

Coupling of Kinetics and Volume Relaxation during Polymerizations of Multiacrylates and Multimethacrylates

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ABSTRACT: A model was developed to describe the kinetics and physical aging during photopolymerizations of diacrylates and dimethacrylates that form highly cross-linked networks. The model incorporates the strong coupling between the volume relaxation and the kinetics observed in these reactions. Model predictions are presented for the reaction kinetics, volume relaxation, radical concentration, and attainment of a maximum conversion as a function of light intensity and relaxation time of the polymer. These results agree qualitatively with experimental observations for photopolymerizations of diacrylates and dimethacrylates. The invalidity of the pseudo-steady-state hypothesis for these reactions is also pointed out.

Introduction

Free-radical polymerizations of multifunctional monomers such as diacrylates and dimethacrylates lead to highly cross-linked polymer structures or networks. These reactions usually exhibit unexpected kinetic behavior, much of which is not observed in polymerizations leading to un-cross-linked or lightly cross-linked polymers. Observations include autoacceleration kinetics,¹⁻⁸ formation of a heterogeneous, glassy polymer,⁹⁻¹⁵ and attainment of a maximum conversion beyond which no significant reaction occurs despite the presence of unreacted initiator and functional groups.^{5,6,8,16-19}

The formation of a highly cross-linked structure can lead to volume relaxation of the polymer during the reaction process, which is of the same or longer time scale than that for the reaction.^{8,19} This phenomenon of volume relaxation of polymers toward their equilibrium specific volume is also known to occur during thermal cycling of polymers where it is referred to as physical aging. In this work we will refer to the volume relaxation during the reaction as physical aging. In glassy polymers, this process is known to occur over long periods of time. When the volume relaxation and the reaction time are of the same scale, the volume shrinkage that accompanies the reaction creates conditions that do not allow equilibrium with respect to the functional group conversion. Polymerization/cross-linking reactions for the production of highly cross-linked or glassy polymers are also accompanied by significantly reduced diffusivities of reacting species^{20,22} and long macromolecular radical lifetimes.^{23,24}

Polymerizations, especially photopolymerizations, of multifunctional monomers are important processes in the production of optical lenses, ultraviolet (UV) curable adhesives, and optical fiber coatings. Photopolymerizations are particularly important in such technologies because of the need for rapid production of a large number of manufactured articles at room temperature. The volume shrinkage behavior of multiacrylates is particularly significant for applications such as specialty lens production where the shape and volume of the polymer are essential to the application.

Physical aging during photopolymerization of tetraethylene glycol was shown by Kloosterboer and Lijten⁶ to play a significant role in the kinetics of the reaction even at very low conversion of the acrylate functional groups. In this reaction the equilibrium specific volume of the polymer with respect to conversion was not maintained. Consequently, the specific volume was greater than the equilibrium value for a long period of the reaction. The

resulting excess volume allowed the reacting species greater mobility and diffusivity than it would have at its equilibrium value. The difference in mobility and diffusivity alters the kinetics of the reaction and, thus, volume relaxation and reaction kinetics are strongly coupled.

In general, the delay in volume shrinkage explains the increase in maximum attainable conversion that is observed with an increasing rate of polymerization. This increase in maximum conversion has been observed by several researchers^{7,8,16,19,25} as a result of increasing reaction rates. The reaction rate is increased by increasing either light intensity (for photopolymerization reactions) or initiator concentration (for either thermal or photopolymerization reactions). At higher reaction rates a larger excess volume prevails, which allows for greater mobility and faster reaction. As the conversion level is approached at which the reaction would stop if it were at equilibrium, the excess volume allows for further reaction and the maximum conversion increases.

For similar reasons the delay in volume shrinkage also accounts for the shift in conversion at which the maximum rate is obtained. This shift has been observed by varying the light intensity during the photopolymerization of bis(hydroxyethyl)bisphenol A dimethacrylate⁸ (HEBDM).

Models to describe autoacceleration in the absence of significant delay in volume shrinkage have been previously developed.^{20,21,26-35} These models were applied successfully to the polymerization of monovinyl and monomethacryl monomers including styrene and methyl methacrylate. These models assume that the equilibrium specific volume is maintained over the course of the reaction and that the maximum conversion is obtained when the fractional free volume of the monomer-polymer mixture reaches 0.025. Due to these assumptions, no dependence of the model-predicted maximum conversion on rate of reaction is observed. The pseudo-steady-state assumption was also used in the development of these models. This assumption, though possibly valid for un-cross-linked systems, was shown to be invalid for the highly cross-linked polymer of ethylene glycol dimethacrylate.²³

Despite significant experimental research and physical interpretation of the coupling of volume relaxation and kinetics, no mathematical model is available for the description of the process. This contribution focuses on the development of a model to predict the kinetics, physical aging, and attainment of a maximum conversion in polymerizations of multifunctional monomers. The model was developed by coupling the reaction and volume relaxation, which are occurring simultaneously in the monomer-polymer system.

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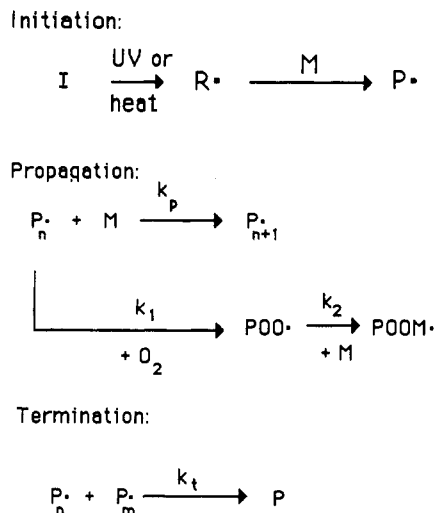


Figure 1. Main steps of a typical photopolymerization reaction of vinyl compounds.

Model Development

The polymerization of multifunctional monomers typically proceeds via the scheme illustrated in Figure 1. In free-radical polymerizations of this type the initiator species decays in the presence of UV light or thermal energy or as the product of a redox reaction into one or more species with free radicals that are then free to react.

The radical species may react with double bonds leading to chain propagation, or they may react with another macromolecular radical to contribute to the termination step of the reaction. These reactions are inhibited by oxygen, as it significantly reduces the radical reactivity. The polymerizations may be accompanied by significant volume shrinkage over the course of the reaction. The volume shrinkage of methyl methacrylate during polymerization to 100% conversion is 21%.²⁶ The shrinkage occurs as the density of the polymer is significantly higher than that of the monomer, and it affects the polymerization behavior as mobility and diffusivity are reduced.

The new model was developed by considering three basic contributions: the expression of the reaction kinetics in terms of a set of coupled differential equations, the change of the kinetic constants as a function of free volume, and the description of the volume relaxation of the monomer-polymer mixture in terms of parameters that are known or can be determined independently from knowledge of the reaction.

Reaction Description. Figure 1 shows a typical polymerization sequence for multiacrylates or multimethacrylates. Description of the reaction involves differential species balances on the initiator, reactive functional groups, and radicals based on this reaction scheme. For the model development it was assumed that oxygen is not present at any time over the course of the reaction. Oxygen is known to inhibit free-radical polymerizations as it reacts with the propagating free radical to form a radical with significantly lower reactivity. The assumption was made that all radicals, including initiator radicals, had equivalent propagation and termination kinetic constants and that termination occurred only by a bimolecular mechanism. This model did not include the common pseudo-steady-state assumption for the radical concentration.

The initiator balance resulting from these assumptions for the photoinitiated reaction scheme in question was²⁷

$$d[A]/dt = -I_0[1 - \exp^{-\epsilon[A]b}] \quad (1)$$

Here, $[A]$ is the photoinitiator concentration, ϵ is the initiator extinction coefficient, b is the reaction vessel

thickness, and I_0 is the light intensity in units of energy per unit volume. The exponential decay of the light through the sample requires the vessel thickness to be present in the calculations. For sufficiently thin vessels the exponential term from eq 1 can be expanded into its truncated Taylor series approximation resulting in

$$d[A]/dt = -I_0\epsilon[A] \quad (2)$$

Here, I_0 is the light intensity in units of energy per unit area and the reaction vessel thickness has been eliminated. For the model development and results, attention will be given only to photoinitiated polymerizations. If other types of initiation are used, they can be incorporated easily into the model.

The kinetic expression for the radical concentration, $[M^\bullet]$, was written as

$$\frac{d[M^\bullet]}{dt} = -2\phi \frac{d[A]}{dt} - k_t[M^\bullet]^2 \quad (3)$$

where k_t is the rate constant for termination and ϕ is the quantum yield for the initiator dissociation and initiation of a growing polymer chain. The factor of 2 indicates that the initiator decays into two equivalent radicals.

The balance on unreacted functional groups, $[M]$, yielded

$$d[M]/dt = -k_p[M][M^\bullet] \quad (4)$$

where k_p is the rate constant for propagation. The rate of polymerization is the rate of consumption of functional groups, $d[M]/dt$. This relation assumes equal reactivity of monomeric functional groups and pendant functional groups.

The kinetic constants k_p and k_t are functions of conversion and state of the system as will be shown later.

Determination of Kinetic Constants. In order to express the kinetic constants as a function of conversion, it was assumed that they were proportional to diffusion coefficients of the reacting species for values below a critical diffusion coefficient.^{20,21} Thus, the kinetic constant for propagation, k_p , was assumed to be proportional to the diffusion coefficient of monomer in the mixture, and the kinetic constant for termination, k_t , is assumed to be proportional to the polymer diffusion coefficient in the mixture.

$$k_p \propto D_M \quad \text{for } D_M < D_{M_c} \quad (5)$$

$$k_t \propto D_P \quad \text{for } D_P < D_{P_c} \quad (6)$$

Here, D_M and D_P are the diffusion coefficients of the monomer and polymer radicals in the polymer-monomer mixture, respectively. The subscript c represents a critical diffusion coefficient corresponding to the onset of the diffusion control region.

The monomer diffusion coefficient in a polymer could be determined from the fractional free volume, v_f , of the monomer-polymer mixture from the following relation:²²

$$D_M = \frac{\phi_0 \delta^2}{6} \exp\left(-\frac{B}{v_f}\right) \quad (7)$$

Also, the polymer chain diffusion coefficient, D_P , in solution could be written as²²

$$D_P = \frac{\phi_0 \delta^2}{k_2 M} \exp\left(-\frac{A}{v_f}\right) \quad (8)$$

where M is the molecular weight of a monodisperse

polymer, ϕ_0 is the jump frequency, δ is the jump distance, and k_2 , A , and B are constants.

The proportionality constant from eq 5 as well as the preexponential constants from eq 7 can be eliminated by letting $k_p = k_{p0}$ at the critical fractional free volume for propagation, $v_{f,cp}$. The result is

$$k_p = k_{p0} \exp \left[-A \left(\frac{1}{v_f} - \frac{1}{v_{f,cp}} \right) \right] \quad (9)$$

where A represents an undetermined constant.

For the termination constant, k_t , a similar relation was obtained from eqs 8 and 6

$$k_t = k_{t0} \left(\frac{M_w}{M_{wc}} \right)^{-\alpha} \exp \left[-B \left(\frac{1}{v_f} - \frac{1}{v_{f,ct}} \right) \right] \quad (10)$$

Here, M_w is the molecular weight of the polymer, M_{wc} is the molecular weight at the point the reaction becomes diffusion controlled, and $v_{f,ct}$ is the fractional free volume at the onset of the diffusion-control region for termination.

For the development of this model it is assumed that segmental diffusion controls the termination rate in these highly cross-linked systems and that there is then no dependence of the termination constant on the molecular weight of the polymer (i.e., in eq 10, $\alpha = 0.0$). The independence of the termination constant from the polymer molecular weight is supported by the studies of others investigators.²⁸⁻³⁰

In order to apply the free-volume model, it is essential to determine the equilibrium fractional free volume as a function of conversion. For this calculation we assumed that the fractional free volume at the glass transition temperature is 0.025, that the free volumes of the monomer and the polymer are added ideally thermodynamically, and that the free volume varies linearly with temperature above the glass transition temperature.^{20-22,31-40}

These assumptions yielded

$$v_{fm} = 0.025 + \alpha_m(T - T_{gm}) \quad (11)$$

$$v_{fp} = 0.025 + \alpha_p(T - T_{gp}) \quad (12)$$

and

$$v_f = v_{fm}\phi_m + v_{fp}(1 - \phi_m) \quad (13)$$

Here, the subscripts m and p represent monomer and polymer, respectively, T is the temperature, T_g is the glass transition temperature, α is the volume expansion coefficient, and ϕ_m is the volume fraction of monomer, which is a function only of conversion.

With models similar to this one for modeling autoacceleration, Marten and Hamielec^{20,21} as well as others³¹⁻⁴¹ have obtained good agreement with experimental reaction profiles of polymerizations of styrene, methyl methacrylate, and other monovinyl monomers that exhibit autoacceleration. Previous models used the steady-state assumption and did not include a volume relaxation term nor could they predict a change in maximum conversion with changing light intensity.

Our model without volume relaxation, like other similar models, appears to be valid for calculating rates of reaction in systems that are not highly cross-linked and whose reactions do not proceed rapidly enough to create a significant excess volume beyond equilibrium. However, many polymerizations exhibit a significant delay in volume shrinkage and hence call for incorporation of physical aging into the corresponding models.

Physical Aging. Polymer glasses are not always in equilibrium with respect to their specific volume or free

volume.⁴²⁻⁴⁹ The volume relaxation that occurs has been referred to as physical aging.⁴² Because of significant volume relaxation during the polymerization reaction, it is necessary to account for the physical aging in addition to the change in equilibrium conditions. Incorporation of physical aging distinguishes this model from those previously developed to model autoacceleration and renders it capable of predicting changes in maximum conversion with reaction rate. The coupling of physical aging and kinetics is essential in order to describe systems that react and relax on similar time scales.

To describe the volume relaxation during the reaction, a single relaxation time model is used as proposed by Kovacs.⁴²⁻⁴⁵ This model states that the rate of change of the specific volume, v , is proportional to the deviation from the equilibrium specific volume, v_∞ . The proportionality constant is characteristic of the system and is inversely related to the relaxation time, τ , so that

$$dv/dt = -(v - v_\infty)/\tau \quad (14)$$

The equilibrium specific volume is determined as a function of conversion, x , the volume concentration factor, ϵ_v , and the specific volume of the monomer, v_m , according to

$$v_\infty = v_m(1 - \epsilon_v x) \quad (15)$$

The contraction factor is determined from

$$\epsilon_v = (v_m - v_p)/v_m \quad (16)$$

Several investigators^{42-46,48,49} found this model to describe physical aging during single contractions. However, it was unable to describe volume expansion or complex thermal histories. Since polymerizations involve a single contraction, it was believed that this model would be adequate with the free-volume dependence of the relaxation time included. It was determined⁴³⁻⁴⁷ that, in order to describe nonlinear behavior with respect to deviation from equilibrium, a free-volume-dependent relaxation time of the form of eq 17 could be used.

$$\ln \tau = C_1 + C_2/v_f \quad (17)$$

This relationship implies that the relaxation time of the polymer may increase dramatically over the course of the reaction as the free volume is consumed. This increase is expected as the relaxation can be nearly instantaneous at low conversions (when the mixture is primarily monomer), while it may take several hours at higher conversions (when the mixture is a glassy polymer).

The final relationship involved relating the actual fractional free volume to the actual specific volume, the equilibrium specific volume, and the equilibrium fractional free volume. All of these can be determined as a function of time and conversion from eqs 13-15.

$$v_f = v_{f_\infty} + (v - v_\infty)/v_\infty \quad (18)$$

Equation 18 is used to determine the actual fractional free volume, which, as opposed to the equilibrium value of the free volume, controls the kinetic constants and the relaxation time. The changes to which this leads are clearly pointed out below as the results of the model are presented, showing the effect of incorporating physical aging into the kinetics.

Results and Discussion

Although the model requires a large number of parameters, most can be determined independently of the reaction considered. Physical properties of the monomer and pure polymer such as thermal expansion coefficients, glass transition temperatures, and densities are easily

Table I
Standard Parameters Input to the Model

Material Properties		
$\nu_m = 1.1 \text{ cm}^3/\text{g}$	$\nu_p = 0.9 \text{ cm}^3/\text{g}$	
$T_{gm} = -60 \text{ }^\circ\text{C}$	$T_{gp} = 380 \text{ }^\circ\text{C}$	
$\alpha_m = 0.001 \text{ }^\circ\text{C}^{-1}$	$\alpha_p = 0.00025 \text{ }^\circ\text{C}^{-1}$	
Kinetic Parameters		
$k_{p0} = 5.0 \times 10^3 \text{ L/mol}\cdot\text{s}$	$\nu_{pc} = 0.085$	$A = 0.5$
$k_{t0} = 4.5 \times 10^6 \text{ L/mol}\cdot\text{s}$	$\nu_{pc} = 0.085$	$A = 0.5$
Initiator Properties		
$\epsilon = 100 \text{ L/mol}\cdot\text{cm}$	$\phi = 0.6$	
Relaxation Parameters		
$C_1 = 0.5$	$C_2 = 0.165$	

determined. In order to determine how the relaxation time behaves as a function of fractional free volume, relaxation times are determined at several different conversions, and the conversion is related to fractional free volume using eq 13. The initiator efficiency and extinction coefficient are determined in a polymerization with known kinetic parameters. This method leaves only the kinetic parameters to be calculated by fitting experimental data to eqs 9 and 10.

If a reaction with very low reaction rates is performed with decoupled kinetics and relaxation, then the kinetic parameters can be determined from that single experiment. All higher rate of reaction experiments are predicted from the model based on the results from the single, low reaction rate experiment.

In the present contribution results are predicted by using the parameters listed in Table I. These parameters are selected to represent as closely as possible the photopolymerization of ethylene glycol dimethacrylate (EGDMA) initiated by 2,2-dimethoxy-2-phenylacetophenone (DMPA). Except for results at varying light intensities, these simulations assume 1.0 wt % DMPA and 0.2 mW/cm² intensity light of wavelength 365 nm at 20 °C.

The polymerization of EGDMA has approximately 18% volume shrinkage extrapolated to 100% conversion of functional groups, exhibits its maximum rate at approximately 80 s (approximately 10% conversion at low reaction rates) and reaches a final conversion of 35% of monomeric functional groups when polymerized with 1.0 wt % DMPA initiated by 0.2 mW/cm² at 20 °C.⁵⁰ The kinetic parameters, specific volumes (shown in Table I), and thermal expansion coefficients of monomer and polymer were selected in order to give agreement with these observations for the photopolymerization of EGDMA. The glass transition temperature of the monomer was set equal to the glass transition temperature of tetraethylene glycol diacrylate,⁶ and the glass transition temperature of the pure polymer (100% conversion of functional groups) was set by adding 100 °C to the observed glass transition temperature of 280 °C in a polymer of EGDMA far from complete conversion.⁵¹ It is known that glass transitions for highly cross-linked materials are not distinct transitions but rather occur over a very broad range. This range gives the approximate character of the polymer sample. The extinction coefficient was set to average values for DMPA at this wavelength,⁵² and the initiator efficiency was set equal to that for azobis(butyronitrile) (AIBN).²⁷ Relaxation parameters are unknown for this monomer-polymer mixture and were set in order to have significant coupling of the kinetics and volume relaxation as observed in this reaction. Currently, experiments are being performed to determine the actual glass transition temperatures of monomer and polymer as well as the relaxation time behavior as a function of free volume for EGDMA.

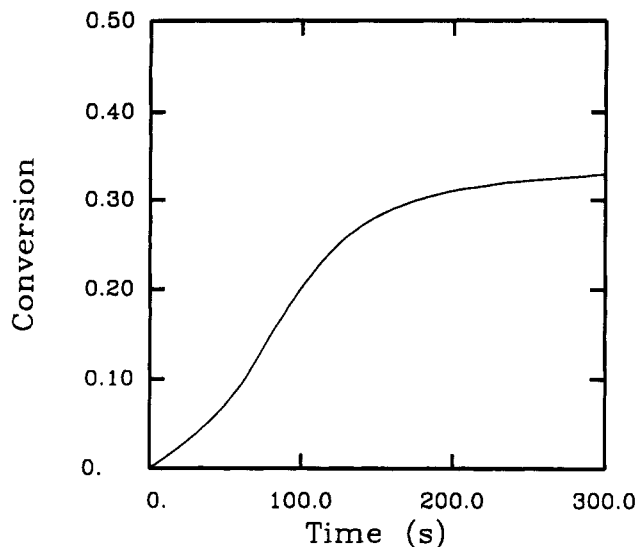


Figure 2. Simulated results of conversion versus time for a polymerization using parameters from Table I at 20 °C and 0.2 mW/cm².

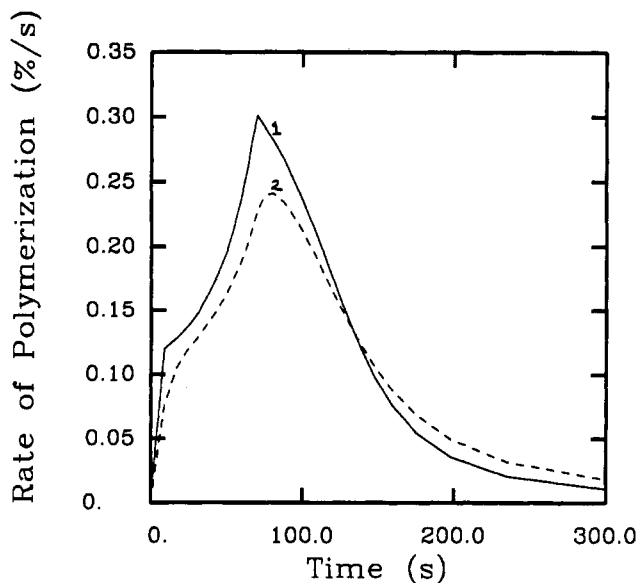


Figure 3. Actual rate of polymerization (curve 1) and rate of polymerization calculated assuming that the equilibrium specific volume is maintained throughout the reaction (curve 2). Rates are in percentage of functional groups consumed per second.

Figures 2–5 illustrate the numerical integration of eqs 1, 3 and 4 with the parameters from Table I. Figure 2 illustrates the model prediction for the conversion versus time behavior of the model system. The curve illustrates the typical S-shaped behavior observed in autoaccelerating systems and also illustrates the attainment of a maximum conversion. If the polymerization is continued, the conversion increases only slightly from its value of 0.33 at 300 s to 0.37 at 10 000 s. The maximum conversion is defined for this model as it was defined experimentally:⁸ when the rate of reaction falls to 1/100th of its maximum value, the conversion is said to have reached its maximum value.

Curve 1 in Figure 3 is intended to resemble the experimental output from performing a photopolymerization in a differential scanning calorimeter (DSC) where the rate of reaction or heat flux is determined as a function of time. Two regions common to polymerizations of multifunctional monomers can be seen in Figure 3. The first region from the start of the reaction until the maximum rate is reached at approximately 75 s is the region known as autoacceleration. Throughout this stage of the reaction,

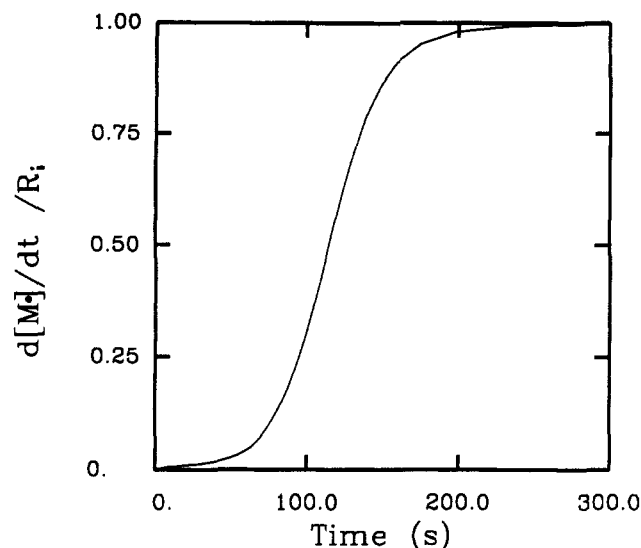


Figure 4. Examination of the PSSA validity as a function of time. The PSSA is valid when the ratio of the rate of change of radical concentration to the rate of initiation is much lower than 1.

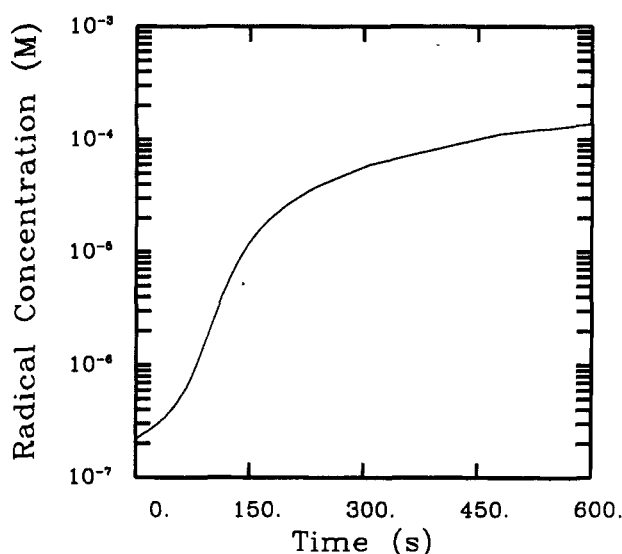


Figure 5. Simulation results for the macromolecular radical concentration as a function of time.

termination is diffusion controlled and the termination constant is continually decreasing. The decreasing termination rate leads to an increase in the number of macromolecular radicals. Because propagation is not diffusion controlled in this regime, the rate of polymerization increases as the radical concentration increases.

The second region begins as the rate of reaction reaches its maximum. This region of the reaction continues until the reaction is stopped and has been referred to as auto-deceleration.⁸ As the rate reaches its maximum, propagation becomes diffusion controlled and begins to decrease dramatically. In this region autoacceleration becomes balanced by autodeceleration. At later stages, autodeceleration dominates. The autodeceleration causes the rate to decrease much more rapidly than can be accounted for by depletion of reactive groups.

The importance of volume relaxation on the polymerization is also shown in Figure 3 where the actual rate of reaction (curve 1) is shown as well as the rate of reaction that would be determined from volume shrinkage measurements. This latter method of calculating the rate is frequently used during polymerizations^{41,53} and assumes that the volume shrinkage is always at equilibrium. This

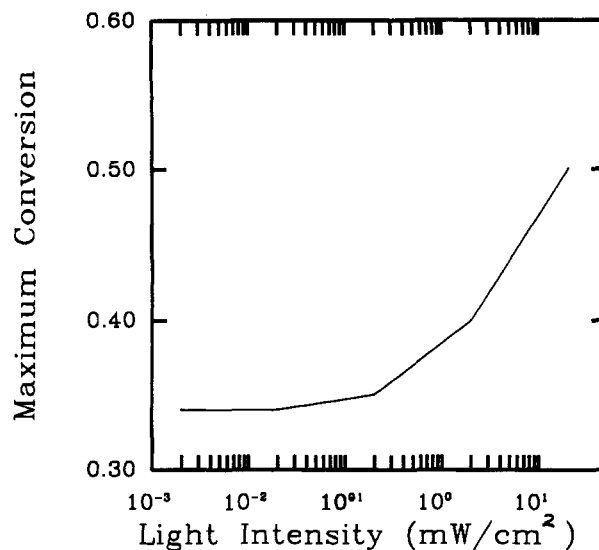


Figure 6. Maximum attainable functional group conversion as a function of the incident light intensity.

assumption has been proven invalid for polymerizations of highly cross-linked materials.⁶ The largest deviation between the actual rate of reaction and the rate measured by volume shrinkage occurs at the maximum reaction rate. At this point, the reaction proceeds far more rapidly than the relaxation can proceed. However, at later stages of the reaction the rate as measured by volume shrinkage actually exceeds the true rate of reaction. Again, this agrees with experimental investigations.⁶ It is explained by noting that the actual reaction rate has been significantly reduced and that the large excess in volume that exists at this time is a driving force toward volume shrinkage.

Past models for the description of autoacceleration have involved the pseudo-steady-state assumption (PSSA) for the radical species. The assumption is equivalent to eq 19, where R_i is the initiation rate.

$$\frac{d[M^*]}{dt} / R_i \ll 1 \quad (19)$$

The model prediction for the ratio of the rate of change of radical concentration to the rate of initiation is shown in Figure 4. For the PSSA to be valid this ratio should be much less than 1.0. It is easily seen that early in the reaction the PSSA is valid but that for times greater than approximately 50 s (approximately 10% conversion) the PSSA is clearly invalid. The PSSA becomes invalid as the rate of termination decreases so that the rate of change of the radical concentration becomes approximately equal to (instead of much less than) the rate of initiation.

The macromolecular radical concentration is shown in Figure 5 as a function of time. As shown by other investigators,²³ the radical concentration during the polymerization of ethylene glycol dimethacrylate increases several orders of magnitude. The model predictions agree well with this observation and the progressive suppression of termination is the primary reason for the invalidity of the PSSA.

The prediction of polymerization behavior at varying light intensities is one of the primary objectives of this model and the present work. The predictions for the behavior of the model system at varying light intensities are given in Figures 6–9. As previously noted, a significant increase in maximum conversion is often observed with increasing light intensity.⁶ For example, in the polymerization of HEBDM the maximum conversion increases from 0.3 at a light intensity of 0.002 mW/cm² to 0.48 at 0.2 mW/cm².⁸ The increase in maximum conversion with

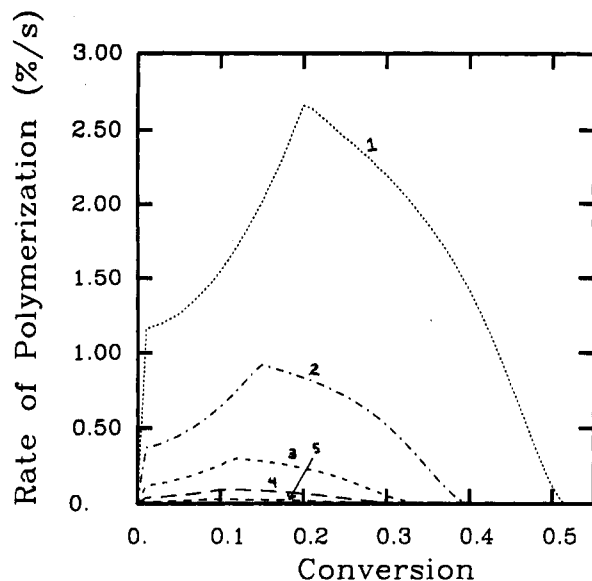


Figure 7. Rate of polymerization (in percentage of functional groups consumed per second) as a function of the functional group conversion for simulations initiated by light intensities of 20 (curve 1), 2.0 (curve 2), 0.2 (curve 3), 0.02 (curve 4), and 0.002 mW/cm² (curve 5).

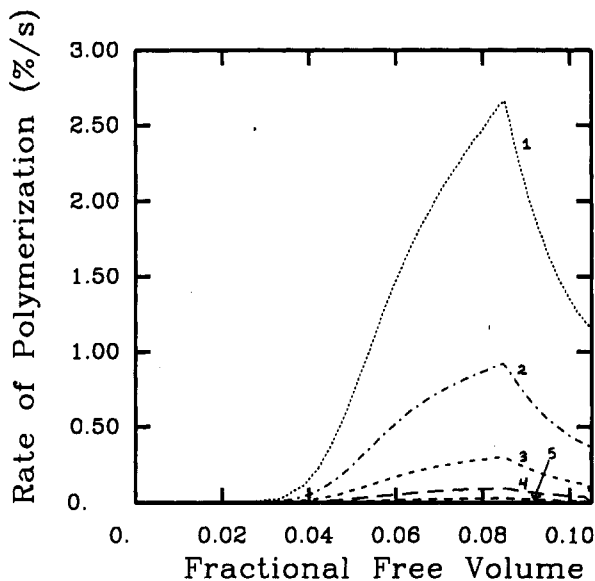


Figure 8. Rate of polymerization as a function of the fractional free volume, which has a value of 0.105 for the pure monomer and decreases as the reaction proceeds for simulations initiated by light intensities of 20 (curve 1), 2.0 (curve 2), 0.2 (curve 3), 0.02 (curve 4), and 0.002 mW/cm² (curve 5).

light intensity is shown in Figure 6 where the maximum conversion is determined as the conversion at which the rate of polymerization drops to 1/100th of the maximum rate.⁸ The expected increase in conversion with light intensity is observed above a 0.2 mW/cm² light intensity. However, below 0.2 mW/cm² a plateau is observed in the maximum conversion. The plateau occurs as the reaction proceeds slowly enough that the volume shrinkage is able to remain near equilibrium during the polymerization. So far this plateau has not been observed experimentally in highly cross-linked polymers. However, at very low light intensities inhibition by trace amounts of oxygen becomes progressively more important. Therefore, it may be difficult to obtain such a plateau.

Figures 7–9 show the interdependence of fractional free volume, reaction rate, and conversion for reaction simulations initiated by different light intensities. As shown by the data in Figure 7, where the reaction rate is given

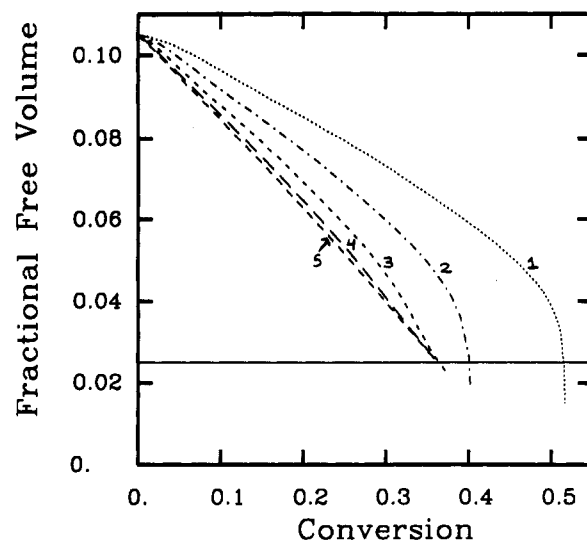


Figure 9. Fractional free volume as a function of conversion for simulations initiated by light intensities of 20 (curve 1), 2.0 (curve 2), 0.2 (curve 3), 0.02 (curve 4), and 0.002 mW/cm² (curve 5). The solid line at a constant fractional free volume of 0.025 crosses the corresponding curves at the conversion where the material vitrifies and the materials become glassy.

as a function of conversion, we find that the curves for different light intensities do not scale with any power of the light intensity due to the volume relaxation. Instead of being a similar shape, the curves shift toward higher conversions when initiated by higher light intensities. This shift is most easily noticed by examining the conversion at which the maximum rate occurs. At 20 mW/cm², the conversion corresponding to the maximum rate is 0.2 while at lower light intensities the maximum rate occurs at conversions below 0.10. If the kinetic constants were controlled by equilibrium conditions or if the equilibrium specific volume of the mixture were consistently maintained, then the curves would appear to be the same or similar shape. Previous models for autoacceleration^{20,21} predicted curves that would scale with different initiation rates.

As reported by other investigators,⁸ the conversion at which the maximum rate occurs is known to shift in the polymerization of HEBDM as the model predicts. However, in the polymerization of tetraethylene glycol diacrylate (TEGDA) the conversion at which the maximum rate occurs does not shift with light intensity. HEBDM is a stiff monomer that is not able to relax as fast as TEGDA, especially at low conversions, so the relaxation of HEBDM is slow even before the maximum rate is obtained. On the other hand, relaxation of TEGDA is very fast before the maximum rate is obtained so that equilibrium is maintained prior to the maximum rate. Because equilibrium is maintained, no shift of the maximum rate conversion is observed.

When the reaction rate is given as a function of fractional free volume (which decreases over the course of the reaction) as in Figure 8, we see that the curves scale approximately with the square root of light intensity. Previous autoacceleration models^{20,21,37–40} predict similar shape of the reaction rate versus conversion curves, but this is not observed experimentally⁸ for polymerizations of certain tetrafunctional monomers. This model predicts that, instead of being like shaped as a function of conversion, the curves resemble each other when shown as a function of free volume.

The excess fractional free volume generated during the reaction is shown in Figure 9. As higher light intensities are used for polymerization, the fractional free volume

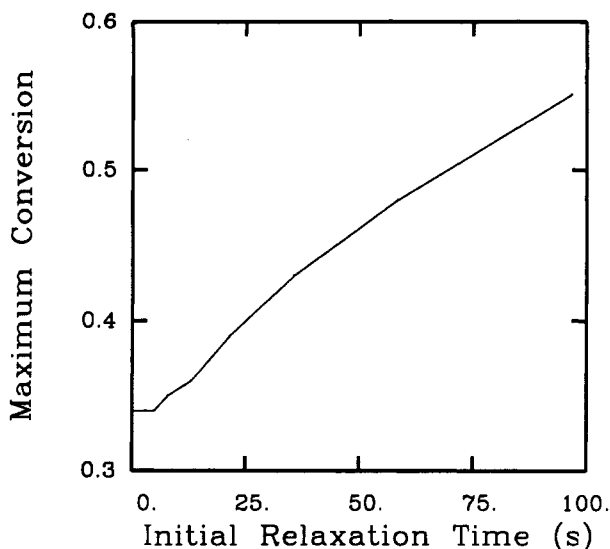


Figure 10. Maximum attainable functional group conversion is shown as a function of the initial relaxation time. This relaxation time is varied by varying C_1 in eq 17. All other parameters are from Table I.

deviates further from its equilibrium. The equilibrium is nearly maintained at low light intensities as shown by the simulation at 0.002 mW/cm^2 . The polymerization at low light intensities typically reach the glassy region with equilibrium fractional free volumes of approximately 0.025 while at higher light intensities higher conversions are reached and the polymer penetrates further into the glassy region.

A plateau similar to that in Figure 6 is demonstrated in Figure 10 where the relaxation time at zero conversion is varied. A constant volume conversion is observed for zero conversion relaxation times of less than 5 s. For short relaxation times the volume shrinkage occurs faster and keeps the monomer-polymer mixture near equilibrium. For longer relaxation times a strong dependence of the maximum conversion on relaxation time is observed. This behavior is not easily verified experimentally as the effect of increasing relaxation time on any experimental system is difficult to determine. Means of affecting the relaxation time such as the addition of a solvent typically affect other properties of the system as well.

Conclusions

A model coupling the relaxation and reaction that occur during thermal and photopolymerization of multifunctional monomers has been presented. The model involves a fractional free volume dependence of the propagation and termination kinetic constants as well as a single relaxation time model for the physical aging or volume relaxation that accompanies the polymerization. The model was presented along with results indicating its ability to predict accurately the volume relaxation, the invalidity of the PSSA for polymerizations of this type, the changing shape of reaction versus conversion curves at different light intensities and the dependence of the maximum attainable conversion on light intensity.

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