reaction behaviour. This coupling of the reaction kinetics and volume shrinkage has been observed experimentally as higher rates of polymerization lead to increased double-bond conversion[5,13,33,34]. As the rate of reaction is increased, the polymerizing system cannot maintain its equilibrium volume (i.e. volume shrinkage is occurring on a much slower timescale than reaction). The excess free volume enhances the mobility in the system, and higher conversions are reached in these systems as compared to equilibrium volume systems. Compared to linear polymers, volume shrinkage plays an increasingly important role in the kinetics of crosslinked network formation, particularly since these networks tend to gel at very low double-bond conversions.

Since the polymerization kinetics of multifunctional monomers are extremely important in determining the final polymeric material properties, it is imperative that the mechanism of the polymerization, as well as reasonable values for the kinetic constants of propagation and termination, over a wide range of conversion be known. This work analyses a series of non-steady-state kinetic experiments carried out at different functional-group conversions, temperatures and rates of polymerization for a variety of multifunctional monomers to provide insight and knowledge about these polymerizations.

EXPERIMENTAL

Materials

The multifunctional monomers chosen for study were a series of commercially available multiacrylates and multimethacrylates. The methacrylates included diethylene glycol dimethacrylate (DEGDMA; Polysciences Inc., Warrington, PA) and trimethylolpropane trimethacrylate (TrMPTrMA; Polysciences Inc.). The acrylates were diethylene glycol diacrylate (DEGDA; Polysciences Inc.), trimethylolpropane triacrylate (TrMPTrA; Polysciences Inc.), pentaerythritol tetraacrylate (PETeA; Polysciences Inc.) and dipentaerythritol monohydroxy pentaacrylate (DPEMHPeA; Polysciences Inc.). *Figure 1* shows the structure for each of these monomers. The photopolymerizations were initiated with 2,2-dimethoxy-2-phenylacetophenone (DMPA; Ciba Geigy, Hawthorn, NY). All chemicals were used as received.

Procedure

Reaction rate profiles were monitored with a differential scanning calorimeter equipped with a photocalorimetric accessory (Perkin–Elmer, DSC-DPA 7, Norwalk, CT). The photocalorimetric accessory included transfer optics to produce full-beam ultra-violet light of varying intensity and a monochromator to produce light of a given wavelength. To characterize the reaction kinetics, monochromatic 365 nm ultra-violet light was chosen, and neutral density filters (Melles Griot, Irvine, CA) were used to control the intensity of the incident light. The d.s.c. cell was attached to a refrigerated recirculating chiller (NESLAB, CFT-25, Newington, NH) to keep the cell cool and isothermal when reactions were performed near room temperature.

Solutions were prepared by dissolving 0.1 wt% DMPA in the appropriate monomer. To study the reaction profiles, 3–5 mg of sample were placed in an uncovered aluminium d.s.c. pan and cured with u.v. light intensities

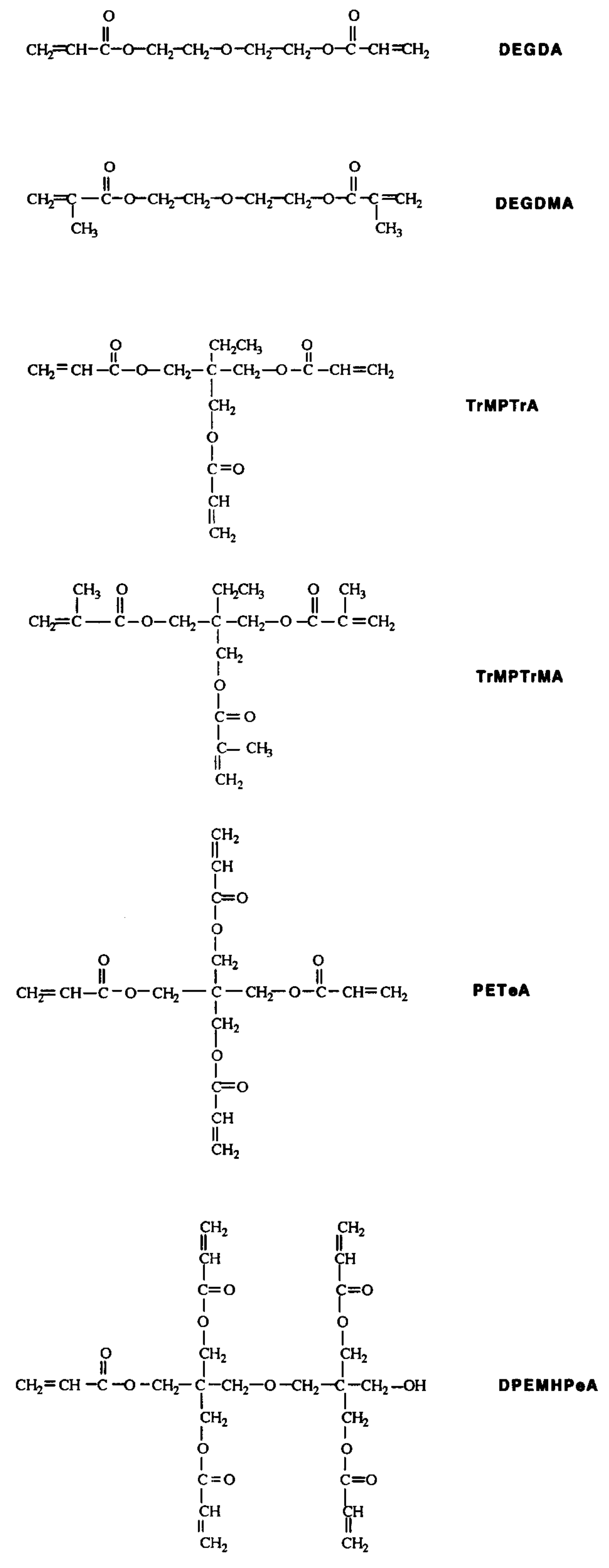

Figure 1 Structures of the multifunctional monomers studied

varying from 0.6 to 4.7 mW cm^{-2} and at various reaction temperatures. Low photoinitiator concentrations and sample masses were used to ensure the applicability of the thin-film approximation for uniform light intensity throughout the sample. Before exposing the samples to the curing light, the d.s.c. cell was flushed with nitrogen for 10 min, since oxygen is known to inhibit these reactions, and nitrogen flushing was continued during the polymerization as well.

The minimum time for nitrogen flushing prior to reaction was determined by flushing the d.s.c. cell with nitrogen for various lengths of time (1, 3, 5, 10, 15 and 30 min) prior to polymerization. When the d.s.c. cell was flushed with nitrogen for less than 10 min prior to polymerization, the reaction rate profiles had lower peak maxima, and a significant delay existed from the time the sample was exposed to the light until the polymerization began. Clearly, significant amounts of oxygen were still present and affecting the reaction behaviour. When nitrogen flushing times of 10 min and greater were used, no differences in the reaction rate profiles were observed. Therefore, 10 min was established as the minimum time to flush the oxygen from the sample cell.

The rate of polymerization was related to the heat flux monitored by the d.s.c., and the conversion as a function of time was determined from the theoretical heat evolved per double bond. For the methacrylate double bond, $\Delta H_{\mathrm{theor}} = 13.1\ \mathrm{kcal\,mol^{-1}}$, and for the acrylate double bond, $\Delta H_{\mathrm{theor}} = 20.6\ \mathrm{kcal\,mol^{-1}}$ (refs. 7, 35, 36). To determine the individual kinetic constants for propagation and termination, a previously developed technique[37,38] was used that combined a steady-state and non-steady-state analysis.

First, the polymerization rate was monitored as a function of time, and the combined kinetic constant, $k_p/k_t^{1/2}$, was determined from a steady-state analysis:

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

The rate of polymerization is represented by R_p, the molar concentration of monomer by [M], the initiator efficiency by ϕ, the incident light intensity in light quanta per area-second by I_0, the absorption coefficient of the initiator by ε and the initiator concentration by [A]. Then, by closing the shutter and stopping radical initiation at various points in the reaction, the individual kinetic constants were determined by monitoring the reaction rate in the dark and applying a non-steady-state analysis:

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

Here, t_0 is the beginning of the dark period, and t_1 is some time later in the dark reaction.

This analysis assumes that the kinetic constants are relatively constant over the time increment $(t_1 - t_0)$ where conversion changes are rather small. For example, in the polymerization of DEGDMA, less than 2% conversion occurs between the time the light is turned off and the time 30 s after the light has been turned off. Additionally, using $t_1 - t_0$ values of 20 or 30 s makes little difference to the kinetic-constant values that are determined from equation (2). Obviously the relative errors from this assumption will be worst in the areas where the kinetic constants are changing most rapidly (i.e. the beginning and end of the reaction), and in these regions the kinetic constants are approximately averages over a small conversion range (i.e. less than 2%).

In addition, equal reactivity of the double bonds is assumed. As discussed previously, the pendent double bonds can have significantly different reactivities than the monomeric double bonds, primarily due to spatial inhomogeneities, but our experimental technique is limited to determining the average propagation reactivity of all double bonds. Termination is unaffected by the pendent or monomeric nature of the double bond. Finally, no attempts were made to measure the initiator efficiency, but rather the propagation kinetic constant reported is lumped together with this efficiency. Thus, the k_p discussed is actually $f^{1/2}k_p$.

RESULTS AND DISCUSSION

A polymerization reaction rate profile of a multifunctional monomer exhibits several typical features. Many of these features are illustrated in *Figure 2* where the rate of polymerization as a function of time is plotted for two photopolymerizations of DEGDMA. These polymerizations were initiated by 4.7 and 0.6 mW cm^{-2} light from a 365 nm monochromatic source. In this figure, three distinct regions can be identified. The initial portion of the curve involves a rapid increase in rate up to a maximum of 0.004 s^{-1} (for the higher intensity) and 0.001 s^{-1} (for the lower intensity). This rapid rise leads to the formation of a shoulder in the rate of polymerization. This phenomenon has been observed by others[5,35] and recently characterized by Cook[28].

The second phase of the polymerization involves a less rapid increase in the polymerization rate and has generally been referred to as autoacceleration. During this portion of the polymerization, the mobility of the radicals is decreasing dramatically and reducing the termination rate. The decreased rate of termination leads to a large build-up in the radical concentration, thus increasing the polymerization rate. It should be noted, as has been shown elsewhere[24–28,38], that, at some point during this autoacceleration region, the termination mechanism becomes reaction-diffusion-controlled. Instead of termination occurring by radicals diffusing together by either segmental or bulk diffusion (both extremely improbable in the crosslinked network that is being formed), the radicals are mobile primarily by reacting with unreacted double bonds present in the system. Finally, the polymerization reaction attains a maximum rate and begins to decrease. This region has generally been referred to as autodeceleration where the vitrification/crosslinking restrict and eventually stop the propagation reaction. During this phase of the reaction, the rate of termination continues to decrease; however, the restriction of propagation dominates the decreasing rate.

Figure 3 illustrates the rate of polymerization as a function of the double-bond conversion for the same polymerizations illustrated in *Figure 2*. In *Figure 3*, two more distinct features of polymerizations of multifunctional monomers are illustrated. The maximum double-bond conversion that is reached increases from 0.48 for the polymerization initiated by 0.6 mW cm^{-2} to 0.56 for the polymerization initiated by 4.7 mW cm^{-2}. The increased double-bond conversion is probably caused by a delay in the volume shrinkage rate[5,13,19,33,34]. The delay in volume shrinkage leads to an increased free volume and, therefore, increased mobility in polymerizations that proceed at faster rates, i.e. those initiated by higher light intensities or higher initiator concentrations. Also apparent from *Figure 3* is the fact that the two curves are not symmetric. The asymmetry is most easily observed as the polymerizations attain a maximum rate. The lower-rate polymerization reaches a maximum rate at 13% conversion, while the higher-rate polymerization reaches a maximum rate at 21% conversion. In general, the curve at higher rates is shifted to higher conversions because of the delay in volume shrinkage. The asymmetry in these curves indicates that the kinetic constants for polymerization are functions of the double-bond conversion as well as the rate at which that double-bond conversion was reached. This fact seems to indicate that previous polymerization models, adequate for linear polymerizations, will not be applicable for polymerizations that produce highly crosslinked polymers. Models of these polymerizations will need to include the dependence of the kinetic constants on not only the double-bond conversion, but also the state of the system.

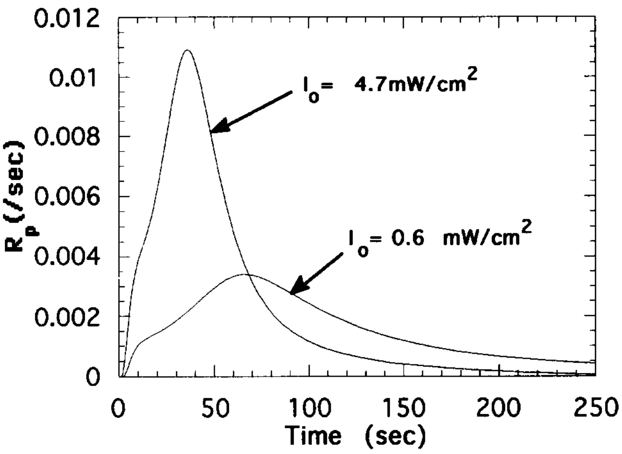

Figure 2 Rate of polymerization as a function of time for DEGDMA polymerized at two different light intensities

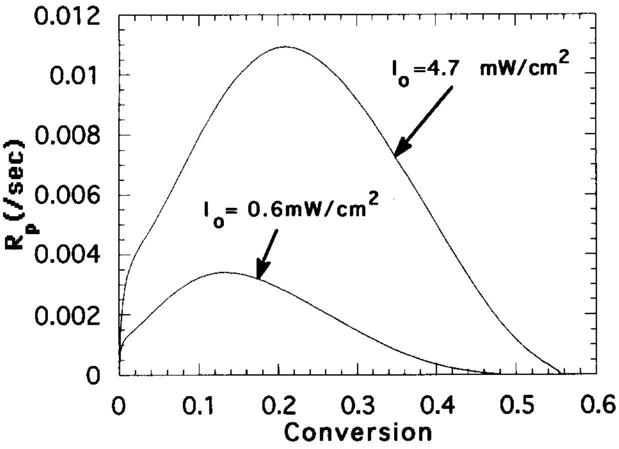

Figure 3 Rate of polymerization as a function of double-bond conversion for DEGDMA polymerized at two different light intensities

In further examining the polymerization of DEGDMA, the kinetic constants of propagation and termination for the polymerization of DEGDMA initiated by 4.7 mW cm^{-2} and 0.1 wt% initiator (DMPA) are presented in *Figures 4* and *5*. In these figures, the dependences of the kinetic constant on conversion and temperature are illustrated. The termination constant as a function of conversion exhibits several unique features, which allude to how the dominant termination mechanism changes throughout the polymerization. From 0 to 15% conversion, the termination kinetic constant decreases rapidly as termination is polymer-diffusion-controlled. Increasing double-bond conversion decreases the polymer diffusivity and, hence, the termination constant. Between

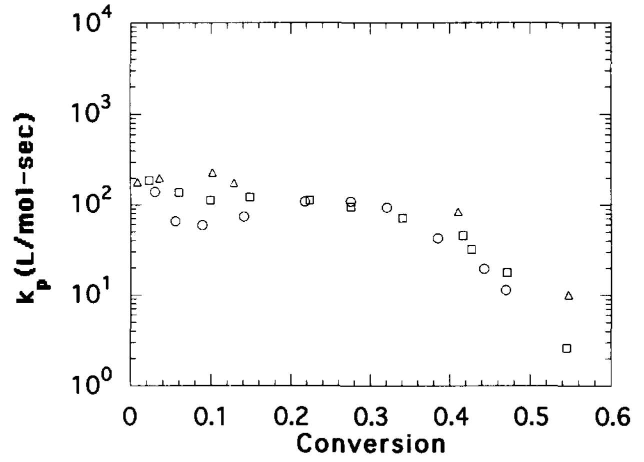

Figure 4 The propagation kinetic constant *versus* double-bond conversion for DEGDMA polymerized with 4.7 mW cm^{-2} light intensity and at different reaction temperatures: 30°C (○), 40°C (□), 50°C (△)

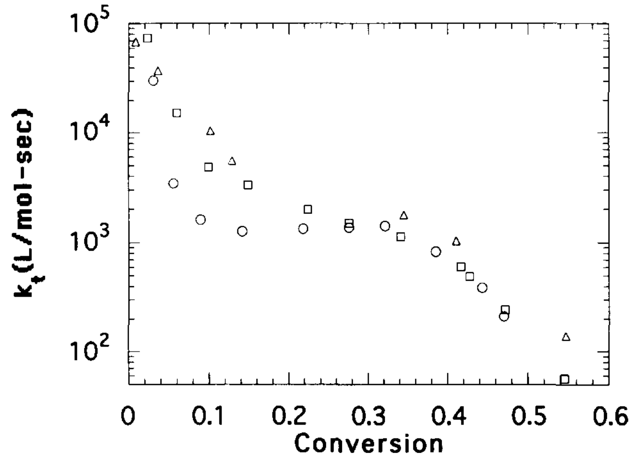

Figure 5 The termination kinetic constant *versus* double-bond conversion for DEGDMA polymerized with 4.7 mW cm^{-2} light intensity and at different reaction temperatures: 30°C (○), 40°C (□), 50°C (△)

15 and 20% conversion, the polymer diffusivity drops to the point that termination becomes reaction-diffusion-controlled, implying that radicals are more mobile through reaction with unreacted double bonds than through simple diffusion. After this point in the polymerization, termination is reaction-diffusion-controlled, and the termination kinetic constant is approximately proportional to the propagation kinetic constant. From 20% to approximately 40% conversion, the termination kinetic constant remains nearly constant since mobility of the radicals through reaction diffusion is nearly constant. At higher conversions, propagation becomes limited and the termination kinetic constant again decreases rapidly. When one examines the effect of conversion on the propagation kinetic constant, it is observed that the propagation constant is nearly constant until the same 40% conversion at which termination decreases (for the second time). The propagation reaction is initially reaction-controlled, but near 40% conversion the methacrylate mobility is reduced to the point that propagation becomes diffusion-controlled.

The effects of temperature on the polymerization rate constants are also illustrated in *Figures 4* and *5* as kinetic constants measured at 30, 40 and 60°C are presented. These results indicate that there is only a slight increase in both propagation and termination as temperature is increased. The most pronounced effect of temperature is observed during the diffusion-controlled region of termination. This fact indicates that the activation energy for this type of diffusion is higher than the other relevant activation energies during the polymerization. One also notices a shift in the plateau region to higher conversions as the reaction temperature is increased. The higher temperatures sufficiently increase the segmental mobility of the system, so termination by segmental diffusion dominates the reaction diffusion mechanism for a greater portion of the initial region.

Figure 6 shows the kinetic constants for propagation and termination for TrMPTrMA, a trimethacrylate monomer, as a function of conversion. These kinetic constants were determined under similar reaction conditions as those for DEGDMA, but with 0.6 mW cm^{-2} of incident light intensity to slow the polymerization rate. Similar behaviour is observed for TrMPTrMA as for DEGDMA; however, certain differences are apparent. First, the initial kinetic constant for termination is significantly lower than for the DEGDMA, although the propagation kinetic constant is similar. This behaviour is related to the higher viscosity and greater diffusion limitations of the polymer radicals in TrMPTrMA as compared to DEGDMA. A further difference is seen in the much shorter plateau region (for termination) and the earlier decrease in propagation, which both begin near 10% conversion as opposed to 40% conversion for the dimethacrylate. This difference is attributed to the additional functional group of the trimethacrylate, which leads to a more highly crosslinked polymer at the same double-bond conversion. The higher crosslink density reduces the diffusivity of both polymer and monomer species.

In addition to characterizing the behaviour of multimethacrylates, this work has focused on the polymerization behaviour of multiacrylates as well. The differences between these types of monomers are illustrated in *Figure 7* where the polymerization rate as a function of time is plotted for both a dimethacrylate and a diacrylate. For both monomers, the polymerizations proceed quite rapidly; however, the acrylate group is more reactive as illustrated by the rate maximum for the diacrylate being over 400% greater than the rate

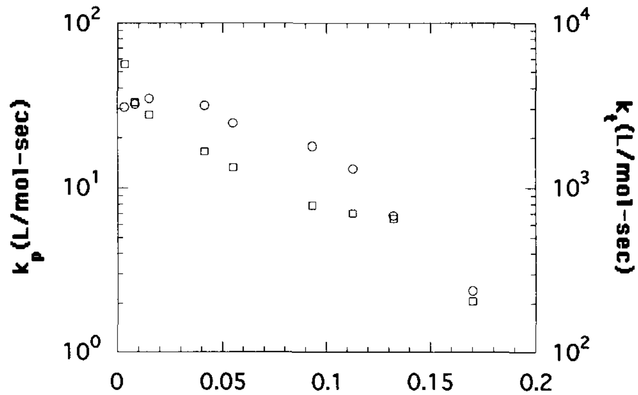

Figure 6 The propagation kinetic constant (○) and the termination kinetic constant (□), as a function of double-bond conversion for TrMPTrMA polymerized at 30°C and with 0.6 mW cm^{-2} light intensity

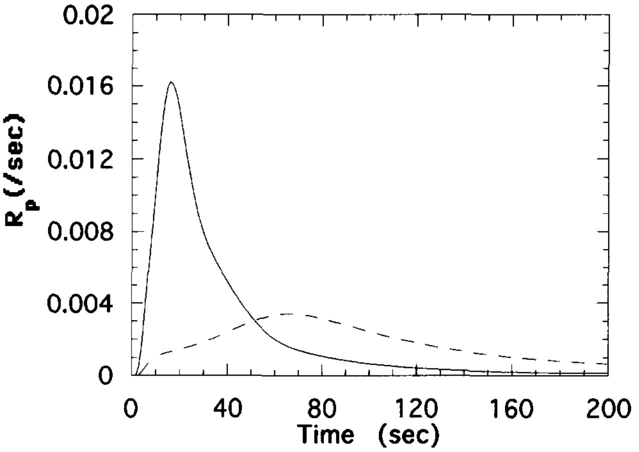

Figure 7 The rate of polymerization as a function of time for DEGDMA (– – – –) and DEGDA (———) at 30°C and with 0.6 mW cm^{-2} light intensity

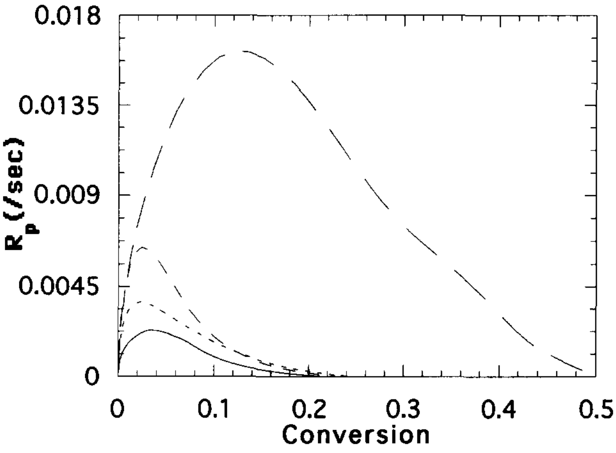

Figure 8 The rate of polymerization *versus* double-bond conversion for DEGDA (———), TrMPTrA (— — —), PETeA (– – – – –) and DPEMHPeA (———) at 30°C and with 0.6 mW cm^{-2} light intensity

maximum for the dimethacrylate. In addition, the diacrylate polymer reaches a higher maximum double-bond conversion than the dimethacrylate (0.51 vs. 0.48). The differences between the two polymerizations are attributed to the increased reactivity of the acrylate groups as well as the increased stiffness of the methacrylate polymers.

Figures 8–10 compare the polymerization behaviour and kinetic constants for a series of multiacrylates ranging from a diacrylate through a tri-, tetra- and pentaacrylate. *Figure 8* illustrates the rate of polymerization as a function of the overall double-bond conversion for each of these monomers. All of these polymerizations were performed under identical conditions of light intensity, initiator concentration and temperature (0.6 mW cm^{-2}, 0.1 wt% and 30°C); however, the diacrylate reacts more than twice as rapidly as any of the other monomers. The high rate of polymerization for the diacrylate is related to the low viscosity of DEGDA monomer when compared with the higher-functionality monomers. Also, for the higher-functionality monomers, propagation becomes diffusion-limited at much earlier conversions, as evidenced by the very low conversion at which the rate maximum is attained (2–3% double-bond conversion for all but the diacrylate). For all of these monomers, increasing the number of functional groups decreases the average reactivity of those functional groups when comparing monomers at identical double-bond conversions. In addition, the maximum conversion increases as the functionality is decreased. The maximum conversion, rate maximum, conversion at the rate maximum and the average number of double bonds reacted per monomer for all of the monomers studied are provided in *Table 1*. From the data in *Table 1*, it is interesting to note that, for all of the monomers except the hexafunctional monomers (the triacrylate and trimethacrylate), the average number of double bonds reacted per monomer is approximately unity.

Finally, *Figures 9* and *10* present kinetic constants for propagation and termination for the series of multiacrylates studied. It is obvious from the data that both termination and propagation kinetic constants, including those at very low conversions, decrease as the functionality of the monomer is increased. This behaviour is caused primarily by the increased viscosity from the increased molecular weight introduced by the higher functionality. Only for DEGDA is a significant plateau observed in either the termination or propagation kinetic constant. However, if the ratio of the propagation to the termination kinetic constant is examined, that ratio becomes a constant for each of these monomers. In addition, this constant was found to be independent of

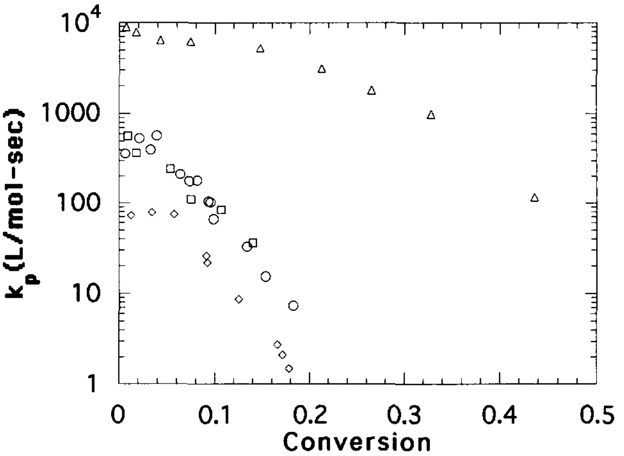

Figure 9 The propagation kinetic constant as a function of double-bond conversion at 30°C and 0.6 mW cm^{-2} light intensity for DEGDA (△), TrMPTrA (□), PETeA (○) and DPEMHPeA (◇)

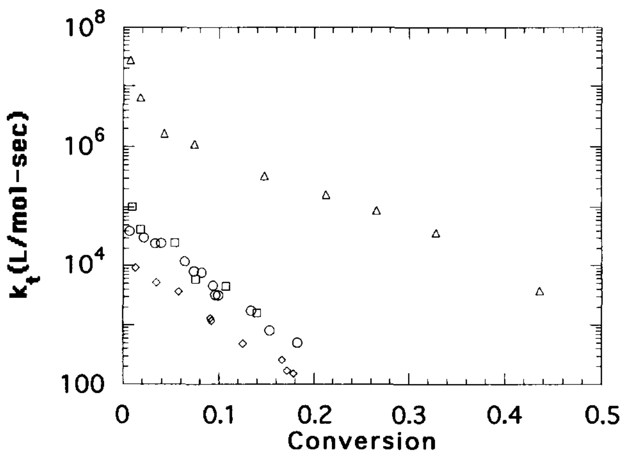

Figure 10 The termination kinetic constant as a function of double-bond conversion at 30°C and 0.6 mW cm^{-2} light intensity for DEGDA (△), TrMPTrA (□), PETeA (○) and DPEMHPeA (◇)

Table 1 Summary of various reaction parameters for the monomers studied

Monomer	X_{max}	Double bonds reacted per monomer	k_{p0} ($l\,mol^{-1}\,s^{-1}$)	k_{t0} ($l\,mol^{-1}\,s^{-1}$)	$R_{p,max}$ (s^{-1})	X at $R_{p,max}$
DEGDMA	0.48	0.96	400	5×10^5	0.0034	0.13
TrMPTrMA	0.19	0.57	40	5×10^3	0.0014	0.025
DEGDA	0.51	1.02	8000	5×10^7	0.0162	0.12
TrMPTrA	0.24	0.72	400	5×10^5	0.0065	0.022
PETeA	0.23	0.92	400	5×10^4	0.0037	0.024
DPEMHPeA	0.21	1.05	100	2×10^4	0.0023	0.035

the monomer structure, degree of functionality and double-bond conversion (after the initial portion of the reaction). This proportional behaviour in the propagation and termination kinetic constants further supports the importance of reaction diffusion and is expanded on in greater detail elsewhere[38].

In considering the type of functionality (i.e. methacrylate *versus* acrylate), a comparison of the kinetic constants for propagation and termination is also possible by comparing the data for DEGDA in *Figures 9* and *10* with the data for DEGDMA in *Figures 4* and *5* or with the data for TrMPTrMA in *Figure 6*. From the data for DEGDA, similar trends are observed in the dominating mechanisms for termination and propagation; however, unlike DEGDMA, DEGDA becomes reaction-diffusion-dominated at very early conversions around 15%. In the case of the trimethacrylate (*Figure 6*), the reason for early domination of reaction diffusion is the severely restricted mobility of the polymer radicals, allowing them to move only through propagation. In the case of DEGDA, it is the extremely rapid propagation that leads to the early reaction diffusion control of termination. The propagation kinetic constant for DEGDA is initially nearly three orders of magnitude greater than that for the trimethacrylate and nearly two orders of magnitude greater than that for DEGDMA. The termination constant is also significantly different for the diacrylate when compared to the dimethacrylate and trimethacrylate. Like propagation, there is a two order of magnitude increase with respect to the dimethacrylate and a three order of magnitude increase with respect to the trimethacrylate for the termination kinetic constant. The fact that the increase is approximately the same alludes to the importance of reaction diffusion at early stages of the reaction, leading to a near-proportionality between termination and propagation kinetic constants.

CONCLUSIONS

This work has characterized the polymerization of multifunctional monomers with respect to rates of polymerization, maximum attainable conversions and kinetic constants for propagation and termination. The effects of number of functional groups and type of functional groups has been explored by studying a dimethacrylate and a trimethacrylate as well as a series of acrylates including a di-, tri-, tetra- and pentaacrylate. The results of this work illustrate the dramatic difference between polymerizations of multifunctional monomers as compared to difunctional monomers. Polymerization results showed a dramatic increase in the maximum attainable double-bond conversion as polymerization rate was increased and the dominance of reaction diffusion termination at early stages of the polymerization. The importance of reaction diffusion was clearly seen as the termination kinetic constant became proportional to the propagation kinetic constant at early conversions and exhibited a long plateau region in which the termination rate was nearly constant. Comparisons of methacrylates and acrylates indicated a several order of magnitude increase in termination and propagation kinetic constants when comparing nearly identical monomers (e.g. comparing DEGDMA to DEGDA). Finally, the characterization of the multiacrylate series indicated that higher-functionality monomers were less reactive than lower-functionality monomers because of their increased viscosities caused by higher molecular weights. It was found for all monomers except the triacrylate and trimethacrylate that the average number of double bonds reacted per monomer (at the maximum conversion) was approximately unity, independent of the type or number of functional groups.

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