Coupling Chain Length Dependent and Reaction Diffusion Controlled Termination in the Free Radical Polymerization of Multivinyl (Meth)acrylates

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ABSTRACT: The importance of kinetic chain length on termination kinetics has been investigated in cross-linking free radical polymerizations both experimentally and using a kinetic model. The model differs from previous multivinyl polymerization models via incorporation of chain length dependent termination (CLDT) kinetics. Experimentally, kinetic chain length distributions were manipulated, and the impact these changes have on the relationship between polymerization rate, R_p, and initiation rate, R_i, was examined over the entire conversion range for both dimethacrylate and diacrylate polymerizations. While the acrylate polymerization exhibits little change, the methacrylate polymerization exhibits significant deviation from the classical dependence of R_p on R_i; this dependence continuously changes throughout polymerization. Once the polymerization becomes reaction diffusion controlled, changes in R_i no longer effect the kinetics. The transition from chain length dependent to independent kinetics is predicted when CLDT is incorporated, thus predicting polymerization kinetics more accurately over a range of polymerization conditions.

Introduction

The termination kinetics of free radical polymerizations are far from simple. Although they have been studied extensively, their complex nature has hindered efforts to establish a comprehensive picture of the polymerization kinetics and all of the mechanisms that underly the kinetics.[1,2] One aspect of the termination kinetics that has received significant attention over the past several decades is the role of the size of the reacting radical. Numerous works have explored the existence of a chain length dependent termination (CLDT) mechanism in monovinyl polymerization systems.[3−15] The importance of such a mechanism in those polymerizations has achieved widespread acceptance although the specifics of the relationship between chain length and the termination kinetic constant continue to be extensively evaluated. Conversely, the importance of such a mechanism in polymerizations that cross-link has long been overlooked. Recently, however, several authors have explored the possibility that, despite the cross-linking nature of the polymerization, kinetic chain length may play a significant role in the termination kinetics.[16−19] These works have laid the groundwork for further investigations and have certainly established CLDT as an important factor in cross-linking polymerizations.

Primary methods for probing the effect of kinetic chain length on the kinetics involve the manipulation of polymerization conditions such that changes are induced in the distribution of chain lengths formed during polymerization. Although discussions of kinetic chain length are traditionally limited to monovinyl polymerization systems, similar relationships will be utilized in this evaluation of cross-linking polymerizations. In the absence of transfer reactions, the kinetic chain length, ν, is simply “the average number of monomers reacting with a given active center from its initiation to its termination”,[20] approximated by the ratio of the rate of monomer consumption, R_p, the polymerization rate, to the rate of radical generation, R_i, which, under pseudo-steady-state conditions, is approximately equal to the termination rate, R_t (eq 1).

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} \tag{1}$$

When transfer is added to the reaction scheme, the kinetic chain length can again be thought of as the number of monomers reacting with an active center during its “lifetime”. In this scenario, an active center produced as a consequence of a transfer reaction is considered a new initiation site and, thus, the start of a new chain.[21−23] Consequently, kinetic chain length in polymerizations where transfer reactions are considered is calculated as follows:

$$\nu = \frac{R_p}{R_i + R_{ct}} = \frac{R_p}{R_t + R_{ct}} \tag{2}$$

where R_{ct} is the chain transfer rate to nonpolymeric species. Again, R_i is approximately R_t under pseudo-steady-state conditions.

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Thus, shifting the distribution of kinetic chain lengths toward lower values can be achieved in several different ways for a given polymerization system. Changes are introduced simply by altering the initiation rate or the chain transfer rate, and the corresponding effect on factors such as the polymerization rate and the termination kinetic constants are then evaluated. Specifically, the dependence of the polymerization rate on the initiation rate is one method for examining this effect. If the termination kinetics are independent of chain length, then the classical dependence of $R_p \propto R_i^{1/2}$ (eq 3) would be expected.

$$R_p = \frac{k_p}{k_t^{1/2}}[M]\left(\frac{R_i}{2}\right)^{1/2} \tag{3}$$

This relationship is based on a second-order bimolecular termination mechanism and does not account for differences in radical reactivity. Thus, if the termination kinetic constant, k_t, depends on the length of the radicals that are participating in the termination reaction, a deviation from the classical picture is expected. Deviations from classical kinetics in monovinyl polymerization systems have been presented via both theoretical predictions and experimentation, with a less than square root dependence of polymerization rate on initiation rate attributed to chain length effects.[3,4,10,24,25]

A number of experimental investigations involving multifunctional (meth)acrylic polymerizations have also reported a nonclassical dependence of polymerization rate on initiation rate.[16,17,26−36] These evaluations have been limited primarily to evaluation of the effect of initiation rate on polymerization rate at a given low conversion or over a range of low conversion values. This deviation has not, however, been thoroughly examined as a continuous function of conversion in those polymerization systems. It is of practical importance not only to establish deviations, or lack thereof, from classical kinetics at low conversion in cross-linking polymerizations, but also to understand how this behavior changes as the polymerization progresses.

The prominence of a reaction diffusion controlled termination mechanism in cross-linking polymerizations of multifunctional (meth)acrylates has been firmly established.[30,37−40] The chain length independent nature of the reaction diffusion process is an aspect of the polymerization that is in stark contrast to the chain length influenced kinetics recently proposed as an important aspect of these polymerizations. Thus, characterization of the role of CLDT during the early stages of the polymerization and the characteristics of the transition to a termination environment dominated by reaction diffusion is critical.

It is the focus of this work to examine the effects of chain length dependent termination in cross-linking free radical systems with polymerization environments that are dominated by a reaction diffusion controlled termination mechanism throughout most of their polymerization. This task has been approached via both experimentation and modeling. The use of these two methods in tandem has been utilized to construct a picture of the kinetics of these systems more complete than is realized with an experimental or modeling approach alone.

Experimental Section

Materials. The monomers used in this study were di(ethylene glycol) dimethacrylate (DEGDMA, Sartomer Co., Exton, PA) and di(ethylene glycol) diacrylate (DEGDA, Sartomer Co., Exton, PA). The GC purity of each monomer is greater than 95%, with a reactive esters content of at least 99%. Polymerizations were performed using 0.1−5.0 wt % of the ultraviolet initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY). All materials were used as received.

Fourier Transform Infrared Spectroscopy (FTIR). Real-time FTIR spectroscopy (Nicolet model 760 Magna series II FTIR, Nicolet, Madison, WI) has been used to monitor the polymerization kinetics. A horizontal transmission accessory was designed to enable mounting of samples in a horizontal orientation for FTIR measurements.[41,42] A MCT/B−XT KBr detector-beam splitter combination was used in conjunction with the rapid scan feature of the spectrometer to obtain temporal resolutions (~30 ms) sufficient for monitoring these polymerizations. All experiments[17,41] and analyses[17,41,43] were conducted as previously described.

An UV light source (Ultracure 100SS, 100 W Hg short-arc lamp, EXFO, Mississaugua, Ontario, Canada) equipped with a liquid light guide and a band-pass filter (320−390 nm, EXFO, Mississaugua, Ontario, Canada) was used to irradiate the monomer/initiator mixtures. The incident light intensity was controlled using the internal aperture of the UV light source. To ensure that the thin-film approximation for uniform light intensity throughout the sample was valid, the sample thickness was minimized (15−20 μm). The molar absorptivity for DMPA at the peak initiating wavelength (365 nm) is 150 L/(mol cm). The initiation rate was calculated assuming an efficiency of one and an exponential decay of initiator (eq 4); correspondingly, R_i (eq 5) during irradiation was incorporated into the analysis of the experimental results.

$$[\mathrm{Ab}] = [\mathrm{Ab}]_0 e^{-2.303\epsilon I_{inc}\lambda t/N_{Av}hc} \tag{4}$$

$$R_i = 2\phi I_{abs} = 2\phi\left(\frac{2.303\epsilon I_{inc}\lambda[\mathrm{Ab}]}{N_{Av}hc}\right) \tag{5}$$

R_i is the initiation rate, ϕ is the initiator efficiency, I_{abs} is the quantity of light absorbed, I_{inc} is the incident light intensity in units of power/area, ϵ is the initiator's molar absorptivity at λ, the wavelength of initiation, [Ab] is the concentration of the initiator, N_{Av} is Avogadro's number, h is Planck's constant, and c is the speed of light. It is important to note that the scaling of the polymerization behavior with initiation rate is of primary importance in these studies, not the absolute value of R_i. The assumption of unity for the efficiency will, thus, have minimal impact on the scaling.

Results and Discussion

Experiment. The impact that kinetic chain length has on the polymerization is examined by evaluating the behavior of a given polymerization system under various conditions. Systematic variation of the kinetic chain length is paramount in discerning its impact on the polymerization kinetics. Several methacrylates and their corresponding acrylates have been examined at conditions that yield different average kinetic chain lengths.[16,17,31] The firmly established differences in the chain transfer characteristics of acrylates and methacrylates[29,44,45] make their comparison a valuable tool for studying chain length effects. The large amount of chain transfer inherent to acrylate polymerizations makes it difficult to impact kinetic chain length significantly during the formation of these networks. It is this characteristic, combined with the absence of a significant chain transfer mechanism in the methacrylate systems, that makes their combined evaluation so valuable to the study of chain length dependent effects in cross-linking polymerizations.

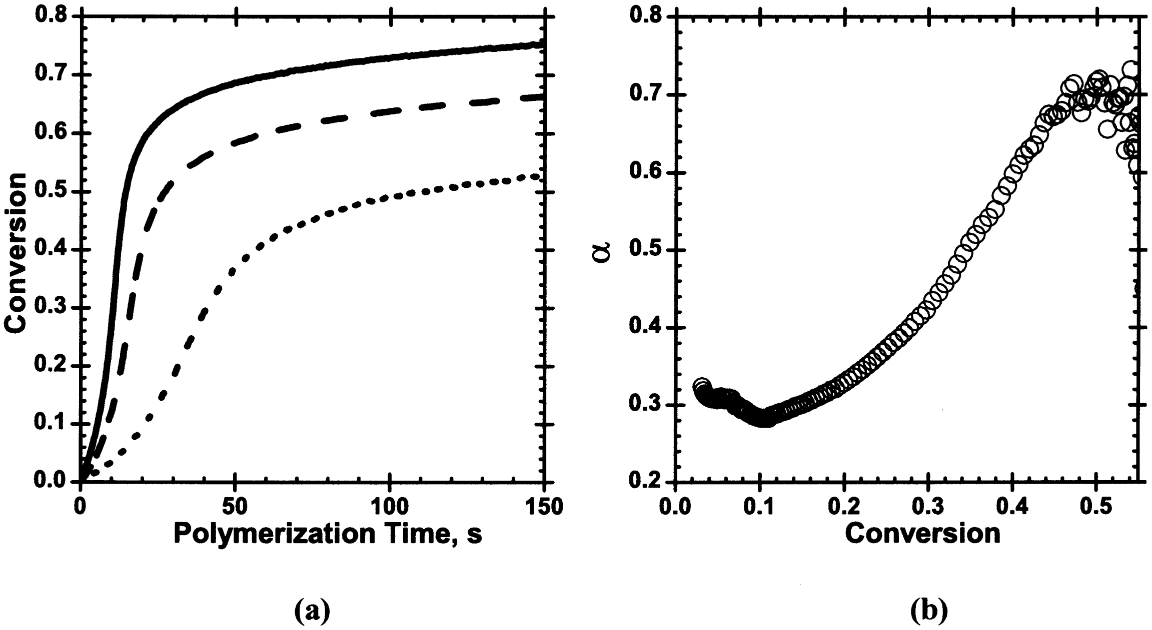


Figure 1. Evaluation of the dependence of polymerization rate on initiation rate for DEGDMA polymerization ($R_i = 4 \times 10^{-5}$ (· · ·), 5.5×10^{-4} (- - -), and 2×10^{-3} mol/(L s) (—)). All polymerizations were initiated at 5 mW/cm^2 with 0.1, 1.25, and 5.0 wt % of the photoinitiator DMPA, respectively. The conversion as a function of time data collected using FTIR is presented **(a)**, as well as the relationship between the polymerization rate and the initiation rate, as expressed by $R_p \propto R_i^{\alpha}$, as a function of conversion **(b)**.

Given that kinetic chain length is approximated by the number of times a radical propagates before it is involved in a chain stopping event such as termination or chain transfer (eq 2), changes are made to the kinetic chain length by modifying the ratio of these events. Since the termination rate is equivalent to the initiation rate under steady-state conditions, changes in the kinetic chain length are induced by changing either the initiation rate, via changes in initiator concentration or the incident light intensity, or the chain transfer rate, via the addition of small quantities of a chain transfer agent. Thus, if a series of polymerizations is carried out over a range of initiation rates, the effect(s), if any, on the kinetics can be explored. It is important to quantify the relationship between polymerization rate and initiation rate as well as to examine changes in that relationship as a function of conversion and correspondingly as a function of the dominant termination mechanism. Although such correlations have been hypothesized previously,[4,17,26,27,30] they have not been explicitly tested.

In a number of systems, an initial scaling exponent has been presented previously,[16,17,26,27,29,30] and it has been acknowledged that the fit is valid, in most cases, for only a small portion of the polymerization. An evaluation of the change in that relationship as the polymerization progresses, as well as a comparison of the location of the transition with changes that have been observed in the underlying kinetics, would provide additional insight into the polymerization process. Specifically, it would assist in defining the polymerization regions where CLDT is most important as well as the relative magnitude of its importance as a function of the polymerization conditions and system.

In a previous study, the polymerization of poly(ethylene glycol) (600) dimethacrylate (PEG(600)DMA) was examined.[16] This system is unique with respect to the other polymerizations that have been studied, as the T_g of the monomer/polymer remains below the cure temperature throughout the entirety of its ambient temperature polymerization. A scaling exponent well below the classical $^1/_2$ was observed throughout the entirety of the polymerization. In fact, when the unsteady-state kinetics of this system at different initiation rates were analyzed,[17] the authors observed a change in the kinetics, not only in the prereaction diffusion controlled termination regime but also for the remainder of the polymerization. It was hypothesized that network formation in this more mobile, rubbery network is controlled by the distribution of the kinetic chains formed during polymerization. Thus, changes in parameters such as the initiation rate and chain transfer rate could be used to alter the kinetic chain length distribution and correspondingly change the underlying structure of the polymer network.

Contrasting the rubbery PEG(600)DMA system with a system that forms a glassy polymer network, such as DEGDMA, provides additional information. Much like the polymerization of PEG(600)DMA, the DEGDMA polymerization exhibits a dependence on the initiation rate that is less than the classical square root dependence ($R_p \propto R_i^{\sim 0.32}$) during the early stages of the polymerization (Figure 1). This identical relationship was also observed by Anseth and co-workers[30] at low conversion for the polymerization of DEGDMA over a range of initiation rates an order of magnitude lower than those studied here. The scaling in that work breaks down at ~10% conversion, compared to ~20% in this study. This discrepancy may be rationalized by the use of an exponentially decaying initiation rate with polymerization time in this contribution (because initiator is consumed) compared to the use of a constant R_i in the scaling of Anseth's data. If analyzed without accounting for this decay, the initial scaling of the data in this study also begins to diverge at ~10% conversion. Accounting for this decay becomes increasingly important as the range over which R_i is examined broadens, i.e., as the difference increases between the constant and

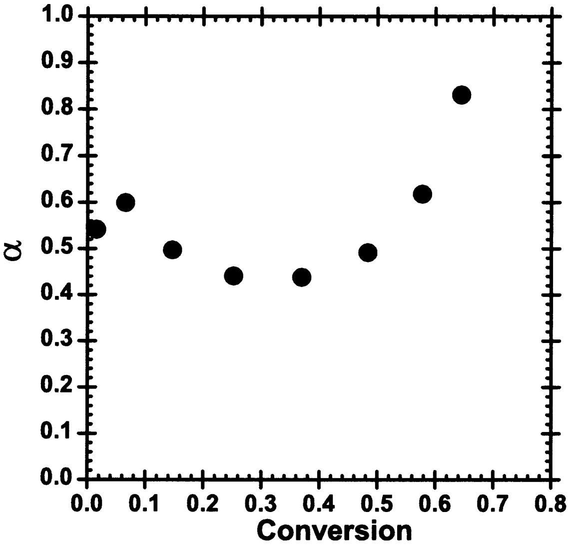


Figure 2. Evaluation of the dependence of polymerization rate on initiation rate for DEGDA polymerization ($R_i = 4 \times 10^{-5}$ and 2×10^{-3} mol/(L s)). Polymerizations were initiated at 5 mW/cm^2 with 0.1 and 5.0 wt % of the photoinitiator DMPA, respectively. Experimental results were obtained using FTIR.

decaying initiation rate cases. Cook also observed a similar relationship, $\alpha = 0.36$, at 5% conversion in the 30 °C visible light; camphorquinone initiated DEGDMA polymerization.[26]

As conversion increases, the relationship between polymerization rate and initiation rate undergoes a transition. The relationship that remained nearly constant for ~20% conversion exhibits a continuously changing dependence of R_p on R_i (Figure 1b). The conversion range over which a significant change in α occurs correlates to the region where this system, under these conditions, has transitioned into a reaction diffusion controlled termination regime (Figure 5).[17] It is not surprising that the dependence on initiation rate observed in this study increases when the dominant termination mechanism shifts. Examination of the corresponding acrylate system also yielded interesting trends (Figure 2). As is expected for an acrylate polymerization, the dependence of R_p on R_i closely follows the classical relationship. In this scenario, $\alpha = {}^1/_2$ is expected for the pure bimolecular termination route.[4] Since the kinetic chain length distribution in the acrylates is dominated by transfer reactions inherent to the polymerization, one would not anticipate a large effect from an increase of this magnitude in R_i. It is worth noting that an $\alpha \geq 0.5$ has been observed in other multivinyl acrylate polymerizations, namely hexanediol diacrylate,[28,29] tripropylene glycol diacrylate,[35] pentaerythritol tetraacrylate,[28] and an aliphatic urethane–acrylate formulation,[32,33] and has been attributed to radical isolation, an effective unimolecular termination process.

Modeling. A natural progression of these investigative efforts into the role of CLDT in cross-linking polymerizations is the incorporation of a chain length dependent mechanism into a model representation of multivinyl polymerization kinetics. Kinetic models exist that are able to describe much of the complex multivinyl monomer polymerization behavior.[46–50] These predictive capabilities are a result of incorporating effects such as diffusion controlled kinetics, free volume considerations, and cyclization. Although the predictive capabilities of these models are ever improving, their current ability to predict kinetics over a broad range of polymerization conditions is still severely lacking. Frequently, second-order bimolecular termination and termination kinetics that are independent of kinetic chain length (or initiation rate) are assumed in the kinetic equations describing multivinyl photopolymerizations. However, the recent experimental observations indicate that previous model failure to predict reaction kinetics accurately over a range of initiation rates is due, in part, to incorporating one or more of the classical kinetic assumptions, specifically, the absence of both CLDT and a transition from CLDT to reaction diffusion controlled termination. What has been learned recently regarding the importance of CLDT in these cross-linking polymerizations will help overcome previous model inadequacies.

On the basis of our experimental observations, a model has been developed that builds upon previous models which incorporated changes in free volume and diffusion controlled kinetics for multivinyl polymerizations.[46–48,50] This model examines the shortcomings of the chain length independent radical termination assumption while retaining the pseudo-steady-state and second-order bimolecular termination criteria. The assumption that radical termination is chain length independent is relaxed by incorporating a CLDT parameter, based on random walk theory as described by Benson and North,[51] into the kinetic equations that describe termination (eqs 6 and 7). A complete description of the kinetic model is presented in Lovestead et al.[19]

In brief, using random walk theory, the dependence of the kinetic constant for termination on the chain length distribution in the polymerization network has been added via a modification of the termination kinetic constant, k_{t0} at infinite free volume, i.e., in the mass transfer limited regime. This change results in an expression for k_{t0} as a function of the length of the two terminating radical chains i and j (eq 6).

$$k_{tij0} = k_{t110}\,\frac{1}{2}\left(\frac{1}{i^{\gamma}} + \frac{1}{j^{\gamma}}\right) \tag{6}$$

Here, γ has generally been assumed to be one-half,[51] which predicts that two radicals terminate at a rate proportional to the sum of the inverse square roots of the chain lengths. Coupling this expression to those that have been developed to account for diffusion controlled kinetics, free volume considerations, and reaction diffusion-controlled termination yields the desired chain length dependent k_{tij} (eq 7).[19]

$$k_{tij} = k_{t110}\left\{1 + \left(\frac{Rk_p[\mathrm{M}]}{k_{t110}} + \mathrm{e}^{-A_t[(1/f)-(1/f_{ct})]}\,\frac{1}{2}\left(\frac{1}{i^{\gamma}} + \frac{1}{j^{\gamma}}\right)\right)^{-1}\right\}^{-1} \tag{7}$$

In this expression, R is the ratio of kinetic constants, $k_t/k_p[\mathrm{M}]$, when reaction diffusion is the dominant termination mechanism. This ratio is referred to as the reaction diffusion coefficient. A_t is a constant that controls the onset and rate of autoacceleration, f_{ct} is the critical free volume where termination becomes controlled by the segmental motion of the active species, and f is the fractional free volume of the system as described by eqs 8−11.[47,48,50,52]

$$f_m = 0.025 + \alpha_m(T - T_{gm}) \quad (8)$$

$$f_p = 0.025 + \alpha_p(T - T_{gp}) \quad (9)$$

$$\phi_m = \frac{1 - X}{1 - X + \frac{\rho_m}{\rho_p}X} \quad (10)$$

$$f = f_m\phi_m + f_p(1 - \phi_m) \quad (11)$$

Here, 0.025 is the fractional free volume at the glass transition temperature,[52] m and p represent monomer and polymer, respectively, α_m and α_p are the volume expansion coefficients, T is the temperature, T_g is the glass transition temperature, ϕ_m is the volume fraction of monomer, X is the conversion, and ρ is the density. These equations combine to predict fractional free volume, and subsequently, termination and propagation, as a function of conversion.

The chain length independent propagation kinetic constant is predicted by eq 12, which takes into account the impact free volume has on monomer mobility.

$$k_p = k_{p0}[1 + \exp[A_p(1/f - 1/f_{cp})]]^{-1} \quad (12)$$

Here, k_{p0} is the propagation kinetic constant at infinite free volume, A_p is a parameter that describes the onset and autodeceleration rate, and f_{cp} is the critical free volume at which propagation changes from being reaction controlled to diffusion controlled. While the impact of chain length on propagation needs to be explored further, for simplicity, this model currently excludes chain length dependent propagation effects.

The incorporation of chain length dependence into the definition of k_t introduces an infinite number of radical species balances, one balance for each radical length. These balances are made more tractable by averaging together longer length radicals and assuming groups of radicals are equally reactive.[8,19] An additional feature of the mass balances that requires further explanation is cross-linking behavior. In this model, monomer consumption is monitored by double-bond concentration depletion; therefore, the model does not take into account which double bond on a monomer unit reacts. As well, the model predicts radical concentrations based on free volume limitations as a function of conversion and not based on radical structure. For these reasons, the model in its current form is applicable to both monovinyl and multivinyl photopolymerizations.

Using the newly derived expression for k_{tij} and the corresponding species balances, the polymerization of DEGDMA was examined. The expansion coefficients for the liquid state minus the expansion coefficient for the glassy state for DEGDMA are assumed to be α_m = 0.0005 °C^{-1} and α_p = 0.000 075 °C^{-1}.[46,48,53] All model predictions were simulated at 25 °C, and the material properties (T_{gm} = −12 °C,[53] T_{gp} = 500 °C,[53] ρ_m = 1.06 g/cm^3,[46,48,53] and ρ_p = 1.32 g/cm^3 [46,48,53]) for DEGDMA were based on literature data. The reaction diffusion parameter, R, is taken from experimental work by Anseth et al. and Berchtold et al.[17,30]

The model parameters for diffusion control and free volume effects are determined utilizing experimental results. When only one polymerization condition is modeled using the chain length independent $\gamma = 0$ case, an exemplary fit is achieved for a given set of polymerization conditions. This outcome is illustrated in Figure 3 where chain length independent model parameters were acquired using the experimental results for DEGDMA polymerization initiated with 5 wt % DMPA at 5 mW/cm^2 (A_t = 0.46, A_p = 0.11, f_{ct} = 0.044, f_{cp} = 0.0219, k_{t110} = 150 000 L/(mol s), and k_{p0} = 100 L/(mol s)). Excellent model prediction of this experimental result is attained up to ~60% conversion. However, the model is entirely unable to capture the observed polymerization behavior for additional polymerization conditions in the absence of a chain length dependent termination mechanism contribution. This model failing is evidenced clearly by the inability of the above parameters to predict polymerization kinetics for initiation conditions other than those used for parameter determination (Figure 3). The chain length independent model predicts that α is one-half and is conversion independent.

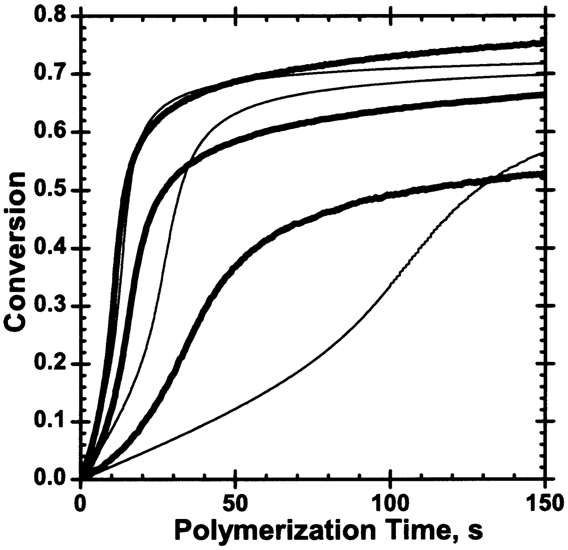
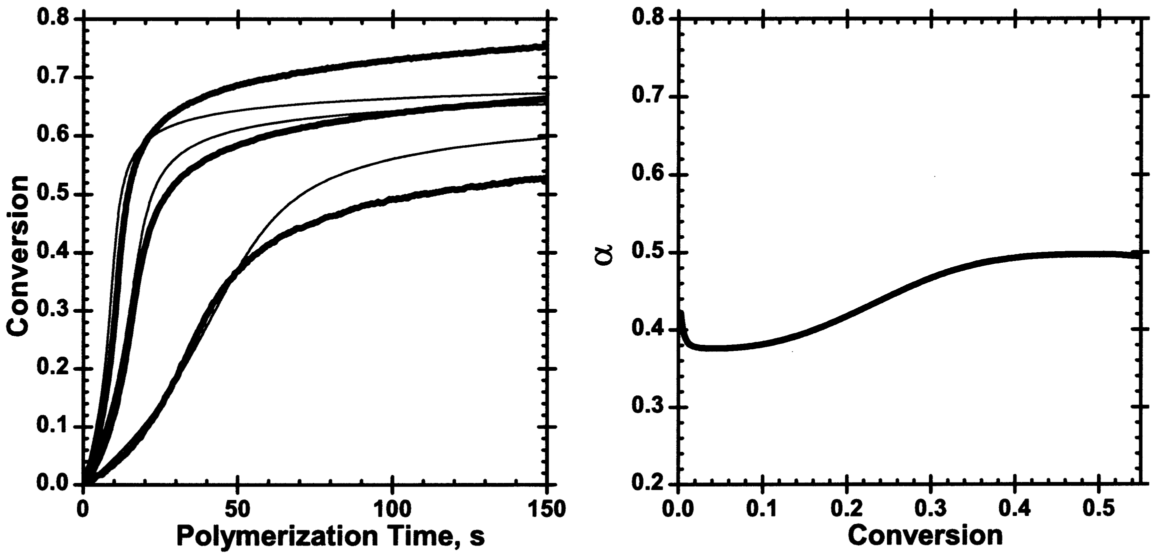


Figure 3. Chain length independent ($\gamma = 0$) model (—) and experimental (━) results for DEGDMA polymerization are presented at three different initiation rates (R_i = 4 × 10^{-5}, 5.5 × 10^{-4}, and 2 × 10^{-3} mol/(L s)), where the longest cure time corresponds to the lowest initiation rate. Model parameters for diffusion control and free volume effects on termination and propagation were fit using experimental data for DEGDMA polymerziation initiated with 5 wt % DMPA at 5 mW/cm^2. All polymerizations were conducted via initiation of samples containing 0.1, 1.25, and 5 wt % DMPA, respectively, at 5 mW/cm^2. Experimental results were obtained using FTIR.

The creation of a model capable of capturing polymerization behavior over a range of initiation and polymerization conditions necessitates both the inclusion of chain length dependent termination and the use of experimental data obtained at a minimum of two different initiation rates. Model parameters for diffusion control and free volume effects on termination and propagation for the $\gamma = {}^1/_2$ case were fit using experimental data for DEGDMA polymerization both with 5 and 0.1 wt % DMPA at 5 mW/cm^2 (A_t = 0.41, A_p = 0.18, f_{ct} = 0.0424, f_{cp} = 0.0227, k_{t110} = 350 000 L/(mol s), and k_{p0} = 110 L/(mol s)). An additional polymerization condition is presented (1.25 wt % DMPA at 5 mW/cm^2) (Figure 4a) that was not used for parameter determination. The initiation rate was assumed to decay exponentially throughout the polymerization. When the polymerization was examined over a range of initiation rates similar to those studied experimentally, the



(a) **(b)**

Figure 4. Chain length dependent ($\gamma = {}^1/_2$) model (—) and experimental (**—**) results for DEGDMA polymerization are presented at three different initiation rates ($R_i = 4 \times 10^{-5}$, 5.5×10^{-4}, and 2×10^{-3} mol/(L s)), where the longest cure time corresponds to the lowest initiation rate. All polymerizations were conducted via initiation of samples containing 0.1, 1.25, or 5 wt % DMPA, respectively, at 5 mW/cm^2. The conversion as a function of time is presented **(**a**)** along with the scaling exponent as a function of conversion as determined by the model **(**b**)**. The scaling exponent reflects the dependence of polymerization rate on initiation rate throughout the polymerization of DEGDMA. Experimental results were obtained using FTIR.

observed dependence of R_p on R_i at low conversion followed the same trend and was numerically similar to the experimentally observed result (Figure 4a).

The CLDT model successfully predicts DEGDMA photopolymerization at low conversions (Figure 4a) for three different initiation rates. The model predictions for the high and low initiation rate systems begin to deviate from experimental results at the onset of autodeceleration. This model has much promise for better prediction of these systems throughout the entire polymerization. Known aspects of cross-linking polymerizations such as chain transfer, primary radical termination, and unimolecular termination (radical trapping), as well as the effect of chain lengths on propagation, have yet to be included in the model. In addition, the CLDT correction to the termination kinetic constant is a general expression that should be explored further. The immediate success of this model with only a simple CLDT parameter inclusion augments the accumulating support for the importance of CLDT in highly cross-linked systems.

Not only is the CLDT model able to predict rates accurately, but how the polymerization rate depends on the initiation rate as a function of conversion is also closely matched with the major discrepancy easily attributable to current model limitations. At low conversions, both the model and experimental results clearly show less than the expected square root behavior (Figures 1b and 4b). Additionally, both methods predict a transition region where α increases steadily as conversion increases. This region is indicative of a transition in the dominant termination mechanism from CLDT to reaction diffusion controlled termination. In the CLDT containing model, only bimolecular termination is considered. Therefore, when reaction diffusion controlled termination dominates the reacting system, α is observed to plateau at the classically predicted relationship between R_p and R_i, where $\alpha = {}^1/_2$, indicative of a chain length independent regime. This classical square root behavior regime is rarely observed experimentally because of the aforementioned phenomena known to happen in polymerization systems. In Figure 1b, α steadily increase to 0.7, which indicates the probable importance of a unimolecular termination mechanism. Around 50% conversion, the experimentally determined α is observed to decrease in value, which can be attributed to the continued decrease in initiation rate. The importance of incorporating “real” behaviors into the model is magnified at high conversion where the greatest deviation between model predictions and experimental results occurs.

The transition from chain length dependent termination kinetics to chain length independent or reaction diffusion controlled termination kinetics is also visible in the kinetic parameters. Using $k_{t,\,avg}$ from the model, as determined by eq 13, the overall ratio of $k_{t,avg}/k_p[M]$ is calculated and compared to the same ratio acquired from unsteady-state experimental data (Figure 5).[17] The model is able to capture key changes in the polymerization features as the initiation rate is varied. Specifically, as initiation rate is increased, an elevation in termination at low conversion is realized, accompanied by the delayed onset of reaction diffusion control, as noted by the plateau of the kinetic constant ratio. Discrepancies between the model predictions and observed experimental results are attributed to the difference between model prediction of $k_{t,avg}$ and experimental results which primarily measure the termination kinetics of the long radical. Using $k_{t,avg}$ always overpredicts the reaction diffusion coefficient, delaying the onset of reaction diffusion. This discrepancy is easily observed in Figure 5.

$$\frac{d[R^\bullet]}{dt} = -k_{t,avg}[R^\bullet]^2_{total} \qquad (13)$$

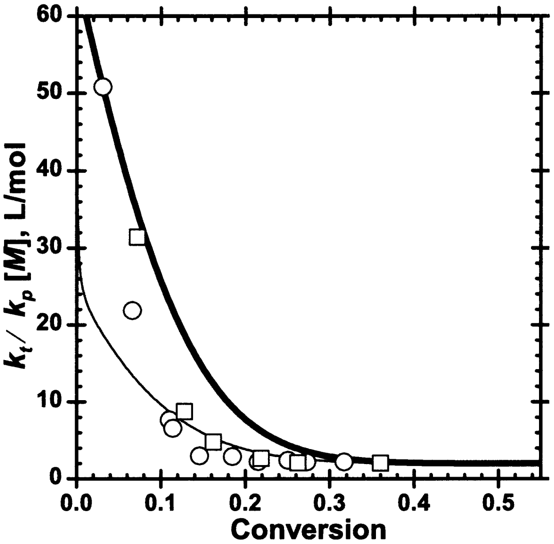


Figure 5. Ratio of kinetic constants as a function of conversion for the polymerization of DEGDMA. Model (–, —) and experimental [○, □] results for polymerization at two different initiation rates, $R_i = 4.36 \times 10^{-5}$ mol/(L s) (–, ○) and 2.18×10^{-3} mol/(L s) (—, □) are presented. Polymerizations were initiated at 5 mW/cm^2 with 0.1 and 5.0 wt % of the photoinitiator DMPA, respectively. Experimental results were obtained using FTIR.

Conclusions

This paper presents both experimental and modeling results that indicate the importance of considering CLDT when evaluating the polymerization kinetics in highly cross-linked multivinyl photopolymerizations. The model builds on previous models developed for multivinyl photopolymerizations, with the incorporation of a CLDT parameter based on random walk theory[51] into the kinetic model. To investigate the effects of CLDT, kinetic chain length distributions were systematically manipulated by changing the initiation rate. The impact this change has on the relationship between R_p and R_i was examined over the entire conversion range for both DEGDMA and DEGDA. While the acrylate polymerization was minimally affected by the alterations in polymerization conditions, a significant change was observed in the methacrylate system both experimentally and theoretically, via the CLDT inclusive ($\gamma = {}^1/_2$) model. At low conversions, the methacrylate system exhibits significant deviation from the classical square root dependence on initiation rate. As the polymerization continues, the dependence of R_p on R_i continuously changes. Once the polymerizing system becomes reaction diffusion controlled, the kinetics are no longer visibly influenced by changes in kinetic chain length. While the chain length independent ($\gamma = 0$) model predictions for DEGDMA polymerization provide excellent prediction of the polymerization kinetics at the initiation rate used to determine the parameters (5 wt % DMPA at 5 mW/cm^2), the impact of initiation rate changes is not predicted. The chain length independent model incorrectly predicts that α is one-half and is conversion independent. Thus, this paper demonstrates qualitatively the importance of CLDT incorporation into the model equations that describe termination for improved prediction of experimental results over a range of cure conditions.

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References and Notes

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