Using Changes in Initiation and Chain Transfer Rates To Probe the Kinetics of Cross-Linking Photopolymerizations: Effects of Chain Length Dependent Termination

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ABSTRACT: The importance of incorporating chain length dependent termination (CLDT) behavior into the interpretation of the kinetics of cross-linked systems has been examined. Kinetic chain length distributions were varied in a variety of di(meth)acrylate photopolymerizations via the manipulation of the initiation rate and the chain transfer rate. Shifting the kinetic chain lengths toward shorter chains has little visible effect on multiacrylate systems. In contrast, similar changes in the corresponding multimethacrylate polymerizations changed the kinetics significantly. Shorter kinetic chains led to the delayed onset of reaction−diffusion-controlled termination behavior, as well as an increase in the ratio of k_t/k_p[M] at all conversions prior to the onset of reaction−diffusion control. Additionally, the magnitude of the kinetic constant ratio in the reaction−diffusion-controlled regime was affected by the kinetics at low conversion in the polymerization of a rubbery system, PEG(600)DMA. This behavior was independent of the method used to alter the kinetic chain length distribution and thus implies that CLDT may potentially impact the network formation in polymerizations occurring above the T_g of the system. These results illustrate that, although counterintuitive, CLDT is an important factor in cross-linking free radical polymerizations.

Introduction

For the past several decades, researchers have understood that the length of the macroradical undergoing termination has a significant effect on the termination rate in linear free radical systems.[1−3] Benson and North were two of the first authors to discuss the significance of chain length dependent termination (CLDT). In their classic 1962 paper,[2] they concluded that the termination process is diffusion-controlled and that the length of the growing polymer chain has a pronounced effect on its termination kinetic constant, especially at short chain lengths. Since that time, numerous researchers have investigated the termination process in linear free radical systems, and a review exists that describes the development of CLDT theory in detail.[4] In brief summary, as the free radical polymerization progresses, the length of the macroradicals increases and the mobility of the chains decreases. With the development of long, less mobile chains, the termination kinetic constant is suppressed. For example, theory predicts that two chains, which are newly formed and relatively "short" in length, will terminate much more rapidly than two "long" chains. Numerous models that include chain length dependent termination mechanisms continue to be developed. These models can be divided into two primary categories: those that focus on the steady-state kinetics of linear polymerization systems[5−11] and those that approach the problem via simulation of the pseudostationary kinetics of these systems, i.e., a modeling perspective of pulsed laser polymerization (PLP)[12−16] or rotating sector[17] type experiments. In conjunction with theoretical developments, the development and refinement of pulsed laser[18−23] and low-frequency pulsed laser[19,24] techniques have enabled experimental verification of the influence of chain length on termination. In a fashion similar to the approach used in pseudostationary polymerizations, molecular weight distributions of low conversion steady-state polymerizations have also been utilized to gain experimental insight into the chain length dependent termination process.[25] Though extensive research has been done to understand the CLDT process, debate continues over the proper way to model these systems and the underlying diffusion mechanisms and how to properly test the validity of those models.[26,27]

Despite the numerous works that have examined CLDT in linear polymerizations, the effect of macroradical chain length on the termination kinetics of multifunctional systems is one that has been little explored. The absence of such discussions in the literature can be attributed to the nature of network formation in cross-linking polymerizations. Mobility becomes limited at very low functional group conversions, leading to diffusion-controlled kinetics throughout most of the polymerization. Thus, in contrast to monovinyl polymerizations, even those that undergo gelation, a significant "high mobility" conversion range is typically absent from cross-linking polymerizations. The mobility of these systems becomes so limited, often at conversions much less than 20%, that radicals can no longer move together via center-of-mass diffusion to terminate. Necessarily, termination becomes controlled by movement of radicals through the network via propagation

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through unreacted double bonds (monomer or pendant vinyl groups) until they are close enough to terminate. Since its introduction by Schulz in 1956,[28] this termination mechanism, now called reaction−diffusion, has received significant attention. When reaction−diffusion is the dominant termination mechanism, the kinetic constant for termination, k_t, is proportional to the propagation frequency (eq 1), i.e., the product of the propagation kinetic constant, k_p, and the double bond concentration, [M].[29−32] The constant of proportionality is referred to as the reaction−diffusion coefficient, R.

$$k_t = Rk_p[M] \quad (1)$$

Given that this chain length independent process dominates termination throughout the majority of a cross-linking polymerization, it is easy to understand why discussions of the possible importance of CLDT in these systems have long been neglected.

From a theoretical perspective, a single work by Zhu[33] is the lone contribution that presents methodology specific to cross-linking polymerizations, although some of the modeling work that has been presented from a linear free radical polymerization perspective[6,10] clearly presents a solid basis for expansion to the even more complex scenario involving cross-linking reactions. Zhu's work focuses on the effect of CLDT on the molecular weight development and gelation behavior of cross-linking systems by building on Saito's[34] model for predicting molecular weight distributions in systems that undergo random cross-linking. The model predicts that CLDT will always delay the gel point since the favored short−short termination process does not contribute to the molecular weight buildup. Furthermore, it predicts that gel growth, though delayed, will actually occur at a much faster rate, with fewer radical centers remaining in the sol fraction when CLDT is included. Though the model admittedly incorporates numerous simplifying assumptions, the work has taken the bold step of applying the notion of a chain length dependent termination mechanism to cross-linking systems.

The same reasons that make it difficult to imagine that a chain length controlled mechanism impacts cross-linking systems significantly also make it difficult to test any theory involving chain length dependent termination in a cross-linked network. In the polymerization scenario that includes cross-linking reactions, the molecular weight analysis that accompanies most experimental protocols developed to probe CLDT is impractical given the infinite network formation characteristics of cross-linking systems. Thus, experimental contributions that explore the importance of CLDT in cross-linking polymerization are few.[35,36]

A recent paper[36] has addressed the importance of CLDT in cross-linking polymerizations. In that work, changes in the initiation rate and the addition of small amounts of a chain transfer agent were used to impact chain length distributions during the photopolymerization of multifunctional (meth)acrylates. The relationship between the initiation rate and the polymerization rate was evaluated and compared to classical behavior, where termination is bimolecular and radical reactivities are assumed independent of chain length. A deviation from the classical dependence, $R_p \propto R_i^{1/2}$, was observed in the polymerization of several dimethacrylate systems over a broad range of initiation rates. This dependence is similar to those measured and theorized for linear polymerizations that exhibit CLDT, i.e., $R_p \propto R_i^{\sim 1/3}$.[4−6,37,38] Chain transfer agent addition was also used to impact chain length and correspondingly termination kinetics for systems where CLDT is important. Changes in polymerization rate as a function of chain transfer agent concentration provided additional evidence regarding the importance of CLDT in cross-linking systems. This study indicated that polymerization kinetics are intimately linked to those factors that affect the chain length distribution in the polymerizing media. This information is valuable to substantiating the importance of accounting for CLDT in cross-linking polymerizations and directs us toward future studies to clarify and understand this behavior more completely.

To probe the polymerization behavior further, this contribution expands upon the steady-state evaluations pursued in the previous work[36] and examines how the addition of a chain transfer agent and changes to the initiation rate can impact the underlying kinetics of multifunctional (meth)acrylate systems. Evaluation of the unsteady-state kinetics[39−41] of these polymerization systems provides insight into the aspects of the polymerization that are affected most by chain length and the potential inpact that variations in chain length can have on network formation.

Experimental Section

Materials. The monomers used in this study were diethylene glycol dimethacrylate (DEGDMA, Sartomer Co., Exton, PA), diethylene glycol diacrylate (DEGDA, Sartomer Co., Exton, PA), 1,6-hexanediol dimethacrylate (HDDMA, Aldrich, Milwaukee, WI), 1,6-hexanediol diacrylate (HDDA, Aldrich, Milwaukee, WI), poly(ethylene glycol) (600) dimethacrylate (PEG(600)DMA, Sartomer Co., Exton, PA), and poly(ethylene glycol) (600) diacrylate (PEG(600)DA, Sartomer Co., Exton, PA). The numeric notation in the PEG monomers refers to the average molecular weight of the ethylene glycol chain of the macromer. The GC purity of the lower molecular weight compounds, DEGD(M)A and HDD(M)A, is greater than 95%. The higher molecular weight systems have a greater than 90% purity with respect to the percent di(meth)acrylate monomer contributing to the 600 average molecular weight ethylene glycol based backbone. All reagents are composed of at least 99% reactive esters. Polymerizations were performed using 0.1−5.0 wt % of the ultraviolet initiator 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba Geigy, Hawthorne, NY). The chain transfer agent, 1-dodecanethiol (ACROS, NJ), was used. All materials were used as received.

Fourier Transform Infrared Spectroscopy. Real-time Fourier transform infrared (RT-FTIR) spectroscopy provides a means for monitoring changes in the vibrational absorbance(s) associated with a system's reactive functionalities as a function of polymerization time. Changes in the peak area attributed to the stretching vibration of the (meth)acrylate carbon−carbon double bond, ca. 1637 cm^{-1}, were used to measure double-bond conversion directly as a function of time and gather kinetic information. The use of infrared spectroscopy for this purpose was pioneered by Decker[42−45] with his use of real-time infrared (RTIR) spectroscopy to monitor polymerizations occurring too rapidly for accurate evaluation with differential scanning calorimetry.[45,46] Modern FTIR spectrometers possess a combination of high-frequency sampling rates and cooled detectors capable of handling those rates while maintaining high signal-to-noise output. These capabilities provide all of the advantages realized with the RTIR technique with the benefits of FT data collection. FTIR supplies the complete vibrational spectra of the monomer-to-polymer transition during polymerization and, correspondingly, real-time information about baseline shifts, peak convolution, and evolution and decay of other absorbances due to vibrational transitions relevant to the reaction in question.

A FTIR spectrophotometer (Nicolet model 760 Magna series II FTIR, Nicolet, Madison, WI) equipped with a MCT/B−XT

KBr detector−beam splitter combination was used to monitor the polymerization kinetics. A temporal resolution of ~30 ms is obtainable using the rapid scan feature of the spectrometer. A horizontal transmission accessory was designed to enable mounting of samples in a horizontal orientation for FTIR measurements.[39,47] The horizontal sample orientation allows measurements on thick samples or low-viscosity films without the flow problems inherent to the standard vertical arrangement. This accessory also facilitates irradiation of samples from a near-normal incidence from above without interfering with the IR source.

Samples 15−20 μm thick were prepared by sandwiching a 5 μL drop of monomer/initiator between two NaCl crystals. The use of this sample geometry ensured uniform irradiation of the polymerization system and an essentially isothermal polymerization environment, using the IR transparent NaCl crystals as efficient heat sinks for the heat released during the polymerization of the thin film.[40,45] All polymerizations were run at room temperature. An UV light source (Ultracure 100SS 100 W Hg short-arc lamp, EFOS, Mississaugua, Ontario, Canada) equipped with a liquid light guide was used to irradiate the monomer/initiator mixtures in the sample chamber of the FTIR. The incident light intensity was controlled using the internal aperture of the UV light source. The molar absorptivity of the photoinitiator, DMPA, at the peak initiating wavelength, 365 nm, is 150 L/(mol cm). The initiation rate for each polymerization was calculated[48] from the following expression:

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

where R_i is the initiation rate, ϕ the initiator efficiency (assumed one for all calculations), I_{abs} the quantity of light absorbed, ϵ the initiator's molar absorptivity at λ, the wavelength of initiation, I_{inc} the incident light intensity in units of power/area, [Ab] the concentration of the initiator, N_{Av} Avogadro's number, h Planck's constant, and c the velocity of light.

Unsteady-state experiments were used to probe the underlying kinetics and the reaction−diffusion process. In these experiments, the initiating light source is extinguishing during photopolymerization, and the polymerization is monitored "in the dark". In the absence of initiation (i.e., after the light is extinguished), the kinetics can be described by species balances on the radicals and double bonds present in the system:

$$\frac{d[R^\bullet]}{dt} = -2k_t[R^\bullet]^2 \tag{3}$$

$$\frac{d[M]}{dt} = -k_p[M][R^\bullet] \tag{4}$$

where t is time and $[R^\bullet]$ is the radical concentration. An expression for $[R^\bullet]$ as a function of time is obtained via integration of the radical population balance, eq 3, where the lower integration limit of $[R^\bullet]$ at time = 0 in the dark is $[R^\bullet]_0$ or $R_{p0}/(k_p[M])$. The resultant radical concentration expression, eq 5, is then substituted into the balance on double bonds, eq 4.

$$[R^\bullet] = \frac{R_{p0}/(k_p[M])}{2R_{p0}R(t - t_0) + 1} \tag{5}$$

The resulting expression is then simplified, and the reaction−diffusion coefficient can be obtained directly from the following result:[40]

$$\Delta[M] = \frac{1}{2R}\ln(2RR_{p0}t + 1) \tag{6}$$

where R_{p0} is the rate of polymerization at time = 0 in the dark, $\Delta[M]$ is the change in double bond concentration, and t is the time for which the change in double bond concentration is monitored in the absence of initiation. The details of this analysis have been published previously.[40]

Results and Discussion

Discussions of kinetic chain length are typically limited to the evaluation of linear polymerizations. For the purpose of this discussion, its definition will be broadened to include the systems and mechanisms that may be important during the free radical polymerization of multifunctional systems. A logical starting point is with a definition that is accepted for polymerization in the absence of transfer reactions. Thus, kinetic chain length, ν, is simply "the average number of monomers reacting with a given active center from its initiation to its termination",[49] represented by the ratio of the rate of monomer consumption, R_p the polymerization rate, to the rate of radical generation, R_i the initiation rate:

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

The initiation rate is approximately equal to the termination rate under pseudo-steady-state conditions.

When transfer is added to the reaction scheme, differences in the definition of kinetic chain length exist.[48−51] The discrepancies resolve around whether a "new" radical formed via a transfer reaction constitutes a new kinetic chain. In this work, chain transfer will be defined as a chain breaking mechanism where the newly formed active site is the start of a new kinetic chain or new initiation site.[50−52] Thus, the kinetic chain length can be approximated as the number of double bonds a radical reacts with before it is involved in a reaction that stops chain growth, e.g., termination or chain transfer, eq 7.

$$\nu = \frac{R_p}{R_i + R_{ct}} = \frac{R_p}{R_t + R_{ct}} \tag{7}$$

where R_p is the polymerization rate, R_t is the termination rate, and R_{ct} is the chain transfer rate. R_i is approximately R_t under pseudo-steady-state conditions.

Examining polymerizations of different systems over a range of conditions can assist in elucidating the impact of kinetic chain length on the kinetics of cross-linking polymerizations. Methacrylates and their corresponding acrylate polymerizations were chosen for study both because of their similarities and differences. Such pairs allow comparison of systems with almost identical initial physical characteristics. The initial double bond concentration, viscosity, density, molecular weight, optical density, monomer size, and monomer makeup are essentially the same; however, the evolution of kinetic chains during the polymerization of these systems is quite different. Factors such as differing radical and monomer reactivities and different chain transfer rates contribute to markedly different polymerization rates.[49]

The differences in the inherent chain transfer characteristics of acrylate and methacrylate polymerizations[53−55] have been firmly established and are thus a very useful tool for characterizing effects that may be due to factors linked to chain transfer. Abstraction of α-hydrogens readily occurs during acrylate polymerization. This reaction leads to the formation of midchain radical sites and correspondingly polymer that functions as a chain transfer agent. This behavior, however, does

not play a significant role in methacrylate polymerization where the α-position is occupied by a methyl constituent from which abstraction is not likely. Thus, the marked differences between the chain transfer characteristics of these two systems can be used as a tool to examine the role of chain length on the polymerization process.

As a result of the differences in the chain length distributions naturally formed during these polymerizations, it has been hypothesized that the effect of CLDT on the kinetics of cross-linking methacrylate photopolymerizations will be more easily observed than its effect on the corresponding acrylate polymerizations, as the chain length distribution in the acrylate systems is naturally controlled by the inherent chain transfer reactions that dominate the polymerization environment. The polymerization kinetics of acrylates and the corresponding methacrylates have been examined over a range of polymerization conditions designed to impart different kinetic chain lengths to validate this hypothesis. Namely, initiation and chain transfer rates have been varied and the resulting impact on the kinetics quantified.

The use of unsteady-state experimentation to evaluate the termination behavior of these systems provides a logical extension to a previous work[36] that examined the impact of R_i and R_{ct} on polymerization rate behavior. This type of experimentation can be used to determine the effect of varying the kinetic chain length on the kinetic constants for propagation and termination as well as the effect on the reaction−diffusion behavior[29−32] of the polymerization system. Additional evidence in support of CLDT would be manifested by changes in the kinetic parameters. Variations in the magnitude of the ratio of the kinetic parameters, k_t/k_p[M], as a function of conversion prior to termination becoming reaction−diffusion-controlled, the double bond conversion at the onset of reaction−diffusion-controlled termination, and the magnitude of the ratio of kinetic parameters once reaction−diffusion is the dominant termination mechanism provide valuable insight into the CLDT process. If CLDT effects are observed, they are expected to be prior to the onset of reaction−diffusion-controlled termination. Although the onset of reaction−diffusion control may be shifted to higher conversions, chain length should not impact the reaction−diffusion-controlled termination mechanism.

Kinetics of Rubbery Systems. As the initiation rate was increased in the polymerization of PEG(600)DMA, the ratio of the kinetic constants, k_t/k_p[M], increased. Figure 1a illustrates the response of k_t/k_p[M] as a function of conversion when the initiation rate is changed. At the onset of polymerization, before any significant amount of initiator has been consumed, a 200-fold difference in R_i is enough to decrease the kinetic chain length by a factor of ∼60, given a comparison of the two systems at 5% conversion.[56] This change has a pronounced effect on the kinetics and is clearly observed in the behavior of k_t/k_p[M] as a function of the double bond conversion. Interestingly, examining the polymerization of PEG(600)DA over a similar range of initiation rates yields little effect on the observed kinetic parameters (Figure 1b). From the first obtainable data point using unsteady-state analysis, the ratios of k_t/k_p[M] for the diacrylate polymerizations at different R_i's are experimentally indistinguishable.

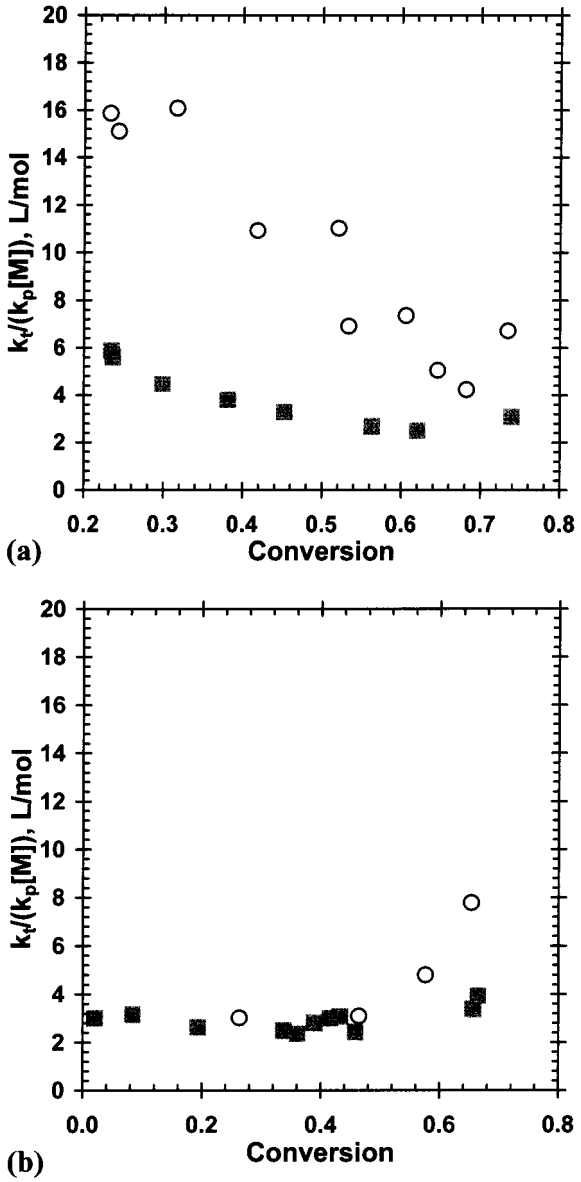

Figure 1. Ratio of kinetic constants as a function of conversion for the polymerization of (a) PEG(600)DMA at two different rates of initiation (R_i (■) = 4.6×10^{-5} mol/(L s) (5 mW/cm^2, 0.1 wt % DMPA), R_i (○) = 9.1×10^{-3} mol/(L s) (100 mW/cm^2, 1 wt % DMPA) and (b) PEG(600)DA at two different rates of initiation (R_i (■) = 4.6×10^{-5} mol/(L s) (5 mW/cm^2, 0.1 wt % DMPA)), R_i (○) = 7.1×10^{-3} mol/(L s) (78 mW/cm^2, 1 wt % DMPA).

The use of initiation rate to impart changes in the kinetic chain length is not ideal. The rapid consumption of initiator that occurs with high irradiation intensities leads to initiation rates that are not constant throughout the polymerization. In fact, for data obtained utilizing 100 mW/cm^2 of irradiating light and 1.0 wt % of the initiator DMPA, the initial initiation rate, $\sim 9 \times 10^{-3}$ mol/(L s), drops by more than 90% over the first 10 s (∼65% conversion) of the polymerization, assuming an initiator efficiency of one. The initiation rate for the polymerization under those conditions remains higher than that of the 5 mW/cm^2, 0.1 wt % DMPA polymerization until reaching ∼80% conversion, after which time the initiation rate has decayed to a value nearly equivalent to the polymerization initiated with 5 mW/cm^2. Thus, a comparison is being made between polymerizations with different initiation rates and corre-

spondingly different kinetic chain length distributions; however, the magnitude of the difference between the conditions is constantly changing over the course of the polymerization. Despite the difficulties associated with utilizing such high light intensities to obtain high rates of initiation, these data indicate that the increased rate and correspondingly decreased kinetic chain length distribution have a dramatic effect on the kinetics, as is exhibited by the elevation of the ratio of $k_t/k_p[M]$ with increased R_i.

It is, therefore, also important to examine other methods for changing the kinetic chain length. The polymerization kinetics of acrylates and the corresponding methacrylates have also been examined with and without the addition of a chain transfer agent to the reaction. The effect of chain transfer agent is also transient during the polymerization, as the chain transfer agent, like the initiator, is also consumed during polymerization. However, this information can be utilized in conjunction with the initiation rate studies to demonstrate the importance of the kinetic chain length as the variable that is contributing to the observed changes in the kinetics.

The addition of a chain transfer agent, even at concentrations as low as 0.1 wt %, to the polymerization of a multifunctional methacrylate has a dramatic effect on the polymerization rate, whereas concentrations much greater than 1.0 wt % are needed to invoke a change of similar magnitude in the corresponding acrylate system.[36] The rate of chain transfer to polymer in the acrylate systems is large enough to dominate and control the kinetic chain length even in the presence of a small amount of chain transfer agent. Thus, the addition of a small amount of chain transfer agent to the acrylate polymerization has little effect on the kinetic chain length distribution during polymerization and consequently little effect on the observed kinetics. Conversely, in the methacrylate polymerization, the factor that controls the kinetic chain length should shift with the addition of a chain transfer agent. The chain transfer rate will easily become much larger than the termination rate, which is approximately equivalent to the initiation rate, as the amount of chain transfer agent introduced into the system is increased for polymerizations initiated at the same rate.

The addition of the chain transfer agent to the polymerization of a rubbery acrylate, PEG(600)DA, yielded the expected result (Figure 2b). Essentially no change was observed in the behavior of the ratio of the kinetic constants. The system was reaction−diffusion-controlled from the earliest data point acquired, and the magnitude of the reaction−diffusion coefficient, which is noted by the plateau value of the ratio of kinetic constants ($k_t/k_p[M]$), was experimentally equivalent for both cases. Conversely, addition of a chain transfer agent to the corresponding methacrylate polymerization of PEG(600)DMA had a substantial effect on the behavior of the ratio of the kinetic constants throughout the polymerization (Figure 2a).

A dramatic difference in the magnitude of the ratio of $k_t/k_p[M]$ is observed at low conversion. As the chain length distribution, even during the formation of this highly cross-linked network, is shifted toward shorter lengths, the radicals that are participating in the termination reaction exhibit a higher mobility than is observed at the same conversion in the absence of the chain transfer agent. This behavior also leads to a delay

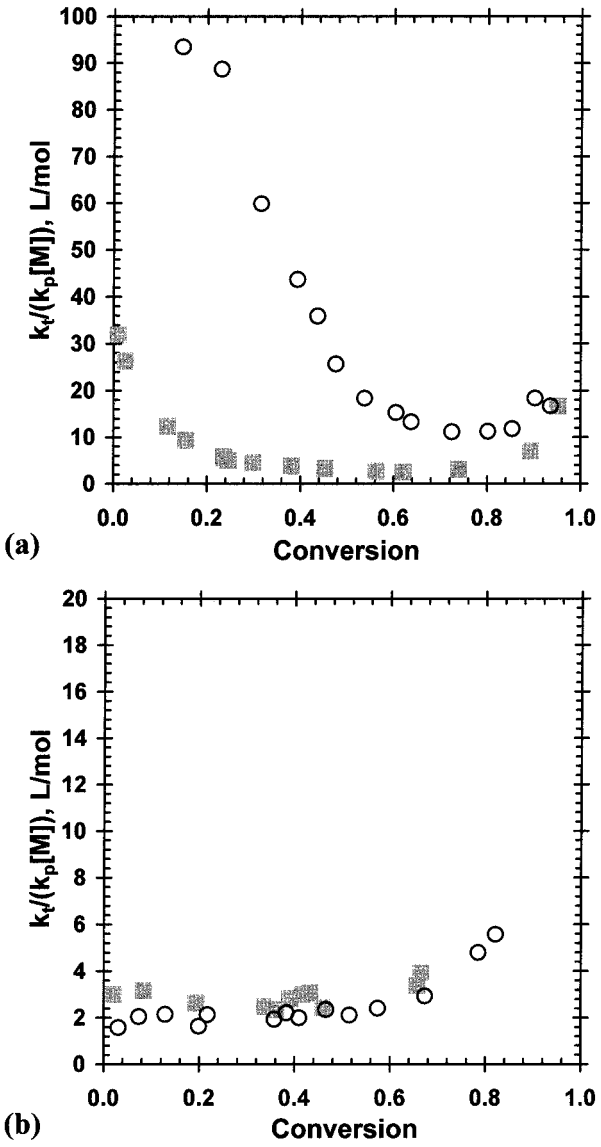

Figure 2. Ratio of kinetic constants as a function of conversion for the polymerization of **(**a**)** PEG(600)DMA with 1.0 wt % of the chain transfer agent 1-dodecanethiol (○) and without the addition of a chain transfer agent (■) and **(**b**)** PEG(600)-DA with 1.0 wt % of the chain transfer agent 1-dodecanethiol (○) and without the addition of a chain transfer agent (■). All polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

in the onset of reaction−diffusion-controlled termination, which is noted by the conversion where the ratio of kinetic constants plateaus. Additionally, the magnitude of the reaction−diffusion coefficient is elevated with the addition of the chain transfer agent in the PEG(600)DMA system. One might expect that if kinetic chain length was important, it would have a significant influence early in the polymerization, prior to the system becoming reaction−diffusion-controlled; thus, the change in the magnitude of the plateau value is surprising. Although the change in the magnitude of the reaction−diffusion coefficient is small in comparison to that which is observed prior to reaction−diffusion dominating the termination reaction, it is experimentally significant.

The change in the plateau value of the kinetic constant ratio implies that the variations in the kinetic chain length that were induced early in the polymerization continue to have an impact on the kinetics well

into the reaction−diffusion-controlled termination regime. It is logical to suspect that this result may be a consequence of the presence of the chain transfer agent and the corresponding R_{ct} and not evidence of, as one might imagine, a possible change in the network so dramatic that even the kinetics in the diffusion-controlled regime are affected. Since the chain transfer reaction is not halted with the extinction of the irradiation source, its effect on the unsteady-state kinetics may be notable. Verification of this result using different means to vary kinetic chain length is necessary to understand the cause of the changed diffusion-controlled kinetics. Ideally, the use of a mechanism that is inactive during the dark period is necessary for kinetic constant determination. This approach would allow the behavior of the species formed during polymerization to be monitored without continuous creation of low molecular weight radical species during the dark experiment.

As previously noted, the impact of changing R_i on the kinetics of the PEG(600)DMA polymerization system is significant. Unfortunately, the decay of initiator over the course of the polymerization makes it difficult to impact the kinetic chain length significantly throughout the entire polymerization. The aforementioned study where R_i was changed primarily through a variation in light intensity led to a polymerization where $R_{i,high} \approx R_{i,low}$ before the $R_{i,high}$ system became reaction−diffusion-controlled. Thus, the effect, if any, on the eventual plateau value of the kinetic constant ratio was not obtained. In light of the result obtained via the introduction of the CT agent, it is desirable to characterize this system more completely over the course of the entire polymerization, including the evaluation of its response at high conversions. A system was chosen that would have both a high initiation rate and initiator decay characteristics that would allow a comparison of the $R_{i,high}$ polymerization to the $R_{i,low}$ experiment throughout the polymerization, i.e., $R_{i,high} \gg R_{i,low}$ for the entire conversion range. This experimental protocol was achieved by using initiator content to manipulate R_i.

Changing R_i in this manner also leads to a delay in the onset of reaction−diffusion-controlled termination, and in a fashion similar to the system containing a CT agent, the magnitude of the reaction−diffusion coefficient is also elevated (Figure 3). It is again apparent from this result that the effect of the change in the kinetic chain length distribution is still evidenced well into the time after the initiation reaction has been stopped, even when the system has become diffusion-controlled. The elevation in k_t/k_p[M] at these conversions is somewhat puzzling, especially considering that the measurements are taken during a dark period, i.e., when $R_i = 0$. This behavior implies that at the same conversion samples that have been initiated at different rates either have radical populations that are different from each other or form networks that are different in nature, such that the kinetics are effected throughout the polymerization. It seems unreasonable that the radical structures would be markedly different in these two systems considering the time frame of the "in the dark" analysis (∼12−60 s.). This time period spans numerous normal radical lifetimes, and thus the difference in the radical length distribution at these extended dark times should not be significantly different for the two systems.

Another characteristic of the kinetic constant ratio, k_t/k_p[M], vs conversion data that deserves mention is

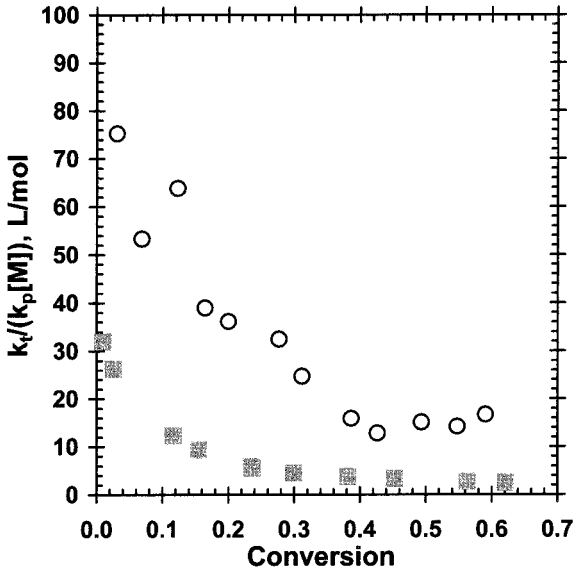

Figure 3. Ratio of kinetic constants as a function of conversion for the polymerization of PEG(600)DMA at two different rates of initiation (R_i (■) = 4.6×10^{-5} mol/(L s) (5 mW/cm^2, 0.1 wt % DMPA), R_i (○) = 2.3×10^{-3} mol/(L s) (5 mW/cm^2, 5 wt % DMPA).

the often observed increase from its reaction−diffusion plateau value at high conversion. This behavior can be attributed to a combination of factors: the changing role of chain transfer in the polymerization system and the nature of the experimental technique. Radicals present in the system have at least three different mechanisms for movement during polymerization: diffusion, propagation, and chain transfer. As the polymerization progresses, a shift in the dominant means of radical mobility occurs. The inherent nature of the three-dimensional cross-linked network at high conversion limits radical mobility via diffusion. At high conversions, propagation is limited because of low diffusion rates and the relatively low and continually decreasing double bond concentration in the system. Thus, as conversion increases, chain transfer plays an ever increasing role in radical mobility and, correspondingly, termination; i.e., termination will be dependent on both the propagation frequency, movement through reaction with carbon−carbon double bonds, and the chain transfer rate.[41] These FTIR experiments, however, use only double bond consumption to monitor the polymerization kinetics. This method does not quantify mobility events that occur in the absence of double bond consumption, i.e., chain transfer. Thus, R will appear to increase as R_{ct} becomes the dominant mechanism for radical mobility; i.e., the instance of termination relative to chain propagation is increased as a result of the presence of chain transfer in the system.

Kinetics of Glassy Systems. Identical experiments were also run on several other systems, including two glassy methacrylate/acrylate pairs: one based on diethylene glycol and the other hexanediol. The polymerizations of the diethylene glycol-based systems were analyzed to compare the polymerization of a glassy system with that of its rubbery PEG(600) counterpart while maintaining the same ethylene glycol-based monomer structure. Alternatively, the hexanediol-based monomers were used to examine what effect, if any, the ethylene glycol monomer backbone was having on the observed chain length dependent characteristics. Since the ethylene glycol units are slightly more prone to

chain transfer reactions themselves, as a result of the decreased dissociation energy associated with the carbon−hydrogen bonds adjacent to the ether linkages, the examination of a monomer with a pure alkyl chain of similar size to the diethylene glycol chain serves as a control. If the primary contribution to the observed changes in the kinetics was due to reactions occurring as a result of the ethylene glycol chains, then the response of the hexanediol-based systems to changes in R_i and R_{ct} during polymerization would differ from that of the ethylene glycol-based systems.

The observed response of these glassy systems to changes in their kinetic chain length distributions was similar to that of their rubbery counterparts. The acrylate polymerizations again exhibited little change in the kinetic parameters measured as a function of conversion. Conversely, the methacrylate kinetics were influenced by both the addition of a chain transfer agent and changes in the initiation rate. Prior to the onset of reaction−diffusion control, $k_t/k_p[M]$ increased at a given conversion in both the DEGDMA (Figure 4a) and the HDDMA (Figure 5) systems. Additionally, the conversion where reaction−diffusion becomes the dominant termination mechanism, i.e., where the kinetic constant ratio reaches its plateau value, is also delayed in both systems with chain transfer agent addition and increased initiation rate. These results indicate that the trends observed in the kinetic parameters do not seem to be affected by the nature of the chain transfer characteristics of the monomer backbone. This behavior also appears independent of the method used to vary kinetic chain length (R_{ct} vs R_i). The kinetics of HDDMA as a function of the amount of chain transfer agent added (Figure 6) illustrate that the delay in reaching the reaction−diffusion plateau is a function of the magnitude of change in the kinetic chain length. As the concentration of chain transfer agent is increased, the conversion where reaction−diffusion control is realized also increases. Unlike the PEG(600)DMA system, the magnitude of the reaction−diffusion coefficient in the plateau region is essentially unchanged in these systems. Each polymerization ultimately returns to the same kinetics, independent of the method used to vary the kinetic chain length. This result conforms to the initial hypothesis that the influence of chain length dependent kinetics would occur at low conversions, prior to the onset of reaction−diffusion-controlled termination.

Comparison to Steady-State Results. The results of this work can also be correlated with the results of the previous steady-state examination of these systems.[36] In that work, Berchtold[36] evaluated the relationship between R_p and R_i as a function of conversion and used the characteristics of that dependence as evidence of CLDT's impact on the kinetics. Using $R_p \propto R_i^{\alpha}$ as the measurable quantity, an α of $<1/2$ was realized throughout the entirety of the PEG(600)DMA polymerization. The large conversion range over which essentially a single exponent at the less than classical level was valid is very much in agreement with the characteristics of the kinetic parameters over the same conversion range, i.e., that the impact of a changed initiation rate was realized over the entire conversion range. In contrast, the significant impact on the glassy systems studied occurred at early conversions, prior to the onset of reaction−diffusion control of the termination process as evidenced by the plateau of the kinetic

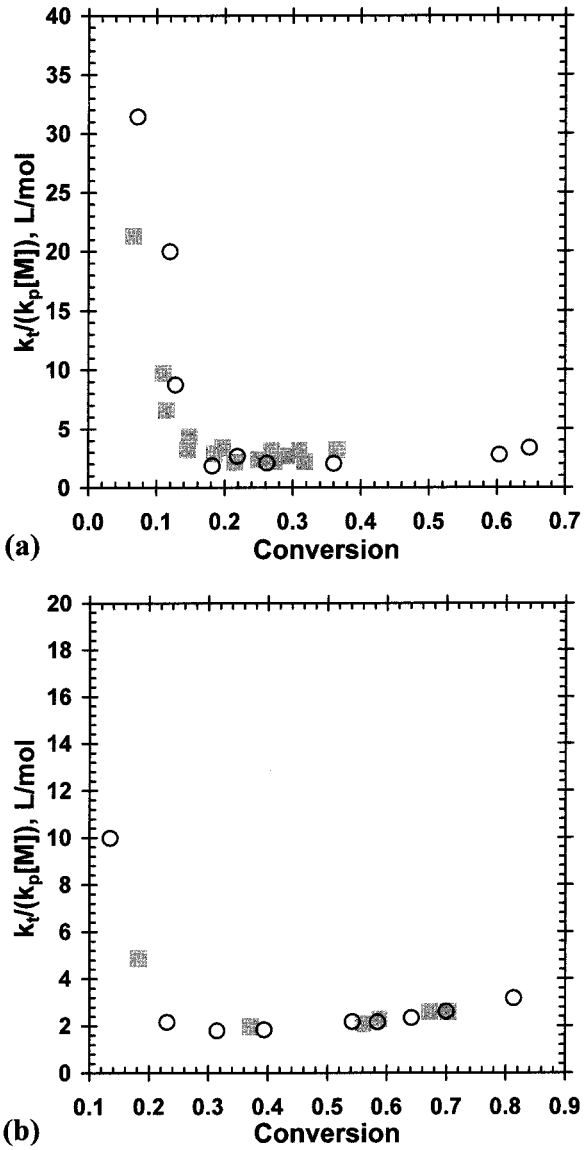

Figure 4. Ratio of kinetic constants as a function of conversion for the polymerization of **(**a**)** DEGDMA at two different initiation rates (R_i (■) = 4.6×10^{-5} mol/(L s) (5 mW/cm^2, 0.1 wt % DMPA), R_i (○) = 2.2×10^{-3} mol/(L s) (5 mW/cm^2, 5 wt % DMPA) and **(**b**)** DEGDA at two different initiation rates (R_i (■) = 4.6×10^{-5} mol/(L s) (5 mW/cm^2, 0.1 wt % DMPA),), R_i (○) = 2.2×10^{-3} mol/(L s) (5 mW/cm^2, 5 wt % DMPA).

constant ratio. This same factor was also visible in the steady-state analysis of these systems. The dependence of R_p on R_i changed significantly at approximately the same conversion where differences in the kinetic constant ratio for polymerization over the same range in initiation rate were measured. Therefore, if we hold α constant at the value that conforms to the early conversion data, a deviation form the fit is observed when the dependence of R_p on R_i changes (Figure 5).

Conclusions

To date, the incorporation of CLDT into the interpretation of the kinetics of cross-linked systems has not been thoroughly explored. The use of initiation and chain transfer rates to manipulate the kinetic chain length distributions in a variety of di(meth)acrylate polymerizations was examined. Changing the kinetic chain length had little visible effect on the photopolymerization of acrylates. In contrast, inducing shorter

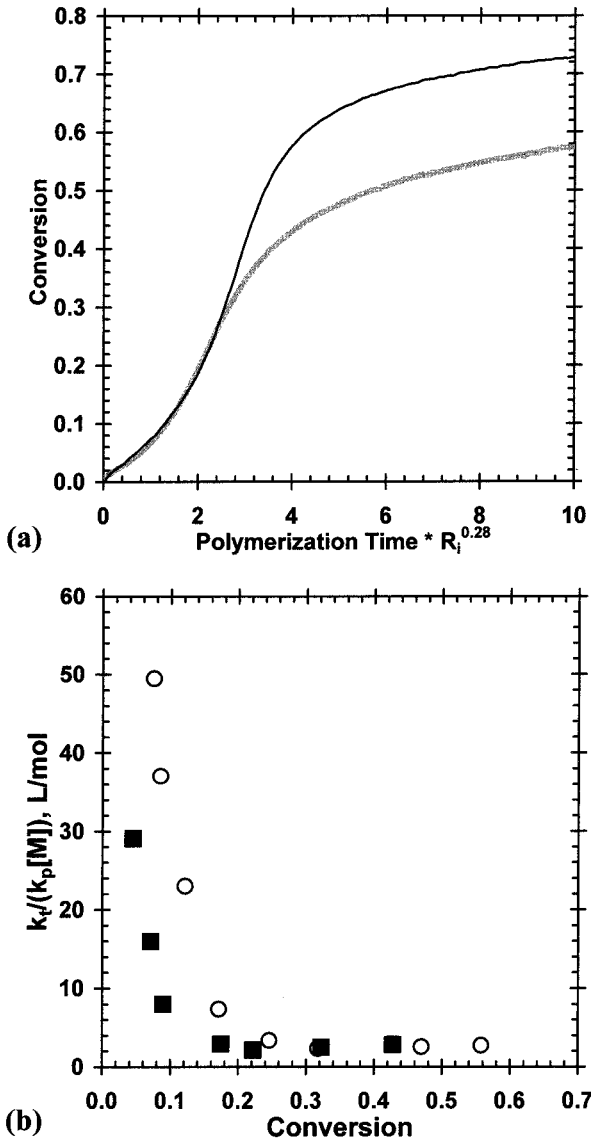

Figure 5. Comparison of data from steady-state evaluation (a) with unsteady-state evaluation (b) for the polymerization of HDDMA at two different initiation rates (R_i (■, —) = 4.6 × 10^{-5} mol/(L s) (5 mW/cm^2, 0.1 wt % DMPA), R_i (○, ⎯) = 2.2 × 10^{-3} mol/(L s) (5 mW/cm^2, 5 wt % DMPA).

kinetic chain lengths in the polymerization of the corresponding methacrylates increased the ratio of $k_t/k_p[M]$ at low conversions, prior to the onset of reaction−diffusion-controlled kinetics and delayed the conversion where the system became reaction−diffusion-controlled. The plateau value of the kinetic constant ratio was independent of R_{ct} and R_i for the polymerization of glassy dimethacrylates but was elevated for the rubbery PEG(600)DMA system regardless of the method used to alter the kinetic chain length distribution. This result implies that CLDT may impact the network formation in polymerizations occurring above the T_g of the system. These results indicate that CLDT is an important factor in these cross-linking free radical polymerizations.

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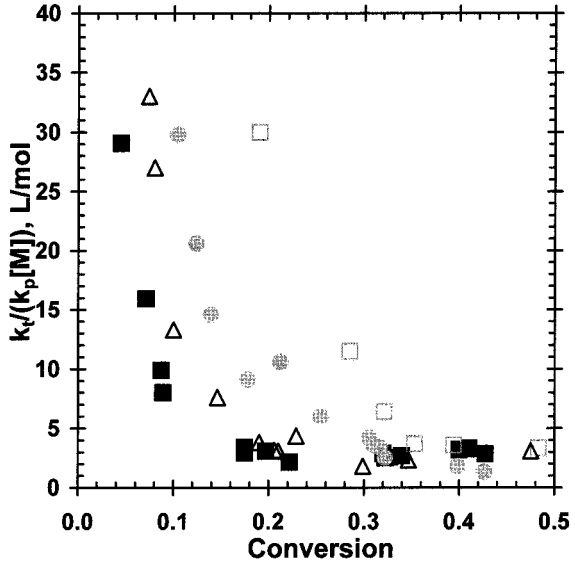

Figure 6. Ratio of kinetic constants as a function of conversion for the polymerization of HDDMA with 0 (■), 0.5 (△), 2.0 (●), and 5.0 wt % (□) of the chain transfer agent 1-dodecanethiol added. Polymerizations were initiated with 0.1 wt % DMPA at 5 mW/cm^2.

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