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Kinetics of 'living' radical polymerizations of multifunctional monomers

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Abstract

The polymerizations of multifunctional monomers with an iniferter, *p*-xylylene bis-(*N*,*N*-diethyldithiocarbamate) (XDT), were studied with differential photocalorimetry. The iniferter was used to simulate a 'living' radical polymerization. The normal autoacceleration behavior that is often observed in the polymerization of multifunctional monomers was not evident in the reactions with the iniferter. The reversible reaction between the propagating polymer chain and the sulfur radical from the XDT molecule dominated the reaction and drastically decreased the rate of polymerization. Various parameters of the reaction (length between functional groups in the monomer, iniferter concentration, UV light intensity, and temperature) were investigated to determine the effect on the polymerization. The rate of polymerization and the final conversion of the polymer were increased significantly by increasing the temperature, initiator concentration and UV light intensity, and decreasing the length between functional groups. Mechanical properties of the resulting polymers were also examined. It was concluded that the presence of the iniferter during the polymerization of the multifunctional monomers had no effect on the heterogeneity of the polymer network. This was in agreement with previous modeling results. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Iniferter; Poly(ethylene glycol)dimethacrylate; Photopolymerization

1. Introduction

Increasingly, research in polymer science has focused on controlling the macromolecular structure of polymers synthesized by free-radical techniques, both linear and crosslinked [1]. In addition, there is an increased interest in developing tailored block copolymer, graft copolymers and star polymers by radical polymerizations. Free-radical polymerization techniques are used to synthesize a variety of polymers because of their fairly easy manufacturing techniques, fast reaction times, and the immediate formation of high molecular weight polymers [2].

However, free-radical polymerizations lack the control of the macromolecular structure that can be achieved in anionic, cationic, and coordinative polymerizations [3]. 'Living' radical polymerizations have proven very promising for the synthesis of low polydispersity linear polymers, block copolymers and star polymers [4–10]. Typically, the trade-off for attaining these controlled structures is the time of polymerization, as the living radical polymerizations take much longer than the conventional radical polymerizations. This area of polymer research is becoming increasingly popular and new initiators and catalysts are continually being introduced in order to optimize the polymerization process.

The lack of control of the macromolecular structure is due to termination reactions by diffusion-controlled radical combination and disproportionation. The formation of dormant polymers from the termination reaction leads to polymers with various sizes. One method to achieve control of the polymer architecture is to eliminate the termination reaction [11]. This method has been used with great success in anionic and cationic polymerizations. Therefore, it has been proposed to carry over these ideas to free-radical polymerizations to create new materials with specified compositions, functionality, and architectures.

The primary definition of a living polymerization is that termination and chain transfer reactions do not occur. It can be extremely difficult to meet all of these criteria in a free-radical polymerization, especially the criterion of lack of termination. Realistically, irreversible termination is only minimized and, therefore, these free-radical polymerizations are termed controlled instead of living polymerizations [6]. Numerous methods have been introduced for controlled radical polymerizations [8,12–15]. Matyjaszewski and coworkers [4,6,8,9] introduced a method of controlled

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radical polymerization through the use of atom transfer radical polymerization (ATRP) with various catalysts. Otsu and Yoshida [12,13] introduced the iniferter for synthesis of more controlled polymerizations.

Of primary interest in this paper is controlled UV free-radical polymerization. Therefore, this work focuses on the iniferters originally developed by Otsu et al. [12,13]. The goal of their work was to synthesize highly designed polymer structures. They introduced the idea of using an initiator that would have a high reactivity for chain transfer to the initiator and a high reactivity for primary radical termination, thus avoiding bimolecular terminations. Otsu and Kuriyama [16,17] found that initiators containing carbon–sulfur or sulfur–sulfur bonds served as excellent photoiniferters and induced living radical polymerization such that the polymers with the iniferter-terminated ends could further function as iniferters.

Fig. 1 shows the ideal polymerization mechanism proposed by Otsu and Yoshida [12]. The key to this polymerization process is that the polymer chain must dissociate into a reactive, propagating carbon radical and a less reactive sulfur radical. This then allows for successive insertion of monomer molecules. Initiators with S–S bonds and initiators with C–S bonds have both been used successfully for photopolymerizations. In Fig. 1, R_2 is the sulfur-containing group and R_1 may be either a carbon- or a sulfur-containing group. Generally, the most successful iniferter initiators are those that decompose to form a reactive carbon radical to initiate propagation and a less reactive sulfur radical [18]. One of the most intriguing and exciting applications of the iniferter technology is in the formation of block copolymerizations. To do this, a polymer with reactive end groups is formed by the sulfur radical and then used as a macroinitiator.

One area that has not been researched considerably is the effect of the living radical polymerization on highly crosslinked and network polymers. The ideal polymeric network consists of a homogeneous, crosslinked network with little variation in the molecular weight between crosslinks, M_c. Realistically, there is a wide distribution of M_c in the network and numerous cycles exist, which may lead to degradation in material properties of the polymer. There are applications where a homogeneous network is desired, particularly in hydrogels for controlled release. If a more uniform network could be developed, the swelling behavior could more accurately be predicted and the release of a biomolecule could be more accurately controlled because the mesh size of the network was uniform throughout.

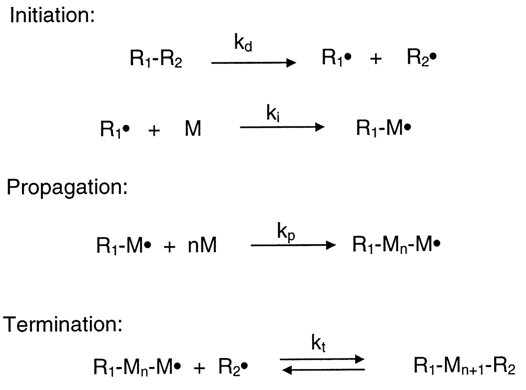

Fig. 1. General mechanism for iniferter kinetics proposed by Otsu and Yoshida. R_2 is usually a sulfur radical. R_1 may be either a sulfur radical or a carbon radical.

Kannurpatti et al. [19] examined the kinetics of polymerizations of 2-hydroxyethyl methacrylate (HEMA), diethylene glycol dimethacrylate (DEGDMA) and poly(ethylene glycol)200 dimethacrylate (PEG200DMA) with the iniferter *p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate) (XDT). They concluded that iniferter HEMA polymerizations were characterized by four stages. In the first stage, irreversible termination between two carbon radicals dominated at low conversion. As the reaction proceeded, there was a decrease in the irreversible termination rate and an increase in radical concentration, which led to an autoacceleration. Next, the reversible termination between the carbon radical and dithiocarbamyl radical increased and was not diffusion limited because of the mobility of the dithiocarbamyl radical. Finally, the propagation reaction eventually became diffusion limited and thus decreased the rate of polymerization. In their polymerizations of the multifunctional methacrylates, they found the reversible termination reaction dominated, even at low conversions.

Kannurpatti et al. [20–22] also used the iniferter to examine the network heterogeneity as a function of conversion. Their aim was to determine mechanical properties of DEGDMA, PEG600DMA and *n*-octyl methacrylate as a function of conversion. They used the iniferter to react with any remaining radicals so the materials at low conversion could be heated and not react further. In their analysis, they concluded that the presence of the iniferter did not change the structure of the material.

In this work, we aim to expand upon the work of Kannurpatti et al. to examine the kinetics of iniferter living radical polymerizations of multifunctional monomers. Specifically, we have examined poly(ethylene glycol) dimethacrylates in order to focus on potential hydrogel materials. Various parameters, including length between functional groups, concentrations, and temperature, have been examined in order to determine the effect on the polymerization with the iniferter compared to polymerization with a conventional photoinitiator.

2. Experimental

The multifunctional monomers used in these experiments were ethylene glycol dimethacrylate (EGDMA), tetraethylene glycol dimethacrylate (TEGDMA), PEG200-DMA, poly(ethylene glycol) 400 dimethacrylate (PEG400-DMA), and poly(ethylene glycol) 600 dimethacrylate

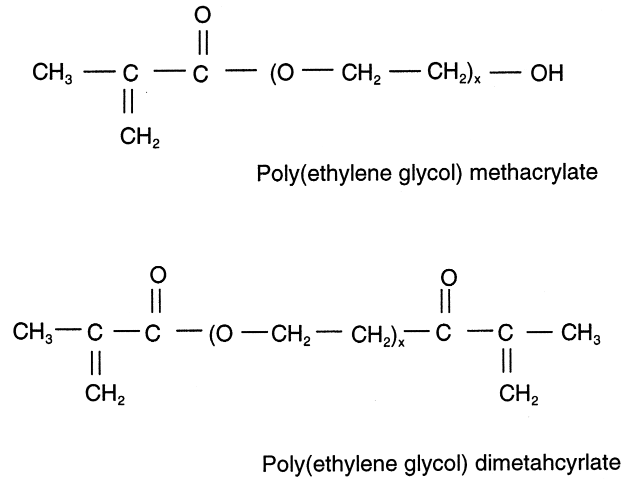

Fig. 2. The chemical structure of poly(ethylene glycol) methacrylate (top) and poly(ethylene glycol) dimethacrylate (bottom).

(PEG600DMA). The numbers 200, 400 and 600 refer to the molecular weight of the poly(ethylene glycol) chain between the methacrylate groups. Fig. 2 displays the chemical structure of the monomers. By utilizing these monomers, the length between the functional groups of the monomer could be varied. Some experimental studies were also conducted with the monomethacrylates PEG200MA and PEG400MA. All monomers were used as received (Polysciences, Warrington, PA).

The iniferter used for this study was *p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate) (XDT, 3M, Minneapolis, MN). The chemical structure of XDT is shown in Fig. 3. UV polymerizations were also conducted with a conventional initiator, 2,2-dimethoxy-2-phenyl acetophenone (DMPA) (Aldrich, Milwaukee, WI).

Kinetic studies were conducted in differential photocalorimeter (DPC, TA Instruments, Model DPC930, New Castle, DE). A sample of 2–6 mg of the monomer dissolved with iniferter or initiator was placed in a small aluminum pan after first being bubbled with nitrogen. The pan was covered with a clear disk of polyethylene in order to prevent evaporation of the monomer. The apparatus was purged with nitrogen to prevent inhibition of the polymerization due to the presence of oxygen.

In a typical experiment, the monomer mixture in the pan was placed in the DPC, equilibrated at 30 °C for 10 min and then irradiated with UV light at 1.2 mW/cm^2. The heat evolved was measured as a function of time. The theoretical enthalpy for the polymerization of the monomer solution was then used to calculate the rate of polymerization, R_p, in units of fractional double bond conversion per second. For the methacrylate groups, an enthalpy of -13.1 kcal/mol was used [23]. The heat evolved from the reaction of the methacrylate group is very large, especially in comparison with the other possible side reactions. It was assumed that other side reactions would not have a significant effect on the heat released and thus the polymerization rate. Integration of the R_p curve versus time provided the conversion as a function of time.

Photopolymerizations were also conducted at different temperatures. In all cases, the monomer and initiator mixture was first equilibrated at the operating temperature for 10 min prior to irradiation. The intensity of the UV light was changed using neutral-density filters.

Mechanical properties of the polymers were measured with variable temperature dynamic mechanical analysis (DMA, TA Instruments, Model DMA 983, New Castle, Delaware). Polymers were prepared in thin films by placing the monomer mixture with initiator between two glass slides separated by 0.9 mm Teflon® spacers. The polymerization took place under a nitrogen environment and the monomer solution was bubbled with nitrogen prior to the polymerization to remove any oxygen. A spot cure UV light source (EFOS Acticure, Mississauga, Ont.) was used to irradiate the sample for 10 min at approximately 10 mW/cm^2. For the samples with the initiator XDT, the polymerization was conducted on top of a hot plate set to 70 °C.

DMA experiments were performed in the resonant frequency mode with an oscillation amplitude of 0.20 mm. Sample lengths were adjusted to give an average resonant frequency of 5.5 Hz. The storage, G'_e, and the loss, G''_e, moduli were determined for the copolymer sample. The damping factor, tan δ, is the ratio of the loss modulus to storage modulus. The glass transition temperature, T_g, is measured as the temperature at which tan δ is a maximum. The tan δ peak is also a measure of the heterogeneity [22]; the wider the peak is, the more heterogeneous the sample is.

3. Results and discussion

3.1. Kinetic studies of multimethacrylates

The kinetics of the polymerization of multifunctional monomers with the iniferter XDT was studied extensively. First, the kinetics of a polymerization with the conventional initiator DMPA was compared to the polymerization with

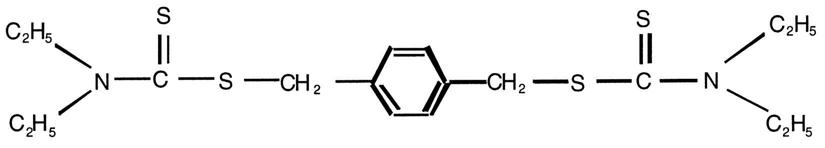

Fig. 3. Molecular structure of the iniferter *p*-xylylenebis(*N*,*N*-diethyl dithiocarbamate) (XDT).

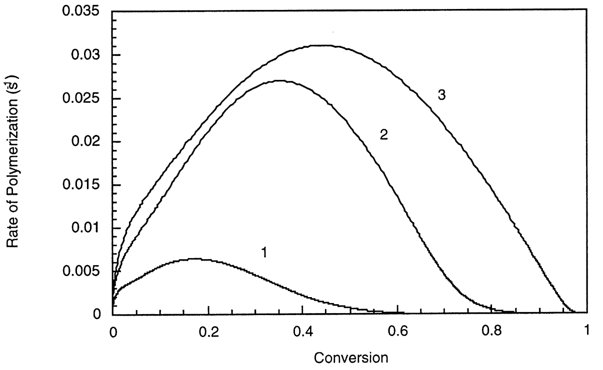

Fig. 4. Rate of polymerization as a function of conversion for the polymerizations of: (1) EGDMA, (2) TEGDMA, and (3) PEG400DMA. All polymerizations were conducted with 1 wt% DMPA and at 1.21 mW/cm^2.

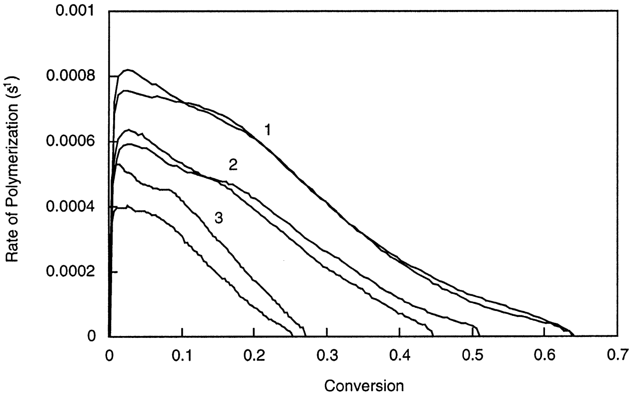

Fig. 5. Rate of polymerization as a function of conversion for the polymerizations of: (1) PEG200DMA, (2) PEG400DMA, and (3) PEG600DMA. All polymerizations were conducted with 0.1 wt% XDT and at 1.1 mW/cm^2.

XDT. Fig. 4 displays the rates of polymerization as a function of time for polymerizations of EGDMA, TEGDMA and PEG400DMA, all with 1 wt% DMPA and at an intensity of 1.2 mW/cm^2. As the number of ethylene glycol units between double bonds increased from 1 to 4 to 9, the final conversion increased from 68 to 87 to 98%, respectively. This was consistent with the results reported by Anseth et al. [24]. This finding was attributed to an increase in mobility of the longer chains because of a lower crosslinking density.

In the classical free-radical polymerization, termination reactions between two radicals result in a ‘dead’ polymer that cannot react anymore. In the living radical polymerizations, a reversible termination is introduced. The termination by combination of two carbon radicals may still occur, resulting in a dead polymer. However, if a carbon radical reacts with the thiol radical introduced from the XDT, this does not result in a dead polymer. Instead, this is termed a reversible termination because further irradiation breaks the bond between the carbon group and the sulfur group and reintroduces a carbon radical and a thiol radical into the reaction.

Fig. 5 displays the rates of polymerization as a function of conversion for multimethacrylate polymerizations in the presence of 0.1 wt% iniferter XDT. A complete summary of all XDT polymerizations can be seen in Table 1. The rates of polymerizations reported for these polymerizations were 100 times smaller than the polymerizations with DMPA and there was not an autoacceleration behavior, only an autodeceleration. The polymerizations with XDT also took a significantly longer time, an indication that the reversible termination with the thiol radical dominated the reaction. When DMPA was used as an initiator, polymerizations were completed in minutes. The polymerizations initiated with XDT were not completed until almost an hour later. The final conversions were also significantly decreased in the presence of XDT.

The autoacceleration phenomenon was not observed in these polymerizations due to the reversible termination reaction with the thiol radical. Because R_p continually decreased throughout the reaction, it was believed that termination with the thiol radical dominated throughout the reaction. In polymerizations with multifunctional monomers, termination becomes difficult and propagation dominates the reaction. The rate of propagation was slowed considerably in the XDT polymerizations because the radicals were reacting with the thiol radical instead of with other functional groups. The thiol radical is very small compared to the other species present and therefore extremely mobile, contributing to the increase in the reversible termination reaction.

Another observation from Fig. 5 is that as the length between functional groups was increased, R_p and the final conversion decreased, opposite of what is typically observed in conventional photopolymerizations. Generally, the polymerization with longer chained monomers will have a decrease in crosslinking density and thus polymerization will occur at a much faster rate. However, in the presence of XDT, it is believed that the polymerization had been slowed so much that the size of the monomer influenced the polymerization. Since the crosslinking density is increasing at a much slower rate in the presence of the iniferter, the crosslinking density is not as important and instead the location of the functional groups in proximity to the radicals is more important. Thus, the smaller monomers with the functional groups closer to each other see an increase in the rate of polymerization and a subsequent increase in the final conversion.

Fig. 5 shows multiple runs of the same polymerization in order to point out the error that is often observed in these iniferter polymerizations. It should be noted that it was more difficult to reproduce polymerization kinetics for the XDT-initiated polymerizations than for those initiated with DMPA. The presence of the sulfur groups may have contributed to the error. The polymerizations with XDT took a long time, over an hour in most cases, due to the reversible

Table 1
Summary of the kinetic data for the multimethacrylate polymerizations with the iniferter XDT

Monomer	XDT (wt%)	Intensity (mW/cm^2)	Temperature (°C)	$R_{\mathrm{p,max}}$ (s^{-1}) $\times 10^{3}$[a]	Final conversion (%)[a]
EGDMA	0.1	1.1	30	5.2 ± 0.04	25 ± 6.0
			50	0.95	62
			70	1.55	56
		5.35	30	0.9	23
		9.36	30	1.15	21
	0.25	1.1	30	0.79 ± 0.096	35 ± 7.4
	0.5	1.1	30	0.90	40
	1.0	1.1	30	1.1	47
PEG200DMA	0.1	1.1	30	0.85 ± 0.092	55 ± 16
			50	1.2 ± 0.12	70 ± 6.0
			70	1.2 ± 0.15	93 ± 13
		2.4	30	1.25	56.2
			50	1.9	83
			70	2.8 ± 0.32	92 ± 10
		5.4	30	1.59	61
			70	3.0	91
		9.4	30	2.1 ± 0.28	55 ± 16
	0.25	1.1	30	1.17 ± 0.24	55 ± 12
			50	1.6	80
			70	2.1 ± 0.19	92 ± 4.0
	0.5	1.1	30	1.1 ± 0.8	61 ± 5.0
	1.0	1.1	30	1.5 ± 0.15	61 ± 5.0
PEG400DMA	0.1	1.1	30	0.59 ± 0.093	43 ± 7.0
			50	1.0 ± 0.23	69 ± 10
			70	1.1 ± 0.17	80 ± 11
		2.4	30	1.3	67
			50	1.22 ± 0.17	71.1 ± 14
			70	2.0	91
		5.35	30	1.3	56
		9.36	30	1.8	70
	0.25	1.1	30	0.98 ± 0.066	56 ± 6.6
			50	1.4	72
			70	1.6	86
	0.5	1.1	30	1.3	55
	1.0	1.1	30	1.7	69
PEG600DMA	0.1	1.1	30	0.56 ± 0.084	27 ± 4.5
			50	1.1 ± 0.36	61 ± 11
			70	1.6 ± 0.21	80 ± 1.4
		2.42	30	0.99	21
			50	0.36	46 ± 11
			70	2.4	73
	0.25	1.1	30	1.1 ± 0.14	49 ± 5.0
			50	1.6 ± 0.25	74 ± 20
			70	1.7	83
	0.5	1.1	30	1.5 ± 0.28	55 ± 15
	1.0	1.1	30	1.7	60

[a] Errors are only included for polymerizations that were run more than twice at the same conditions.

termination. The presence of numerous reactions may have contributed to the difficulty in reproducing the experiments. In addition, the continuous reactions between the sulfur groups and the propagating chains probably did have some effect on the exothermic heat recorded by the DPC that was not accounted for in the theoretical enthalpy used for the calculations.

Another possible reason for error was the presence of oxygen. Oxygen acts as an inhibitor and it was believed to have a significant effect on the XDT polymerizations. Experimental observations indicated that if the monomer mixture was not adequately bubbled with nitrogen and then placed in the DPC pan in a nitrogen environment, results would differ considerably. Therefore, every attempt was made to conduct all experiments in the same manner and to remove as much oxygen as possible.

Different parameters were varied in these polymerization studies. One major concern of these polymerizations was

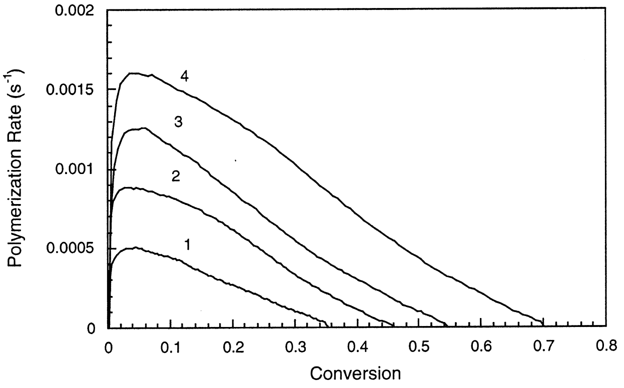

Fig. 6. Rate of polymerization as a function of conversion for the polymerization of PEG400DMA with: (1) 0.1 wt% XDT, (2) 0.25 wt% XDT, (3) 0.5 wt% XDT and (4) 1.0 wt% XDT. All polymerizations were conducted at 1.1 mW/cm^2 and 30 °C.

the low final conversion. Therefore, the polymerizations were studied to determine how to increase the final conversion.

As indicated in Table 1, increasing the concentration of XDT resulted in an increase in the final conversion and an increase in R_p. Fig. 6 displays the results for the various XDT concentrations for the polymerization of PEG400-DMA. The initiator concentration was set at 0.1, 0.25, 0.5 and 1.0 wt%. The corresponding maximums in R_p for the samples were 0.005, 0.009, 0.0013 and 0.0017 s^{-1}. The corresponding final conversions were 38, 50, 55 and 70%. Increasing the initiator concentration from 0.1 to 1 wt% resulted in a tripling in R_p and almost a doubling of the final conversion. Similar observations were shown for the polymerizations of the other multifunctional monomers.

Increasing the initiator concentration led to an increase in propagating chain centers. In addition, the viscosity increases at a slower rate with the increased XDT concentration because with the increased propagating chains, the molecular weight decreases. This in turn increases the rate of polymerization, as evident in the R_p curves.

Finally, in order to increase conversion, it was attempted to heat the monomer mixture during polymerization. All of the previous experiments had been conducted at 30 °C. It was attempted to conduct a thermal polymerization to ascertain if XDT would initiate the polymerization. There was no reaction just by heating the mixture. However, if the monomer mixture was heated and irradiated, the final conversion increased. Fig. 7a displays the kinetic data for PEG200DMA at 30, 50 and 70 °C. The corresponding data for PEG400DMA and PEG600DMA are in Fig. 7b and c, respectively. In all of the cases, increasing the temperature increased R_p and the final conversion.

The PEG200DMA polymerization showed signs of an autoacceleration at 50 and 70 °C. The rate of polymerization started out high initially, decreased and then increased slightly before autodecelerating. The PEG400DMA showed a very slight autoacceleration at 50 °C and a more prominent autoacceleration at 70 °C. The PEG600DMA did not show an autoacceleration.

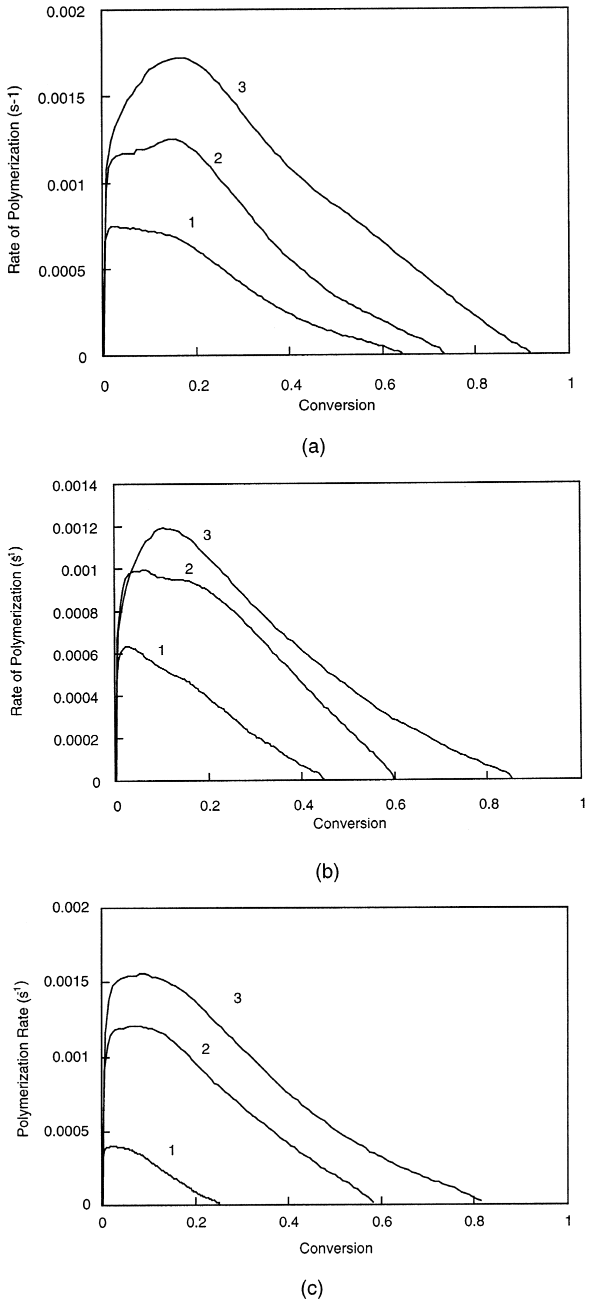

Fig. 7. Rate of polymerization as a function of conversion for the polymerization of PEG200DMA (a), PEG400DMA (b), and PEG600DMA (c) with 0.1 wt% XDT at: (1) 30 °C, (2) 50 °C, and (3) 70 °C. All polymerizations were conducted at 1.1 mW/cm^2.

For the PEG200DMA polymerization, the increased temperature led to reaction behavior more similar to a classical free-radical polymerization. Increasing the temperature more than the previous experiments means that the sample will have different material properties during polymerization.

As the length of the monomer was increased from

PEG200DMA to PEG400DMA, the autoacceleration effect was only evident at the highest temperature. Autoacceleration was not evident for the polymerization of PEG600DMA because it was a larger molecule. The thiol radicals are extremely small and mobile and therefore dominated the reaction.

3.2. Material properties of polymultimethacrylates

Variable temperature DMA was used to examine the properties of polymers synthesized from multimethacrylates with the iniferter XDT. For these studies, copolymerizations of PEG200DMA and PEG200MA were investigated and the amount of the crosslinking agent PEG200DMA was varied.

Fig. 8 shows the tan δ as a function of the effective temperature above the T_g for copolymers of 75 wt% PEG200DMA and 25 wt% PEG200MA. A major concern for comparing material properties was the final conversion of the polymer. If both materials are not at the same conversion, they cannot be compared. The kinetic analysis indicated that polymers initiated with XDT did not reach as high of conversion as polymers initiated with DMPA. Therefore, the polymerizations with XDT were conducted on a hot plate at 70 °C in an attempt to increase the final conversion. The glass transition temperatures for these two materials were 55 °C for the DMPA-initiated polymer and 60 °C for the XDT-initiated polymer.

The tan δ curves for the two polymers were very similar. Generally, the damping factor is a measure of the heterogeneity. The wider the peak is, the more heterogeneous the crosslinked polymer is. The basis for comparing the widths is the width at one half the peak tan δ. Fig. 8 indicates that the width of the tan δ peak is very nearly the same for both polymers. This corresponds with the kinetic gelation model results described in a previous study [25]. In the highly crosslinked polymeric networks, the living radical polymerization does not have an effect on the pendent double bond reactivity. It appears that the living radical polymerization just slows the polymerization down, as indicated by the kinetic studies.

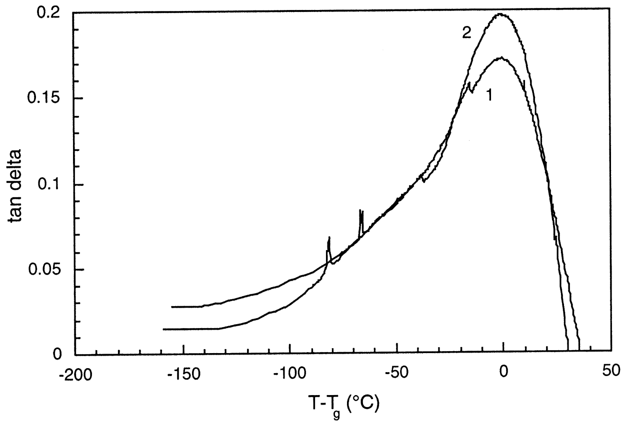

Fig. 8. The damping factor, tan δ, as a function of the effective temperature above T_g for polymers with 75 wt% PEG200DMA and 25 wt% PEG200MA synthesized with: (1) DMPA and (2) XDT.

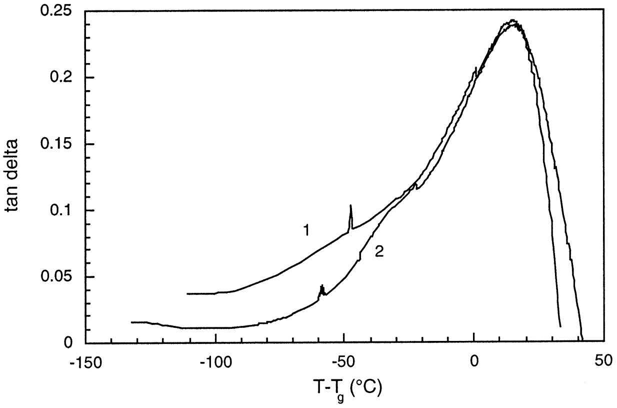

Fig. 9. The damping factor, tan δ, as a function of the effective temperature above T_g for polymers with 50 wt% PEG200DMA and 50 wt% PEG200MA synthesized with: (1) DMPA and (2) XDT.

Fig. 9 shows tan δ for the copolymers of 50 wt% PEG200DMA and 50 wt% PEG200MA. The values of T_g for the different polymers were 27 °C for the DMPA-initiated polymer and 23 °C for the XDT-initiated polymer. Again, there is not a noticeable difference in the widths of the damping factors for the two polymers synthesized by the classical free-radical technique or the living radical technique. Similar results were observed for samples with only 25 wt% PEG200DMA.

4. Conclusions

The kinetics of the polymerizations of multimethacrylates in the presence of the iniferter XDT was examined. It was found that this living radical polymerization drastically decreased the rate of polymerization as compared to polymerization by the classical UV free-radical technique. In addition, the prominent autoacceleration effect that is observed with the polymerization of multifunctional monomers was not apparent in the living radical polymerization. One concern was the low conversions attained with the living radical polymerization. Various parameters of the polymerization could be changed to increase the conversion, including increasing the amount of iniferter, increasing the intensity and increasing the temperature.

The damping factors of the polymers synthesized by living radical polymerizations were also examined. It was concluded that this new polymerization technique did not have an effect on the network heterogeneity of the highly crosslinked polymers. The presence of an irreversible termination due to the iniferter does not have an effect on the network structure because the pendent double bond reactivity is not affected. In the polymerization of multifunctional monomers, very tightly formed microgel regions are formed and it is not possible to alter the pendent double bond reactivity by introducing a living radical polymerization.

Acknowledgements

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