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Kinetics of Primary Cyclization Reactions in Cross-Linked Polymers: An Analytical and Numerical Approach to Heterogeneity in Network Formation

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ABSTRACT: It is difficult to characterize the kinetics of cyclization reactions during free radical photopolymerization of multivinyl monomers because of the varying pendant double bond reactivities and inhomogeneities in the system. Primary cyclization, where a pendant double bond reacts intramolecularly with the propagating active center that formed it, leads to formation of microgels in the network. A new analytical and numerical approach is presented that solves the differential kinetic equations and can be used to investigate the factors influencing cyclization versus cross-linking reactions. Data are presented comparing two approaches, one based on numerical integration of the appropriate balances and one based on an analytical solution.

Introduction

Free radical polymerization of multifunctional monomers produces densely cross-linked networks. Because of the cross-linking, these polymers exhibit abnormal kinetic behavior, including autoacceleration, autodeceleration, reaction diffusion-controlled termination, limiting functional group conversion, and anomalous pendant reactivity.[1,2] Understanding the network formation of these cross-linked polymers is complex, exhibiting abnormalities related to increasing viscosity and decreasing species mobility with conversion and the heterogeneous distribution of reacting species. Additionally, pendant double bond cyclization reactions play a significant role in these highly cross-linked systems as these reactions determine how cross-linked the network will be.[1]

Chain polymerization of multivinyl monomers results in pendant double bonds on the growing polymer chains. These pendant double bonds can react with propagating radicals by three different reaction mechanisms: primary cyclization, secondary cyclization or multiple cross-linking, and cross-linking (Figure 1). In primary cyclization reactions a pendant double bond reacts intramolecularly with the radical on its own propagating chain, i.e., the radical which created the pendant double bond (by monomer consumption) and then continued to propagate. Secondary cyclization or multiple cross-linking reactions occur when a pendant double bond reacts with a radical on a chain in which it is already cross-linked. In cross-linking reactions a pendant double bond reacts intermolecularly with another growing polymer chain. In particular, primary cyclization reactions are important reactions to be accounted for in cross-linked polymers.[1,3,4] Primary cyclization causes small loops to be formed in the network, which causes microgels and heterogeneity to occur in the polymer. Further, primary cyclization can lead to a reduction in the effective cross-linking density, as these small cycles do not contribute significantly to the overall network structure. This reduction is often pronounced, leading to a significant delay in the gel point conversion, a dramatic change in the kinetics of polymerization (since cycles hinder mobility less than cross-links), and a reduction in some properties such as mechanical strength, solvent resistance, and glass transition temperature.[5−8] Understanding pendant reactivity during the reaction is an important step in being able to predict the degree of heterogeneity in the final network structure.[9]

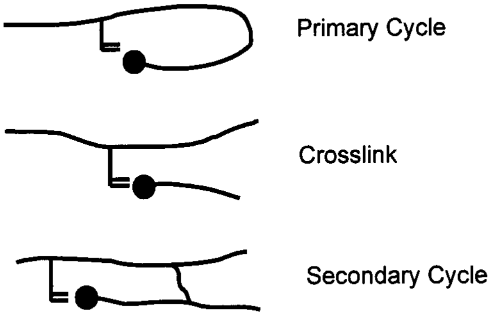

Figure 1. Three possible ways pendant double bonds react.

Understanding the polymerization kinetics and the resulting material properties of cross-linked polymers is important because of the wide array of industrial and scientific applications for these materials. In particular, many of these materials are photopolymerized. Photopolymerization has the advantage of rapid processing time, spatial control of the polymerization, ambient processing temperature, solventless processing, and increased energy efficiency. Applications for cross-linked photopolymers exist in the photolithography and microelectronics area, protective and decorative coatings, dental restorative materials, aspherical lenses, contact lenses, and optical fiber coatings.[10−12] Further understanding of the relationship between processing conditions and network formation would facilitate better material development for these applications.

To date, a comprehensive kinetic model, which predicts the abnormal kinetics of primary cyclization reactions, does not exist.[1] Specifically, the kinetics of cyclization reactions occurring during free radical photopolymerization of multifunctional monomers are difficult to characterize because of the varying pendant

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reactivity and inhomogeneities of the system. Previously, models to predicts the structural evolution, the gel point conversion, and sol and gel fractions have been developed for chain polymerizations which form cross-linked polymers;[2−5,7,8,13−19] however, these models generally include the effects of cyclization on cross-linked polymer structure without providing a methodology for determining cyclization rates. Further, except for percolation type models, a mean-field approach is often used whereby all the double bonds are assumed to be equivalently reactive. In this work we will present a first principles non-mean-field kinetic model for calculating the rates of primary cyclization throughout the polymerization. The non-mean-field approach allows the model to capture the inhomogeneities of the network formation. Additionally, the kinetic expressions include the effects of diffusion control, anomalous pendant reactivity, and the resulting cyclization rates.

This work will focus on two novel modeling approaches, which analytically and numerically solve the differential kinetic equations to investigate the factors influencing cyclization versus cross-linking. The model follows the formation time and lifetime of each pendant double bond added to the polymer, starting when the first double bond on a multifunctional monomer is consumed. The relative local concentration of radicals on the same propagating chain (local radicals) as compared with the concentration of radicals in the bulk is used to determine the rate of reaction of each pendant double bond. In this work primary cyclization, a reaction of the pendants with local radicals, is considered relative to secondary cyclization and cross-linking, both reactions with bulk radicals. Secondary cycles and cross-links both contribute significantly to the overall polymer network properties. Both reactions increase the mechanical strength of the material, but only cross-links lead to gelation. Using the concept of “birth conversion”, which was popularized by Tobita,[17,20] a population balance approach is used to account for varying birth times of each pendant vinyl in the reaction as well as the local radical concentration associated with each pendant vinyl. In this manner it is possible to account for the observed experimental behavior with respect to cyclization as compared to cross-linking.

Background

The effect of cyclization on polymerizations of cross-linked systems has been observed experimentally, including when the actual gel point conversion in a system is significantly greater than that predicted by classical Flory−Stockmayer theory.[4,14,15,21,22] Additionally, evidence of cyclization is seen by the discrepancy between the ideal prediction and experimental value of the sol-fraction yield[23] and viscometric data.[24] It has also been found to lead to lower cross-link densities and higher fractions of fully reacted divinyl monomers than is expected in a homogeneous system.[25]

Dusek and Ilavsky[3] as well as others[1,18] identified that primary cyclization was the dominant reaction of pendant functional groups at low conversions. Other researchers have theorized that the pendant reactivity then decreases with conversion due to the polymer gel forming around the pendants, shielding them from further reaction.[4,25] As direct experimental measurement of cyclization is difficult, various researchers have pursued theoretical models of network formation in cross-linked polymers. Previously, three methods have been used to model free radical polymerization of multifunctional monomers: statistical approaches, computer simulations in space, and kinetic models.

Statistical approaches, where the macrostructure is generated from monomer units in different reaction states, have been used for many years beginning with Flory[26] and Stockmayer.[27] Dusek and Ilavsky[3] developed a model for cross-linking copolymerization, where they applied the cascade theory developed by Gordon and used a scaling theory for contact probability.[28] In their work, reaction probabilities are controlled by the conformational statistics of a growing macroradical chain of a certain length to react with monomeric double bonds, a pendant on its own chain (cycle), or a pendant on another chain (cross-link). In this model, it was assumed that all the pendant functional groups were equivalent in reactivity. The pioneering statistical work to include cyclization was done by Jacobson and Stockmayer.[29] Other work using a statistical approach on cross-linked systems has been done by Landin and Macosko.[30] They amplified the recursive model proposed by Macosko and Miller[31,32] to include cyclization. However, the cyclization rates are approximated rather than predicted.[1]

Simulations in space, namely percolation or kinetic gelation type models which account for varying pendant reactivity in cross-linking chain polymerizations, were first proposed by Mannevile and de Seze[5] and have been utilized and further developed by numerous researchers over the past decade.[7,8,13,33,34] As discussed in work by Kloosterboer,[25] in this model type a lattice structure was assumed to simulate the network structure in space. At each unit of time a neighbor to each site with a radical was chosen, and a chemical bond was formed if the double bonds of the neighboring site were not yet fully reacted. Thus, the model simulates the radicals randomly moving through the lattice connecting monomer molecules. Most importantly, these types of models incorporate the non-mean-field nature of the polymerization reaction. Therefore, these simulations were able to predict successfully the inhomogeneities that existed as microgels formed at low conversions. These microgels form initially because of the high pendant double bond reactivity, which is represented in the lattice model by the closer spatial proximity of pendants to propagating radicals. Thus, more primary cycles are formed at low conversion.

Recently, other researchers have amplified the percolation type simulation to account for additional levels of complexity. Bowman developed a new kinetic gelation model,[33] where a face-centered-cubic lattice was used rather than the simple cubic lattice. Molecules were allowed to occupy more than one site so that the effect of different monomer sizes could be investigated. Anseth further developed this model type to allow the initiator concentration to decay through a first-order decay reaction rather than assuming all radicals are present at the beginning of the reaction.[2,8] Termination of radicals was also included. These assumptions put additional information into the simulations that allowed them to be more accurate. Primary cyclization was allowed to occur in the model, but the relative flexibility or stiffness of monomers in cycling back on themselves was not accounted for. Chiu and Lee[34] also accounted for cyclization in their percolation model. Segmental diffusion was considered additionally because monomers were allowed to occupy more than one site. The Bowman, Anseth, and Chiu models are able to predict qualitatively the experimental trends of pendant double bond conversion and cyclization, and the understanding of highly cross-linked polymerization kinetics was furthered by their work. Computer simulations in space have been the current models of choice for modeling polymerizations that form highly cross-linked polymers. These lattice simulation type models are limited, however, because they use a fixed lattice structure, and there is difficulty in introducing realistic mobility of the reacting species.

Kinetic modeling is the third method for modeling the network evolution of cross-linked polymers. Tobita and Hamielec developed a pseudokinetic modeling approach, where all the important elementary reactions, including primary cyclization, in the copolymerization are considered.[16,17] The kinetics of these reactions are simplified by averaging the effect of chain size into pseudokinetic rate constants that are functions of time. The rate constants account for all the spatial effects in the polymerization. Thus, the kinetic expressions are reduced to be analogous to expressions for a homopolymerization. Okay et al. continued this approach while also including cyclization into the possible kinetic mechanisms, fitting experimental data to the model.[18] This work elucidated the importance of cyclization in the beginning of the reaction, where it was estimated to be 30−60% at zero monomer conversion. Because of the pseudokinetic approach, a constant rate of primary and secondary cyclization and cross-linking is assumed throughout the reaction.[18,19] Other kinetic type modeling was done by Dusek and Somvarksy.[35] Their approach is called the combined method, because it includes kinetics and cascade theory. As the generating kinetic expressions are again transformed into single partial differential equations, these functions become very difficult to evaluate analytically unless strict assumptions are made about cyclization.

Method

Little non-mean-field kinetic modeling has been done because of the difficulty in developing the appropriate differential equations, which are necessary for this system to represent the varying pendant double bond reactivities as a function of conversion. In this work an approach is proposed that develops and solves the relevant species balances and accounts for the difference in reactivity of monomeric double bonds and pendant double bonds throughout the entire polymerization. Using these differential equations, the rate of primary cyclization and cross-linking are determined as a function of reaction time and pendant birth time. The most important contribution of this work is that primary cyclization reaction rates are not input into the model a priori but predicted as a function of the given reaction conditions, monomer size, pendant birth time, and polymerization reaction rate.

In the numerical approach the differential equations for pendant reactivity are developed and numerically evaluated; pendants, which are tracked by birth time, are allowed to form cycles or cross-links throughout the entire reaction. In the analytical approach the differential equations for the cyclization of pendants are integrated analytically for a limited subset of conditions that are based on certain assumptions. The consumption by cyclization is accounted for at the time when the pendants are originally formed.

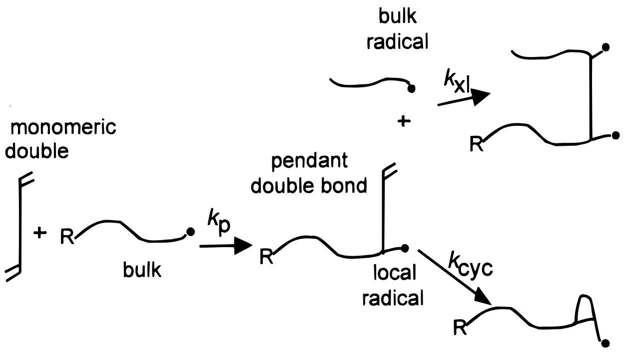

Figure 2. Mechanism of monomeric and pendant double bond reactions.

Both the analytical and numerical approaches account for the varying reactivity in double bonds due to cyclization. Figure 2 illustrates the different pathways for double bonds to react in polymerization of multifunctional monomers. Two mechanisms for pendant double bond reactions are considered: the reaction of double bonds with bulk radicals to form a cross-link or secondary cycle and the reaction of double bonds with local radicals to form primary cycles, where a local radical is considered to be the radical that reacted with the monomeric double bond to form the selected pendant double bond. Monomeric and pendant double bonds are given different reactivities for there are no local radicals for monomeric double bonds.

As shown, the consumption of a monomeric double bond is a function of monomer concentration, bulk radical concentration, and the propagation kinetic constant (k_p), while the reactivity of a pendant double bond is the sum of two competing reactions: cyclization and cross-linking. Pendant vinyls reacting with a radical on the same propagating chain (i.e., a local radical) produce primary cycles while reaction with a bulk radical produces either a secondary cycle or cross-link. Cyclization and cross-linking reactions are controlled by the kinetic constant for cyclization (k_{cyc}) and the local radical concentration and the kinetic constant for cross-linking (k_{xl}) and bulk radical concentration, respectively. Thus, pendants and monomeric double bonds have different reactivities based on differing kinetic constants and radical concentrations.

Local and bulk radicals are concepts introduced to include the cyclization and cross-linking reactions specific to pendant double bonds, but they are not two fundamental different types of radicals. All locals radicals are also bulk radicals, in the sense that they contribute to the total number of radicals in the solution. Every bulk radical is also the local radical for the pendants that hang off its chain. The concept of the “local radical” designates the spatial relationship between a pendant double bond and the radical on the same propagating chain. For pendant double bonds born at a specific birth time, the local radical concentration is a measure of the proximity of the radicals on their propagating chains as a function of time.

The monomeric and pendant double bond species are tracked separately. The overall propagation reaction rate (R_p) can be calculated by solving, analytically or numerically, the differential equations for the rate of monomeric double bond consumption (R_m) and the rate of pendant double bond consumption (R_{pen}) by cyclization and cross-linking.

$$R_p = R_m + R_{pen} \tag{1}$$

Monomeric Double Bond Reactivity. The rate of monomer consumption is defined for a bimolecular reaction as the product of the propagation kinetic constant and the concentration of each of the reactants, monomer [M] and radicals in the bulk solution [R_b].

$$R_m = k_p[M][R_b] \tag{2}$$

The bulk radicals are produced from decaying initiator. Assuming a pseudo-steady state on the bulk radical concentration, the bulk radical concentration ([R_b]) can be expressed as the following:

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

Here, R_i is the rate of initiation and k_t is the termination kinetic constant. This standard method of calculating the radical concentration in free radical polymerizations is used here for simplicity. More accurate numerical calculations are also done when necessary to calculate [R_b] accurately. The rate of initiation is calculated from the initiator concentration, light intensity, and initiator efficiency. The initiator concentration may be assumed to be constant or can be allowed to decay. For all of the model results presented in this paper, the rate of initiation is assumed to be constant; i.e., it is assumed that the initiator concentration is approximately constant.

Pendant Double Bond Reactivity. Using eq 2 for the rate of consumption of monomer, the amount of pendants created by the consumption of monomer is determined for each differential time step in the model. Although the pendant double bonds are generally chemically equivalent to monomeric double bonds, the apparent reactivity of pendant double bonds may be reduced or increased. Initially, after it is created, the pendant double bond may have an enhanced reactivity because of its close proximity to the local radical. Later in the reaction its reactivity may be diminished by steric limitations and/or reduced mobility of the system given that pendants are more likely to be in regions of high polymer concentration and low mobility. Besides the varying pendant reactivity, the pendant double bonds cross-linking and cyclization reactions need to be considered separately in order to understand the contribution of primary cyclization in the reaction.

Thus, the rate of consumption of pendants (R_{pen}) is a function of the consumption by cross-linking and cyclization, which is calculated separately for pendants of each birth time. The rate of consumption of pendants by cross-linking is calculated, analogously to eq 2, by the product of the kinetic constant for cross-linking (k_{xl}) and the concentration of bulk radicals. Consumption of pendants by cyclization is determined by summing of the rate of cyclization of pendants born at each time (t_b). The probability of pendant cyclization is dependent on the proximity of the pendant to its local propagating radical, which is a function of the pendant age. The longer the pendant has existed, the further the radical has propagated away from the radical and the less likely it will be able react intramolecularly in a cyclization reaction. The amount of pendants that cycle of each birth time or age is dependent on the cyclization kinetic constant (k_{cyc}), the concentration of pendant born at that birth time ([Pen(t,t_b)]), and the local radical concentration ([R_l(t,t_b)]), which is a function of how far the radical has propagated away. The total amount of pendant consumed by cyclization is calculated from the summation over all birth times.

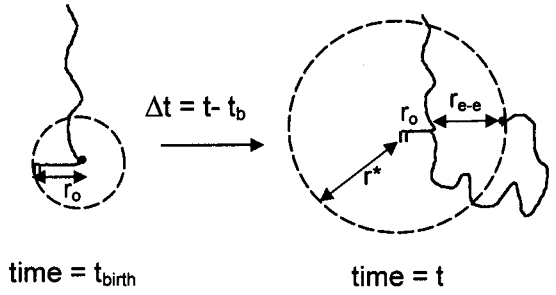

Figure 3. Radius containing the local radical for a particular pendant.

$$R_{pen} = k_{xl}[Pen][R_b] + \sum_{t_b=0}^{t_b=t} k_{cyc}[Pen(t,t_b)][R_l(t,t_b)] \tag{4}$$

For the pendants of each birth time, the local radical concentration is calculated by defining a spherical volume that includes both the pendant vinyl and propagating radical on the same kinetic chain that initially formed the pendant. The volume has a radius, which represents the distance between the pendant double bond and the radical. This radius is assumed to be the average distance between double bonds in a monomer (r_0), plus the end-to-end distance (r_{e-e}) of the polymer that has the same number of repeat units as there are between the pendant and propagating radical (Figure 3). In the absence of termination, the local radical concentration ([R_l]) for the pendant is thus approximated as the moles of radicals, which is one divided by Avogadro's number (N_A), over the volume that contains the pendant on the same chain.

$$[R_l(t,t_b)] = \frac{1}{N_A\left(\frac{4}{3}\pi(r_0 + r_{e-e}(t,t_b))^3\right)} \tag{5}$$

The value of r_0 can be varied to represent different sized monomers. In the results presented in this paper, the polymer end-to-end distance is assumed to have the following Gaussian form based on statistical arguments for the freely jointed chain model:[26]

$$r_{e-e}(t,t_b) \approx n^{1/2} l \tag{6}$$

Non-Gaussian chain distribution expressions could easily be incorporated in the model as well. Also, more accurately, to incorporate molecular details for each cross-linking agent, r_{e-e} as a function of n may be is derived from molecular simulations. Any of these formulations could be used within the structure of this work. The variable l represents the statistical length of a repeat unit and is estimated as 5 Å in the model predictions presented here. The variable $n(t,t_b)$ represents the number of repeat units at time t between the radical and monomeric double bond that reacted to form the pendant at t_b. It is defined as the propagation frequency (η) integrated over the time since the pendant was formed, therefore representing the number of repeating units added since the pendant was formed.

The propagation frequency is calculated from the rate of propagation (R_P) divided by the bulk radical concentration ([R_b]).

$$n(t,t_b) = \int_{t_{birth}}^{t} R_P(t')/[R_b]\,dt' \tag{7}$$

Thus, in the absence of termination the expression for the local radical concentration is given below.

$$[R_l(t,t_b)] \approx \frac{1}{N_A\left[\frac{4}{3}\pi(r_0 + n(t,t_b)^{1/2}l^3\right]} \tag{8}$$

This expression gives local radical concentration at each time (t) for a particular pendant created at t_{birth} (t_b). The radical on the propagating chain of the pendant could terminate before the pendant has an opportunity to cycle. Termination of the local radicals by reaction with bulk radicals is, therefore, important to include in the model. This accounting is especially critical when simulating high light intensities where radical termination occurs at a much higher rate. The termination of local radicals with bulk radicals has the following kinetic rate expression where $F_l(t,t_b)$ represents the fraction of radicals that remain unterminated from their birth at t_b to time t:

$$-\frac{d[F_l(t,t_b)]}{dt} = k_t[F_l(t,t_b)][R_b] \tag{9}$$

This expression is integrated from the pendant birth time (t_b) to the current time (t) to determine the fraction of local radicals which are left, $F_l(t,t_b)$.

$$F_l(t,t_b) = \exp[-kt[R_b][(t - t_b)] \tag{10}$$

The expression for the local radical concentration, eq 8, can then be multiplied by the fraction of local radicals that are left, eq 10, to account for termination reactions as presented in eq 11.

$$[R_l(t,t_b)] = \exp[-kt[R_b](t - t_b)]\frac{1}{N_A\left[\frac{4}{3}\pi(r_0 + n(t,t_b)^{1/2}l)^3\right]} \tag{11}$$

A bimolecular reaction for primary cyclization is assumed where the rate of consumption of pendants depends directly on the local concentration of radicals. Using the concentration of radicals developed in eq 3 and eq 8, the rate of consumption of pendants is the sum of the rate of pendant reaction with bulk radicals and the rate of consumption of pendants with local radicals summed over all birth times.

$$R_{pen} = k_{xl}[Pen(t)]\left(\frac{R_i}{2kt}\right)^{1/2} + \frac{k_{cyc}}{N_A}\sum_{i=0}^{i=t}\frac{[Pen(t,t_b)]}{\left[\frac{4}{3}\pi(r_0 + n(t,t_b)^{1/2}l)^3\right]} \tag{12}$$

Here, k_{xl} is the kinetic constant for cross-linking and k_{cyc} is the kinetic constant for cyclization. This equation is evaluated at each time step for pendants of all previous birth times. The total rate of pendant disappearance is then calculated by summing the R_{pen} for pendants born at all times, before the current time. With calculation of R_m and R_{pen}, the total rate of propagation can be determined from eq 1. The numerical model thus accounts for all important elementary reactions, particularly the formation of pendant double bonds and their subsequent reaction with bulk and local radicals.

In the differential equations for the pendant consumption, the value of the local radical concentration changes much faster with time then the bulk radical concentration, and typically all potential cyclization reactions will occur before there is any significant possibility for cross-linking reactions. The time step of the equation is thus determined by the consumption by cyclization. Additionally, the numerical approach requires that the model calculate the pendant consumption for pendants of each birth time separately. Thus, at each time it performs a material balance on pendants born at all previous times. The model can be simplified and computation time drastically reduced by using an analytical expression for the consumption of pendants by cyclization.

In the analytical approach, the above methodology for calculating the rate of consumption of pendants is simplified by integrating over time the contribution of cyclization to the consumption of pendants born at each time. The total fraction of pendants that react by cyclization is then accounted for immediately. This approach avoids having to evaluate at each time whether the pendants born at all previous times react by cyclization. Additionally, the time step needed for a stable solution can be increased. This approach is valid when kinetic parameters are assumed constant (no diffusion control) and when cross-linking reactions occur much more slowly than the concentration of local radicals decreases. Also, termination of local radicals with bulk radicals is assumed not to occur.

The contribution of pendant consumption by cyclization is given by the second part of eq 4, using the local radical concentration expression from eq 8, and assuming the number of repeat units between the pendant and radical on its same propagating chain, n, is approximated as the propagation frequency, η, times $t - t_{birth}$. Here, η represents the polymerization rate divided by the bulk radical concentration.

$$R_{pen,cyc} = \frac{-d[Pen(t,t_b)]}{dt} = \frac{k_{cyc}[Pen(t,t_b)]}{N_A\left\{\frac{4}{3}\pi[r_0 + (\eta(t - t_{birth}))^{1/2}l]^3\right\}} \tag{13}$$

Eq 13 is integrated from t_{birth} to ∞, where infinite time for cyclization is a very short time because of the rapid decrease in the local radical concentration. This integration gives the following result, where ψ is the fraction of pendants born at a particular birth time that cycle:

$$\frac{[Pen(t_b)]_\infty}{[Pen(t_b)]_0} = \exp\left(\frac{-3k_{cyc}}{4\pi N_A\eta r_0 l^2}\right) = 1 - \psi \tag{14a}$$

At each time step the pendants, which are produced from the consumption of monomer, are immediately evaluated for cyclization over their lifetime by eq 14a, and all primary cyclization is assumed to happen in that same time step. This assumption is reasonable because the effect of propagated away significantly, i.e., when the local radical is highest.

Equation 14a can be simplified with several additional assumptions. Assuming cyclization occurs on a much faster time scale then cross-linking for pendants of each birth time, the bulk environment of the pendants during their lifetime can be assumed to be a constant. Thus, the rate of propagation is approximated as k_p[DB][R_b], where k_p, [R_b], and [DB], the total double bond concentration, are constant over the lifetime of the pendant of a particular birth time. Plugging this into eq 7, the propagation frequency becomes k_p[DB]. And, if the kinetic constant for cyclization is equivalent to the propagation kinetic constant, which will be true for most cross-linking agents, then eq 14a becomes the following:

$$\frac{[\mathrm{Pen}(t_\mathrm{b})]_\infty}{[\mathrm{Pen}(t_\mathrm{b})]_0} = 1 - \exp\left(\frac{-3}{4\pi N_\mathrm{A}[\mathrm{DB}]r_0 l^2}\right) \tag{14b}$$

From this equation several trends in the behavior of cyclization can be noted. The fraction of pendants that cycle, ψ, increases with decreasing, r_0, l, and [DB]. Therefore, the degree of cross-linking is increased using a larger monomer, a monomer that is more extended in the solution, or in lower double bond concentrations.

Thus, eq 14a or 14b is used to calculate the contribution of cyclization to pendant decay, where ψ represents the fraction of pendants born at that time that undergo primary cyclization. The consumption of pendant double bonds by cross-linking is then considered on the concentration of pendants remaining [Pen_{xl}], i.e., pendants produced in this time step that did not cyclize and pendants existing from all previous times for which primary cyclization reactions have already been accounted.

$$R_{\mathrm{pen,xl}} = k_{\mathrm{xl}}[\mathrm{Pen}_{\mathrm{xl}}(t)][\mathrm{R_b}(t)] \tag{15}$$

Using this two-step calculation, involving eqs 14a and 15, the consumption of pendants is determined. This analytical approach accounts for the kinetics of all elementary reactions, particularly the reaction of pendants by cross-linking and cyclization.

Input Parameters and Kinetic Constants. For the model runs presented in this paper, the values of input parameters were taken from experimental data for DEGDMA.[36] Diffusion-controlled kinetics may be incorporated into the model.[37] Data presented in this paper, however, do not include the effect of diffusion control in order to isolate and present only the effect of other parameters on the cyclization kinetics. The propagation and termination kinetic constants are fixed at the non-diffusion-controlled values. As the rate of initiation is also held constant, the bulk radical concentration is unchanging throughout the reaction; therefore, the effect of the local radical concentration can be isolated from the effect of the bulk radical concentration on cyclization.

The kinetic constants for propagation (k_p) and cyclization (k_{cyc}) are assumed to be the same because the reactions are, in essence, identical once the local radical concentration is used for cyclization. The pendant double bond has the same chemical reactivity as the monomeric double bond. An example of when this assumption is not the case is monomers such as divinylbenzene where the pendant vinyl is chemically less reactive because of the change in the conjugated structure of the monomer upon reaction of the monomeric double bond. Additionally, unless specified in the figure, the non-diffusion-controlled data presented in this paper are for the case where $k_{xl} = k_p$ (i.e., assuming that there are not steric or diffusional limitations to the cross-linking).

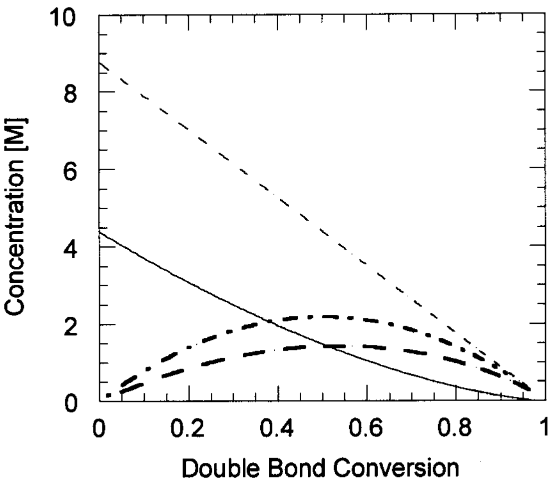

Figure 4. Model prediction of double bond (- - -), unreacted monomer (—), total pendant double bond concentration (— — —), and total pendants double bond concentration for a homogeneous system, i.e., when $k_{cyc} = 0$ (— • —) ($r_0 = 4.5$ Å, light intensity = 1 mW/cm^2).

Results and Discussion

Because of the first principles approach, this kinetic model is able to investigate factors that control primary cyclization in chain polymerizations. Both the numerical and analytical models can predict how cyclization varies as a function of conversion reaction conditions and monomer type. Consistency is found between the analytical and numerical results, except in cases where the assumptions of the analytical model do not hold.

Figure 4 shows the polymerization kinetics predicted by the numerical model. The monomer and double bond concentrations decrease almost linearly with conversion. The amount of pendants present begins at zero and increases as monomer is rapidly consumed. At 50% conversion, the total amount of pendants begins to decrease as the rate of monomer consumption falls off, and more pendants are reacting away then are being formed (Figure 4). The pendant concentration of a homogeneous system (i.e., a system where cyclization reactions are neglected) is also shown in Figure 4, illustrating that pendants are reacting away faster with cyclization then they would be expected to in a homogeneous system. In this homogeneous system k_{cyc} is assumed to be zero.

The model tracks how pendants react at each time. Figure 5 presents the numerical model data for the cumulative fraction of pendants created that react by cyclization or cross-linking. Cyclization is shown to be a very critical mechanism for the consumption of pendants, being between 2−3 times more prevalent then cross-linking in the beginning of the reaction. Cyclization occurs predominantly when a pendant double bond has just been created, and the propagating radical is in close proximity to that pendant functional group. Toward the end of the reaction cross-linking becomes a more competitive mechanism. Radicals have propagated

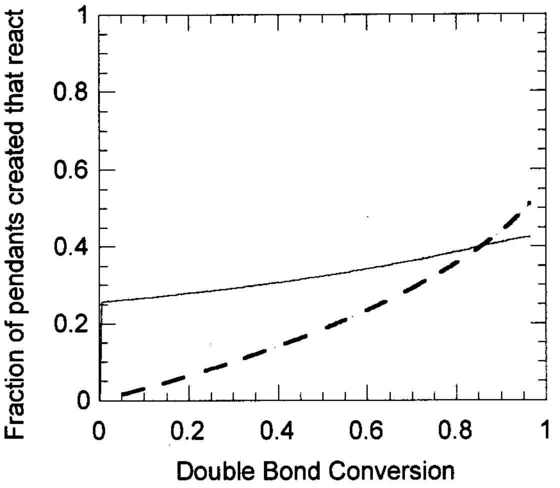

Figure 5. Integral fraction of pendants created that react by cyclization (—) and cross-linking (— — —) ($r_0 = 4.5$ Å, light intensity = 1 mW/cm^2).

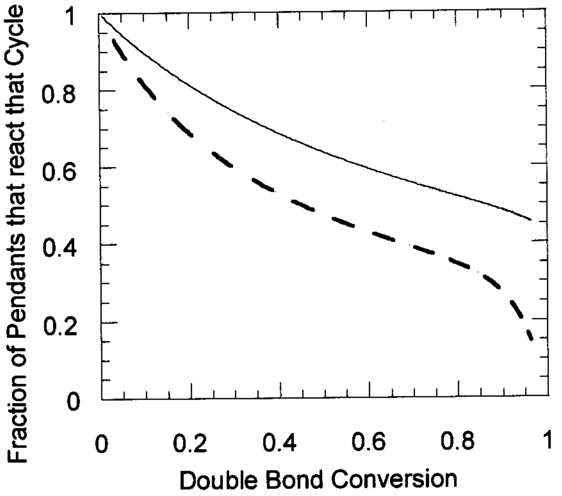

Figure 6. Instantaneous fraction (—) and cumulative fraction (— — —) of reacting pendants forming primary cycles ($r_0 = 4.5$ Å, light intensity = 1 mW/cm^2).

away from earlier incorporated pendants, allowing them to react preferentially by cross-linking. Even still, the contribution of cyclization to the polymerization cannot be neglected. At the end of the reaction about 40% of the potential cross-links (pendants) are lost to cyclization reactions and are not contributing to the overall network structure significantly.

The degree of cyclization changes over the course of the reaction. Figure 5 showed the cumulative fraction of pendants that exist which cycle as a function of conversion. To get a clearer picture of how cyclization rates change over the reaction, the fraction of pendants that react which cycle is plotted. In Figure 6, the instantaneous and cumulative fractions of reacting pendants that form primary cycles as a function of double bond conversion are shown with data from the numerical model. The highest fraction of pendants cycling occurs in the beginning of the reaction because of the limited propagation of radicals away from the newly created pendants (smaller end-to-end distance). As time goes on, the fraction to cycle decreases because of the increasing relative amount of pendants that can react with bulk radicals. The instantaneous fraction of cyclization data illustrates how pendant cyclization varies over the reaction, and the cumulative fraction shows the overall effect on the reaction of the variations in cyclization.

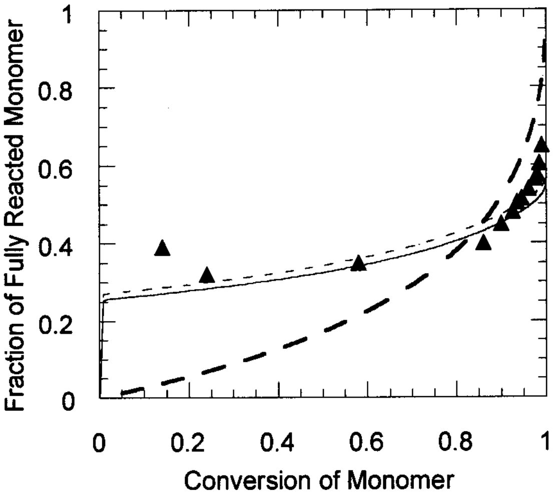

Figure 7. Fraction of fully reacted monomer versus monomer conversion with numerical model (—), analytical model (- - -), numerical model with equal pendant reactivity (— — —), and experimental data for HDDA from Kloosterboer[25] (▲) ($r_0 = 4.5$ Å, light intensity = 1 mW/cm^2, $k_{xl} < k_p$).

Because cyclization is difficult to measure experimentally, very little experimental data are available to test the validity of the model. A study by Kloosterboer about pendant reactivity was used for comparison with the model results.[25] In his work Kloosterboer determined the fraction of fully reacted monomer units as a function of monomer conversion for hexanediol diacrylate (HDDA). The fraction of fully reacted monomer represents the fraction of reacted monomers that have also reacted twice. It could also be called the pendant conversion. In Figure 7 model predictions for both the analytical and numerical approach are compared with mean-field assumption data, where the reactivity of all double bonds is assumed to be equal. For the equal pendant reactivity case, the fraction of fully reacted monomer is calculated as the fraction of monomer in the polymer network that have both double bonds reacted; i.e., it is the fraction of reacted monomer that is fully reacted over the fraction that have at least one double bond reacted. As the first monomeric double bond and the pendant double bond are equally likely to reacted for this case, the expression is $p^2/(p^2 + 2p(1 - p))$, where p is the double bond conversion. For the model results the kinetic constant for cross-linking (k_{xl}) is assumed to be 1 order of magnitude lower than propagation to account for the fact that the pendants available to cross-link are typically buried in regions of high polymer concentration. Model data from both approaches are nearly identical. There is slightly more cyclization accounted for in the analytical model, likely due to the fact that local radical termination is neglected. Both approaches are consistent in trend with the experimental data crossing over the mean-field approximated line at the end of the reaction. The amount of cyclization is approximately 25% at zero conversion.

Investigation of the effect of light intensity on polymerization is limited to using the numerical model. The termination of local radicals by bulk radicals is an important reaction at high light intensities, which is not included in the analytical approach. In Figure 8 the effect of light intensity on the fraction of reacting

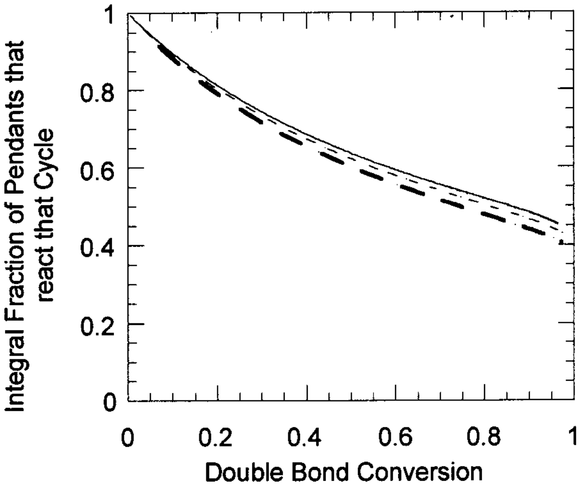

Figure 8. Integral fraction of pendants created that react by cyclization at light intensity = 1 mW/cm^2 (—), light intensity = 50 mW/cm^2 (- - -), and light intensity = 500 mW/cm^2 (— — —) (r_0 = 4.5 Å).

pendant that cycle versus double bond conversion is shown. Increasing light intensity increases the termination rate of radicals. Thus, the rate of cyclization is diminished as the local radicals are consumed more quickly. This effect is small though under the conditions of this simulations. As shown in Figure 8, increasing the light intensity from 1 to 500 mW/cm^2 decreased the integral fraction of reacting pendants that cycle by only 15% at 75% conversion. These results assume an isothermal reaction.

Conclusions

Two kinetic models, one using a numerical approach and the other using an analytical approach, have been developed on the basis of first principles. The models capture the varying pendant reactivity and the competition between cross-linking and cyclization mechanisms by incorporating non-mean-field kinetics. Its most important achievement is that cyclization rates are not input into the model a priori but predicted by the model based on the given reaction conditions, monomer size, pendant birth time, and reaction rate. In the quest to understand the network formation of cross-linked polymers, the models provide a valuable tool. Insight into the factors effecting cyclization during the photopolymerization of multifunctional monomers can be obtained. Initial simulation results presented in this paper already give a fuller picture of the role of primary cyclization in network formation.

Model results demonstrate how pendant reactivity varies with conversion. The instantaneous and cumulative fraction of reacting pendants that form cycles is highest initially, when the radical on the same chain has undergone limited propagation. Additionally, the model is able to predict experimental data for relative rates of consumption of monomeric and pendant double bonds. Increasing the light intensity was found to slightly decrease the rate of cyclization. The effect of monomer size and stiffness, solvent concentration, copolymerization, and monomer functionality can now be evaluated. The model will also be used to investigate the effect of diffusion-controlled kinetics on cross-linked polymerizations to provide more insight into primary cyclization in cross-linked polymer systems.

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