A Modeling Investigation of Chain Length Dependent Termination during Multivinyl Free Radical Chain Photopolymerizations: Accounting for the Gel

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ABSTRACT: A mathematical model of multivinyl monomer free radical photopolymerizations that takes into account chain length dependent termination (CLDT) and gel formation (an infinite network) was utilized to obtain a more accurate picture of network formation and multivinyl monomer photopolymerization kinetics. The model predicts an increased probability that a radical chain is attached to the gel with increasing chain length and double bond conversion. Accounting for CLDT delays radical incorporation into the gel and induces gel formation at earlier double bond conversions. Increasing the initiation rate also delays gel formation. When the model is expanded to account for the probability that a highly mobile sol radical reacts to become a nearly immobile gel radical, the importance of CLDT prior to reaction diffusion-controlled termination is increased. This result is attributed to bimolecular termination occurring between a short (<10-mer) sol radical and a long gel radical (short−long radical termination). The transition from a CLDT important regime to reaction diffusion-controlled termination is characterized by a transition from primarily short−long to primarily long−long (gel−gel) radical termination.

Introduction

Multivinyl monomers photopolymerize to yield highly cross-linked networks with exceptional material properties. Currently, photopolymer networks are used for a variety of applications, including microelectronics, contact lenses, dental restorations, adhesives, and coatings.[1−8] The industrial success of photopolymer networks is due, in part, to the many advantages of photopolymerization, such as spatial and temporal control of a reaction that occurs under ambient conditions with or without a solvent. Additionally, the cure temperature, initiation conditions, comonomer concentration, monomer chemistry, and monomer functionality dictate the final material properties, affording another layer of control and flexibility. Unfortunately, a clear understanding of how changing cure conditions and monomer chemistry affect network formation and the final material properties is lacking. Thus, a priori design of materials and cure conditions to achieve material properties with a specific application in mind requires a more fundamental understanding of photopolymerization kinetics and network formation.

Cross-linking polymerizations are difficult to characterize due to the rapid generation of high molecular weight, cross-linked, and cyclized polymer. At very low double bond conversions a gel of infinite molecular weight forms, which dramatically decreases the reacting species' mobility.[9] These changes lead to diffusion control of the large polymeric radical chains and suppression of their translation through the reacting system, leading to autoacceleration.[10−19] The termination rate decreases with increasing polymer concentration, and radical recombination eventually occurs more rapidly by a radical propagating through nearby vinyl groups until meeting and terminating with another radical. This latter termination regime is referred to as reaction diffusion-controlled termination.[20−25] As the reacting species' mobility decreases further, the small monomer molecule also becomes diffusion-controlled and autodeceleration is observed. When the cure temperature is below the polymer's glass transition temperature, T_g,[26−28] incomplete double bond conversion and the accumulation of persistent radicals often occur.

The termination mechanism is the most complex, and thus, the least understood aspect of multivinyl monomer photopolymerization kinetics. Recently, the importance of chain length dependent termination (CLDT) during network formation has been shown both experimentally[20,29−32] and through the development of a novel kinetic model.[33−35] While these results and predictions suggest that CLDT is important at low double bond conversions, prior to the onset of significant mobility restrictions, they also reveal that CLDT is a complex function of both monomer chemistry and double bond conversion.

This work aims to develop a better understanding of CLDT during network formation via expansion of the CLDT model to include gel formation and growth. Zhu and co-workers[36,37] have investigated gelation, and Zhu[38] has investigated the impact of CLDT and cross-linking on the MWD evolution during free radical photopolymerization; however, no one has investigated the importance of CLDT and gel formation during multivinyl monomer photopolymerization. The model developed here investigates the impact of highly mobile sol radicals reacting to become nearly immobile gel radicals on the photopolymerization kinetics, with the goal of obtaining a better understanding of CLDT and the complex termination kinetics exhibited by network forming monomers.

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Model Development

The model presented here is based on previous models of cross-linking phenomena that account for the effects of increasing polymer concentration (e.g., increased T_g and density and decreased fractional free volume) on the reacting species' mobility and diffusivity via the mathematical expressions for the propagation and termination kinetic constants (k_p and k_t, respectively).[26,33,39−42] This model predicts phenomena that typify multivinyl monomer photopolymerizations, including autoacceleration, reaction diffusion-controlled termination, and incomplete double bond conversion. The model also accounts for radicals of each length, i.e., incorporates CLDT, and thus more accurately predicts the impact of initiation rate changes on the polymerization kinetics. Chain transfer to thiol,[33] chain transfer to polymer,[34] and persistent radical accumulation[35] may also be readily incorporated into the model equations.

One advantage of this model over previous multivinyl monomer (photo)polymerization models is that the pseudo-steady-state assumption (PSSA) is not made. Multivinyl monomer photopolymerization exhibits complex diffusion restrictions from the onset of the reaction due to the rapid formation of an infinite network,[10,43−45] and thus, the rates of radical formation and annihilation are often very different and the PSSA is frequently invalid for the majority of the photopolymerization. Additionally, the classical relationship between the polymerization rate, R_p, and the initiation rate, R_i, is rarely observed (eq 1, where α is $^1/_2$):[9,46]

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

Here, [C=C] is the double bond concentration and α is the scaling exponent that is $^1/_2$ classically. The classical, square root relationship between the polymerization rate and the initiation rate is accurate for bimolecular, chain length independent termination when the PSSA is made.

Nonclassical kinetics is most often attributed to nonclassical termination, i.e., CLDT or persistent radical accumulation. Decreasing radical chain mobility due to the gel and decreasing local vinyl group and radical concentrations all contribute to the accumulation of "trapped" radicals. This phenomenon is modeled frequently via a pseudo-first-order termination mechanism. The annihilation of only one radial in each termination event results in a greater than expected increase in the polymerization rate when the initiation rate is increased; i.e., the scaling exponent α in $R_p \propto R_i^{\alpha}$ is greater than $^1/_2$.

CLDT is another process that contributes to nonclassical kinetics. Increasing the initiation rate increases the number of initiator fragments and, subsequently, the number of radical chains, which shifts the MWD toward a lower average kinetic chain length. When CLDT occurs, the shorter radical chains are more mobile and more readily terminate. Thus, a less than classical increase in the polymerization rate with increased initiation rate is exhibited and α is less than $^1/_2$. Recently, dimethacrylate monomers have been shown to exhibit CLDT.[20,29,30] These experimental results during network formation necessitate CLDT inclusion into the mathematical expressions that describe multivinyl monomer photopolymerization kinetics.

CLDT is incorporated into the equations that describe termination via theory developed by Benson and North.[47] A complete kinetic model description is presented in Lovestead et al.[33] The model takes into account that termination transitions from chemical to diffusion control and that the mechanism of diffusion control transitions from chain length dependent to reaction diffusion-controlled termination as the gel increases. During the transition from CLDT to reaction diffusion-controlled termination, even when the system is gelled, radical termination may occur either between two gel radicals or between a sol radical of low molecular weight (primary radical or initiator radical) and a gel radical. In brief, the chemically controlled termination kinetic constant for two unimers ($k_{t0}^{1,1}$) is modified in the mass-transfer-limited regime to be a function of the terminating radical chain's length, i or j.

$$k_{t0}^{\,i,j} = k_{t0}^{\,1,1}\frac{1}{2}\left(\frac{1}{i^{\gamma}} + \frac{1}{j^{\gamma}}\right) \tag{2}$$

Here, γ describes the degree to which increasing the radical chain length retards its ability to translate through the reacting system to terminate with another radical. Coupling eq 2 to the previously developed equation for the chain length independent termination kinetic constant, which accounts for diffusion-controlled kinetics, free volume considerations, and reaction diffusion-controlled termination, yields the desired CLDT kinetic constant, $k_t^{\,i,j}$.[20,33,34]

$$k_t^{\,i,j} = k_{t0}^{\,1,1}\left\{1 + \left(\left(\frac{1}{2}\left(\frac{1}{i^{\gamma}} + \frac{1}{j^{\gamma}}\right)\right)\exp\left(-A_t\left(\frac{1}{f} - \frac{1}{f_{ct}}\right)\right) + \frac{Rk_p[\mathrm{C{=}C}]}{k_{t0}^{\,1,1}}\right)^{-1}\right\}^{-1} \tag{3}$$

In this expression, A_t is a constant that controls the onset and rate of autoacceleration, f_{ct} is the critical fractional free volume where termination becomes controlled by the diffusion of the radical chains or chain ends, and f is the fractional free volume of the reacting system.[26,42,48,49] Additionally, R is the reaction diffusion coefficient, or the ratio of kinetic constants, $k_t/(k_p[\mathrm{C{=}C}])$, and assumed to be constant when reaction diffusion is the dominant termination mechanism.[40] The chain length independent propagation kinetic constant, initiation rate, and initiator decay are incorporated as appear elsewhere.[33−35]

The present model accounts for radical concentrations of each length in the sol fraction and determines the probability that a sol radical reacts to become a gel radical; thus, the model predicts the kinetic chain length of the sol radicals. The model also accounts for the kinetic chain length distribution of the dead polymer in the sol fraction. The model predicts directly the polymerization rate (eq 4) and the average termination kinetic constant (k_t^{avg}, eq 5).[20,33,34]

$$R_p = -\frac{\mathrm{d}[\mathrm{C{=}C}]}{\mathrm{d}t} = k_p[\mathrm{C{=}C}][\mathrm{P}^{\bullet}]_{\mathrm{tot}} \tag{4}$$

$$k_t^{\,\mathrm{avg}} = \frac{\sum_{i=1}^{\infty}\sum_{j=1}^{\infty} k_t^{\,i,j}[\mathrm{P}^{\bullet}]_i[\mathrm{P}^{\bullet}]_j}{[\mathrm{P}^{\bullet}]_{\mathrm{tot}}^{\,2}} \tag{5}$$

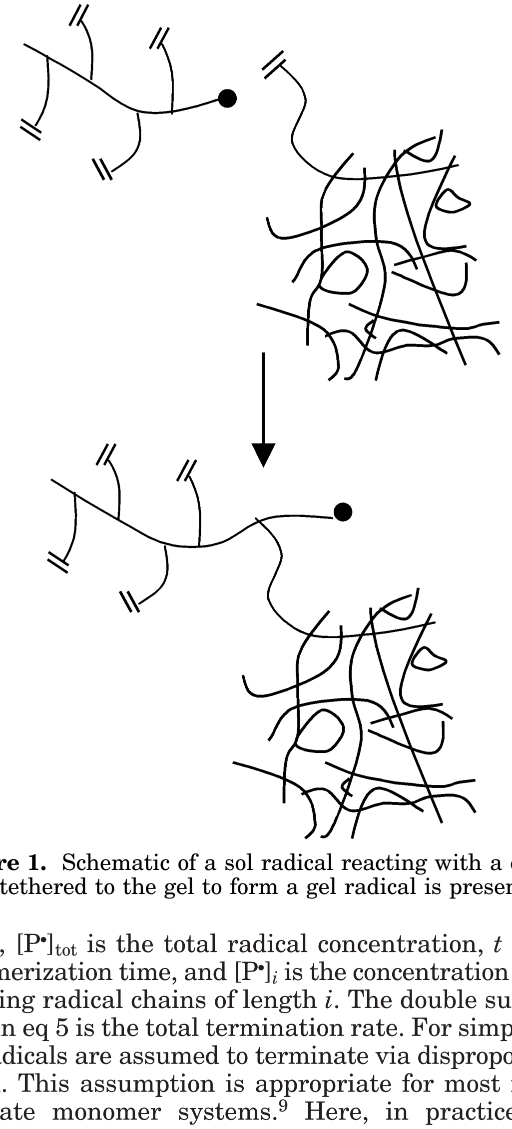

Figure 1. Schematic of a sol radical reacting with a double bond tethered to the gel to form a gel radical is presented.

Here, $[\mathrm{P}^\bullet]_{\mathrm{tot}}$ is the total radical concentration, t is the polymerization time, and $[\mathrm{P}^\bullet]_i$ is the concentration of the growing radical chains of length i. The double summation in eq 5 is the total termination rate. For simplicity, all radicals are assumed to terminate via disproportionation. This assumption is appropriate for most methacrylate monomer systems.[9] Here, in practice, the number of radical concentrations is made more tractable by averaging together longer length radicals and assuming groups of radicals that are similar in chain length are equally reactive.[33,50]

The gel is accounted for utilizing the probability equations developed by Miller and Macosko.[51,52] An example of the reaction of a sol radical with a double bond on a chain tethered to the gel is presented in Figure 1. The instantaneous gel fraction ($E(i)$) is the fraction of chains of length i in the gel. $E(i)$ is a function of the double bond conversion (X) (eq 6) and depends on the probability of a radical propagating rather than undergoing any other reaction (q), which embodies the monomer composition and functionality. For simplicity, q is assumed equal to 0.99. The model predicts the fraction of radicals that are gel radicals (y_{g}) according to eq 8, which takes into account the gel radical concentration ($[\mathrm{gel}^\bullet]$ from eq 7). The model also predicts the number-average gel fraction (φ) or the fraction of the total "alive" and "dead" kinetic chains that are tethered to the gel (eq 9, where $[\mathrm{DP}]_i$ is the concentration of dead polymer chains of length i).

$$E(i) = 1 - \left[\frac{\left(\left(\frac{1-q}{qX} + \frac{1}{4}\right)^{0.5} - \frac{1}{2}\right)^2 + \left(\frac{1-X}{X}\right)}{1 + \left(\frac{1-X}{X}\right)}\right]^i \tag{6}$$

$$[\mathrm{gel}^\bullet] = \sum_{X=0}^{1} \sum_{i=1}^{\infty} [\mathrm{P}^\bullet]_i E(i) \tag{7}$$

$$y_{\mathrm{g}} = \frac{[\mathrm{gel}^\bullet]}{[\mathrm{P}^\bullet]_{\mathrm{tot}}} \tag{8}$$

$$\phi = \frac{\sum_{X=0}^{1} \sum_{i=1}^{\infty} ([\mathrm{P}^\bullet]_i + [\mathrm{DP}]_i) E(i)}{\sum_{X=0}^{1} \sum_{i=1}^{\infty} ([\mathrm{P}^\bullet]_i + [\mathrm{DP}]_i)} \tag{9}$$

Model Parameters

The model is a useful tool for testing hypotheses about the impact of the gel on multivinyl monomer photopolymerization kinetics and network evolution. Diethylene glycol dimethacrylate (DEGDMA) serves as an excellent model system as it gels at low double bond conversion, and its photopolymerization kinetics exhibit chain length dependent termination, autoacceleration, reaction diffusion-controlled termination, and incomplete double bond conversion. DEGDMA's material properties are taken from the literature ($T_{\mathrm{g,m}} = -12$ °C,[53] $T_{\mathrm{g,p}} = 500$ °C,[53] $\rho_{\mathrm{m}} = 1.06$ g/mL,[40,41,53] and $\rho_{\mathrm{p}} = 1.32$ g/mL[40,41,53]), where m and p represent monomer and polymer, respectively, and ρ is density. The reaction diffusion coefficient ($R = 2$ L/mol) was characterized by both Anseth et al. and Berchtold et al.[30,54]

The parameters for the diffusion control and free volume effects on termination and propagation for the CLDT model with the gel ($k_{\mathrm{p0}} = 50$ L/(mol s), $k_{\mathrm{t0}}{}^{1,1} = 800\,000$ L/(mol s), $A_{\mathrm{p}} = 0.18$, $A_{\mathrm{t}} = 0.40$, $f_{\mathrm{cp}} = 0.02$, $f_{\mathrm{ct}} = 0.037$, and $\gamma = 0.8$) were acquired using the previously published CLDT model predictions for the polymerization rate vs double bond conversion at 2.5 mW/cm^2 with 0.1 wt % photoinitiator ($R_{\mathrm{i}} = 2.1 \times 10^{-5}$ L/(mol s)) ($k_{\mathrm{p0}} = 50$ L/(mol s), $k_{\mathrm{t0}}{}^{1,1} = 90\,000$ L/(mol s), $A_{\mathrm{p}} = 0.18$, $A_{\mathrm{t}} = 0.43$, $f_{\mathrm{cp}} = 0.02$, $f_{\mathrm{ct}} = 0.037$, and $\gamma = 0.8$).[35] The initiator concentration is assumed to remain constant throughout all simulations. The chain length independent model parameters ($k_{\mathrm{p0}} = 50$ L/(mol s), $k_{\mathrm{t0}}{}^{1,1} = 75\,000$ L/(mol s), $A_{\mathrm{p}} = 0.18$, $A_{\mathrm{t}} = 0.52$, $f_{\mathrm{cp}} = 0.02$, $f_{\mathrm{ct}} = 0.046$, and $\gamma = 0.0$), along with the parameters for the CLDT model that neglects the gel ($k_{\mathrm{p0}} = 50$ L/(mol s), $k_{\mathrm{t0}}{}^{1,1} = 25\,000$ L/(mol s), $A_{\mathrm{p}} = 0.18$, $A_{\mathrm{t}} = 0.51$, $f_{\mathrm{cp}} = 0.02$, $f_{\mathrm{ct}} = 0.05$, and $\gamma = 0.0$) were acquired using the CLDT model predictions for polymerization rate vs double bond conversion at 2.5 mW/cm^2 with 0.1 wt % photoinitiator ($R_{\mathrm{i}} = 2.1 \times 10^{-5}$ L/(mol s)). Additionally, the model assumes 25 °C and the parameters for the photoinitiator, 2,2-dimethoxy-2-phenylacetophenone (DMPA), a common ultraviolet initiator appear in a previous paper.[33]

Results and Discussion

A fundamental understanding of the mechanism for CLDT during multivinyl monomer photopolymerization is still lacking. The difficulty in characterizing CLDT in these systems lies in the rapid development of an infinite network, or a gel, at very low double bond conversion. A model that was developed previously to investigate the impact of CLDT on multivinyl monomer photopolymerization kinetics and molecular weight distribution (MWD) of the backbone kinetic chains was

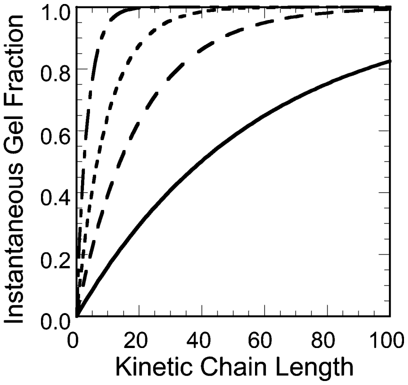

Figure 2. Instantaneous gel fraction is presented as a function of kinetic chain length (up to 100-mers) for 2 (—), 5 (— — —), 10 (- - -), and 25% (– - –) double bond conversions. All photopolymerizations are simulated with 0.1 wt % DMPA at 2.5 mW/cm^2.

expanded to account for gel formation and growth.[33−35] This model describes more completely network formation and, thus, is ideally suited to provide insight into the complex termination mechanism(s) that occur during cross-linking photopolymerization.

The Miller and Macosko[51] theory for gel formation and growth was utilized. Figure 2 presents the probability that a sol radical of a given chain length reacts with a gel vinyl group to become a gel radical for chain lengths up to 100-mers, i.e., a molecule with a kinetic chain length of 100, at 2, 5, 10, and 25% double bond conversions. The probability that a propagating radical chain attaches to the gel increases with both the sol radical chain's length and polymer formation. For example, at 5 and 25% double bond conversions, 99% of 92-mers and 16-mers, respectively, have been reacted into the gel. Furthermore, by 25% double bond conversion, 44% of dimers, i.e., a molecule with a kinetic chain length of 2, are tethered to the gel. Thus, the majority of radicals in the reacting system are gel radicals even at very low double bond conversions and chain lengths. It is important to note that these calculations neglect cyclization, which would decrease the fraction of radical chains attached to the gel.

The gel model takes into account that sol radicals are more mobile and, thus, more readily terminate than gel radicals that are tethered to the infinite network. The fraction of radicals that are gel radicals, i.e., y_g, and the gel fraction are presented in Figure 3. The gel model predicts that the gel forms by 0.6% double bond conversion. Additionally, accounting for chain length dependent termination delays the tethering of radical chains to the gel (Figure 3a). For example, at 0.6% double bond conversion, the gel model with and without accounting for CLDT predicts that 91 and 97%, respectively, of the total radical concentration are gel radicals. The gel model also reveals that the gel fraction increases more rapidly in the double bond conversion domain when CLDT is accounted for; i.e., the model predicts that 99% of the total "alive" and "dead" kinetic chains are incorporated to the gel by 0.7 and 0.9% double bond conversion, when CLDT is accounted for or neglected, respectively (Figure 3b). Thus, CLDT accelerates the gel's growth rate, which was also predicted by Zhu's model of CLDT during free radical polymerization modified with cross-linking.[38]

Multivinyl monomer photopolymerization kinetics and the MWD of the backbone kinetic chains have been shown to depend nonideally on the initiation rate,[33−35] and thus, the impact of the gel on the photopolymerization kinetics was examined. Increasing the initiation rate increases the number of initiator fragments, resulting in a larger number of kinetic chains and, thus, a shorter average kinetic chain length. The gel model reveals that increasing the initiation rate decreases the fraction of radicals that are gel radicals (Figure 4a) and delays gel growth (Figure 4a).

Accounting for the gel also impacts the complex termination mechanism. When the polymerization kinetics depends on the radical kinetic chain length, the polymerization rate increases less than would be expected classically ($\alpha = {}^1/_2$) as the initiation rate is increased due to more facile termination of the shorter kinetic chains. Figure 5 reveals that the gel model predicts that the polymerization kinetics exhibit greater chain length dependencies as determined by examining the dependence of the polymerization rate on the initiation rate, i.e., the scaling exponent, α. For example, at 10% double bond conversion α is 0.22 when the gel is accounted for and 0.33 when the gel is neglected. The scaling exponent α also reveals information about the transition from CLDT to reaction diffusion-controlled termination, a chain length independent termination mechanism. When reaction diffusion-controlled termination is the dominant termination mechanism, α is $^1/_2$. Accounting for the gel does not change the double bond conversion that reaction diffusion-controlled termination becomes the dominant termination mechanism.

The gel model predicts stronger chain length dependencies than the CLDT that neglects the gel, even though most of the radicals in the model are gel radicals by 0.6% double bond conversion. This increased importance of CLDT is due to termination occurring mostly between

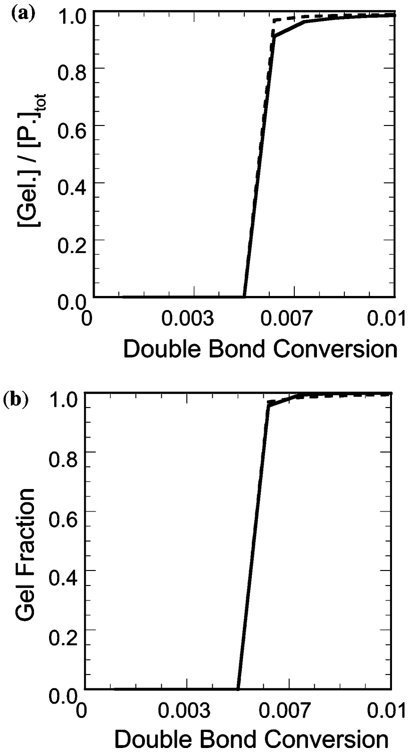

Figure 3. Fraction of radicals that are gel radicals (a) along with the gel fraction (b) are presented as a function of double bond conversion as predicted by the gel model with (—) and without (- - -) accounting for CLDT. All simulations are with 0.1 wt % DMPA at 2.5 mW/cm^2.

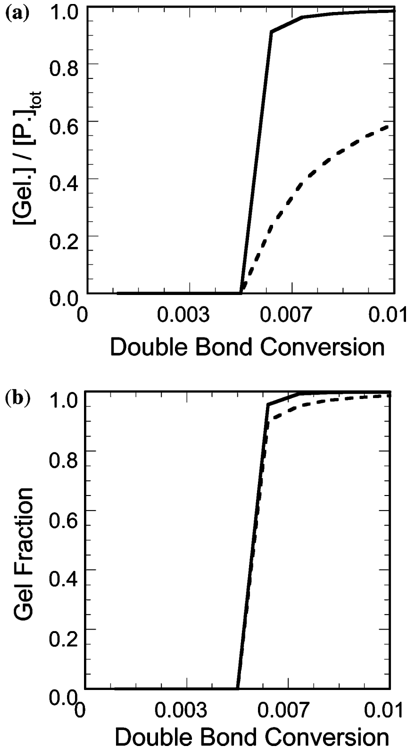

Figure 4. Fraction of radicals that are gel radicals (a) along with the gel fraction (b) are presented as a function of both double bond conversion and initiation rate as predicted by the gel model that accounts for CLDT. All simulations are with either 0.1 wt % DMPA at 2.5 mW/cm², $R_i = 2.1 \times 10^{-5}$ L/(mol s) (—), or 1 wt % DMPA at 20 mW/cm², $R_i = 1.4 \times 10^{-3}$ L/(mol s) (— — —).

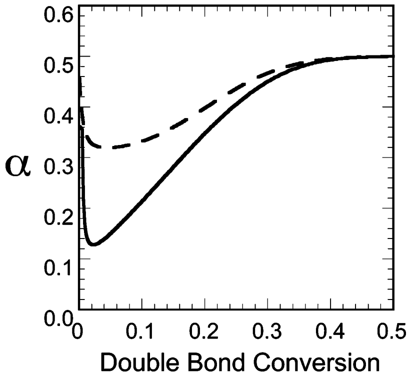

Figure 5. Polymerization rate's dependence on the initiation rate (i.e., α from $R_p \propto R_i^{\alpha}$) is presented throughout polymerization as predicted by the CLDT model with (—) and without (— — —) accounting for the gel. α is calculated for polymerization simulated with 1 wt % DMPA at 20 mW/cm² and 0.1 wt % DMPA at 2.5 mW/cm².

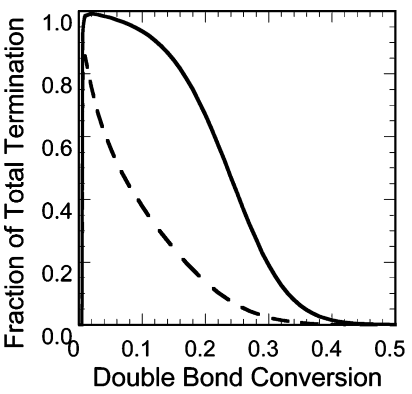

Figure 6. Fraction of total termination that is between a gel radical and a radical that is less than a 10-mer in length is presented as predicted by the gel model that accounts for CLDT for either 1 wt % DMPA at 20 mW/cm² (—) or 0.1 wt % DMPA at 2.5 mW/cm² (- - -).

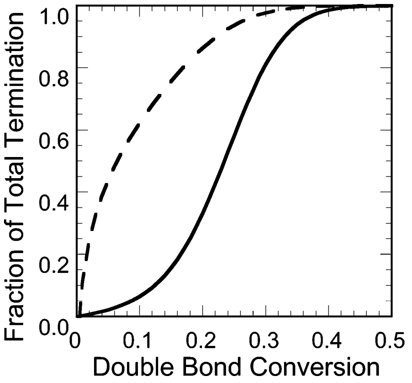

Figure 7. Fraction of total termination that is between two gel radicals is presented as predicted by the gel model that accounts for CLDT for either 1 wt % DMPA at 20 mW/cm² (—) or 0.1 wt % DMPA at 2.5 mW/cm² (- - -).

a short (<10-mer) and a long (gel) radical chain (short–long radical termination) at low to moderate double bond conversions (Figure 6). The gel model reveals that at 1% double bond conversion 99 and 85% of the total termination rate is short–long termination for the simulation with either 1 wt % DMPA at 20 mW/cm² or 0.1 wt % DMPA at 2.5 mW/cm², respectively. The fraction of total termination rate that occurs between a short and a long radical chain decreases with increasing double bond conversion. This decrease in the fraction of total termination that is short–long termination corresponds to the decreased importance of CLDT and the increased importance of reaction diffusion-controlled termination. When reaction diffusion-controlled termination is the dominant termination mechanism, the model reveals that termination occurs solely between two long radical chains (long–long or gel–gel radical termination) (Figure 7). Thus, the gel model reveals that the transition from CLDT to reaction diffusion-controlled termination is due to the bimolecular termination reaction transitioning from short–long to long–long radical termination.

Short–long radical chain termination has also been investigated both theoretically and experimentally as the cause of CLDT exhibited during linear polymerizations.[50,55–57] Russell reveals that the short–long approximation impacts model prediction of an average termination kinetic constant and, thus, the polymerization kinetics, minimally. Additionally, Adams and coworkers were able to apply a short–long radical termination model to evaluate the seeded emulsion polymerization kinetics of styrene. Thus, short–long radical chain termination is one possible explanation for CLDT kinetics exhibited during multivinyl monomer photopolymerizations.

Conclusions

A model of multivinyl monomer photopolymerization kinetics was expanded to account for the gel formation to probe further the complex termination mechanism, specifically the importance of CLDT, during network formation. Radical chain incorporation to the gel significantly increases mobility restrictions on the growing radical chains. The gel forms by 0.6% double bond conversion, and its growth rate is shown to decrease with increasing initiation rate and increase with the incorporation of CLDT into the model equations. The models presented here reveal that accounting for the gel increases the importance of CLDT prior to the onset of reaction diffusion-controlled termination. The increased importance of CLDT when the gel is accounted for is attributed to short−long termination. In conclusion, this paper presents a more accurate picture of network formation, which enables a better understanding of the mechanism of CLDT during network formation.

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