Macromolecules **1996,** *29,* 7310−7315

Kinetic and Mechanistic Studies of Iniferter Photopolymerizations

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Received December 28, 1995; Revised Manuscript Received August 9, 1996[⊗]

ABSTRACT: An investigation of the rate behavior of bulk photopolymerizations of methacrylates initiated by *p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate) (XDT) is presented. Kinetic studies of photopolymerizations of monomethacrylates and dimethacrylates were performed by differential scanning calorimetry. A comparison of the polymerization rate behavior between the iniferter polymerizations and the conventional radical polymerizations is presented to propose a mechanism for the kinetics of the iniferter polymerization. The iniferter polymerization mechanism involves two termination pathways: (1) carbon−carbon radical combination and (2) carbon−dithiocarbamyl (DTC) radical termination. At lower conversions, when the viscosity of the polymerizing system is lower and thus diffusional resistance to termination is low, path 1 is the significant termination mechanism. As the viscosity increases with further conversion, path 2 begins to dominate termination. Therefore, the characteristic autoacceleration effect observed in polymerizations of the mono- and multifunctional methacrylates studied with regular initiators is dramatically reduced or absent in some cases. Additional evidence for preferential cross-termination (i.e., carbon−DTC radical termination) in the presence of an excess of DTC radicals is presented by examining polymerization initiated by a combination of XDT and tetraethylthiuram disulfide (TED). Further, the effects of varying concentration of XDT, intensity of initiating ultraviolet light, and reaction temperature on the rate behavior were examined. The reaction behavior observed in these studies is well explained by the proposed mechanism.

Introduction

Iniferter polymerizations or “living” radical polymerizations are of considerable interest as they can be used to produce block copolymers and polymers of relatively low polydispersity.[1−4] Recently, iniferter polymerizations have also found application as a useful method for studying the structure/property evolution of highly cross-linked polymers.[5] To enable the effective use of these novel polymerizations, a good understanding of the kinetics and the mechanism of the reaction is necessary. In this work, an investigation of bulk photopolymerizations of methacrylates initiated by *p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate) (XDT) is reported.

Iniferter polymerizations, like conventional radical polymerizations, involve initiation, propagation, and termination steps. Figure 1 compares the structures of the iniferter (XDT) and a conventional photoinitiator (DMPA). The XDT molecule absorbs UV light and generates a carbon radical and a sulfur-based dithiocarbamyl (DTC) radical, unlike DMPA, which decays to produce two carbon radicals. The carbon radicals produced in these reactions are extremely reactive and initiate the polymerization by reacting with a monomeric double bond, while the dithiocarbamyl radical is relatively less reactive and does not participate significantly in initiating polymerization.[4,6,7]

Propagation occurs by addition of monomers or double bonds to the active centers. In the iniferter polymerizations, the carbon radicals constitute the active centers because the dithiocarbamyl radical is stable and relatively unreactive to propagation.[4,6,7] Lambrinos *et al.*[6] concluded by performing polymerizations of *n*-butyl acrylate with tetraethylthiuram disulfide (TED) that the dithiocarbamyl radicals are mainly radical terminators and the propagation by these radicals is negligible. Similar behavior was noted by Turner *et al.*[8] while polymerizing acrylates. In this work, 2-hydroxyethyl methacrylate (HEMA) has been studied, and to verify the reactivity of the DTC radicals with HEMA, TED-initiated polymerization of HEMA was examined. Almost no reaction was observed while polymerizing HEMA with TED (at higher light intensities and for longer times than the XDT-initiated polymerizations studied for this work), suggesting that the DTC radicals do not initiate polymerization and can be considered unreactive *relative* to the carbon radicals.

The termination mechanism, however, is considerably different in these nonconventional radical polymerizations as there are two possible mechanisms for termination: (i) carbon−carbon radical termination and (ii) carbon−dithiocarbamyl radical termination. The carbon−carbon bimolecular radical termination results in a dead unreactive polymer while the carbon−dithiocarbamyl radical termination forms a “macroiniferter” which can reinitiate by absorbing light and decaying back into radicals. It is expected that the kinetic constants for these two termination reactions are significantly different because of the difference in reactivity of the carbon and the dithiocarbamyl radical. In the absence of diffusional limitations, the kinetic constant for carbon−dithiocarbamyl radical termination, i.e., k_{ts}, is expected to be at least an order of magnitude lower than the kinetic constant for carbon−carbon radical termination (k_{tc}).

Lambrinos *et al.*[6] investigated the mechanism of XDT-initiated solution polymerizations of *n*-butyl acrylate. They reported that the reaction lacked the true living character that was expected and also presented some possible schemes of side reactions that affect the living character. In our effort, the same iniferter (XDT) is used in bulk photopolymerizations of methacrylates, and thus the monomer concentration is 2.5 times higher than that used by Lambrinos *et al.*[6] This increased

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[⊗] Abstract published in *Advance ACS Abstracts,* October 15, 1996.

S0024-9297(95)01914-0 CCC: $12.00

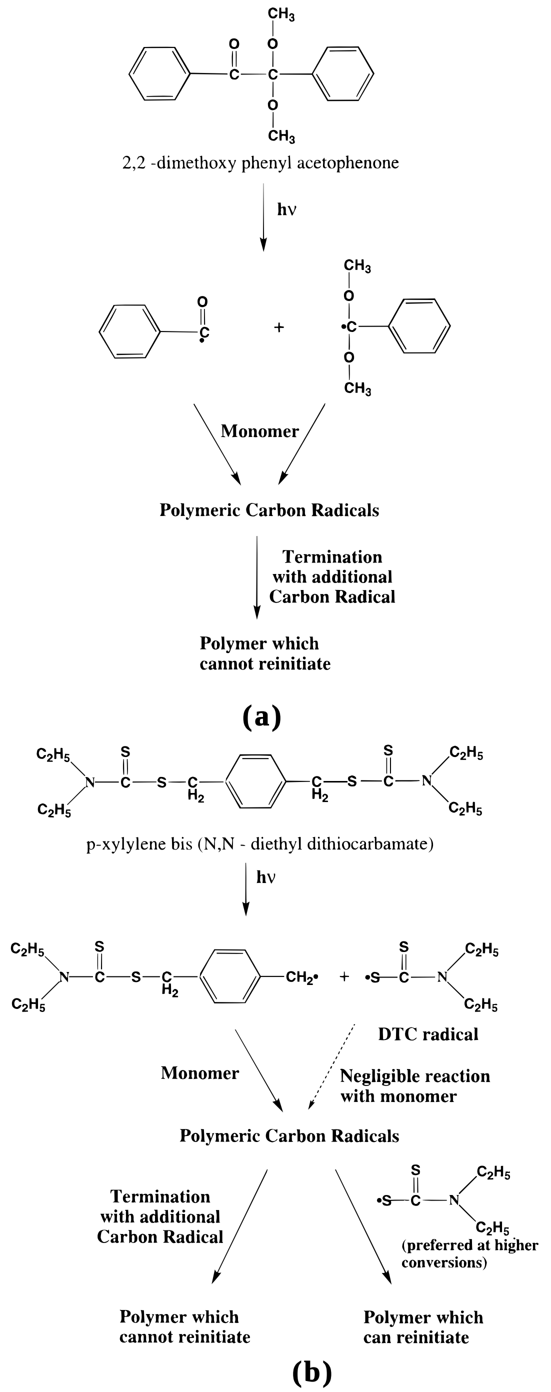

Figure 1. (a) Conventional initiator polymerization mechanism and (b) iniferter polymerization mechanism.

monomer concentration has been noted by others[9] to assist the living nature of the polymerization and favor formation of high-functionality polymers by keeping the reaction times small. The dependence of the kinetic behavior on the concentration of XDT, initiating light intensity, polymerization temperature, and monomer functionality is characterized. From such studies and from studies of polymerizations initiated by a combination of XDT and TED, conclusions are drawn on the reaction mechanism of these iniferter polymerizations, especially the role of the DTC radicals.

Experimental Section

Differential scanning calorimetry (DSC) has been used extensively in characterizing the kinetics of polymerizations by several researchers.[10,11] In this work, a differential scanning calorimeter equipped with a photoaccessory was used to monitor the rate of polymerization in these photoinitiated iniferter reactions. The rate of polymerization is monitored by following the rate of heat evolved in these highly exothermic reactions. The standard heat of reaction for methacrylates is −13.1 kcal/mol.[12] As a result, the heat evolved during the polymerization is very large, making the technique highly sensitive to the polymerization reaction. Other side reactions which occur to much lesser extents will not have a pronounced affect on the heat released or the translation of that into polymerization rate.

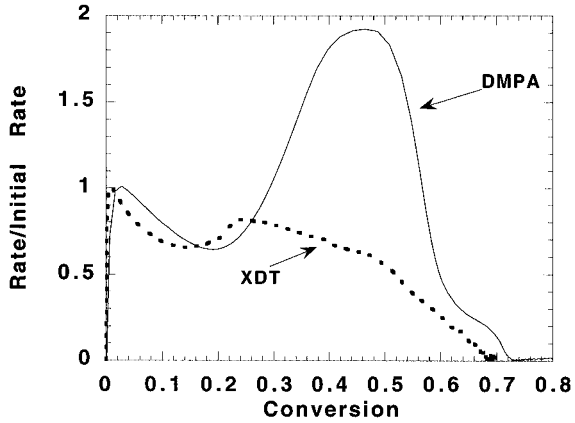

Figure 2. Comparison of conventional initiator polymerization (using DMPA) and the iniferter polymerization (XDT) rate behavior of HEMA at 30 °C. In both polymerizations, 0.1 wt % initiator was used. The rates are normalized by the initial rates. The initial rate of polymerization of HEMA with DMPA is 12 times as fast as the initial rate of polymerization of HEMA with XDT.

Monomers studied include 2-hydroxyethyl methacrylate (HEMA), diethylene glycol dimethacrylate (DEGDMA), and poly(ethylene glycol)-200 dimethacrylate (PEG200DMA). HEMA was obtained from Aldrich and was used after passing over Dehibit 100 resin (Polysciences Inc.) to remove the hydroquinone inhibitor. The other monomers were obtained from Polysciences Inc. and used as received. The iniferter used in this work was *p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate) (XDT), which was provided by 3M. Tetraethylthiuram disulfide (TED) used in the studies was purchased from Aldrich. All polymerizations in the DSC were initiated by a Hg lamp or an EFOS Ultracure fiber optic source. The intensity of the initiating light was varied by using neutral-density filters.

Experiments were performed at various temperatures to study the effect of reaction temperature. Before performing these experiments, XDT-initiated polymerizations of HEMA in the absence of UV light at elevated temperatures (>70 °C) were attempted. No significant heat of polymerization was observed, confirming that thermal initiation by XDT was negligible. Studies were restricted to temperatures below 60 °C to prevent error in results due to loss of monomer by evaporation. In addition, experiments were performed to observe the effect of changing iniferter concentration and initiating light intensity. In all the DSC experiments, care was taken to satisfy the thin-film approximation and thus maintain the light intensity constant through the sample. The role of the DTC radicals was investigated by performing a series of experiments in which HEMA polymerizations were initiated by a combination of XDT and TED.

Results and Discussion

Iniferter polymerizations are significantly different from and slower than conventional radical polymerizations. Figure 2 compares the iniferter polymerization behavior and the conventional free-radical polymerization behavior of HEMA. In the figure, the rate of polymerization normalized by the initial rate is plotted as a function of conversion. It should be noted that under these conditions the initial rate of conventional free-radical polymerization is about 12 times that of the iniferter polymerization. Taking a closer look at the figure, one can see that for the first 20% conversion the rate behavior of the two types of polymerizations is similar, indicating that the reaction mechanism is similar. Thus, initially, it appears that in the iniferter polymerizations, the more reactive carbon radicals propagate through the double bonds and are also involved in the termination mechanism. However, this observation does not preclude the cross-termination of carbon−DTC radicals early in the reaction. As the conversion approaches 15%, the viscosity of the system reaches a certain critical value which results in the diffusional resistance becoming the dominant mechanism for the carbon−carbon radical termination reaction. Therefore, the carbon radical concentration increases, resulting in an increase in the rate of polymerization. This effect is seen very distinctly in the case of conventional polymerizations and is called autoacceleration or the gel effect.[10,11,13] The autoacceleration behavior provides further evidence that carbon−carbon termination is significant at this stage of the polymerization. If carbon−DTC termination were solely responsible for the termination, then no autoacceleration would occur.

In Figure 2, one can see that this trend is seen in the iniferter polymerization as well; however, the autoacceleration behavior continues for only a small range of conversion. Thus, the autoacceleration effect in the iniferter polymerization is not as prominent as the one seen in the case of conventional free-radical polymerizations. A reduction or an absence of gel effect has also been observed by Zaremskii *et al.*[14] during iniferter polymerizations of methyl methacrylate and styrene. This reduced autoacceleration may be explained by a change in the termination mechanism in the XDT-initiated polymerizations. As the carbon−carbon radical termination becomes more hindered (because of increased diffusional resistance), the carbon−DTC radical termination reaction becomes more prominent and dominates termination. Termination with the DTC radical is not affected by diffusion to the degree that carbon−carbon radical termination is because the DTC radical remains small (as it does not propagate and grow) and mobile.

The carbon−DTC radical termination keeps the radical concentration from increasing dramatically, and thus, the rate of polymerization decreases slowly as more double bonds are reacted away. As the polymerization proceeds, the viscosity of the reaction mixture increases further and the propagation reaction becomes diffusion limited. This diffusional resistance to propagation leads to a decrease in the rate of polymerization until the reaction eventually ceases. The same final trend is observed in both conventional and iniferter polymerizations, with the conventional polymerization reaching slightly higher conversion.

Additional evidence exists in the literature which supports this type of a mechanism. In a study of the polymerization of *n*-butyl acrylate initiated by XDT, Lambrinos *et al.*[6] found that the average molecular weight data followed a linear trend with respect to conversion but had a large positive intercept. The positive intercept indicates that the termination mechanism at the beginning of the reaction involves a rapid buildup of molecular weight as seen in conventional free-radical polymerization. This feature would be expected if the carbon−carbon termination mechanism were dominant in the early stages of the reaction. Following this initial rapid increase in molecular weight, a linear trend is observed when the termination is dominated by carbon−dithiocarbamyl radical combination. This linear dependence of molecular weight on yield or conversion is expected in such “living” polymerizations.

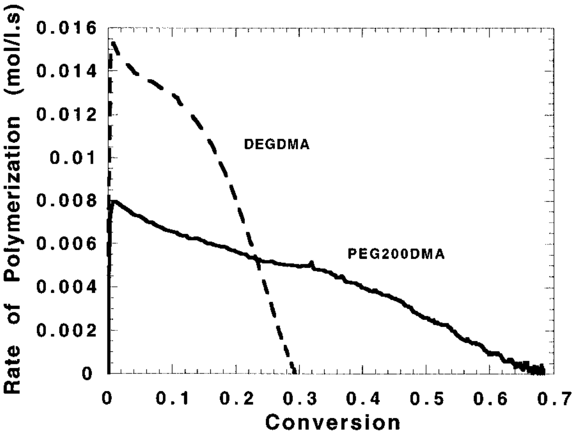

Figure 3. Polymerization behavior of DEGDMA and PEG200DMA with 0.1 wt % XDT at 30 °C.

Homopolymerizations of dimethacrylates were performed to examine the features of iniferter polymerizations of these network-forming monomers. Polymerizations of multifunctional monomers are in general characterized by even more pronounced autoacceleration and autodeceleration.[10,11,13] In addition, these diffusion-controlled reactions result in networks which are highly heterogeneous containing unreacted monomer and pendant double bonds. Typical final conversions in this type of reaction vary from 0.4 to 0.8 for polymerizations of DEGDMA and PEG200DMA.[11] Using XDT to polymerize the same monomers, final conversions of 0.3 and 0.7 were obtained. The rate behavior of these reactions is depicted in Figure 3. As seen in the polymerization of HEMA, the autoacceleration behavior is absent and the rate of polymerization of these tetrafunctional methacrylates is much lower than regular polymerization rates. Because absolutely no autoacceleration is observed, it is likely that the termination mechanism is dominated by carbon−dithiocarbamyl combination from the early stages in the reaction. This dominance may be further justified by recalling that the polymerizations of multifunctional monomers are controlled by diffusional resistances and the carbon−carbon radical termination constant for these systems rapidly decreases as a function of conversion. As a result, it is expected that the carbon−DTC termination reaction will begin to dominate even at very low conversions.

The termination mechanism was further investigated by performing a series of experiments in which HEMA polymerizations were initiated by a combination of XDT and TED. By keeping the concentration of XDT constant and varying the concentration of TED, the role of the DTC radicals in the mechanism can be elucidated from an analysis of the initial rates of polymerization. The TED in the system can (a) react as an inhibitor (or chain transfer agent), (b) dissociate to DTC radicals that participate in the termination reaction, or (c) have no significant participation in terminating carbon radicals. As this analysis is concerned only with the initial rate of polymerization, the reaction of the products (P) of these reactions is neglected. The scheme below depicts the initiation and inhibition/termination steps in the mechanisms considered:

Case a: Inhibition by TED

$$\mathrm{XDT} \rightarrow \mathrm{R_C}^{\bullet} + \mathrm{R_S}^{\bullet}$$

$$\mathrm{R_C}^{\bullet} + \mathrm{TED} \rightarrow \mathrm{P}$$

Case b: Cross-termination by DTC radicals

$$\mathrm{XDT} \rightarrow \mathrm{R_C}^{\bullet} + \mathrm{R_S}^{\bullet}$$

$$\mathrm{TED} \rightarrow 2\mathrm{R_S}^{\bullet}$$

$$\mathrm{R_C}^{\bullet} + \mathrm{R_S}^{\bullet} \rightarrow \mathrm{P}$$

Performing mass balances on the carbon ($\mathrm{R_C}^{\bullet}$) and DTC ($\mathrm{R_S}^{\bullet}$) radicals and assuming pseudo steady state on the radical concentrations, it can be shown that the initial rate of polymerization is inversely proportional to the concentration of TED in case a and inversely proportional to the square root of the TED concentration in case b. Using this analysis, experiments were designed in which the TED concentration was varied while maintaining the XDT concentration and other factors constant.

Figure 4 is a log−log plot of the initial rate of polymerization versus the concentration of TED. The slope of the straight line is approximately −0.5, indicating that the initial rate is dependent on the inverse square root of the TED concentration. This analysis strongly suggests that the cross-termination of the carbon and DTC radicals is the significant termination mechanism when XDT and TED are used in combination. Considering this evidence, it is conceivable that in a polymerization initiated by XDT, the carbon−DTC radical cross-termination mechanism is present even at low conversions. However, this cross-termination reaction becomes a dominant mechanism at higher conversions because there is an excess of DTC radicals as the carbon radicals terminate by two pathways. In a study of end groups during polymerizations of butyl acrylate, Dika Manga *et al.*[9] found that preferential cross-termination occurred even at low conversions. However, based on the observed autoacceleration behavior in HEMA polymerizations initiated just by XDT, it is clear that the carbon−DTC radical termination is not the only reaction responsible for the termination in these systems.

To understand further the reaction mechanism, experiments were performed to determine the dependence of the rate behavior on XDT concentration. Figure 5 depicts the rate behavior of HEMA polymerizations at various concentrations of XDT. As the concentration of XDT is increased, two important features are observed in the polymerization rate behavior. First, the initial rate of polymerization increases approximately with the square root of XDT concentration. Secondly the autoacceleration effect becomes less prominent as the concentration of XDT increases until finally it almost disappears.

One can also observe that the onset of autoacceleration is delayed as the concentration of the iniferter is increased and the onset of the dominance of carbon−dithiocarbamyl termination is delayed to higher conversions at higher concentrations of XDT. For the transition to carbon−dithiocarbamyl radical termination from carbon−carbon radical termination to take place, the carbon−carbon radical termination rate constant (k_{tc}) has to drop to a value lower than the carbon−dithiocarbamyl radical termination rate constant (k_{ts}). The k_{tc} decreases as the viscosity of the reacting system increases. A dramatic decrease in the k_{tc} is observed when the viscosity reaches a critical value. The delay in the onset of autoacceleration as the XDT concentration is increased may be explained by recalling that as the concentration of XDT increases, the concentration of active propagating centers increases, decreasing the average molecular weight, and therefore, the viscosity builds up more slowly compared to polymerizations with lower iniferter concentrations. Thus, the critical value for diffusion-controlled termination is reached at later times. Subsequently, the time required (and thus, conversion) to reach the critical viscosity that favors carbon−dithiocarbamyl radical termination relative to carbon−carbon radical termination increases.

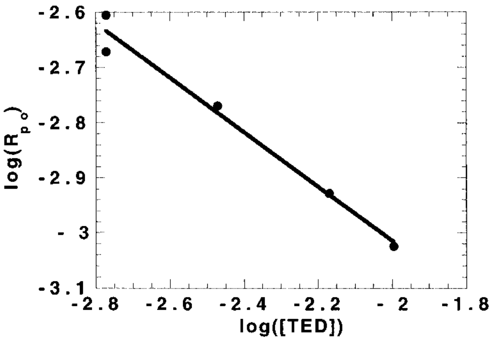

Figure 4. Plot of log of initial polymerization rate versus the log of concentration of TED (in L mol^{-1}). Slope of the straight line is approximately −0.5, strongly suggesting that the cross-termination of the carbon and DTC radicals is the significant mechanism of termination.

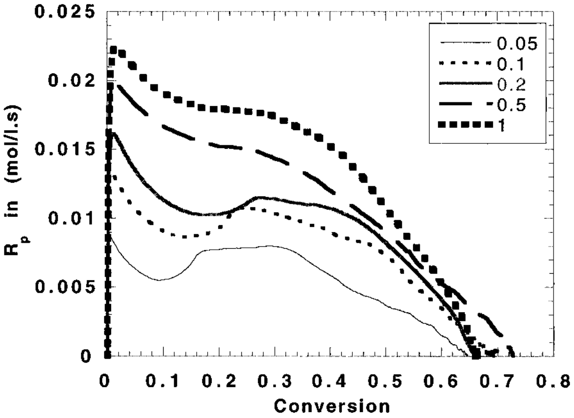

Figure 5. Rate behavior of HEMA polymerizations with varying concentrations of XDT. Legend shows the concentrations of XDT in weight percent.

To analyze further the data in Figure 5, the rate of polymerization normalized by the square root of concentration of XDT is plotted as a function of the conversion in Figure 6. It can be seen that there is good agreement in the rate behavior at the beginning and the end of the polymerizations, while in the region where there is (a) transition between termination mechanisms and (b) indication of the presence or absence of autoacceleration, there is little agreement in the rate behavior. Also, the final conversions achieved do not change significantly with XDT concentration.

To verify further the effects of initiation rate, studies on the effects of light intensity were performed. Figure 7 shows the rate of polymerization versus conversion

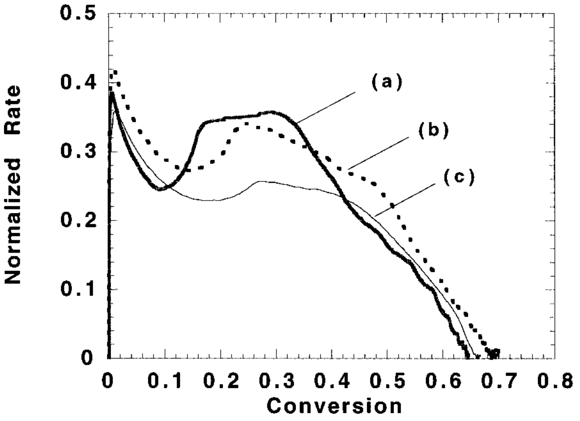

Figure 6. Normalized rate (rate divided by square root of XDT concentration) of polymerization of HEMA vs conversion for (a) 0.05, (b) 0.1, and (c) 0.2 wt % XDT concentrations.

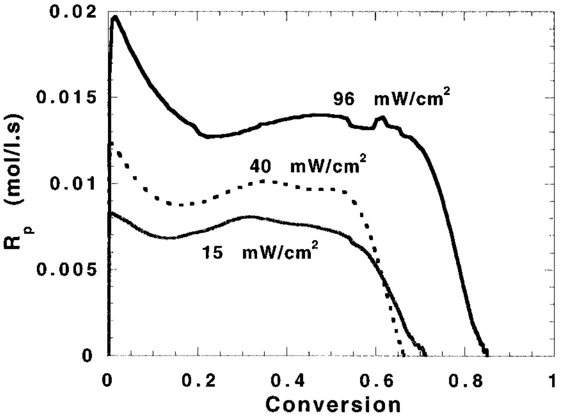

Figure 7. Dependence of polymerization behavior of HEMA on initiating light intensity at 365 nm.

curves at various light intensities for the polymerization of HEMA. The light intensity was varied from 96 to 15 mW/cm^2. As the light intensity increases, the transition from carbon—carbon radical termination to carbon—dithiocarbamyl radical termination is delayed to higher conversions. This delay is expected because at higher light intensities the critical viscosity for diffusion limitations to carbon—carbon radical termination is achieved only at higher conversions, just as observed with increasing the iniferter concentrations. Also, one can see that the autoacceleration effect diminishes as the light intensity increases. This decrease could be a result of an increase in the dithiocarbamyl radical concentration at higher light intensities which would facilitate a rapid transition from carbon—carbon termination to carbon—dithiocarbamyl termination.

These polymerizations slow down and eventually stop because of diffusion limitations which prevent the monomer from reacting with a propagating carbon radical. The diffusion limitations are determined by the viscosity of the reacting system. At higher light intensities, there are more active propagating centers. Therefore, it takes longer (higher conversion) to build the viscosity. Upon reaching a critical value, the mobility is decreased to such an extent that the diffusion of monomer to the active centers is restricted and thus, the polymerization (propagation) is stopped. As a result, at higher light intensities one observes a higher final conversion as the critical viscosity to prevent propagation is reached at later times or conversions. By similar arguments, it may be concluded that increasing iniferter concentration should lead to an increase in the final conversion of monomer. Interestingly, however, such an increase in the final conversion was not observed when the XDT concentration was increased.

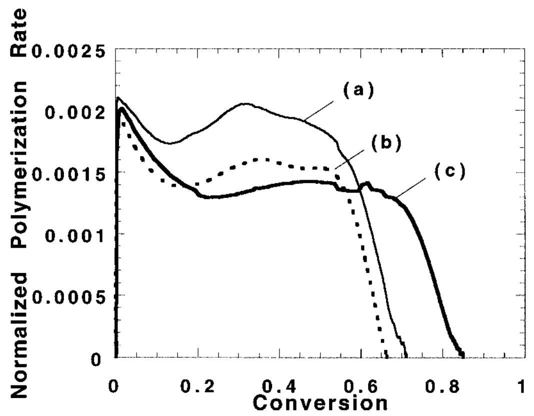

Figure 8. Rate of polymerization of HEMA normalized by square root of light intensity vs conversion. (a) 15, (b) 40, and (c) 96 mW/ cm^2.

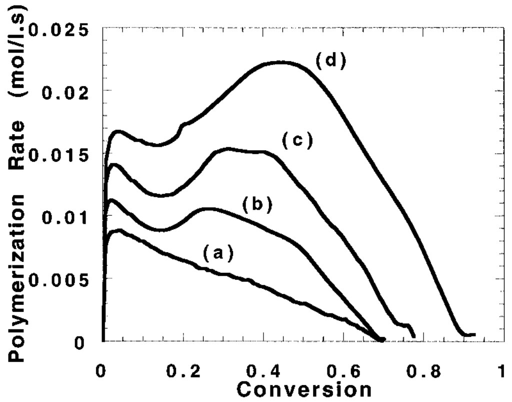

Figure 9. Rate behavior of HEMA polymerizations at (a) 0, (b) 30, (c) 45, and (d) 53 °C.

In conventional free-radical polymerizations, the termination mechanism is by bimolecular reaction of propagating carbon radicals. This mechanism results in a rate of polymerization that is proportional to the square root of the light intensity. If the termination mechanism in the iniferter polymerizations is by combination of two radicals that are independently propagating or mobile in the system, then when the rate of polymerization normalized by the square root of the light intensity is plotted as a function of conversion, the normalized rates and the trends should match. However, if the iniferter mechanism involved propagation of a radical pair and unimolecular termination, the normalized rates will not match.

In Figure 8, the normalized rate is graphed as a function of conversion. The initial normalized rates are nearly identical and there is reasonable agreement (within experimental error) in the trends as well. This observation precludes the unimolecular termination (*i.e.*, radical pair) mechanism. It is also observed that there is not good agreement at higher conversions as the dominant termination pathway becomes the carbon—DTC reaction. This disagreement may be expected as the concentrations of carbon and DTC radical are not equal and thus do not follow square root dependence on the light intensity or the rate of initiation.

In addition to the effects of initiation rate, the polymerization rate behavior of HEMA was studied at temperatures ranging from 0 to 53 °C. In Figure 9, the reaction rate of HEMA with 0.1 wt % XDT is plotted as

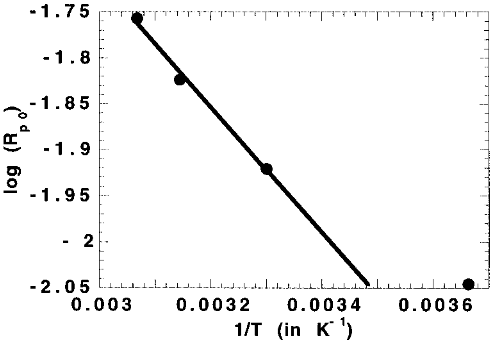

Figure 10. Logarithm of the initial rate of polymerization versus inverse temperature (in K^{-1}). The point corresponding to polymerization at 0 °C deviates from the straight line formed by points corresponding to higher temperatures.

a function of monomer conversion for four different temperatures. The initial reaction rate increases as the temperature is increased. This increase is expected as the initial rate is dependent only on the chemical reaction rate constants of the reactions. One of the important features that is observed is that the autoacceleration behavior becomes increasingly prominent as the temperature of the reaction increases. As the temperature increases, the mobility of the reacting polymer chains increases, and therefore, the carbon radicals are mobile until higher monomer conversions are achieved. As a result, the transition from carbon–carbon radical termination to carbon–dithiocarbamyl radical termination is extended to higher conversions. This delayed transition results in more significant autoacceleration behavior at higher temperatures.

When the initial rates were graphed on an Arrhenius plot as shown in Figure 10, the reaction rates at the higher temperatures formed a straight line, while the point corresponding to the 0 °C reaction deviated. The apparent activation energy found at higher temperatures from such a plot was approximately 13 kJ mol^{-1}, which is in the range of the apparent activation energies observed during conventional polymerizations. This observation strongly suggests that at higher temperatures, early in the reaction the carbon–carbon radical reaction is the significant termination pathway while at lower temperatures the carbon–DTC radical is dominant very early in the reaction.

Another feature that is observed from these experiments is that the final conversion of the polymerizations increases with increasing temperature. This feature is as expected. As the temperature increases, the mobility of the system increases and consequently, the diffusion limitation to propagation is delayed to higher conversions. Therefore, higher final conversions are obtained at higher temperatures.

Conclusions

In this paper, HEMA has been used as a model monomethacrylate and the kinetics of iniferter polymerization using XDT have been studied. In this effort, the effects of varying the concentration of XDT, the initiating light intensity, and the temperature of the reaction on the rate behavior have been examined. A mechanism has been proposed to describe the various characteristics of the rate behavior. To summarize, one can observe the following four stages in the iniferter polymerizations of bulk monomers: (1) termination dominated by carbon–carbon radical combination at low conversions (this does not imply that carbon–DTC termination does not take place); (2) a decrease in the carbon–carbon radical termination rate, resulting in an increase in radical concentration and thus an increase in the rate of polymerization (autoacceleration); (3) change in termination mechanism to one dominated by carbon–dithiocarbamyl radical combination which is not diffusion limited; and (4) diffusion limitations to propagation eventually decrease the overall rate of polymerization.

Based on this hypothesis, separate regimes have been identified during the reaction where the termination mechanism is dominated by carbon–carbon reaction and carbon–dithiocarbamyl radical reaction. At certain conditions, for example the polymerization of HEMA at 0 °C, it has been noted that the termination is dominated entirely by carbon–dithiocarbamyl combination leading to a "living" free-radical polymerization. Further, it has also been noted that in highly diffusion-limited polymerizations of tetrafunctional monomers, the autoacceleration behavior, which is an important characteristic of these reactions, is entirely absent. Polymerizations initiated by a combination of XDT and TED were examined to elucidate that the cross-termination is preferred even in the early stages of the polymerization if there is an excess of DTC radicals in the reacting system.

The effect of initiation rate (by altering XDT concentration as well as the initiating light intensity) on the polymerization behavior was examined. At higher rates of initiation, the autoacceleration effect was delayed and was also very much reduced. While a square root dependence of the rate of polymerization on the rate of initiation is valid in the earlier stages of the reaction, at later stages, when the carbon–dithiocarbamyl radical termination dominates the mechanism, the dependence is not straightforward. Studies of the reaction behavior at various temperatures suggest that the activation energy for carbon–carbon radical termination is higher than that of carbon–dithiocarbamyl radical termination.

Acknowledgment. We thank Steve Brinduse of 3M for the XDT. We also acknowledge 3M and DuPont for their support of this work and the National Science Foundation for its support of this work through the Presidential Faculty Fellowship to C.N.B. (CTS-9453369).

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