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Effects of Composition and Reactivity on the Reaction Kinetics of Dimethacrylate/Dimethacrylate Copolymerizations

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ABSTRACT: The bis-GMA (2,2-bis[4-(2-hydroxy-3-methacryloyloxypropoxy)phenyl]propane) and TEGDMA (triethylene glycol dimethacrylate) copolymerization has been often used as the organic phase of dental composites and is a good example of a dimethacrylate/dimethacrylate polymerization involving a viscous monomer and a reactive diluent. This work focuses on the kinetic behavior of this monomer system and the effect of monomer structure, viscosity, and comonomer concentration on the mobility and reactivity of the evolving network. Unsteady-state polymerizations were performed using various compositions of bis-GMA/TEGDMA to obtain the kinetic parameters as a function of double-bond conversion. Furthermore, TEGDMA and bis-GMA were hydrogenated, i.e., the double bonds were saturated, and utilized to study the effect of each reactive component on the copolymerization. The results suggest that reaction diffusion-controlled termination dominates as the reaction progresses and that bis-GMA plays a more controlling role in the kinetics than TEGDMA. In addition, the hydrogenated monomers were used to determine the effect of viscosity on the homopolymerization of dimethacrylates. It was shown that the addition of a solvent, i.e., hydrogenated TEGDMA, to the bis-GMA system had a more pronounced effect on the polymerization kinetics than TEGDMA polymerized in the presence of viscous hydrogenated bis-GMA. The difference in the kinetic behavior was attributed to the relative mobilities of each monomer.

Introduction

Within the dental materials industry, dimethacrylate copolymers incorporating bis-GMA (2,2-bis[4-(2-hydroxymethacryloyloxypropoxy)phenyl]propane) are often used as the organic phase of dental restorative materials because of their high strength and hardness. However, due to the high viscosity of the monomer and low final conversion of homopolymerized bis-GMA, a reactive diluent, such as TEGDMA (triethylene glycol dimethacrylate), is often added to improve the viscosity, reactivity, and final conversion of these materials. Though bis-GMA-based copolymers have been used and studied as dental restorative materials since the 1960s, many problems still exist with these materials. In addition to polymerization shrinkage upon cure and water uptake upon exposure to the oral environment, the material exhibits low final double-bond conversions (55−75%)[1−3] upon exposure to ultraviolet or visible light. In addition, researchers have found that up to 6% residual monomer remains in a bis-GMA/TEGDMA system after curing.[4] This unreacted monomer could be extractable and leach into the body where various fates are possible. For example, a recent study found that the release of TEGDMA from resin composites stimulated the growth of bacteria around the restoration.[5] Furthermore, any unreacted monomer that remains in the restoration may act as a plasticizer and decrease the mechanical properties of the system when compared to a fully cured specimen.

Recent research has focused on varying experimental factors, such as light intensity, initiator concentration, and polymerization temperature, to improve the final conversion, mechanical properties, and curing rate of bis-GMA-based copolymers. This work, however, will focus on obtaining a greater understanding of the underlying mechanisms of the copolymerization by quantifying the kinetic parameters as a function of conversion. The discussion of the kinetic behavior of this copolymerizing system will focus on the effects of monomer structure, viscosity, and comonomer concentration on the mobility and reactivity of the evolving network.

Furthermore, this work will provide valuable insight into the kinetic behavior of viscous dimethacrylates and how the kinetic behavior changes with the addition of a reactive diluent. Many industrial applications utilize the addition of less viscous comonomers to improve the final conversion of viscous multi(meth)acrylates,[1−4] but little research has been done to understand the kinetic behavior of these complex, diffusion-controlled systems. The viscosity of the initial monomer mixture and the chemical structure of the monomers involved are both important variables in the kinetic behavior of these copolymerizations. However, it is difficult to separate these two effects in a typical polymerization. Therefore, this work will attempt to discern between the effects of monomer structure and viscosity by using a procedure that saturates the double bonds of each comonomer to give an unreactive product. By using an unreactive species as the second component in the system, one can study the reactivity of each monomer in a medium that mimics the initial viscosity of the typical comonomer system.

Background

Homopolymerizations of dimethacrylates have been studied in much detail. These multifunctional systems have been shown to exhibit complex features such as

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autoacceleration and autodeceleration,[6,7] limiting double-bond conversion,[6,8−10] a reaction diffusion-controlled termination mechanism,[11−15] and kinetic parameters that are a function of the rate of polymerization.[6,16] These polymerizations exhibit complex kinetics due to the fact that the mobility of the reacting medium varies as the polymerization proceeds. At very low conversions, propagation and termination are chemically controlled. However, as the network forms, segmental movements of the radicals are restricted, and termination becomes diffusion-limited. A decrease in the termination rate leads to an increase in the population of radicals and a corresponding increase in the propagation rate. This elevation of the rate has been termed autoacceleration and commonly occurs in dimethacrylate systems. As the system continues to react, the environment becomes even more restricted, and the propagation reaction also becomes diffusion-controlled. The rate then drops off substantially since both propagation and termination are diffusion-limited. This decline in rate has been called the autodeceleration effect. The diffusion-controlled kinetics of these polymerizations lead to double-bond conversions less than unity, especially in glassy systems, and kinetic rate parameters that are a function of conversion.[6,16]

Furthermore, Anseth et al.[15] have shown that reaction diffusion-controlled termination dominates throughout most of the polymerization (beginning as early as 5% conversion) for multifunctional acrylates and methacrylates. Reaction diffusion occurs when the radicals, in a restricted environment, are unable to segmentally move toward each other. Instead, the radicals propagate through unreacted monomer and pendant double bonds in order to diffuse toward each other and terminate. This mode of termination is labeled reaction diffusion-controlled termination, and within this regime, the propagation, k_p, and termination, k_t, kinetic constants are unchanging and related to each other through a reaction diffusion constant, R:

$$k_t = Rk_p[M] \tag{1}$$

where [M] is the concentration of double bonds. For a wide variety of multiethylene glycol dimethacrylate homopolymerzaions, the proportionality constant, R, has been determined to be a value between 2 and 3.[17]

Other researchers have also studied homopolymerizations of multimethacrylates and found that solvent concentration, cross-linking density, and monomer structure all have significant effects on the kinetics. Scranton et al.[18] found that the time before the onset of autoacceleration increased and the maximum rate decreased as the solvent concentration or pendant chain length was increased. However, the addition of even a small amount of dimethacrylate cross-linking agent to a monomethacrylate polymerization caused an increase in the autoacceleration effect. All of these observations were explained in the context of the mobility of the growing radical chains. Increasing solvent and pendant chain length increases the mobility of the reacting media whereas the addition of a cross-linking agent to the system decreases the mobility of the growing chains.

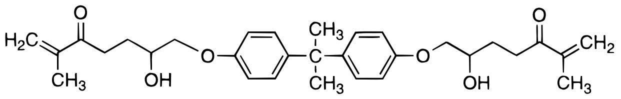
Okay and co-workers [19,20] have also published a series of works in which they investigated the effect of cross-linker (ethylene glycol dimethacrylate, EGDMA) concentration on the polymerization of methyl methacrylate and explained their results in terms of cyclization. Cyclization is a characteristic feature of free-radical cross-linking polymerizations and can be divided into two areas: primary cyclization in which the macroradical attacks the pendent double bonds in the same chain and secondary cyclization in which the radical attacks double bonds pendant on other chains already incorporated in the network. They showed that cyclization has two competing effects on the termination rate of polymer radicals in a system containing up to 4 mol % cross-linker.[19] For one, it decreases the coil size of macroradicals and therefore increases the rate of termination. However, the cross-links, which form inside the macroradical coil, tend to decrease the mobility of the segments and decrease the termination rate. At higher EGDMA concentrations (up to 75 mol %), they reported an increase in cyclization which leads to the formation of compact “primary particles” which limit access of the radical centers and pendant vinyl groups to other polymer molecules.[20] As a result, the diffusion-controlled termination rate constants decrease with increasing cross-linker concentration.

In addition, Cook[7] has studied the effect of monomer structure on the kinetics of dimethacrylates by utilizing a series of bisphenol A based dimethacrylate monomers in which the spacer group flexibility between the phenyl ring core and the methacrylate functional group was increased by the addition of ethylene glycol groups. In general, he found that the maximum conversion increased as the spacer group flexibility increased. However, bis-GMA did not follow this trend, and the extent of cure was generally lower than the identical monomer which did not contain a hydroxyl group (diethoxylated bisphenol A dimethacrylate). This behavior was explained by the hydrogen bonding in the bis-GMA network which reduces the mobility of the bis-GMA backbone and hence the final conversion.

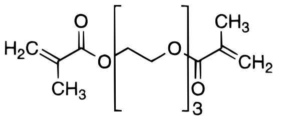
Homopolymerizations of dimethacrylates and polymerizations of methacrylates with a dimethacrylate cross-linker have been studied extensively, and much work has been published on the diffusion-controlled kinetics of these systems; however, less research has been done to understand the complex kinetics of highly cross-linked, dimethacrylate copolymer systems such as bis-GMA and TEGDMA. Since bis-GMA has a far greater viscosity than TEGDMA and a chemical structure with a stiff central core and hydroxyl groups in the backbone, the relative concentration of each monomer can have a marked effect on the mobility and hence kinetics of the reaction. Other researchers have investigated the effects of temperature, composition, and initiator concentration on the cure behavior of bis-GMA based dental resins and composites.[3,4,21−26] However, efforts need to be made to apply the extensive knowledge of the diffusion-controlled kinetic behavior of dimethacrylates to bis-GMA based copolymer systems.

Experimental Section

Materials and Methods. As shown in Figure 1, two monomers, 2,2-bis[4-(2-hydroxymethacryloyloxypropoxy)phenyl]-propane (bis-GMA, Cook Composites and Polymers, Kansas City, MO) and triethylene glycol dimethacrylate (TEGDMA, Polysciences Inc., Warrington, PA), were used for these experiments. The heat released from the polymerization was monitored on a photodifferential scanning calorimeter (Perkin-Elmer, DSC, Norwalk, CT) with a refrigerated recirculating chiller to facilitate isothermal reactions at 25 °C (NESLAB, RTE-111, Newington, NH). A photocalorimetric accessory capable of producing 365 nm monochromatic light (Perkin-Elmer, DPA 7, Norwalk, CT) was employed as a light source



(a) 2,2-bis(4-(2-hydroxy-3-methacryloxyprop-1-oxy)propane (bis-GMA)



(b) triethyleneglycol dimethacrylate (TEGDMA)

Figure 1. Monomer structure of bis-GMA (a) and TEGDMA (b).

for these experiments. The light intensity ranged from 2.5 to 4 mW/cm^2. Furthermore, the initiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorn, NY, 0.036 wt %), was used instead of the visible light initiating system of camphorquinone and a tertiary amine to simplify the initiation step of the polymerization. In addition, all the samples were purged with nitrogen for 10 min before cure as well as throughout the reaction to ensure that oxygen did not inhibit the polymerization. Finally, to ensure that the thin-film approximation for uniform light intensity throughout the sample was valid, the sample size was maintained between 1 and 2 mg.

The exothermic heat flux obtained from the DSC was transformed into the rate of polymerization by using the heat of reaction per methacrylate double bond (13.1 kcal/mol).[7] The rate versus time data were then numerically integrated to give the polymerization rate as a function of double-bond conversion. To aid in comparing the various compositions, the rate of polymerization was normalized by the initial double-bond concentration and reported in units of inverse time.

Determination of the Kinetic Parameters. To obtain the kinetic parameters as a function of double-bond conversion, a series of unsteady-state experiments were performed. The light was extinguished at a given time, but the polymerization rate was still monitored on the DSC even after extinguishing the light. The decrease in rate over time after the light was removed was used to obtain a value for R, the reaction diffusion parameter (the ratio of the termination kinetic constant to the propagation kinetic constant times the double-bond concentration). A value for R, combined with an expression for the steady-state rate of polymerization just before the light was extinguished, was then used to decouple the kinetic parameters. The details of this analysis have been previously published by others[15,17] and will not be discussed further here. However, it is important to note that some assumptions were made in the analysis of the kinetic parameters. For one, the efficiency of the initiator, ϕ, was assumed to be one. Therefore, all of the propagation (k_p) and termination (k_t) kinetic constants reported are actually $k_p\phi$ and $k_t\phi$, respectively. The actual values of propagation kinetic constants may be lower than reported. Furthermore, the pseudo-steady-state assumption was applied on the radical concentration in the calculation of the kinetic parameters. It is also worth noting that even though four types of propagation reactions are possible (bis-GMA or TEGDMA monomer adding to either the bis-GMA or TEGDMA radical), we have assumed that all combinations are equally reactive. Similarly, the various termination reactions were also assumed to have the same reactivity. Therefore, the reported k_p and k_t values are average values for the kinetic parameters.

By performing a series of unsteady-state runs with increasing light exposure times, one is able to monitor the kinetic parameters over a wide range of conversions. To monitor the effect of composition on the kinetic parameters, partial cures were performed on samples that ranged from 100 wt % bis-GMA to 100 wt % TEGDMA in 25 wt % increments of TEGDMA.

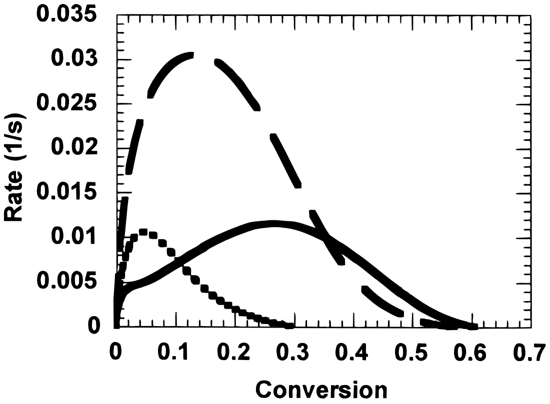


Figure 2. Example of full cure polymerizations of TEGDMA (—), bis-GMA(···), and 50/50 bis-GMA/TEGDMA (- - -) performed at 25 °C and 3 mW/cm^2.

Saturation of Double Bonds. The procedure for hydrogenation of dimethacrylates has been used previously to obtain FTIR calibration curves for calculation of degree of conversion.[27] The selective reduction of the methacrylate C=C bonds provides materials that are almost identical structurally to the monomers but are not polymerizable. A solution of 2 g of monomer was combined with 100 mL of ethyl acetate and 1 g of 3% Pd on activated carbon. Within an enclosed hydrogen atmosphere, the reaction was complete within 6−8 h. The hydrogenated product was isolated by filtration through Celite and evaporation of the solvent under reduced pressure. Finally, the material was washed with a small amount of methylene chloride and then refiltered to ensure removal of all the activated carbon. The reaction products were verified by FTIR and NMR analysis.

DSC Experiments Using Hydrogenated Species. Hydrogenated bis-GMA was combined with untreated TEGDMA in mixtures of 25, 50, and 75 wt % TEGDMA. Hydrogenated TEGDMA was mixed with untreated bis-GMA in the same manner. DMPA was used as the UV initiator at a concentration of 0.036 wt %. A randomized factorial experimental design was employed to monitor the effect of the hydrogenated comonomer on the polymerization of bis-GMA/TEGDMA. By using a randomized factorial design, one can analyze the results using analysis of variance. Analysis of variance, or ANOVA, is a powerful statistical tool, which allows one to separate the variation observed into assignable and random causes. If the variation can be attributed to an assignable cause within a 95% confidence limit, the variable is said to have a significant effect on the results.[28] Furthermore, unsteady-state experiments were performed as previously described to obtain the kinetic parameters as a function of double-bond conversion.

Results and Discussion

Representative DSC Results. Figure 2 illustrates the characteristic behavior of TEGDMA, bis-GMA, and 50/50 TEGDMA/bis-GMA photopolymerizations. The dramatic increase in rate in the early stages of all three polymerizations is attributed to diffusion limitations to termination, which is termed the autoacceleration effect. As the reaction progresses and the system becomes more cross-linked, the mobility of the radicals continues to decrease, and the propagation step of the reaction also becomes diffusion-controlled. Diffusion limitations to propagation lead to a decline in the rate, and autodeceleration is observed. Finally, because of vitrification and additional cross-linking, the radicals become quite immobile, and the rate eventually tapers off to zero, leaving residual unreacted monomer and double bonds. Therefore, diffusion limitations to propagation are usually responsible for the apparent end of the polymeri-

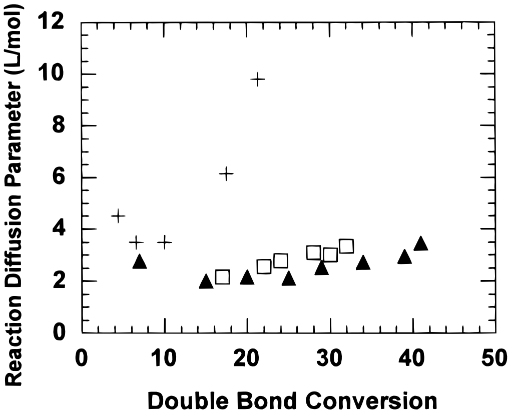


Figure 3. Reaction diffusion parameters for bis-GMA (+), 75/25 bis-GMA/TEGDMA (□), and 50/50 bis-GMA/TEGDMA (▲) polymerized at 25 °C and 3.5 mW/cm^2 light intensity.

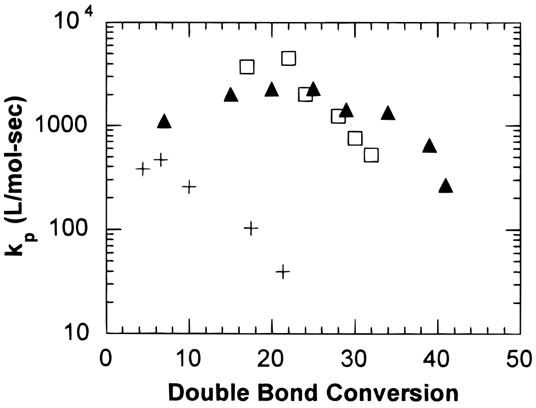


Figure 4. Propagation kinetic constant, k_p, as a function of conversion for bis-GMA (+), 75/25 bis-GMA/TEGDMA (□), and 50/50 bis-GMA/TEGDMA (▲) polymerized at 25 °C and 3.5 mW/cm^2 light intensity.

zation instead of complete reaction of double bonds. This type of behavior has been reported for many multiethylene glycol dimethacrylate systems (MEGDMA),[17] and the polymerization of TEGDMA shown here is quite similar to those results. When TEGDMA is polymerized, the maximum rate is low ($\approx$0.01 s^{-1}) and occurs at approximately 25% conversion. The polymerization of bis-GMA shows an immediate autoacceleration region, caused in this case by the extremely hindered reaction environment, and the maximum rate ($\approx$0.01 s^{-1}) occurs before 6% of the double bonds are reacted. Interestingly, if one combines the two in an equal weight mixture, there is a dramatic increase in rate ($>$0.03 s^{-1}), and the final conversion mimics that obtained by TEGDMA alone. This behavior suggests that bis-GMA is a highly reactive monomer when it is used in conjunction with a reactive diluent such as TEGDMA. TEGDMA increases the mobility of the system, thereby allowing the material to reach a much higher double-bond conversion.

Copolymerization Kinetics. In addition to probing the full cure behavior of polymer systems, one can utilize differential scanning calorimetry to learn more about the polymerization mechanism and reaction kinetics. As discussed in the experimental methods section, unsteady-state reactions were performed to obtain the reaction diffusion and kinetic rate constants for various copolymer compositions as a function of conversion. Figures 3, 4, and 5 give the reaction diffusion parameter (R), propagation kinetic constant (k_p), and termination kinetic constant (k_t) for copolymer systems of 50 wt % or greater bis-GMA. These formulations are similar to what would be seen clinically since relatively large concentrations of bis-GMA are needed to maintain the desired mechanical properties.

Figure 3 illustrates that reaction diffusion-controlled termination plays a dominant role in the kinetics of copolymer mixtures, which contain high amounts of viscous dimethacrylate. For mixtures with 50−75 wt % bis-GMA the reaction diffusion parameter remained between 2 and 4 for the entire conversion range studied (5−40%). In previous work,[17] it has also been shown that the reaction diffusion parameter drops to a constant value (2−3 for MEGDMA) as the reaction progresses. However, an initial decline in the reaction diffusion parameter was reported in which segmental diffusion of the polymer chains was the predominant route for termination to occur. No such decline is evident in mixtures with 50 wt % or greater bis-GMA, suggesting that termination, even at low double-bond conversions, is reaction diffusion-controlled.

It is interesting to note that the reaction diffusion parameter for pure bis-GMA exhibits a noticeable increase as the reaction progresses and has a higher value than the other mixtures shown in Figure 3. The homopolymerization of bis-GMA is quite unusual since the high viscosity of the material greatly hinders the mobility of the reacting chains and limits the final conversion to less than 30%. The restricted mobility of the forming network may allow for another mode of termination to dominate, especially at the end of the polymerization. The kinetic analysis supports this claim since the regression fit to the unsteady-state polymerization for the reaction diffusion parameter deviates from linearity at 20% conversion. However, more studies need to be conducted to determine what mode of termination is dominant.

The kinetics of copolymerized dimethacrylates are similar to other homopolymerizations that have been studied.[17] At the beginning of the polymerization, the propagation mechanism is not diffusion-controlled, but chemically controlled, so the value of k_p remains relatively constant. However, as the polymerization progresses and a cross-linked network forms, the propagation kinetic constant becomes diffusion-controlled and drops off by an order of magnitude or more over a fairly small change in conversion. The decline in the propagation kinetic constant causes a decrease in the termination kinetic constant as well. Eventually, the values become so small that no further increase in the conversion can be measured, although a significant amount of unreacted double bonds still remains in the system. For a typical dimethacrylate polymerization,[17] the termination kinetic constant, k_t, initially decreases because termination is limited by the rate at which the polymer segments diffuse together. However, as the polymerization progresses, reaction diffusion becomes the dominant termination mechanism and the value of k_t plateaus. Then, k_t drops off as the propagation kinetic constant decreases.

The propagation and termination kinetic constants shown in Figures 4 and 5 exhibit unique trends as the amount of reactive diluent (TEGDMA) in the mixture is increased. The high initial viscosity of pure bis-GMA suppresses the kinetic parameters by an order of magnitude even at low conversions. Furthermore, k_p declines rapidly after only 10% conversion for pure bis-

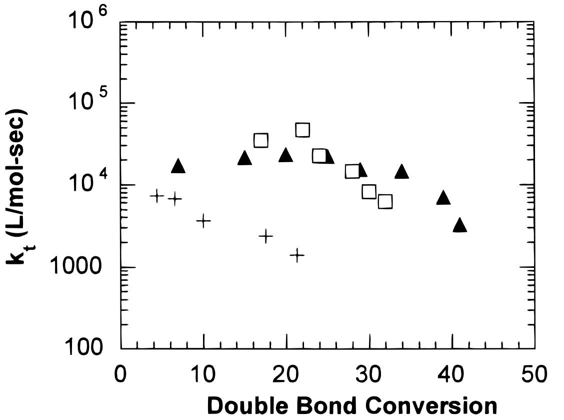


Figure 5. Termination kinetic constant, k_t, as a function of conversion for bis-GMA (+), 75/25 bis-GMA/TEGDMA (□), and 50/50 bis-GMA/TEGDMA (▲) polymerized at 25 °C and 3.5 mW/cm^2 light intensity.

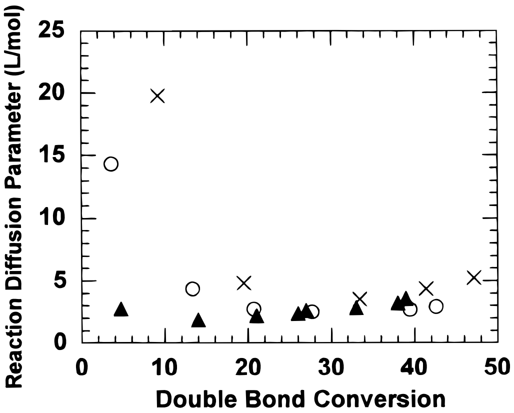


Figure 6. Reaction diffusion parameters for TEGDMA (×), 25/75 bis-GMA/TEGDMA (○), and 50/50 bis-GMA/TEGDMA (▲) polymerized at 25 °C and 2.5 mW/cm^2 light intensity.

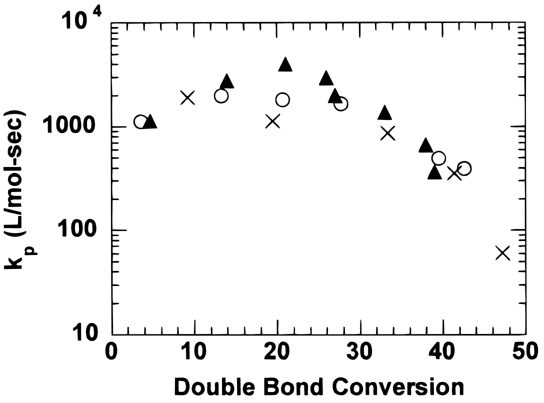


Figure 7. Propagation kinetic constant, k_p, as a function of conversion for TEGDMA (×), 25/75 bis-GMA/TEGDMA (○), and 50/50 bis-GMA/TEGDMA (▲) polymerized at 25 °C and 2.5 mW/cm^2 light intensity.

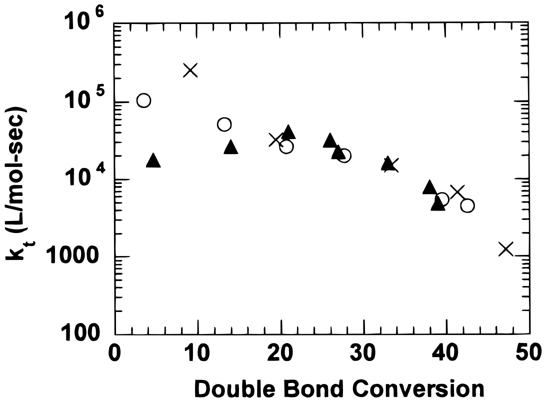


Figure 8. Termination kinetic constant, k_t, as a function of conversion for TEGDMA (×), 25/75 bis-GMA/TEGDMA (○), and 50/50 bis-GMA/TEGDMA (▲) polymerized at 25 °C and 2.5 mW/cm^2 light intensity.

GMA, but adding TEGDMA to the system shifts the diffusion control of propagation to longer reaction times (higher conversions). The addition of a less viscous dimethacrylate allows for greater mobility of the monomer molecules and delays the onset of diffusion-controlled propagation. Furthermore, the presence of TEGDMA spurs the reaction on at later conversions, allowing for increased double-bond conversion. In addition, all of the mixtures with 50 wt % or less TEGDMA do not exhibit elevated k_t values at the beginning of the reaction which supports the conclusion that reaction diffusion-controlled termination dominates over the entire course of the polymerization.

To investigate the copolymerization mechanism completely, mixtures with a high concentration of the reactive diluent were also prepared. These compositions are less important from an applications standpoint but illustrate how the kinetics change as the mobility of the reacting system is increased. Figure 6 gives the reaction diffusion parameter (R) as a function of conversion for mixtures with 50 wt %−100 wt % TEGDMA. Similar to Figure 3, the reaction diffusion parameter falls to the constant value of 2−4 for all comonomer mixtures studied. However, the samples with high amounts of TEGDMA are unique since an initial region exists where reaction diffusion-controlled termination is not dominating. The elevated R values at the beginning of the reaction for mixtures with more than 75 wt % TEGDMA suggest termination through segmental diffusion. This result is expected since TEGDMA has a low viscosity that leads to a less hindered reaction environment. Furthermore, TEGDMA lacks the stiff central core and strong intermolecular hydrogen bonding present in bis-GMA, so it forms a less sterically hindered network. A more mobile reaction environment promotes segmental movement of the macroradicals for a longer time during the polymerization. However, as the cross-linked network forms, diffusion limitations suppress macroradical movement and promote reaction diffusion-controlled termination in all the dimethacrylate mixtures studied.

The onset of reaction diffusion-controlled termination is accelerated even when only 25 wt % bis-GMA is present. As shown in Figure 6, pure TEGDMA terminates predominately through segmental diffusion of the macroradicals up to 20% conversion. However, the addition of 25 wt % bis-GMA hinders segmental termination and causes the predominate mode of termination to shift to reaction diffusion at earlier conversions (approximately 10%).

Figures 7 and 8 give the propagation (k_p) and termination (k_t) kinetic constants as a function of conversion for mixtures containing 50 wt % or greater TEGDMA. Even though the mode of termination is affected by the concentration of bis-GMA in the initial mixture, Figure 7 suggests that the propagation mechanism is relatively insensitive to compositions up to 50 wt % bis-GMA. The similarity in the k_p values suggests that the monomers have enough mobility to add onto the macroradical and propagate regardless of the restrictions the macroradicals encounter during termination.

The k_t values given in Figure 8 support the finding that termination through segmental diffusion decreases as bis-GMA is added to the mixture. Even though the k_t values seem independent of composition during the latter stages of the polymerization, the mixtures containing 0−25 wt % bis-GMA show initial termination that is not reaction diffusion-controlled. Once again, these differences can be attributed to the relatively high mobility of polymerizing TEGDMA compared to that of bis-GMA.

The dominance of reaction diffusion-controlled termination throughout the polymerization for mixtures with 50−75 wt % bis-GMA explains the impressive autoacceleration seen in the full cure polymerizations (e.g., Figure 2). The large amount of bis-GMA in the comonomer mixture decreases the initial mobility of the system and causes a rapid decrease in the mobility of the reacting media at the beginning of the polymerization. This lower mobility leads to a significantly lower termination rate, which is also reaction diffusion-controlled. The suppression of the termination reaction facilitates a more rapid polymerization of the comonomer mixtures compared to the individual reactions of each monomer. However, it is important to realize that the restricted mobility of the reaction environment can also negatively impact propagation and cause final conversions significantly less than unity.

The change in the kinetic parameters as a function of the reaction illustrates the complex mobility issues that govern the copolymerization of a viscous dimethacrylate and a reactive diluent. The initial viscosity of the comonomer mixture is very important for several reasons. On the one extreme, an undiluted system lacks the mobility to propagate well even though the monomer is intrinsically reactive. However, a well-diluted mixture exhibits initial termination through segmental diffusion which hampers autoacceleration and increases the polymerization time. Therefore, an optimum viscosity exists in which the monomer has enough mobility to propagate well, but the reaction environment is restricted enough to prevent the dominance of termination through segmental movements of the macroradicals.

Furthermore, it is important to realize that the viscosity of the reacting medium changes as the polymerization progresses. Since these monomers form cross-linked networks, the mobility of the reaction environment decreases as the reaction progresses. Therefore, the conversion of the network is also a significant parameter in determining the overall mobility of the reacting polymer. Interestingly, the initial composition will affect how rapidly the mobility changes as a function of conversion.

In addition to the initial viscosity and copolymer composition, the relative reactivity of each monomer appears to play an important role in the kinetics of the bis-GMA/TEGDMA system. The polymerization studies suggest that bis-GMA is a reactive species once enough TEGDMA is added to the mixture to facilitate propagation. However, it is difficult to discern whether the initial viscosity of the mixture or the reactivity of bis-GMA contributes more to the impressive autoacceleration that the slightly diluted mixtures exhibit.

Copolymerizations of Bis-GMA, TEGDMA, and Hydrogenated Monomers. To determine whether the chemical structure or viscosity of bis-GMA has a more significant effect on the polymerization behavior of bis-GMA/TEGDMA mixtures, a series of experiments were performed in which one of the comonomers was made unreactive by hydrogenating the C═C double bond. As illustrated in Figure 9, a 50/50 mixture of unreactive TEGDMA and reactive bis-GMA was compared with a mixture of the same composition but with reactive TEGDMA and unreactive bis-GMA. By examining the various rate curves, one can ascertain the different effects of the viscosity of the system and the chemical reactivity. When bis-GMA and TEGDMA are copolymerized in an equal weight mixture, autoacceleration is immediate, and the maximum rate has occurred by 12% conversion. When bis-GMA is polymerized in a media containing an equal weight of hydrogenated TEGDMA, the initial polymerization behavior mimics that of the regular 50/50 mixture. Autoacceleration occurs instantaneously, and the maximum rate occurs at 9% conversion. However, the final conversion is greater since the growing polymer chains are more mobile in the hydrogenated system, which acts like a plasticizing solvent. When TEGDMA is polymerized in a system with an equal amount of hydrogenated bis-GMA, the maximum rate is approximately half of the other 50/50 systems and is delayed until 20% conversion. The full cure behavior of these systems suggests that the reactivity of the bis-GMA monomer has a more significant effect on the copolymerization than the initial viscosity of the reacting media. It is likely that in the reactive 50/50 mixture bis-GMA plays a dominant role in the kinetics early in the reaction.

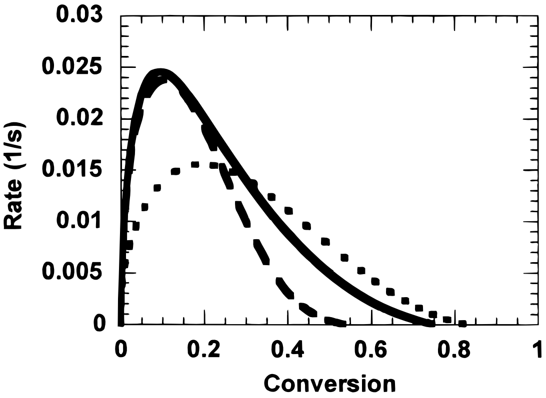


Figure 9. Copolymerization of 50/50 bis-GMA/TEGDMA (- -), 50/50 bis-GMA/hydrogenated TEGDMA (—), and 50/50 hydrogenated bis-GMA/TEGDMA (··). The polymerization conditions were 25 °C and a light intensity of 3.9 mW/cm^2.

The polymerization rate data of mixtures composed of 25, 50, and 75 wt % hydrogenated bis-GMA (remainder of sample is TEGDMA) and hydrogenated TEGDMA (remainder of sample is bis-GMA) were analyzed using analysis of variance (ANOVA)[28] with the choice of hydrogenated species and the amount of TEGDMA, whether reactive or not, as the two factors. The statistical analysis confirmed that the choice of hydrogenated species had a significant effect on the conversion at which the maximum rate was obtained. All samples that contained reactive bis-GMA autodecelerated at earlier conversions than the mixtures where TEGDMA remained the only reactive species. Furthermore, both the choice of hydrogenated species and the amount of TEGDMA significantly affected the final conversion of the system. The mixtures with reactive TEGDMA reached higher conversions than their reactive bis-GMA counterparts due to the increased mobility of the

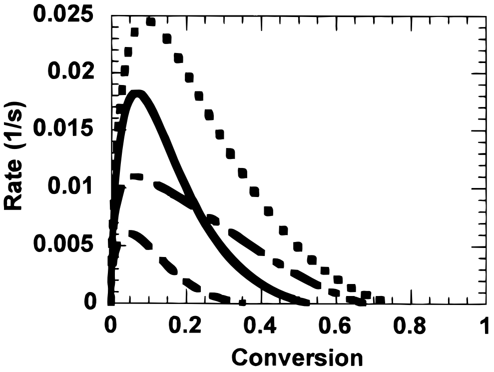


Figure 10. Polymerizations of pure bis-GMA (- - -) and bis-GMA in 25 wt % (—), 50 wt % (···), and 75 wt % (- —) hydrogenated TEGDMA. Polymerization conditions were 25 °C and 3.5 mW/cm^2 light intensity.

TEGDMA chains. On the basis of these observations, one can conclude that the initial viscosity of the comonomer mixture is not the controlling issue in the diffusion-controlled kinetics of these polymerizations. Instead, the chemical structure of bis-GMA, which exhibits fast reactivity and network formation, seems to play the more dominant role.

Effect of Hydrogenated TEGDMA. In addition to providing useful information about the effect of each comonomer on the bis-GMA/TEGDMA copolymerization, the hydrogenation experiments provide a unique opportunity to investigate the effect of viscosity on the homopolymerizations of dimethacrylates. Figure 10 depicts the polymerization of bis-GMA in increasing concentrations of hydrogenated TEGDMA. Since TEGDMA is far less viscous than bis-GMA, it can be thought of as a solvent. As was previously shown in Figure 2, the homopolymerization of bis-GMA has a very low maximum rate and a final conversion of approximately 30%. Increasing the amount of hydrogenated TEGDMA in the system from 0 to 50 wt % causes a dramatic increase in the maximum rate (5-fold increase at 50 wt %) and increases the final conversion to over 70%. In this case, the "solvent" is increasing the mobility of the viscous bis-GMA and allowing it to react faster and reach a higher final conversion. However, diffusion-controlled kinetics still dominate the polymerization, and autoacceleration is enhanced with the addition of a solvent instead of reduced as is typical with other MEGDMA systems.[18] However, when the mixture is composed of 75 wt % hydrogenated TEGDMA, the maximum rate declines to 0.01 s^{-1} and the rate drops off linearly with conversion (double-bond concentration) from this peak value. This type of behavior for the 75 wt % hydrogenated TEGDMA system suggests that the reaction is no longer diffusion-controlled since the solvent has given the monomer an even greater amount of mobility. The lack of diffusion-controlled kinetics is further supported by the fact that the propagation and termination kinetic constants remain unchanged during the course of the polymerization.

Figure 10 illustrates the significance of diffusion-controlled kinetics on the maximum rate of polymerization. The extreme limits of mobility are in the polymerizations of pure bis-GMA and bis-GMA in 75 wt % hydrogenated TEGDMA. In the pure bis-GMA case, the maximum rate is suppressed due to the low mobility of the system. However, the 25/75 bis-GMA/hydrogenated TEGDMA case also exhibits a low maximum rate since the high mobility of the reacting media prevents autoacceleration. These findings suggest that, when adding a solvent to a viscous dimethacrylate, a balance should be maintained between increasing the mobility of the monomer and retaining the autoacceleration effect to ensure a desirable final conversion within a short reaction time.

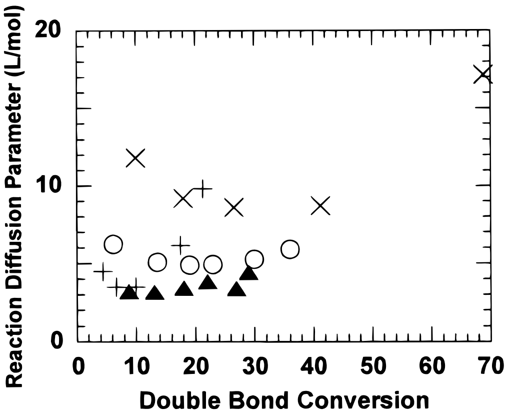


Figure 11. Reaction diffusion parameter, as a function of conversion, of pure bis-GMA (+) and bis-GMA in 25 wt % (▲), 50 wt % (○), and 75 wt % (×) hydrogenated TEGDMA at 25 °C and 3.5 mW/cm^2 light intensity.

The effect of increasing the "solvent" concentration on the reaction diffusion parameter of the bis-GMA homopolymerization is shown in Figure 11. Anseth et al.[17] have reported the reaction diffusion parameter for DEGDMA (diethylene glycol dimethacrylate) polymerized with PEG400 (poly(ethylene glycol)) as the solvent. They found the reaction diffusion constant remained unchanged even when the solution contained 50 wt % PEG400. However, for the polymerization of bis-GMA, one sees an increase in the reaction diffusion constant from 3 to 9 as the amount of hydrogenated TEGDMA is increased. The main difference in these two systems is the monomer structure and viscosity. Bis-GMA contains a stiff central core and hydroxyl groups that inhibit cyclization and cause diffusion-controlled kinetics to occur immediately upon exposure to light. DEGDMA, on the other hand, polymerizes in a manner similar to TEGDMA and possesses an initial region where the main method of termination is segmental movement of the macroradicals. These mobility differences may explain the unique behavior of each monomer in a solvent. The effect of a solvent on the kinetics of a bis-GMA system appears to be much greater than other MEGDMA systems studied since the reaction diffusion constant increases quite dramatically.

Effect of Hydrogenated Bis-GMA. Figure 12 graphically illustrates the effect of adding hydrogenated bis-GMA to a homopolymerization of TEGDMA. In this case, the bis-GMA is far more viscous than the TEGDMA monomer and acts as a viscosity modifier to increase the viscosity of the environment in which TEGDMA is polymerized. Interestingly, increasing the amount of unreactive bis-GMA from 0 to 75 wt % causes a 3-fold increase in the maximum rate of polymerization. This pronounced change in the autoacceleration effect is due to the diffusion limitations imposed on the reaction by the presence of the viscous hydrogenated bis-GMA. Adding a viscosity modifier to the system encourages autoacceleration to happen at an earlier conversion and with a greater rate since it is more difficult for the polymer segments to move toward each other and terminate. Once 75 wt % hydrogenated bis-GMA is added to the system, TEGDMA reacts fully.

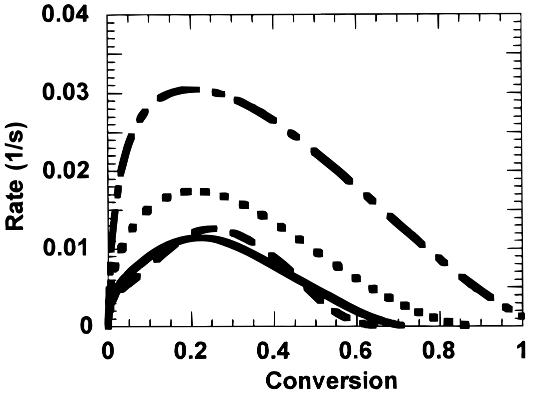


Figure 12. Polymerizations of pure TEGDMA (- - -) and TEGDMA in the presence of 25 wt % (—), 50 wt % (···), and 75 wt % (- —) hydrogenated bis-GMA at 25 °C and 3.5 mW/cm^2 light intensity.

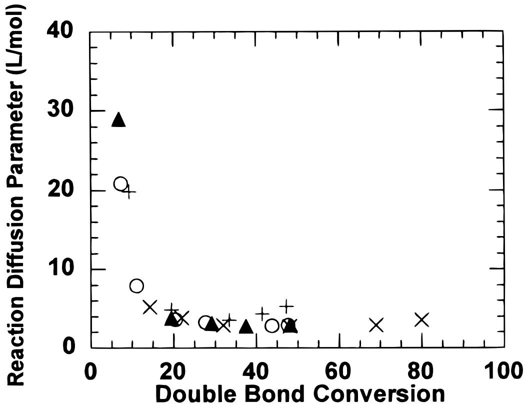


Figure 13. Reaction diffusion parameter, as a function of conversion, of pure TEGDMA (+) and TEGDMA in 25 wt % (▲), 50 wt % (○), and 75 wt % (×) hydrogenated bis-GMA at 25 °C and 3.5 mW/cm^2 light intensity.

Even though there is a remarkable difference in the polymerization rate versus double-bond conversion for mixtures with increasing amounts of hydrogenated bis-GMA, the same cannot be said for the values of the reaction diffusion constant. Figure 13 illustrates that the reaction diffusion parameter of TEGDMA does not appear to change as a function of conversion as one increases the amount of hydrogenated bis-GMA in the system. The fact that the reaction diffusion parameter drops to the same constant value regardless of the amount of hydrogenated bis-GMA in the system suggests that the reaction diffusion termination mechanism in TEGDMA is unaffected by the presence of the hydrogenated bis-GMA.

Conclusions

This work, which probed the reaction kinetics of a viscous dimethacrylate (bis-GMA) copolymerized with a reactive diluent (TEGDMA), illustrates the complex issues that exist when reacting two multifunctional monomers with vastly different viscosities and chemical structures. The initial viscosity, relative reactivity of each monomer, and copolymer composition are all important parameters in the kinetics of these polymerizations. A mixture containing an equal weight of TEGDMA and bis-GMA is a good balance between the highly reactive bis-GMA and the more mobile TEGDMA. The hydrogenation of each species provided valuable insight into the different roles initial viscosity and chemical structure of the monomer play in the kinetics. It was shown that the high reactivity and quick network formation of the bis-GMA constituent had a significant effect on the copolymer kinetics.

It was also illustrated that the mobility of the reacting species has a significant effect on the kinetics. A reaction environment is needed that promotes the mobility of the monomer molecules for propagation but hinders the movement of macromolecular segments so that reaction diffusion-controlled termination dominates throughout the polymerization. Restricted termination allows for an increase in the radical concentration, which ensures that these materials cure quickly. However, as the cross-linked network forms, propagation also becomes diffusion-controlled and the rate decays before complete conversion. If copolymer systems could be developed that allow for greater propagation with the same degree of restricted termination, increased double-bond conversions would be achievable within the desired reaction times.

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