

A Kinetic Model for Radical Trapping in Photopolymerization of Multifunctional Monomers

Mei Wen and Alon V. McCormick*

Department of Chemical Engineering & Materials Science and Center for Interfacial Engineering,
University of Minnesota, Minneapolis, Minnesota 55455

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ABSTRACT: An improved kinetic model is presented which accounts for radical trapping during the photopolymerization of multifunctional monomers such as diacrylates and dimethacrylates. Following earlier suggestions, the model assumes that trapping of radicals behaves as a unimolecular first-order reaction. The novel feature is that the trapping rate constant is presumed to increase exponentially with the inverse of the free volume; this treatment is qualitatively consistent with the free volume dependence previously proposed for the other rate constants. This improved model predicts the experimental reaction rate trends as well as previous models developed in the literature; more importantly, though, this improved model newly predicts, as no other model has, the following experimental trends in the trapped and active radical concentrations: (1) that the active radical concentration passes through a maximum while the trapped radical concentration increases monotonically; (2) that a higher light intensity leads to a lower fraction of trapped radicals at a given conversion of functional groups but to a higher trapped radical concentration at the end of the reaction. Moreover, unlike its antecedents, the improved model correctly predicts that the polymerization rate depends more on light intensity the higher the conversion and that higher light intensity can lead to a higher final conversion.

Introduction

The free-radical polymerization of multifunctional monomers such as diacrylates and dimethacrylates forms highly cross-linked, rigid, and glassy polymer networks with high modulus and solvent resistance for protective and decorative coatings, photoresists, printing, and biomaterials.^{1,4–6} Generally, these materials are prepared by radiation (e.g., ultraviolet (UV)) curing of liquid monomer mixtures since photopolymerization can take place rapidly at room temperature with good spatial control.

One problem with such cross-linking systems is that the conversion of reactive functional groups usually remains incomplete because of dramatic drops in the mobility of radicals and functional groups during polymerization. Such dramatic drops in mobility also lead to characteristic kinetic features such as autoacceleration, autodeceleration,^{7–11} and the early onset of what has been called reaction–diffusion behavior.^{12–16}

The analysis of such diffusion-controlled features might be simplified by classifying two types of free radicals: the active and the trapped. Electron spin resonance (ESR) spectroscopy shows that active (mobile) radicals give a 13-line spectrum and trapped (static) radicals give a nine-line spectrum.^{17,18} The presence of the two different types of radicals is explained by the heterogeneous nature of the cross-linking free radical polymerization. Those on cross-linked, large linear, and branched polymer chains are shielded by a “solid” environment, wherein diffusion is highly hindered. In contrast, those on relatively small chains are relatively mobile. Here we define trapping of radicals as the conversion of active radicals to inactive ones as mobility is lost.

Qualitatively, radical trapping has been considered as a pseudo-first-order termination process.^{1–3} Such an

approach, combined with a pseudo-steady-state approximation, has been used to rationalize the experimental finding that the photopolymerization rate can depend more on light intensity than might be expected without trapping at high conversions.^{1–3} However, there has been no thorough exploration of the quantitative implications of this idea. Particularly, we wish to test whether such a simple idea alone (neglecting even volume relaxation) is capable of correctly predicting trends in the concentrations of active and trapped radicals and the effect of light intensity.

What makes this question interesting is that it is known that a higher light intensity can lead to a higher final conversion, and this has been attributed to delayed volume shrinkage.^{7,15,19,20} Delayed volume shrinkage leads to the formation of excess free volume, which preserves mobilities of reactive species. Volume relaxation has been incorporated into the polymerization kinetics to predict the effect of light intensity on the final conversion.^{13,16,21} However, to our knowledge, without the inclusion of volume shrinkage, no kinetic model has been able to predict this effect. Because the inclusion of radical trapping can explain how reaction rate depends on the light intensity, the effect of this treatment alone on the final conversion needs to be investigated to distinguish between radical trapping effects and volume shrinkage effects.

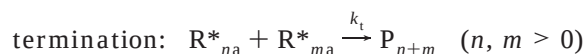
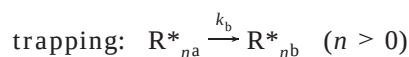
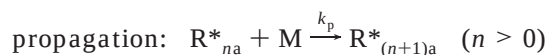
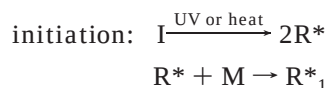
Clearly, a kinetic model that ignores trapping will fail to predict the following important experimental observations. (1) It has been shown experimentally¹⁸ that whereas the concentration of trapped radicals increases monotonically with functional group conversion, the concentration of active radicals increases initially and then drops at high conversions. (2) A higher light intensity leads to a lower fraction of trapped radicals at a given conversion but to a higher trapped radical concentration at the end of the reaction.¹⁸ The objective of this work is to propose and test a physically mean-

* To whom correspondence should be addressed.

ingful model for the trapping rate constant that, with a kinetic approach, at least semiquantitatively predicts the behavior of the concentrations of active and trapped radicals. Moreover, we want to test whether the inclusion of radical trapping alone, even without any account of volume relaxation, might help explain the increased final conversion with increasing light intensities. Following previous work, trapping is considered as a unimolecular first-order reaction. Here, though, we attempt to incorporate its acceleration with growing diffusion limitation; the rate constant of trapping is taken as rising as the system becomes more and more solidlike.

Model

The functional-group reaction scheme of a free-radical polymerization of multifunctional monomers with the formation of trapped radicals is shown below.



Here I is an initiator, R^* is a primary radical, R^*_{1a} is a chain initiating radical, R^*_{na} and R^*_{nb} are active and trapped (buried) radicals with n functional groups reacted, M is a functional group, P_{n+m} is a dead polymer with $(n + m)$ functional groups reacted, k_p is the rate constant for propagation, k_b is the rate constant for radical trapping (burying), and k_t is the rate constant for termination.

In the initiation step, the initiator splits into two primary radicals R^* , each of which reacts with a functional group to form a chain initiating radical R^*_{1a} . Because reactions by trapped radicals are defined in this model as very much slower than the reactions by active radicals, propagation and termination can be taken to involve only active radicals. Propagation consists of the growth of active radicals by the successive addition of functional groups. Radical trapping is presumed to take place by a unimolecular first-order reaction. Because radical trapping is presumed to be permanent, it affects the rate in a manner similar to unimolecular termination.

We have adopted a number of simplifying assumptions: (1) initiation produces two equally reactive radicals, (2) chain transfer reactions are neglected, (3) the rate constants for radicals of different sizes are assumed identical, (4) the propagation rate constant k_p , termination rate constant k_t , and the rate constant for radical trapping k_b are all simple functions of free volume as discussed below, and (5) there is no excess free volume. These simplifications should not interfere with our investigation of the question at hand—whether such a simple treatment of trapping correctly predicts the active and trapped radical concentrations and the effect of light intensity. In principle, this model can be

applied to thermal initiated or photoinitiated systems, but the development here focuses on photoinitiation.⁴³

The material balance equations for the initiator, the functional group, the active radical, and the trapped radical concentrations are

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

$$d[M]/dt = -k_p [M][R_a] \quad (2)$$

$$d[R_a]/dt = 2fI_0 b \epsilon [A] - k_b [R_a] - 2k_t [R_a]^2 \quad (3)$$

$$d[R_b]/dt = k_b [R_a] \quad (4)$$

where $[A]$ is the current (not initial) photoinitiator concentration, $[M]$ is the functional group concentration, $[R_a]$ is the active radical concentration, $[R_b]$ is the trapped radical concentration, I_0 is the incident light intensity in the units of einstein/(L s),²⁷ b is the film thickness which will be canceled out when it is multiplied by I_0 , ϵ is the extinction coefficient of initiator at the applied wavelength, and f is the initiator efficiency. The initiation term in eq 3 assumes only weak absorption (e.g., $\epsilon[A]b \ll 1$).

Rate Constant Models Adapted from Previous Work

Initiation. The initiator efficiency is the fraction of radicals produced upon decomposition of the initiator that actually initiate propagating chains. It may be in the range of 0.3–0.8 even at the beginning of polymerization²⁸ because some of the radicals recombine to form compounds that are (relatively) stable and also because some primary radicals terminate with radicals on growing polymer chains (which is not included in the termination reaction above). Because the viscosity of the reacting medium rises as reaction proceeds and so the diffusivity of primary radicals falls, radical recombination is more and more favored until the initiator efficiency finally falls to zero. Several models of this behavior of initiator efficiency can be found in the literature.^{28–32} We use the following model to describe it: we take the initiator efficiency f as a function of the diffusivity of primary radicals:²⁹

$$f = \left[1 - \frac{D_{i0}}{D_i} \left(1 - \frac{1}{f_0} \right) \right]^{-1} \quad (5)$$

where f_0 and D_{i0} are the initiator efficiency and the diffusion coefficient of primary radicals at the beginning of polymerization, respectively, and D_i is the current diffusion coefficient of primary radicals in the course of polymerization. By assuming that the diffusivity is exponentially proportional to the inverse of system fractional free volume v_f ,³³ eq 5 becomes

$$f = \left[1 - \left(1 - \frac{1}{f_0} \right) e^{A_i(1/v_f - 1/v_{f0})} \right]^{-1} \quad (6)$$

where A_i is the dimensionless activation volume which governs the rate at which initiator efficiency falls in the diffusion-controlled period, and v_{f0} is the fractional free volume at the beginning of the polymerization.

Propagation and Termination. The propagation rate constant k_p and the termination rate constant k_t are calculated as functions of free volume following a model developed by Anseth and Bowman.^{11,13} In their

model, the two constants are calculated by summing different resistances for diffusion, intrinsic reaction, and reaction–diffusion (for termination).

$$k_p = \frac{k_{p0}}{1 + e^{A_p(1/v_f - 1/v_{fcp})}} \quad (7)$$

$$k_t = k_{t0} \left(1 + \frac{1}{\frac{Rk_p[M]}{k_{t0}} + e^{-A_t(1/v_f - 1/v_{fct})}} \right)^{-1} \quad (8)$$

where A_p is the dimensionless activation volume which governs the rate at which propagation rate constant decreases in the diffusion-controlled period, v_{fcp} is the characteristic fractional free volume at which the diffusional resistance equals the intrinsic reaction resistance for propagation, k_{p0} is a preexponential factor, A_t is the dimensionless activation volume which governs the rate at which termination rate constant decreases in the diffusion-controlled period, v_{fct} is the characteristic fractional free volume at which the diffusional resistance equals the intrinsic reaction resistance for termination, k_{t0} is a preexponential factor, and R is the reaction–diffusion parameter.⁴⁴

Fractional Free Volume. The fractional free volume is the sum of the equilibrium fractional free volume and the excess fractional free volume. In this work, we consider only the case without excess free volume. Therefore, the system fractional free volume, which equals the equilibrium fractional free volume, is simply a function of conversion:²¹

$$v_f = v_{fm}(1 - \phi_p) + v_{fp}\phi_p \quad (9)$$

where

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

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

$$\phi_p = \frac{x(1 - \epsilon_v)}{1 - x\epsilon_v}$$

Here, the subscripts m and p denote monomer and polymer, respectively, T is the reaction temperature, T_g is the glass transition temperature, α is the volume expansion coefficient, ϕ_p is the volume fraction of polymer, which is a function of conversion x , and ϵ_v is the contraction factor determined by $(V_m - V_p)/V_m$, where V is the specific volume.

Novel Features of the Rate Constant Model

Radical trapping becomes more and more severe as polymerization proceeds; thus, the rate constant for radical trapping k_b should increase with the extent of reaction. Because no model is available to predict how k_b changes during the course of polymerization by a mean-field method, we presume that it is inversely proportional to the diffusion coefficient of active radicals. This simple assumption is reasonable because active radicals become less and less mobile as their diffusion coefficient drops. This leads to radical trapping. Here, we postulate that segmental diffusion controls the trapping process. Consequently, the diffusivity is not a function of polymer radical molecular

Table 1. Parameters Used in This Model

$V_m = 0.943 \text{ cm}^3/\text{g}$	$\epsilon_v = 0.197$
$T_{gm} = -100 \text{ }^\circ\text{C}$	$T_{gp} = 225 \text{ }^\circ\text{C}$
$\alpha_m = 0.0005 \text{ }^\circ\text{C}^{-1}$	$\alpha_p = 0.000075 \text{ }^\circ\text{C}^{-1}$
$[M]_0 = 8.7 \text{ mol/L}$	$R = 2$
$k_{p0} = 1.3 \times 10^4 \text{ L}/(\text{mol s})$	$A_p = 0.5$
$v_{fcp} = 0.057$	$k_{t0} = 1.2 \times 10^7 \text{ L}/(\text{mol s})$
$A_t = 2.8$	$v_{fct} = 0.089$
$k_{b0} = 7.79 \times 10^{-7} \text{ 1/s}$	$A_b = 0.7$
$f_0 = 0.3$	$\epsilon = 150 \text{ L}/(\text{mol cm})$
$A_i = 0.411$	

weight but changes with the fractional free volume exponentially:

$$k_b = k_{b0}e^{A_b/v_f} \quad (10)$$

where A_b is the dimensionless activation volume which governs the rate at which radical trapping increases as a function of fractional free volume and k_{b0} is the preexponential factor. This relationship implies that the rate of radical trapping increases dramatically with the loss of free volume. (Trapping is accelerated with decreasing free volume, in contrast to the slowing of propagation and termination.)

Experimental Section

The bifunctional monomer used in this work, diethylene glycol dimethacrylate (DEGDMA), and the photoinitiator 2,2-dimethoxy-2-phenylacetophenone (DMPA) were obtained from Aldrich (Milwaukee, WI) and were used without further purification. A solution was prepared by dissolving 0.1 wt % DMPA in the DEGDMA monomer.

Reaction rate was monitored with a differential scanning calorimeter adapted with a photocalorimetric accessory capable of producing monochromatic ultraviolet light (Perkin-Elmer, DSC-DPA 7, Norwalk, CT). The light intensity was controlled by neutral density filters (Melles Griot, Irvine, CA). 365 nm ultraviolet light was selected. Approximately 1 mg of sample was placed in uncovered aluminum DSC pans. The DSC cell was continuously flushed with nitrogen. Nitrogen flushing started 10 min before exposing the sample to UV light to completely purge the DSC cell before polymerization. Curing took place at the temperature of 25 °C, and continuous irradiation of UV was used. The rate of polymerization was determined from the heat flux monitored by the DSC and the theoretical heat of reaction for double bond, 13.1 kcal/mol.⁸

Results and Discussion

Parameters. Listed in Table 1 are the parameters used to model the photopolymerization of DEGDMA initiated by 0.1 wt % DMPA at 365 nm UV, $T = 25 \text{ }^\circ\text{C}$. The glass transition temperatures and the thermal expansion coefficients of monomer and polymer were obtained from the literature.¹¹ The monomer specific volume was obtained from the Sartomer (West Chester, PA) catalog. The volume contraction factor was calculated on the basis of the volume shrinkage of 22.5 cm³ per mole of double bonds converted.³⁵ The initial initiator efficiency f_0 ³⁶ and the extinction coefficient of initiator ϵ ¹³ were obtained from the literature. The dimensionless activation volume governing the initiator efficiency, A_i , was taken from Kurdikar and Peppas's prediction of 0.05 at 0.4 conversion.¹⁶

The kinetic parameters were selected to represent closely the polymerization of DEGDMA at 0.42 mW/cm² UV intensity measured by photo-DSC (Figure 1). The preexponential kinetic constants k_{p0} and k_{t0} were selected to match the initial rate of polymerization and with the rate in the region identified following proce-

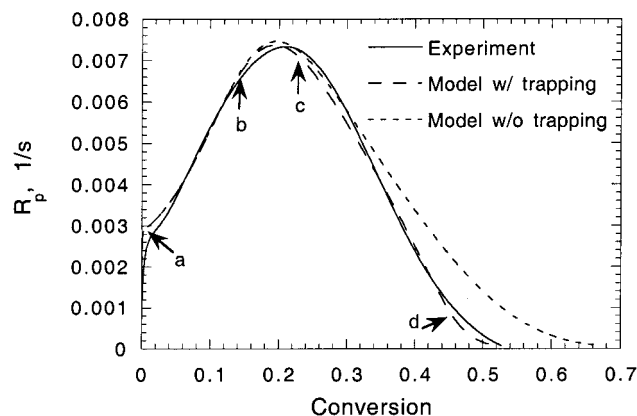


Figure 1. Predicted reaction rate with and without radical trapping and the actual reaction rate measured by photo-DSC versus conversion of double bonds during the polymerization of DEGDMA with 0.42 mW/cm² light intensity and 0.1 wt % DMPA. The markers on the predicted curve with radical trapping are (a) onset of autoacceleration, (b) reaction–diffusion becoming dominant for termination, (c) radical trapping becoming dominant, and (d) propagation becoming diffusion-controlled.

dures described by Goodner et al., i.e., the region where termination was reaction–diffusion-controlled, but propagation was still not diffusion-controlled and radical trapping was still not severe.¹¹ The dimensionless activation volumes, A_t and A_p , were selected to match the shape of autoacceleration and autodeceleration periods. The characteristic fractional free volume for termination v_{fct} was taken as only slightly higher than at the onset of the reaction. The characteristic fractional free volume for propagation v_{fcp} was selected to match the conversion at the maximum reaction rate. The reaction–diffusion parameter R was taken from the literature.³⁷ The dimensionless activation volume A_b and the preexponential parameter k_{b0} were selected to match the rate (with conversion) of radical trapping in ref 18.

Predicted Rate and Concentration Profiles. Figures 1–10 illustrate the numerical integration of eqs 1–4 with the parameters listed in Table 1. The “final” conversion was chosen to be that when the reaction rate had fallen to 1% of its maximum value, a typical criterion used in this highly diffusion-controlled reaction.^{1,21}

Figure 1 shows the predicted polymerization rate versus conversion, which is compared with the experimental data of polymerization of DEGDMA at UV intensity of 0.42 mW/cm² obtained from photo-DSC.

Autoacceleration takes place from the beginning of the reaction. Initially, termination of active radicals is diffusion-controlled, and the termination rate constant falls continuously. The decreasing termination rate constant leads to an increase of the active radical concentration while the trapped radical concentration is still low. When the termination resistance by segmental diffusion equals that by reaction–diffusion, termination becomes reaction–diffusion-controlled.

The rate of reaction reaches its maximum at 0.2 conversion. Shortly after that, around 0.23 conversion, the radical trapping becomes severe as the active radical concentration starts to drop. Propagation becomes diffusion-controlled very late; the system reaches the characteristic fractional free volume at 0.45 conversion. The radical trapping and the diffusion-controlled propagation that follows it cause the rate to decrease much more rapidly than the rate which can be accounted for

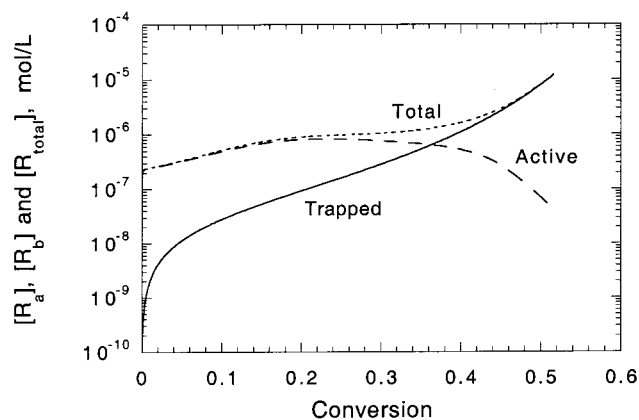


Figure 2. Concentrations of active, trapped, and total radicals versus the conversion of double bonds during the polymerization of DEGDMA with 0.42 mW/cm² light intensity and 0.1 wt % DMPA.

by the depletion of functional groups—we term this autodeceleration.

Also shown in Figure 1 is the polymerization rate without radical trapping ($k_{b0} = 0$). Obviously, the reaction rate before 0.23 conversion is not appreciably affected by the radical trapping. After that, the reaction rate without trapping appears to be higher than with trapping. Trapping severely lowers the active radical concentration. As a result, the final conversion is raised.

Changes in both active and trapped radical concentrations as well as the total radical concentration as a function of conversion are shown in Figure 2. At the beginning of the reaction, the trapped radical concentration is much lower than the active radical concentration because segment mobility (free volume) is high and initiation leads to a “steady-state” active radical concentration. At low conversions, the termination of active radicals slows severely as it becomes diffusion-controlled, and this causes the active radical concentration to rise rapidly with conversion. The rate constant for radical trapping is still low.

When termination becomes reaction–diffusion-controlled at around 0.14 conversion, the drop of the termination rate constant slows down. This leads to a slower increase of active radical concentration. When the trapping rate constant becomes high enough (around 0.23 conversion), the rate of forming active radicals becomes zero—here is a maximum in the active radical concentration. After that, radical trapping becomes dominant. The rate of forming active radicals becomes negative, leading to a drop of the active radical concentration. Finally, the drop of the active radical concentration, as well as the drop of the propagation rate constant, leads to an immeasurably slow reaction rate.

The trapped radical concentration increases monotonically. It surpasses the active radical concentration at around 0.36 conversion. From this point, the trapped radicals start to dominate the overall radical population. The behavior of trapped radicals is the result of the decreasing radical mobility as the system becomes more solidlike.

The total radical concentration increases monotonically with conversion during reaction. The increase is dominated by the active radicals at low conversions and by the trapped radicals at high conversions. At 0.2–0.3 conversion, the total radical concentration rises very slowly because the drop of the active radical concentra-

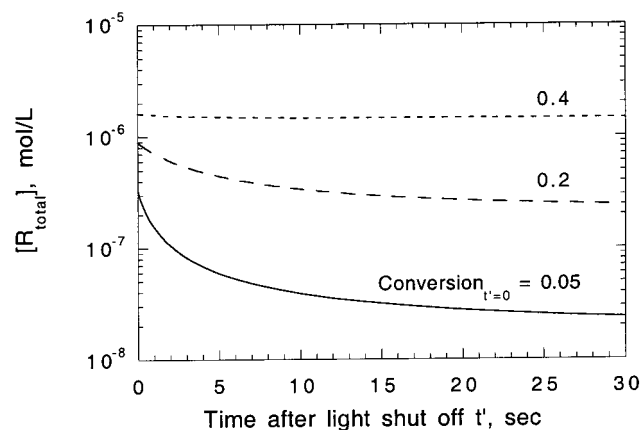


Figure 3. Total radical concentration as reaction proceeds after initiation (with 0.42 mW/cm² light intensity) is stopped at different conversions, 0.05, 0.2, and 0.4, as a function of time in the dark polymerization of DEGDMA with 0.1 wt % DMPA.

tion is almost balanced by the increase of the trapped radical concentration.

The predicted trend of active and trapped radical concentrations agrees qualitatively with experimental studies.¹⁸ However, the model overpredicts the growth of trapped radical concentration at high conversions. Experiment shows that the increase of the trapped radical concentration with respect to conversion slows down at the later stage of the reaction.¹⁸ This might be caused by the termination of trapped radicals, which is absent in this model. Trapped radicals can move slowly to react further. This might be important in affecting the growth of trapped radicals at the late stage of reaction.

Figure 3 shows the predicted total radical concentration change after the initiation has stopped (i.e., dark reaction when the light is shut off) at different conversions. The total radical concentration decays with time because of the termination of active radicals. After the active radicals have terminated each other, the final stable radical concentration represents that of trapped radicals. At a higher conversion, the overall total radical concentration increases, and the decay becomes less pronounced because of the formation of more and more trapped radicals. This predicted trend in the total radical concentration agrees with the experimental observations by Anseth et al.¹⁸ and Zhu et al.¹⁷

The agreement between the model and these experimental observations indicates that radical trapping can be represented by a unimolecular first-order reaction with a rate constant that rises as free volume is lost, even though this simple treatment ignores the microscopic details of radical trapping. For instance, trapping of radicals at low conversions is usually attributed to formation of what are called microgels, which shield the radicals from further polymerization.^{3,18} Also, at high conversions, radicals can be trapped by virtue of their substantially reduced mobility as microgel regions extend throughout the macroscopic gel.^{18,38} Nevertheless, both mechanisms contribute to the loss of free volume. It appears that the free volume concept works fairly well in predicting the radical trapping even without taking these details into account.

Predicted Behavior of the Rate Constants as the Conversion Changes. Figure 4 shows the kinetic constants k_p , k_t , k_b , and the initiator efficiency f as functions of conversion at typical values of the model

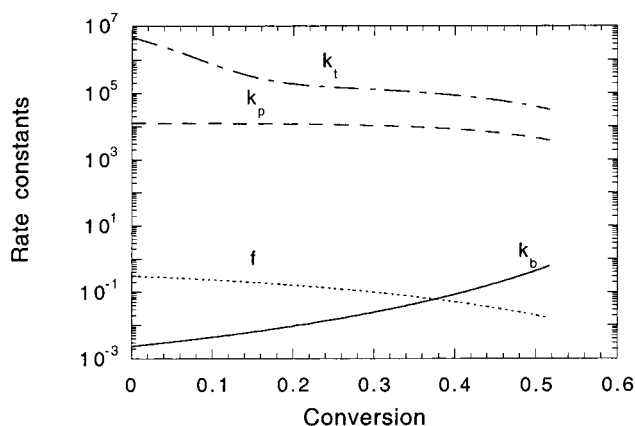


Figure 4. Rate constants for propagation k_p , for termination k_t , for radical trapping k_b , and initiator efficiency f versus the conversion of double bonds during the polymerization of DEGDMA with 0.42 mW/cm² light intensity and 0.1 wt % DMPA.

parameters. The propagation rate constant drops slowly before the system reaches the characteristic fractional free volume at 0.45 conversion, below which diffusion of the smaller monomer molecules remains unhindered. Then, k_p begins to decrease. The decrease of k_p is not severe because the active radicals are highly reactive throughout the reaction. The termination rate constant k_t changes more during the reaction. At the beginning, termination is limited by segmental diffusion; thus, k_t drops rapidly due to the loss of free volume. As conversion reaches around 0.14, the termination mechanism changes from segmental diffusion to reaction–diffusion. Thus, k_t gradually becomes proportional to k_p , with a proportionality determined by the product of the reaction–diffusion parameter R and the functional group concentration $[M]$.

The rate constant for radical trapping k_b increases with conversion as the active radicals gradually lose their mobility. At low conversions, k_b is very small since most radicals still have high mobility. As conversion reaches 0.23, k_b becomes significant enough to cause the drop of the active radical concentration.

In the present model, k_p and k_t depend on conversion less severely than in the models that do not have a separate equation for trapped radicals.^{11,13} This is because in the latter case radical trapping is considered as the diffusion limitation to both propagation and termination. Such a simplification loses important information such as the concentrations of trapped and active radicals during polymerization.

The diffusion-dependent initiator efficiency f drops severely during the course of polymerization. This is because more and more primary radicals formed by the decomposition of initiator recombine to form inactive molecules. The drop of the initiator efficiency severely lowers the total radical concentration at high conversions according to the sum of eqs 3 and 4.

Predicted Effects of Light Intensity on Rate and Concentration Profiles. Figures 5–10 show the effects of light intensity on the polymerization kinetics. As shown in Figure 5, the curves at different intensities have similar shapes. However, the polymerization rate scales with light intensity, following a power law relationship with an exponent ranging monotonically from 0.5 to close to 1.0 as conversion rises (Figure 6). This can be understood with eq 3.

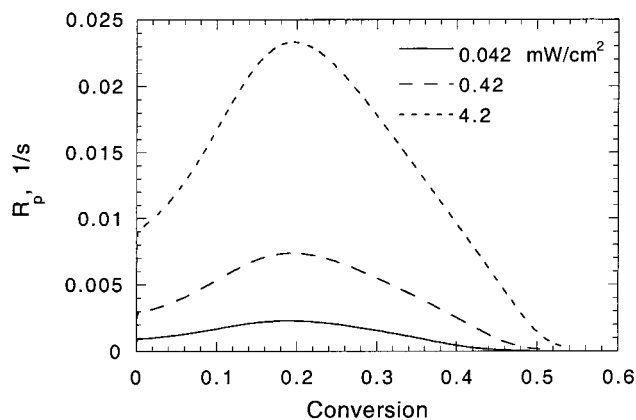


Figure 5. Reaction rate versus conversion of double bonds during the polymerization of DEGDMA with different light intensities, 0.042, 0.42, and 4.2 mW/cm², at 0.1 wt % DMPA.

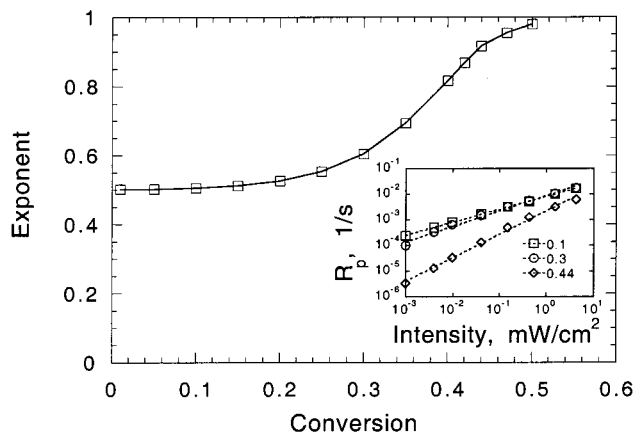


Figure 6. Exponent by which the propagation rate is proportional to the light intensity (ranging from 0.001 to 4.2 mW/cm²) at different conversions. Because of the limited final conversion, at 0.47 conversion, the exponent was examined from 0.01 to 4.2 mW/cm² of light intensity; at 0.5 conversion, the exponent was examined from 0.1 to 4.2 mW/cm² of light intensity. The inset shows the actual data fit by power relation at three different conversions: 0.1, 0.3, and 0.44.

At low conversions, the rate constant for radical trapping is still small, but the rate constant for termination is still high. Thus, radical trapping term is much smaller than the termination term. If one could apply the pseudo-steady-state assumption, the active radical concentration would be proportional to the light intensity to the power of 0.5. So would the reaction rate, which would be proportional to the active radical concentration.

At high conversions, the rate constant of radical trapping becomes significant, and the radical termination term can be ignored. Therefore, the active radical concentration and the reaction rate change linearly with light intensity. This scaling agrees with the experimental studies of photopolymerization of 1,6-hexanediol diacrylate (HDDA)³⁹ and diallyl oxydiethylene dicarbonate,² where a typical value increasing from 0.5 to 1.0 was found.⁴⁵

Figure 5 shows an increased final conversion (e.g., 0.49 in 0.042 mW/cm², 0.52 in 0.42 mW/cm², and 0.54 in 4.2 mW/cm²) at a higher light intensity, even though volume relaxation is not included in this model. The enhanced final conversion with light intensity has been observed experimentally in the photopolymerization of many multifunctional acrylates and methacrylates.^{1,7,15,41}

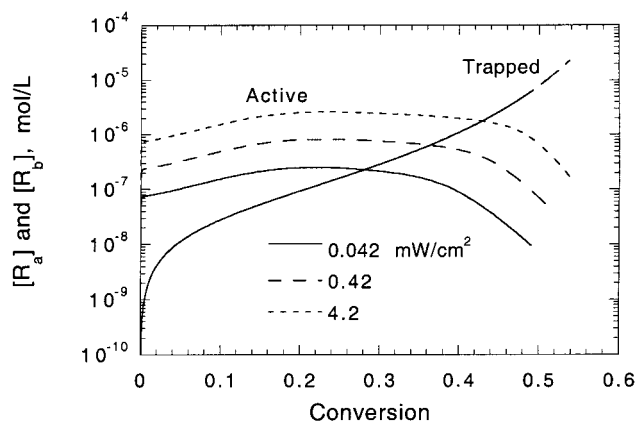


Figure 7. Concentrations of active and trapped radicals versus conversion of double bonds during the polymerization of DEGDMA with different light intensities, 0.042, 0.42, and 4.2 mW/cm², at 0.1 wt % DMPA.

Since the final conversion is generally chosen to be that when the reaction rate reaches a certain fraction (here, 1%) of the maximum reaction rate, the rate change during the autodeceleration period is what mainly determines the final conversion. The polymerization rate changes with light intensity by an increasing power from 0.53 at the maximum reaction rate to close to 1.0 at the end of reaction; thus, the final conversion must increase as light intensity rises. Models that ignore trapping, or treat trapping as diffusion limitation, would not predict this trend if volume relaxation is not included. Moreover, such models with a pseudo-steady-state approximation must always predict that the polymerization rate changes with light intensity following a power law relationship with an exponent of 0.5.

With increasing intensity, the overall active radical concentration rises, and the crossover of the trapped and active radical concentrations occurs at a higher conversion (Figure 7). The latter is caused by the raised active radical concentration. Interestingly, the trapped radical concentration at a given conversion does not depend on the light intensity. This is due to the following relation, derived from eqs 2 and 4,

$$\frac{d[R_b]}{dx} = \frac{k_b}{k_p(1-x)} \quad (11)$$

where x is the fractional conversion of functional groups. Therefore, $[R_b]$ is a function of x and should not depend on the light intensity. This behavior of trapped radicals needs to be tested with careful measurement of conversion and trapped radical concentration. With increasing light intensity, the trapped radical concentration reaches a higher value at the end of reaction.

Figure 8 shows the fraction of trapped radicals as a function of conversion while intensity is changed. Clearly, the fraction of the trapped radicals increases with conversion monotonically, reaching almost unity at the end. At a given conversion, the fraction of trapped radicals drops when light intensity is raised due to the higher active radical concentration. This has been observed experimentally.¹⁸

Figures 9 and 10 show the fractional conversion of photoinitiator and the total radical concentration as a function of polymerization time at different light intensities. The decomposition of photoinitiator follows an exponential decay according to eq 1. Because of the

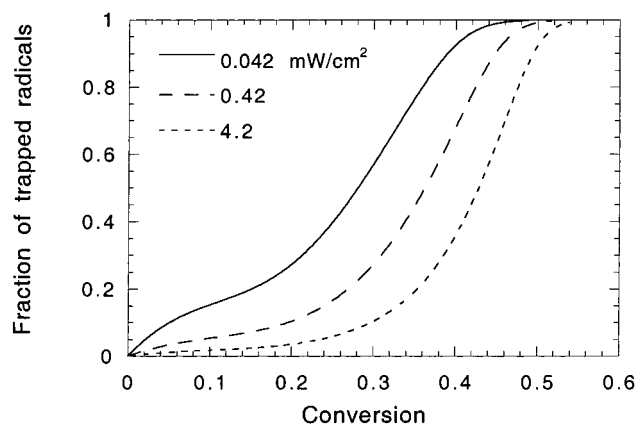


Figure 8. Fraction of trapped radicals versus conversion of double bonds during the polymerization of DEGDMA with different light intensities, 0.042, 0.42, and 4.2 mW/cm², at 0.1 wt % DMPA.

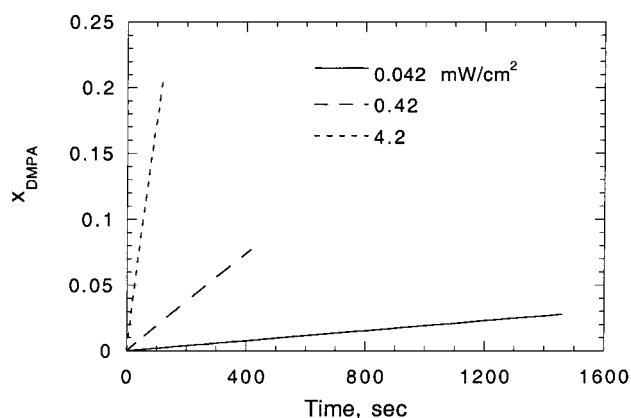


Figure 9. Conversion of photoinitiator DMPA during the polymerization of DEGDMA with different light intensities, 0.042, 0.42, and 4.2 mW/cm², at 0.1 wt % DMPA (initial weight fraction).

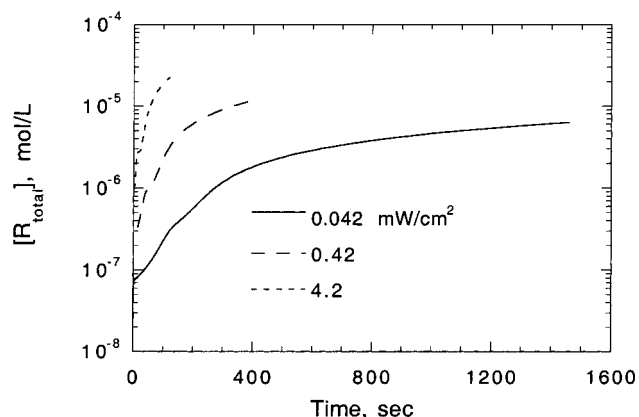


Figure 10. Total radical concentration change during the polymerization of DEGDMA with different light intensities, 0.042, 0.42, and 4.2 mW/cm², at 0.1 wt % DMPA.

small initiation rates, the decomposition seems to decay linearly with time (Figure 9). At the end of the reaction, there is only a small amount of initiator decomposed, i.e., 2.8% at 0.042 mW/cm² light intensity, 7.7% at 0.42 mW/cm² light intensity, and 20.8% at 4.2 mW/cm² light intensity. The higher the light intensity, the more the initiator decomposed.

The total radical concentration increases with time monotonically. At the beginning of the reaction, it suddenly reaches a "steady-state" concentration. The

total radical concentration then increases rapidly because of the increase in the active radical concentration by autoacceleration. This is followed by the slower formation of more and more trapped radicals, which also drives the increase of the total radical concentration. A similar trend in the total radical concentration was obtained experimentally.¹⁸ However, the measured initial steady-state period is longer than our prediction. As intensity is raised, the total radical concentration increases faster with time, and the system ends up with a higher radical concentration. This was also observed experimentally.¹⁸

In general, our model tends to underestimate the radical concentrations. Our calculation shows that if termination and changing of initiator efficiency are turned off ($f = 0.3$ at all conversions), the maximum radical concentrations at 300 s of irradiation under the light intensities of 0.2 and 0.02 mW/cm² are 6.7×10^{-5} and 6.8×10^{-6} mol/L, respectively. However, the measured total radical concentrations were 4×10^{-4} and 2×10^{-5} mol/L, respectively. Nevertheless, our model shows the right trends.

Our proposed treatment of radical trapping contributes to explaining why there is an enhanced final conversion at high intensity, but trapping alone probably underestimates the magnitude of this effect. In our photo-DSC experiment, we observed that when light intensity was raised from 0.42 to 4.2 mW/cm², the final conversion increased by 0.06. However, our model predicts that the final conversion increases only by 0.02. This indicates that volume relaxation is still needed to simulate this polymerization as a function of intensity. The excess free volume left by the slow volume relaxation enhances the mobility of reactive species; thus, an even higher final conversion is obtained.

Figure 5 shows that the conversion at the maximum reaction rate does not depend on the light intensity. This is different from the observation that the conversion at the maximum reaction rate shifts to a higher conversion at a higher light intensity in the polymerization of DEGDMA.^{8,37} This again is due to the absence of volume relaxation in this model. Bowman et al. have clearly demonstrated that, with the inclusion of volume relaxation, the conversion at the maximum reaction rate shifts to a higher conversion as intensity rises.²¹ The presence of a larger amount of excess free volume at a higher reaction rate enhances the mobility of functional groups, postponing the maximum reaction rate to a higher conversion.

Conclusions

An improved treatment of radical trapping during the photopolymerization of multifunctional monomers has been presented. The treatment assumes the trapping of radicals as a unimolecular first-order kinetic reaction and that the rate constant of this reaction increases exponentially with the inverse of the free volume. This functional form qualitatively captures the increasing diffusion resistance to further propagation.

The model is consistent with experimental measurements of polymerization rate and of the concentrations of trapped and active radicals in that (1) the concentration of trapped radicals increases with conversion monotonically, (2) the concentration of active radicals first increases, then reaches a maximum value, and drops, and (3) in agreement with experimental results, at a given conversion, the fraction of trapped radicals

decreases with light intensity (but always ultimately reaching almost unity). The model predicts a higher final conversion of functional groups with increasing light intensity even though volume relaxation process is not included. However, the underestimation of the increased final conversion and the invariant conversion at the maximum reaction rate as light intensity is raised support the additional role of volume relaxation.

This model does not accurately represent reaction behavior over the time scale that allows "trapped" radicals to react. (This time scale is defined such that further reaction by the "trapped" radicals does not contribute significantly to the overall propagation rate.) Though trapped radicals have low mobility, they are not permanently inactive. They can move slowly and react with the functional groups and radicals left in the system. This process can be enhanced when temperature rises during application. Consequently, "untrapping" will occur. Further modification to the model presented might incorporate this process to account for the late-stage decay of trapped radicals¹⁸ and the slow postpolymerization.⁴²

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- However, this model does not apply to the polymerization of liquid monomers in polymeric matrixes^{22,23} since the transfer reactions of radicals to the polymer binder are absent here. Note also that this model does not apply to iniferter ("living" radical) polymerization,^{24–26} which involves a reversible reaction between small stable radicals generated by iniferters and the free radicals on polymer chains.
- In this model, the exponential function of the diffusion-controlled term was developed on the basis of the dependence of diffusivity on free volume³³ and the Smoluchowski rate expression. Though Anseth and Bowman developed this model to predict the behavior of all the radicals (including the trapped ones), we presume that it can be applied to the active radicals by changing the parameters. Note that recently Michael Goodner et al. developed a model that incorporates the termination between primary radicals and macroradicals to account for the dependence of reaction rate on the light intensity under high intensities.³⁴ However, the recombination of primary radicals outside the solvent cage, which might be significant in affecting the primary radical concentration, was not included. Moreover, volume relaxation, which is very important to affect the reaction rate at very high intensities, was absent in their model. Once further modification is done, their model could certainly be incorporated.
- For the polymerization of DEGDMA, Cook et al. found that the intensity exponent changes from 0.36, 0.45, to 0.65 when the conversion increases from 0.05, 0.2, to 0.4 (cured at 50 °C).⁴⁰ Though our model predicts the trend of the increasing exponent with conversion, it overestimates the overall value for this system. This might be caused by the primary radical termination,³⁴ which lowers the exponent to zero.