Modeling Primary Radical Termination and Its Effects on Autoacceleration in Photopolymerization Kinetics

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ABSTRACT: In industrial photopolymerization processes, high light intensities are used to achieve fully cured products in short exposure times. Under these conditions, a high concentration of primary radicals—those radicals derived directly from the photocleavage of the initiator—is established. These high concentrations can lead to a phenomenon known as primary radical termination, in which growing macroradicals are terminated by primary radicals instead of other macroradicals. This mechanism violates the pseudo-steady-state assumption used in most radical polymerization modeling. While previous research has demonstrated the effects of primary radical termination on low conversion, linear polymerizations, little has been done to describe its effects on diffusion-controlled polymerizations and high conversion systems. To improve our understanding of primary radical termination on photopolymerization kinetic behavior, a previously developed kinetic model is extended to include the primary radical termination mechanism. In the initial simulations, the primary radical termination kinetic constant (k_{tp0}) is varied to determine its effects on the polymerization rate, the macroradical and primary radical concentrations, and the dominant mode of termination. The effect of primary radical termination on autoacceleration is addressed in particular. In a second series of predictions, k_{tp0} will be held constant as the light intensity is varied to demonstrate its effects on the polymerization rate profile. Last, the phenomenon of rate saturation is reproduced and explained using the kinetic model.

1. Introduction

At the moderate light intensities and initiator concentrations used in the vast majority of the radical photopolymerization studies reported in the open literature, nearly all termination events occur through a bimolecular reaction between macroradicals; i.e., two growing polymer chains come in close enough proximity to react and terminate by either combination or disproportionation. As a result, some bulk polymerization systems show diffusion-controlled polymerization behavior such as autoacceleration and autodeceleration. Autoacceleration occurs due to the increasing double-bond conversion in the system; as monomer is converted to polymer, the increase in viscosity leads to a reduction in the mobility of large molecules, such as the growing radical chains. Because the macroradicals can no longer diffuse into close enough proximity to react, the number of radicals in the system increases, which subsequently causes the increase in the rate of polymerization known as autoacceleration. Autodeceleration occurs when increased viscosity and vitrification effects begin to limit the mobility of small molecules such as monomer. Under these conditions, monomer can no longer easily diffuse to the reactive sites, and the rate of polymerization drops precipitously.

Most models describing this polymerization behavior utilize the pseudo-steady-state assumption to characterize the polymerization kinetics. In this assumption, the macroradical population is found by setting the rate of generation of radicals through photoinitiation equal to the rate of consumption of radicals through the bimolecular termination mechanism. Then the polymerization rate (R_p) is given by

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

where k_p and k_t are the kinetic constants for propagation and termination, respectively, R_i is the rate of decomposition of the initiating species, ϕ is the initiator efficiency, and [M] is the instantaneous concentration of double bonds. In this approach, autoacceleration and autodeceleration are accounted for by k_t and k_p, respectively, decreasing with increasing conversion in the system. For studies using moderate light intensity and initiator concentrations, the linear dependence on double-bond concentration and the square root dependence on rate of initiation predicted by eq 1 hold for experimentally determined polymerization rates. However, studies have also shown that at high initiation rates the dependence on initiation rate drops below the half-order prediction, and a greater than first-order dependence on double-bond concentration is displayed.[1] These features have been attributed to a phenomenon known as primary radical termination.

At low initiation rates, the population of primary radicals—those radicals derived directly from photocleavage of the initiator molecule—is very low, and macroradicals are much more likely to undergo termination with another macroradical than with a primary radical. In this case, the pseudo-steady-state assumption is valid, and eq 1 describes the polymerization kinetics. At high rates of initiation, however, the large primary radical population increases the likelihood of primary radical−macroradical termination events. When the rate of these reactions become significant, the pseudo-steady-state assumption is violated, and the deviation from ideal kinetic behavior (as predicted by eq 1)

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becomes pronounced. Furthermore, there can also be a pronounced effect on autoacceleration in the system. The primary radicals limit the buildup of macroradicals, thereby mollifying the rate increase normally seen during autoacceleration. While many photopolymerization studies are carried out under modest light intensities and initiator concentrations, most industrial photopolymerizations are carried out under "extreme" conditions, causing primary radical termination effects to manifest. In fact, primary radical termination, along with degradative chain transfer, has been referred to as "the most important (cause) of non-ideality in vinyl polymerization".[2] Therefore, due to both the dearth of research into the effect of primary radical termination on diffusion-controlled systems and the prevalence of high initiation rates in industrial photopolymerization processing, the effect of primary radical termination on photopolymerization kinetics, with particular focus on autoacceleration, will be addressed in this work.

Several researchers have examined the effect of primary radical termination in a variety of linear polymer-forming systems. Bamford[1] formulated an analytical treatment to predict the polymerization rate in the presence of primary radical termination. In the analytical method, one of two simplifying assumptions was utilized to make the math tractable. The two were the omission of primary radical recombination and the geometric mean postulate (in which the primary radical termination kinetic constant is the geometric mean of the bimolecular termination kinetic constant and the primary radical recombination constant). Polymerizations of styrene initiated thermally with 2,2′-azobis-(isobutyronitrile) (AIBN) in *N*,*N*′-dimethylformamide were used to compare predictions with experiment. Both formulations gave good agreement with the experimental trend observed: the rate dropped below the classical prediction (square root dependence on initiation rate) at higher initiator concentrations. While the two formulations do not describe the same series of reactions, they were both found to be adequate approximations. This work leads to the conclusion that primary radical recombination outside the solvent cage is negligible.

Okamura and Manabe[3] studied the effect of primary radical termination on the rate and degree of polymerization in styrene photopolymerizations self-initiated by γ radiation. They found that the dependence of polymerization rate upon radiation intensity decreased at high intensities, to the point of the polymerization rate becoming independent of intensity above a critical value (a phenomenon referred to in this work as "rate saturation"). A simple model offered to explain the experimental results also predicts the existence of a ceiling intensity, albeit at a much higher value than seen in the experiments. This discrepancy was attributed to the kinetic constant for primary radical termination being much higher than the kinetic constant for bimolecular termination in the real system. They also found that while primary radicals participated in chain termination reactions, the recombination of primary radicals outside of the solvent cage was negligible and did not effect the polymerization kinetics. A later monograph supported this conclusion, further showing that only systems containing greater than 50 vol % solvent show significant primary radical recombination effects in the polymerization rate profile.[4] They conclude that under normal conditions primary radical interaction is negligible when compared with the rate of primary radical termination.

Allen and Patrick[5] analytically treated primary radical termination in "diffusion-controlled" systems. In their work, a diffusion-controlled system is defined as a system in which diffusion is the rate-limiting step in the termination process over the entire course of the polymerization. However, their formulation does not allow the diffusivity (i.e., the termination kinetic constant) to change over the course of the reaction. Their predictions also show the existence of the rate saturation effect for high values of the primary radical termination kinetic constant. It is also noted that as the bimolecular termination kinetic constant is lowered, the effects of primary radical termination become more pronounced, a feature which proves important in vitrifying systems where bimolecular termination decreases over the course of the polymerization.

Deb[2,6−12] spearheaded a campaign to analytically determine the effects that primary radical termination and degradative chain transfer have on polymerization kinetics. In this series of papers, styrene, methyl methacrylate, and vinyl acetate were thermally polymerized using benzoyl peroxide and AIBN as initiators both in bulk and in solvent. In addition to experimental studies that were carried out over a wide temperature range to determine activation energies for chain initiation and primary radical termination, an analytical method was developed to determine a lumped kinetic constant that describes the extent of primary radical termination. It is also shown that while primary radical termination manifests at high initiation rates, at low initiation rates, degradative chain transfer is seen. Degradative chain transfer is similar to primary radical termination in that the polymerization rate is reduced from the classically predicted values, but the mechanism is that of chain transfer to solvent, producing a new radical that has a much lower reactivity than the primary radicals generated by initiator decomposition.

While this profusion of research has been carried out for linear polymerizations performed at low conversions, scant attention has been given to high conversion, cross-linking, or linear polymerizations in which diffusion-controlled kinetics plays a major role. In the aforementioned studies, the polymerization rates reported are initial rates; the dependence on double-bond concentration is determined by changing the solvent-to-monomer ratio and finding the new initial rate. No experimental studies focusing on primary radical termination in diffusion-controlled systems have been reported, and few attempts at predicting primary radical termination effects in these systems have been made. In the modeling field, the main thrust thus far has been to incorporate primary radical termination into termination kinetics that depend on chain length.[13] In such a formulation, primary radicals are treated as polymer chains of the shortest possible length, zero repeat units. While such a method will inherently capture the diffusion-controlled kinetics associated with primary radical mobility in the polymerizing system, treating primary radicals as short polymer radicals neglects the difference in reactivities between alkane-like radicals (the chain ends) and initiator-generated radicals, which can often have unsaturated, aromatic, or heteroatom substituents. The effect due to radical type may not be particularly large, but it is the more general case and thus merits consideration. More importantly, primary radicals will show markedly different reaction behavior than even the shortest oligomeric radicals in cross-linked systems.

In these systems, the oligomeric radicals will have a high probability of being attached to the growing polymer network and thus will have a greatly restricted mobility compared to that of primary radicals.

In this work, a previously developed kinetic model[14,15] is extended to include the mechanism of primary radical termination and to elucidate its effects on radical photopolymerization kinetics, with particular focus on its effects on autoacceleration. In a series of simulations, the primary radical termination kinetic constant (k_{tp}) will be varied to determine its effect on the polymerization rate, the macroradical and primary radical populations, and the dominant mode of macroradical termination. In the following simulations, k_{tp} will be held constant as the incident light intensity is varied; these results will show the effect that primary radical termination can have on photopolymerizations at high light intensities. These simulations are performed for a monofunctional monomer but are applicable for any polymerization showing diffusion-controlled kinetics, especially cross-linking polymerizations where diffusion limitations dominate the cure behavior. Last, predictions will be made for a difunctional monomer system with relatively fast propagation and termination kinetics. These predictions will be compared qualitatively to experimental results reported by Decker.[16]

2. Model Development

The kinetic model is based upon the following reaction mechanism:

initiation*:*

$$\mathrm{I} \xrightarrow{h\nu} 2\mathrm{R}^\bullet \tag{2a}$$

$$\mathrm{R}^\bullet + \mathrm{M} \xrightarrow{k_i} \mathrm{P}_1^\bullet \tag{2b}$$

propagation*:*

$$\mathrm{P}_n^\bullet + \mathrm{M} \xrightarrow{k_p} \mathrm{P}_{n+1}^\bullet \tag{2c}$$

termination*:*

$$\mathrm{P}_n^\bullet + \mathrm{P}_m^\bullet + \xrightarrow{k_t} \mathrm{P}_{n+m}\ (\mathrm{P}_n + \mathrm{P}_m) \tag{2d}$$

$$\mathrm{P}_n^\bullet + \mathrm{R}^\bullet \xrightarrow{k_{tp}} \mathrm{P}_n\mathrm{R} \tag{2e}$$

In the above equations, I is the initiator, M represents monomer, $R^\bullet$ and $P_n^\bullet$ are primary radicals and growing chains of length n, respectively, and both P_n and P_nR represent polymer without an active center.

The initiation process consists of two steps. In the first step (2a), the initiator undergoes photolysis upon absorbing a photon to produce two radicals. For this simulation, both radicals will be considered identical with respect to their reactivity. The rate of this step is given by

$$R_i = \frac{\epsilon I_0[\mathrm{I}]}{E'} \tag{3}$$

where ϵ is the molar absorptivity of initiator, I_0 is the incident light intensity, and [I] is the instantaneous initiator concentration. E' is the energy per mole of photons (based on 365 nm ultraviolet light for this work) and is necessary to convert the light intensity from an energy quantity (mW/cm^2) to a molar quantity (mol/(s cm^2)). Note that eq 3 assumes Beer's law governs the light absorption; i.e., only a small fraction of the incident light is absorbed. For high initiator concentrations or thick samples, light absorption must be treated more rigorously. The second step in initiation is chain initiation (2b), in which primary radicals react with a monomer unit to form a growing polymer radical one repeat unit in length. The kinetic constant for this step is k_i, the chain initiation kinetic constant.

The propagation step is given by eq 2c. In this step, monomer is added to the growing polymer chain with kinetic constant k_p. Two separate paths exist for termination. Normal bimolecular termination, in which two growing macroradicals come together and terminate, is given by eq 2d. Termination can occur by either combination or disproportionation; however, the specific mode does not effect the polymerization kinetics, so termination will be treated with one lumped kinetic constant k_t.

The second path for termination (2e) is that of primary radical termination, the focus of this work. In this step, a growing macroradical reacts with a primary radical to form inactive polymer. Note that the kinetic constant for this step (k_{tp}) will in general be different from that for the bimolecular termination step for two main reasons. First, the chemistry involved in the two reactions can be considerably different, as the primary radical can have a very different reactivity than the chain end radical. Also, the diffusion-controlled character of the two reactions will be quite distinct, as the primary radicals are much smaller, and therefore much more mobile, than the growing macroradicals. Also note that primary radical recombination is not included in the model. This assumption simplifies the system to reduce the number of kinetic parameters in the model and is in accordance with the observations that primary radical recombination events are negligible compared to other reactions.[1,4]

The form for the diffusion-controlled propagation and termination kinetic constants will be identical to that used in the previously developed model:[14,15,17]

$$k_p = \frac{k_{p0}}{1 + e^{A_p(1/f - 1/f_{cp})}} \tag{4a}$$

$$k_t = \frac{k_{t0}}{1 + \left(\dfrac{Rk_p[\mathrm{M}]}{k_{t0}} + e^{-A_t(1/f - 1/f_{ct})}\right)^{-1}} \tag{4b}$$

In the expression for k_p, k_{p0} is the true kinetic constant for propagation, i.e., the value of k_p in the absence of diffusional limitations. f is the average fractional free volume of the system, which is calculated using the free volume correlations utilized in Goodner et al.[14] f_{cp} is the critical free volume for propagation; this represents the value of f at which k_p will be half of k_{p0}. A_p is a parameter that determines how quickly the diffusion-controlled kinetic constant decreases once diffusional limitations manifest. The parameters appearing in the expression for k_t are similar, with an extra term representing the contribution from reaction−diffusion. Within this term appear the instantaneous double-bond concentration, [M], and the reaction−diffusion parameter, R.

The expressions for k_i and k_{tp} will incorporate diffusion-controlled kinetics in the same manner as k_p; therefore, they will have the same form as eq 4a.

Table 1. Material and Kinetic Properties for HEMA and PUA[a]

Material Properties for HEMA		
$\rho_m = 1.073$ g/cm^3	$\rho_p = 1.15$ g/cm^3	$[M]_0 = 8.2$ mol/L
$T_{gm} = -60$ °C	$T_{gp} = 55$ °C	
$\alpha_m = 0.0005$ °C^{-1}	$\alpha_p = 0.000075$ °C^{-1}	
Kinetic Parameters for HEMA		
$R = 4$ L/mol		
$k_{p0} = 1000$ L/(mol s)	$A_p = 0.66$	$f_{cp} = 0.042$
$k_{t0} = 1.1 \times 10^6$ L/(mol s)	$A_t = 1.2$	$f_{ct} = 0.060$
$k_{i0} = 1000$ L/(mol s)	$A_i = 0.66$	$f_{ci} = 0.042$
k_{tp0} = varies	$A_{tp} = 0.66$	$f_{ctp} = 0.042$
Kinetic Parameters for PUA		
$R = 2$ L/mol		
$k_{p0} = 1.0 \times 10^4$ L/(mol s)	$A_p = 0.60$	$f_{cp} = 0.047$
$k_{t0} = 1.0 \times 10^7$ L/(mol s)	$A_t = 2.0$	$f_{ct} = 0.090$
$k_{i0} = 1.0 \times 10^4$ L/(mol s)	$A_i = 0.6$	$f_{ci} = 0.047$
$k_{tp0} = 1.0 \times 10^8$ L/(mol s)	$A_{tp} = 0.6$	$f_{ctp} = 0.047$

[a] The material properties for PUA are identical to those for HEMA; the choice of values for the kinetic parameters for PUA are discussed in the text.

Because the kinetic parameters governing chain initiation and primary radical termination are difficult to determine experimentally, the values of the related kinetic parameters will be estimated. Since the diffusion-controlled characteristics of chain initiation and primary radical termination both depend on the diffusion of small molecules (primary radicals and monomer for chain initiation, primary radicals for primary radical termination), the diffusion-related kinetic parameters will be set equal to those for propagation, which depends on the diffusion of monomer. Thus, $A_i = A_{tp} = A_p$ and $f_{ci} = f_{ctp} = f_{cp}$. The non-diffusion-limited value of the chain initiation kinetic constant, k_{i0}, will likewise be set to the corresponding value of k_{p0}, as chain initiation is effectively a propagation reaction. While this assumption may underestimate the value of k_{i0} in a real system, the characteristic quantity governing primary radical termination is (k_{tp}/k_ik_p),[8] and thus the selection of a reasonable k_{i0} should not effect the model predictions qualitatively. The value of k_{tp0} will be varied throughout this work to elucidate the effect of primary radical termination on photopolymerization kinetics.

In this work, photopolymerization of 2-hydroxyethyl methacrylate (HEMA) initiated by 2,2-dimethoxy-2-phenylacetophenone (DMPA) will be simulated. The kinetic parameters for propagation and termination in HEMA polymerization have been experimentally determined elsewhere[14] and are presented along with the physical parameters in Table 1. The six material properties listed are required to calculate the fractional free volume at a given conversion. These parameters are the monomer and polymer densities (ρ_m and ρ_p), the glass transition temperatures (T_{gm} and T_{gp}), and the differences between the expansion coefficients in the rubbery and glassy states (α_m and α_p).

In the simulation, the time-dependent species balances on all the reacting species (I, M, $R^\bullet$, $P_n^\bullet$, P_n and P_nR) form a set of six coupled ordinary differential equations. These equations are numerically integrated using a commercial software routine for solving stiff sets of differential equations (Numerical Algorithms Group, Oxford, UK).

3. Results and Discussion

3.1. Model Predictions of HEMA Polymerization.

Figure 1 shows predicted rate profiles for bulk HEMA polymerization as the primary radical termination kinetic constant is varied. In the absence of primary radical termination, the traditional profile shape is seen. Initially, the rate decreases slightly as monomer is consumed. At approximately 20% conversion, however, the rate begins to increase dramatically. This increase is referred to as autoacceleration; it occurs due to the mobility limitations of the growing macroradicals. Because of vitrification and increasing viscosity in the polymerizing system, growing chains can no longer come together to terminate through the normal bimolecular mechanism, and as a result, the macroradical population (and thus the polymerization rate) increases. This rate increase persists up to nearly 45% conversion, at which point autodeceleration sets in. At this point, increasing viscosity and vitrification cause monomer mobility to drop, slowing the diffusion of double bonds to the reactive chain ends. Finally, a limiting conversion of approximately 85% is reached, signifying that unreacted monomer is trapped in the vitrifying polymer and cannot diffuse to any reactive site on the time scale of the observation.

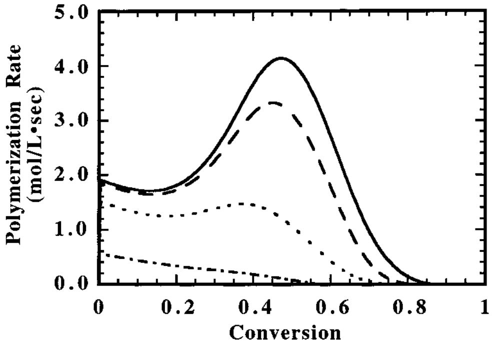

Figure 1. Polymerization rate profiles for several levels of primary radical termination. The lines correspond to k_{tp0} = 0.0 (solid), 1.0×10^6 L/(mol s) (dashed), 1.0×10^7 L/(mol s) (dotted), and 1.0×10^8 L/(mol s) (dash–dot). Light intensity is 500 mW/cm^2, and the initiator concentration is 0.2 M.

At nonzero values of the primary radical termination kinetic constant, a change in polymerization rate behavior is seen. At the lowest level of primary radical termination ($k_{tp0} = 10^6$ L/(mol s)), the initial rate is identical to the profile in the absence of primary radical termination. However, once autoacceleration starts, the effect of primary radical termination can easily be seen. The rate increase in the autoacceleration regime is mollified as the still mobile primary radicals scavenge the growing chains, thereby lessening the buildup of macroradicals. This trend can be clearly seen in Figure 2a,b, which shows the macroradical and primary radical populations as a function of conversion for the rate profiles plotted in Figure 1.

The reason that primary radical termination effects do not manifest until autoacceleration begins is best explained by examining the species balance on the macroradical population:

$$\frac{d[P_n^\bullet]}{dt} = k_i[R^\bullet][M] - 2k_t[P_n^\bullet]^2 - k_{tp}[R^\bullet][P_n^\bullet] \quad (5)$$

In this equation, the first right-hand-side term is macroradical generation via chain initiation. The second and third terms represent macroradical consumption through bimolecular termination and primary radical termination, respectively. In the absence of primary

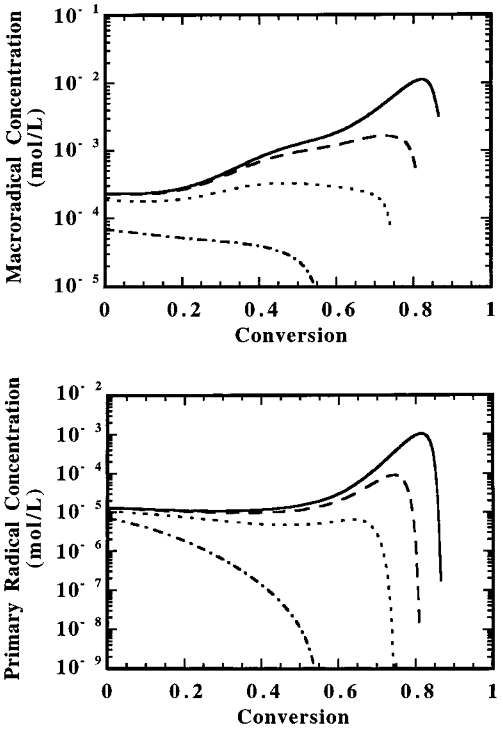

Figure 2. (a, top) Macroradical concentration for the polymerization profiles shown in Figure 1. The lines correspond to the same levels of primary radical termination as in Figure 1: $k_{tp0} = 0.0$ (solid), 1.0×10^6 L/(mol s) (dashed), 1.0×10^7 L/(mol s)(dotted), and 1.0×10^8 L/(mol s) (dash−dot). Light intensity is 500 mW/cm^2, and the initiator concentration is 0.2 M. (b, bottom) Primary radical concentration for the polymerization profiles shown in Figure 1. The lines correspond to the same levels of primary radical termination as in Figure 1: $k_{tp0} = 0.0$ (solid), 1.0×10^6 L/(mol s) (dashed), 1.0×10^7 L/(mol s) (dotted), and 1.0×10^8 L/(mol s) (dash−dot). Light intensity is 500 mW/cm^2, and the initiator concentration is 0.2 M.

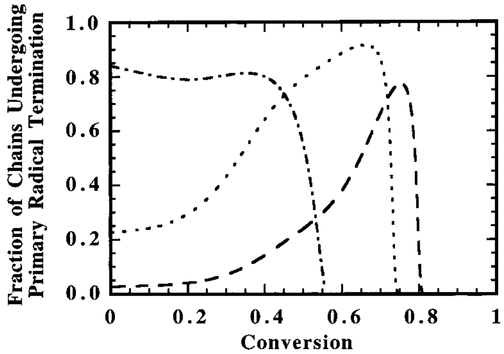

Figure 3. Relative importance of primary radical termination mechanism as indicated by the fraction of polymer radicals undergoing primary radical termination. The lines correspond to the polymerizations shown in Figure 1: $k_{tp0} = 1.0 \times 10^6$ L/(mol s) (dashed), 1.0×10^7 L/(mol s) (dotted), and 1.0×10^8 L/(mol s) (dash−dot). Light intensity is 500 mW/cm^2, and the initiator concentration is 0.2 M.

radical termination, macroradical consumption drops off as k_t decreases in the autoacceleration regime, leading to the build of macroradicals (at approximately 25% conversion in Figure 2a). With primary radical termination occurring, a drop in k_t may initially cause a buildup of radicals; however, once the bimolecular termination term drops below the value of the primary radical termination term, primary radical termination becomes the dominant mode of termination, and the buildup of macroradicals will be mitigated (around 40% conversion in Figure 2a). This occurrence is also shown in Figure 3, which shows the fractions of polymer radicals terminated by primary radicals.

At the end of the polymerization, a slight decrease is also seen in the final double-bond conversion. This feature is a result of monomer and primary radicals "competing" for the growing macroradicals. In the absence of primary radical termination, the macroradicals continue to add monomer units, albeit at a slow rate, until mobility restrictions stop diffusion of monomer to reactive sites on the time scale of the polymerization. With primary radical termination occurring, primary radicals continue to scavenge the macroradicals, reducing the final number of monomer units that will be incorporated as the system vitrifies.

As the primary radical termination kinetic constant is increased ($k_{tp0} = 10^7$ L/(mol s)), the reduction in autoacceleration is clearly seen along with a reduction in the initial polymerization rate. At the lower value of k_{tp0} (10^6 L/(mol s)), primary radical termination did not become the dominant mechanism of macroradical termination until after the bimolecular termination kinetic constant (k_t) dropped because of diffusional limitations. At the increased value of k_{tp0} (10^7 L/(mol s)), primary radical termination contributes to a reduction in the macroradical population from the start of the reaction. Returning to the macroradical species balance, eq 5, it can be seen that the last term, the primary radical termination term, is now significant from the onset of polymerization, causing the drop in macroradical concentration seen in Figure 2a. In Figure 3, it is shown that over 20% of all termination reactions occur by primary radical termination at the start of the reaction, and this percentage increases as diffusional limitations reduce macroradical mobility, inducing a decrease in k_t.

As the value of k_{tp0} is increased even further (to 10^8 L/(mol s)), the polymerization rate is reduced considerably throughout the entire reaction, and a much lower final conversion is reached. In this case, the number of primary radical termination events limits not only the macroradical population but also the primary radical concentration, as the primary radicals are consumed preferentially through this termination mechanism. As a result, the number of growing chains initiated by primary radicals is reduced, leading to the large reductions in both radical populations as seen in Figure 2a,b. The much lower final conversion reached is attributed to the reaction proceeding at a much slower rate until finally all the photoinitiator is consumed, and the reaction ceases. In addition to reducing the extent of polymerization, this behavior would have the effect of reducing the kinetic chain length, and thus the molecular weight, of the polymer produced. For example, the kinetic chain length of the polymer produced at 500 mW/cm^2 light intensity in the absence of primary radical termination is approximately 20 repeat units at the start of the reaction and increases to 90 at 50% conversion. When k_{tp0} is 10^8 L/(mol s), the initial kinetic chain length is only 10; only short oligomeric chains are created before termination occurs through the primary radical mechanism.

The previous results show the effect of changing the primary radical termination kinetic constant on the polymerization rate with the goal of giving a better understanding of the primary radical termination mechanism. In a real system, however, the kinetic constants are fixed by the monomer or monomer/solvent combination used. A more realistic way to examine the effect of

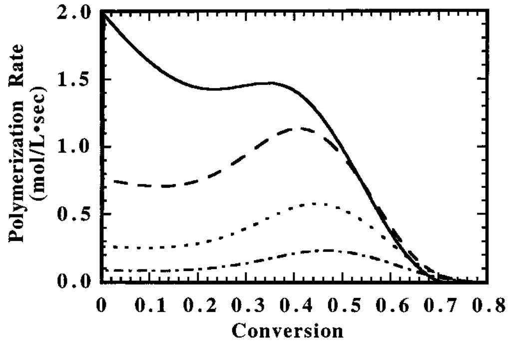

Figure 4. Polymerization rate profiles for several light intensities with a fixed level of primary radical termination ($k_{tp0} = 1.0 \times 10^7$ L/(mol s)). The lines correspond to decreasing incident light intensity: 1000 mW/cm^2 (solid), 100 mW/cm^2 (dashed), 10 mW/cm^2 (dotted), and 1 mW/cm^2 (dash−dot). Initiator concentration is 0.2 M.

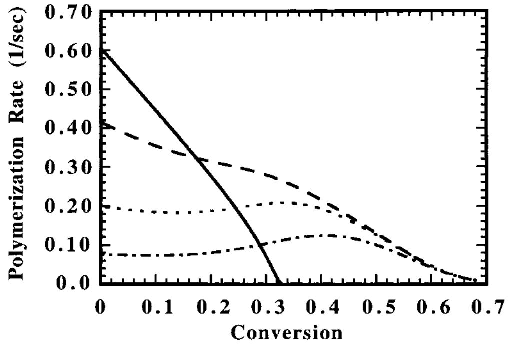

Figure 5. Polymerization rate profiles for several light intensities with a fixed level of primary radical termination greater than that shown in Figure 4 ($k_{tp0} = 1.0 \times 10^8$ L/(mol s)). The lines correspond to decreasing incident light intensity: 1000 mW/cm^2 (solid), 100 mW/cm^2 (dashed), 10 mW/cm^2 (dotted), and 1 mW/cm^2 (dash−dot). Initiator concentration is 0.2 M.

primary radical termination is to vary the controllable factors in the polymerization, i.e., the light intensity or initiator concentration. Figures 4 and 5 illustrate the effect that light intensity has on photopolymerizations in which primary radical termination can occur.

In Figure 4, the primary radical termination kinetic constant is fixed at a level 1 order of magnitude greater than the bimolecular termination kinetic constant ($k_{tp0} = 10^7$). At lower light intensities (1 and 10 mW/cm^2), the traditional diffusion-controlled rate profile is seen, with a non-diffusion-limited region, autoacceleration and autodeceleration. As the light intensity is increased to 100 mW/cm^2, primary radical termination starts to limit the rate increase seen in the autoacceleration region. At 1000 mW/cm^2, the autoacceleration peak is nearly eliminated. This occurs because higher light intensities correspond to greater decomposition of the photoinitiator into primary radicals. While the primary radical termination mechanism was present at the low light intensities, the population of primary radicals was small enough that even in the diffusion-controlled regimes, macroradical termination would occur through reaction diffusion before a primary radical was encountered in order to terminate. At the higher light intensities, the high concentration of primary radicals drives primary radical termination to become the dominant termination mechanism earlier in the reaction.

Furthermore, the occurrence of primary radical termination leads to a reduction in kinetic chain length (and thus molecular weight of the final polymer) similar to that mentioned in the discussion of Figure 2. For comparison, when the light intensity is 1 mW^2/cm and primary radical effects are negligible, the kinetic chain length varies between 400 and 1300 over the course of the reaction. However, for the polymerization carried out at 1000 mW^2/cm, in which primary radical termination is the dominant termination mechanism, the kinetic chain lengths are well below 100 for the majority of the polymerization. Thus, primary radical termination leads to lower molecular weight polymer in addition to a reduction in the overall polymerization rate.

Similar polymerization rate behavior is shown in Figure 5, which displays rate profiles for a system with a higher value of k_{tp0} (10^8). In this series of predictions, the effects due to primary radical termination manifest at lower light intensities due to the greater reactivity of the primary radicals as reflected in the increased kinetic constant. At the highest light intensity, 1000 mW/cm^2, both the concentration and the reactivity of the primary radicals are so great that the reaction is quenched considerably. While an initially high polymerization rate is achieved, it drops quickly as the macroradical population dies out.

Several factors are responsible for this feature. First, initiator is decomposed quickly by photolysis as the polymerization proceeds, leading to ever decreasing numbers of primary radicals to initiate radical chains. Second, the primary radicals that are generated are far more reactive toward the chain end radicals than they are toward the monomer; thus, they preferentially terminate macroradicals as opposed to initiating new growing chains. It should be noted that while the model does not allow primary radical recombination, a photopolymerization operating at this high of light intensity (and therefore high primary radical concentration) could have a significant proportion of primary radicals undergoing recombination reactions outside the solvent cage.

3.2. Comparison with Experimental Studies. In this section, the mechanism of primary radical termination will be used to explain the phenomenon of rate saturation. In particular, model predictions will be compared qualitatively to experimental polymerization kinetic studies reported by Decker.[16] In that work, photopolymerizations of a telechelic poly(urethane) acrylate (PUA) displayed rate saturation as the incident light intensity was increased above 100 mW/cm^2. A likely explanation of rate saturation involving primary radical termination will be set forth in the discussion concerning Figure 6.

To simulate the polymerization of PUA, the kinetic parameters and physical properties needed in the model had to be estimated, as they have not been reported. Without any particular information driving the choice of physical properties, the values for the model were set to those used previously for the HEMA polymerization. The values of the kinetic parameters were chosen to yield approximately the same polymerization kinetics as observed by Decker at low light intensities: a slow but steady reaction at lower light intensities, greater than 50% conversion in less than a second at high light intensities, and rate saturation above a critical value of the light intensity. The kinetic parameters used in this work are reported in Table 1. Note that only qualitative agreement between model predictions and experiments was sough for; to reproduce the exact

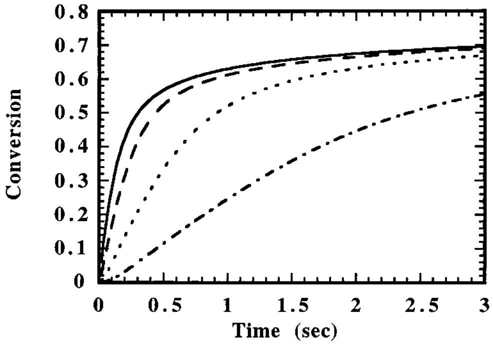

Figure 6. Simulated photopolymerization profiles for PUA. The lines correspond to decreasing incident light intensity: 1000 mW/cm^2 (solid), 100 mW/cm^2 (dashed), 10 mW/cm^2 (dotted), and 1 mW/cm^2 (dash–dot). Initiator concentration is 0.2 M.

polymerization behavior would require not only a more thorough description of the kinetic parameters and physical properties but also a model accounting for temperature variations, as polymerization in Decker's system proceeds in a nonisothermal manner.

The effect of rate saturation in the simulated polymerization of PUA is shown in Figure 6. The rate of polymerization increases considerably as the light intensity is increased from 1 to 10 mW/cm^2. In fact, the rate (time derivative of conversion) scales with the square root of light intensity, as predicted by the classical kinetic analysis represented by eq 1. However, further increases in light intensity show smaller increases in polymerization rate. By the time 200 mW/cm^2 has been reached, the rate no longer increases, and the conversion profiles become coincidental and the saturation intensity has been achieved. Therefore, rate saturation can be reproduced by a simple kinetic model incorporating primary radical termination.

The reason why rate saturation occurs is most easily explained by returning to the differential mass balance on the macroradical population, eq 5. When the primary radical concentration is low (at low light intensities), the primary radical termination term will be small compared to the bimolecular termination term. The balance is then between chain initiation and bimolecular termination, and setting the two terms approximately equal (the pseudo-steady-state assumption[18]) gives the result of the macroradical population scaling with the square root of the primary radical population (and therefore the light intensity, as the primary radical population is directly proportional to the light intensity):

$$2k_t[P_n^\bullet]^2 \approx k_i[R^\bullet][M] \propto I_0 \qquad (6a)$$

Since the rate is first order in the macroradical concentration, the rate displays a square root dependence on the light intensity, the classical result expressed by eq 1.

At high light intensities, the primary radical population will be large, and primary radical termination will be the dominant mode of termination. In this case, chain initiation will be balanced by primary radical termination, again using the pseudo-steady-state assumption[18] to set the two terms in the species balance approximately equal:

$$k_{tp}[R^\bullet][P_n^\bullet] \approx k_i[R^\bullet][M] \qquad (6b)$$

In this case, the primary radical populations on each side of the balance cancel, leaving the macroradical population independent of the primary radical population and, thus, independent of the light intensity. This situation is the one that occurs above the saturation intensity. It should also be noted that decreasing initiator efficiency (through primary radical recombination) could also contribute to the rate saturation effect in the polymerization profiles reported by Decker. This effect was not addressed in this work.

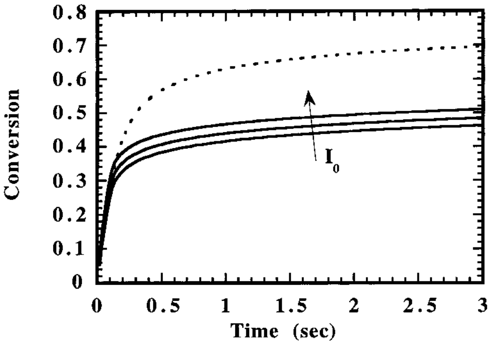

Figure 7. Dark polymerization profiles for PUA polymerization. Illumination is stopped at 0.1 s. The solid lines indicate profiles for increasing light intensities of 500, 1000, and 5000 mW/cm^2. For reference, the dotted line represents the full cure behavior (i.e., continuous illumination) above the saturation intensity. Initiator concentration is 0.2 M.

From a processing standpoint, the existence of a saturation intensity might look grim. If processing time is limited because of throughput requirements or equipment availability, then higher light intensities will not provide the extra curing required in a short time span. However, after illumination ceases, dark polymerization takes over. Primary radicals that were generated while the light was on will continue to initiate new chains as well as to terminate macroradicals. The continuing chain initiation will allow the polymerization to proceed, albeit at a much slower rate than while the light was on. Higher light intensities when the light was on translate into higher primary radical concentrations after the light is extinguished, which, in turn, leads to a greater rate of polymerization in the dark. This feature is shown by the model predictions presented in Figure 7. While the polymerization rate is limited to the saturation rate while the light is on, greater light intensities lead to a greater degree of curing in the dark. In Figure 7, the difference in conversion over an order of magnitude light increase is only 5%, but Decker's experimental studies on PUA display an increase of 30% conversion with a mere 6-fold increase in light intensity.[16] The discrepancy between the model predictions and the experiments most likely stems from either the uncertainty in the kinetic parameters used in the model or the isothermal restriction used in the model development.

4. Conclusions

A kinetic model incorporating primary radical termination has been presented. For the simulated polymerization of HEMA at a fixed light intensity and initiator concentration, increasing the value of the primary radical termination kinetic constant leads to a decrease in the polymerization rate throughout the course of the entire polymerization. This decrease occurs due to primary radicals scavenging macroradicals, thereby quenching the polymerization. This decrease in macroradical concentration is most evident in the reduction of the autoacceleration peak, with elimination of the peak occurring for the highest values of k_{tp0}. Increasing k_{tp0} also leads to a reduction in the final conversion, a feature that is also due to macroradical scavenging by primary radicals. Simulations varying the incident light intensity for fixed values of k_{tp0} show similar results. As the light intensity is increased, causing an increase in the primary radical concentration, the increase in rate in the autoacceleration regime is reduced, as is the final conversion at the highest light intensities.

The kinetic model is also used to reproduce the rate saturation effect. In this scenario, the rate of polymerization reaches a maximum as light intensity is increased. This feature results from a change in the dominant mode of termination and thereby a change in the dependence of the macroradical population on the light intensity. At low light intensities, bimolecular termination dominates, resulting in a square root dependence of the macroradical population on the light intensity. At high light intensities, primary radical termination dominates, and the macroradical population becomes independent of the light intensity. While operating at light intensities above the saturation intensity does not afford greater rates of polymerization while the sample is illuminated, higher light intensities cause higher primary radical populations, which in turn may lead to enhanced polymerization after illumination ceases.

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