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The effect of wavelength on the polymerization of multi(meth)acrylates with disulfide/benzilketal combinations

L.G. Lovell, B.J. Elliott, J.R. Brown, C.N. Bowman*

Department of Chemical Engineering, University of Colorado at Boulder Engineering Centre, ECCH 111, Campus Box. 424, Boulder, CO 80309-0424, USA

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Abstract

As an alternative to asymmetric iniferters like XDT (*p*-xylylene bis(*N*,*N*-diethyldithiocarbamate), the use of DMPA (2,2-dimethoxy-2-phenylacetophenone) in combination with TED (tetraethylthiuram disulfide) has been proposed as a means of studying living radical polymerizations and creating crosslinked polymers without trapped radicals. This dual initiator system ideally could imitate XDT. The DMPA would photocleave and initiate the reaction via carbon radicals while the TED would photocleave and terminate via dithiocarbamyl (DTC) radicals. In this contribution, we report that for the case of TED and DMPA photoinitiated systems, the nature of the living polymerization and the polymerization kinetics are dependent on the wavelength of light used. Kinetic studies of TEGDMA (triethylene glycol dimethacrylate) photocured with monochromatic light at wavelengths 290, 310, 324, and 365 nm were performed using differential scanning calorimetry. TED was added in incremental amounts to determine its effect on the polymerization as a function of wavelength and concentration. The results suggest that termination via DTC radicals becomes more prominent as the irradiating wavelength is increased. A model was developed that incorporates three modes of chain breaking, where carbon–carbon termination, carbon-DTC termination, and chain transfer to TED are all referred to as chain breaking reactions. The model fit the data well after the maximum rate of polymerization. Furthermore, the model predicts that termination involving TED and its derivatives dominates over carbon radical–carbon radical termination when the ratio of TED:DMPA is 1:2 or higher in TED. Therefore, TED:DMPA combinations can be used as an alternative to conventional iniferters as long as a sufficient amount of TED has been added so that carbon–sulfur chain breaking reactions dominate over traditional termination. Infrared analysis of several samples proved that TED:DMPA combinations greater than 1:2 can prevent trapped carbon radicals from persisting in polymer networks after cure. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Dimethacryaltes; Tetraethylthiuram disulfide; Iniferters

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1. Introduction

Iniferter polymerizations, or “living” or “controlled” radical polymerizations, have been investigated as a means of producing block copolymers with low polydispersity during a controlled free radical synthesis. The term “iniferter” was established by Otsu to represent compounds that could initiate, chain transfer and terminate radical polymerizations [1]. This step-like reaction leads to narrow polydispersities and polymers that contain no trapped radicals in the final polymer. Because polymers can be produced that contain no trapped radicals, iniferters as well as disulfide/iniferter combinations have been used as a method of studying crosslinked polymer network formation using dynamic mechanical analysis [2]. Before this technique was developed there was no practical means of analyzing photocured crosslinked polymers without the complication of post-curing by trapped radicals during the analysis.

Several researchers have investigated the fundamentals of iniferter polymerizations and contradicting reports of termination mechanisms are claimed in the literature [3,4]. In this contribution we report that for the case of tetraethyldiuramdisulfide (TED) and 2,2-dimethoxy-2-phenylacetophenone (DMPA) photoinitiated systems, the nature and kinetics of the living polymerization and the carbon–sulfur chain breaking rate are dependent on the wavelength of light used. This work is a systematic study to investigate the use of monochromatic light at varying wavelengths to initiate iniferter polymerizations. This study demonstrates that, for the case of DMPA and TED combinations, these reactions are highly dependent on initiation source. The end goal of using DMPA and TED combinations is to provide a faster alternative to traditional iniferter polymerizations and still create crosslinked polymer samples that do not contain residual trapped radicals.

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* Corresponding author. Tel.: +1-303-492-3247; fax: +1-303-492-4341.
E-mail address: christopher.bowman@colorado.edu (C.N. Bowman).

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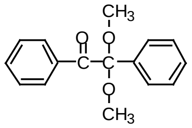
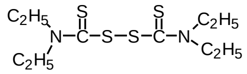
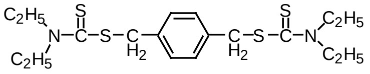


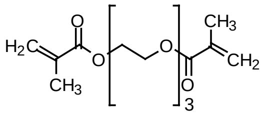
(a) 2,2-dimethoxy-2-phenyl acetophenone - DMPA



(b) tetraethylthiuram disulfide - TED



(c) p-xylylene bis(N,N-diethyldithiocarbamate) - XDT



(d) triethyleneglycol dimethacrylate - TEGDMA

Fig. 1. Molecular structure of (a) DMPA; (b) TED; (c) XDT; and (d) TEGDMA.

Iniferters are generally classified into two categories: compounds that dissociate into two different radicals and compounds that generate two identical radicals. An extensive review of iniferters has been written [1] so, in this report, we will only focus on the three initiators we studied. 2,2-dimethoxy-2-phenyl acetophenone is a standard initiator that generates two carbon radicals. The molecular structure of DMPA is shown in Fig. 1.

Tetraethylthiuram disulfide is a disulfide that photocleaves into two dithiocarbamyl (DTC) radicals. These radicals can, although extremely slowly, initiate (meth)acrylate and vinyl polymerizations. TED can also be thermally degraded to form DTC radicals above 60°C, but the reaction is far slower than conventional free radical initiators [5]. The DTC radicals can also terminate the carbon radicals on propagating chains. This terminated polymer chain can reinitiate upon further ultraviolet light exposure to reform the carbon radical and DTC radical. The molecular structure of TED is also shown in Fig. 1.

The iniferter *p*-xylylene bis(*N*,*N*-diethyldithiocarbamate) (XDT) is a symmetric molecule in which each half can photocleave into a carbon radical and a DTC radical. This molecule initiates via the carbon radicals generated upon irradiation. Although the DTC radicals can initiate vinyl polymerizations, they are much less reactive than carbon radicals. Therefore, initiation by DTC radicals is negligible for XDT systems as compared to initiation by carbon radicals. The DTC radicals can terminate the propagating chains forming an endgroup that can be reinitiated as in the case of TED. The molecular structure of XDT is also given in Fig. 1.

The monomer, triethylene glycol dimethacrylate (TEGDMA) was used in this study since it forms a glassy, crosslinked polymer at room temperature. The molecular structure of TEGDMA is also shown in Fig. 1. Highly crosslinked dimethacrylates, such as TEGDMA, exhibit diffusion limitations during cure. Both the propagation and termination reactions become diffusion controlled and the predominant mode of termination shifts to reaction diffusion controlled termination as the cure progresses (past 20% conversion) [6,7]. Reaction diffusion controlled termination occurs when the carbon radicals, in a restricted environment, are unable to segmentally move toward each other. Instead, the radicals are more mobile by propagating through unreacted double bonds than they are by either segmental or bulk diffusion.

Diffusional limitations to termination lead to the presence of trapped carbon radicals within the polymer network. These trapped radicals may remain in the sample for at least a year after cure, depending on the nature of the crosslinked network [7–9]. Therefore, post cure often occurs during sample heating that is common during mechanical or other types of testing. Iniferters, such as XDT, have been successfully used to prevent post cure, but the polymerization is quite slow [2]. Therefore, as an alternative, the use of DMPA in combination with TED has been proposed as a means of studying living radical polymerizations. This dual initiator system ideally could imitate XDT. The DMPA would photocleave and initiate the reaction via carbon radicals while the TED would photocleave and terminate via DTC radicals. Once this carbon-sulfur bond was formed by the addition of a DTC radical, the polymer endgroup could be reinitiated with light. One potential problem would be if one of the initiators did not photocleave at the desired rate to match the production of the other radical type. If the TED does not photocleave rapidly enough, the reaction will behave more like a standard photopolymerization. The non-cleaved TED may also act as a chain transfer agent.

Kannurpatti and co-workers studied XDT initiated versus conventional DMPA initiated photopolymerizations of methacrylates [3]. They reported that for polymerizations of hydroxyethyl methacrylate (HEMA) using XDT, termination was dominated by carbon–carbon radical combination at low conversions and carbon–sulfur radical combination (cross-termination) at high conversions. This change in the dominant mode of termination was attributed to the mobility becoming diffusion limited at the onset of autoacceleration. Further studies on diethylene glycol dimethacrylate (DEGDMA) and poly(ethylene glycol200) dimethacrylate (PEG200DMA) indicated that these highly crosslinked systems exhibited cross (carbon to sulfur) termination from low conversions and throughout the polymerization [3]. This result was consistent with the conclusion that when the reacting system becomes diffusion limited, cross termination dominates. Based on these findings, it is expected that for the TEGDMA and XDT polymerizations presented in this paper, cross termination will dominate from the onset of reaction.

In an article on the mechanism of the polymerization of *n*-butyl acrylate initiated by iniferters, Dika Manga et al. [4] challenge the scheme originally proposed by Otsu [10]. They claim that non-reversible termination and initiation by DTC radicals must not be neglected. They cite the works of Otsu [11], Turner et al. [12] and themselves [13] where DTC radicals were found to polymerize various monomers. Dika Manga et al. also report that definitive termination (carbon radical to carbon radical) reactions took place simultaneously with (but more slowly than) the reversible termination reactions [4]. Their conclusion was that the iniferter polymerization was only partially living because of these numerous side reactions.

In an additional study of the polymerization of styrene, methyl methacrylate and butyl acrylate initiated by iniferters, Dika Manga et al. reported that these polymerizations were like “living” reactions, but not ideal [14]. The main differences between the three monomers were attributed to kinetic deviations. For one, it was difficult to control the molecular weight of butyl acrylate since it exhibited a much faster propagation kinetic rate (compared to initiation) than styrene and methyl methacrylate. However, butyl acrylate displayed a low rate of initiation by DTC radicals, thereby diminishing the amount of end-groups leading to irreversible termination [14].

Otsu has published many articles [1,15–17] concerning iniferters including an extensive review [1]. In one, the elucidation of mechanisms for living radical polymerizations of styrene was obtained by a spin trapping technique [15]. Similar to the results of Dika Manga et al., they also reported that living polymerizations of methyl acrylate were not possible with benzyl *N*,*N*-diethyldithiocarbamate (BDC) as the iniferter due to the dominance of bimolecular termination over the iniferter reactions [16]. Therefore, they proposed the use of the BDC initiator in combination with TED, which acts as a chain transfer agent, to perform the desired living polymerization of methyl acrylate successfully [16]. In another work, Otsu and coworkers found that the wavelengths between 350 and 390 nm must be important in the photodissociation of the BDC molecule [17].

The photoinitiator DMPA is a benzilketal that has been shown to be extremely effective at generating radicals under ultraviolet light irradiation [18]. This molecule undergoes an α-cleavage (Norrish type I) into a benzoyl-α,α-dimethoxybenzyl radical pair. The α,α-dimethoxybenzyl radical subsequently decays into a highly reactive methyl radical [18]. Through sensitization and quenching studies the α-cleavage was found to proceed through a short-lived triplet excited state [18]. For Norrish type I reactions, absorption of light by a carbonyl chromophore leads to two electronic transitions: the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ [19]. The UV–Vis absorption spectra of DMPA contains a main peak at 250 nm due to the $\pi \rightarrow \pi^*$ excitation and a smaller peak at 332 nm due to the $n \rightarrow \pi^*$ excitation [20].

When a conventional initiator, such as DMPA, is used in conjunction with a disulfide, such as TED, several different reactions are possible due to the presence of carbon [M·] and dithiocarbamyl [DTC·] free radicals. Typical carbon–carbon radical termination is expected (1). Furthermore, the addition of TED into the system provides for chain-transfer (2) to the TED molecule and cross-termination involving the combination of carbon and DTC radicals (3). By performing mass balances on the carbon and DTC radicals and assuming pseudo steady state on each radical concentration, one can predict the rate of polymerization for various TED concentrations. Several authors [3,5,21] have performed similar analysis on polymerizations initiated by iniferters only. In a recent study, one group [5] showed that styrene and methyl methacrylate polymerizations thermally initiated by tetramethylthiuram disulfide (TMTD) exhibited initiation by the DTC radical, cross-termination (styrene and methyl methacrylate) and recombination (methyl methacrylate only) of the DTC radicals. The recombination effect was due to the large accumulation of DTC radicals in the system caused by the low initiation rate of methyl methacrylate by TMTD. Since DMPA is being used to initiate the polymerization in our study, we do not believe a significant buildup of DTC radicals will form and are thus neglecting recombination of DTC radicals as a dominant mode of termination for our system since it will occur at a very low rate. Furthermore, initiation by DTC radicals, and other types of termination (unimolecular, primary radical termination, etc.) are also being neglected since the rates of these reactions are much lower than the dominant modes of propagation and termination that have been discussed. Clearly, TED can initiate polymerizations; however, using DMPA in conjunction with TED facilitates predominately carbon-radical initiation. In addition, the analysis will be performed after the maximum rate of polymerization has been achieved.

Possible chain-breaking reactions are as follows:

$$\mathrm{M}\cdot + \mathrm{M}\cdot \xrightarrow{k_t} \mathrm{M{-}M} \qquad \text{Carbon–carbon termination} \qquad (1)$$

$$\mathrm{M}\cdot + \mathrm{TED} \xrightarrow{k_{ti}} \mathrm{M{-}DTC} + \mathrm{DTC}\cdot \qquad \text{Chain-transfer} \qquad (2)$$

$$\mathrm{M}\cdot + \mathrm{DTC}\cdot \xrightarrow{k_{tx}} \mathrm{M{-}DTC} \qquad \text{Cross-termination} \qquad (3)$$

2. Experimental

2.1. Materials

The monomer used in this investigation was triethylene

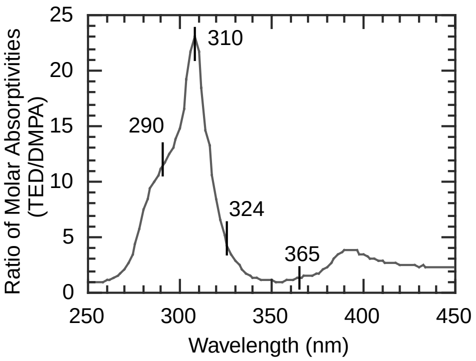


Fig. 2. Ratio of molar absorptivities of TED to DMPA obtained by UV–Vis spectroscopy. The highlighted values denote the wavelengths at which the polymerizations were performed.

glycol dimethacrylate (TEGDMA, Polysciences, Warrington, PA, USA). Photopolymerizations were performed using 2,2-dimethoxy-2-phenylacetophenone (DMPA, Ciba-Geigy, Hawthorne, NY, USA) as the initiator. Tetraethylthiuram disulfide (TED, Aldrich Chemical Co., Milwaukee, WI, USA) was added to generate DTC radicals. As a comparison, the iniferter, *p*-xylylene bis(*N*,*N*-diethyldithiocarbamate) (XDT, 3M Company, Minneapolis, MN, USA), was also studied.

2.2. UV–Vis spectroscopy

The UV–Vis spectra were obtained for DMPA and TED in methylene chloride. Due to the high molar absorbtivities, quartz glass sample holders with a path length of 1.0 or 0.1 mm were used (NSG Precision Cells, Inc. Farmingdale, NY, USA). The quartz sample holders were placed in the chamber of a Hewlett-Packard 8452A-diode array spectrophotometer (Hewlett-Packard, Palo Alto, CA, USA) and a background spectrum was taken. Solutions of DMPA and TED (0.004 M) in methylene chloride were added to the quartz holders and the spectrums were taken over a range from 190 to 800 nm.

2.3. Differential scanning calorimetry

The polymerizations were performed at 25°C in a differential scanning calorimeter (Perkin–Elmer, DSC, Norwalk, CT) with a refrigerated recirculating chiller to facilitate isothermal reactions near room temperature (NESLAB, RTE-111, Newington, NH). A photocalorimetric accessory capable of producing monochromatic light (Perkin–Elmer, DPA 7, Norwalk, CT) was employed as a light source for these experiments. The four wavelengths (290, 310, 324, and 365 nm) were chosen based on the absorbance behavior of DMPA and TED, as described in the following section. At each wavelength, TEGDMA was polymerized with DMPA only (0.01 wt%) and DMPA/TED combinations (0.01/0.001, 0.01/0.005, and 0.01/0.01 wt%). All of the samples were irradiated for 8–25 min, depending on the speed of the reaction. Furthermore, the DSC chamber was purged with nitrogen for 10 min prior to initiation and during the reaction to ensure that oxygen did not inhibit the polymerization. Small sample sizes (1–2 mg) and low initiator concentrations were chosen so that the thin film approximation for uniform light intensity through the sample could be applied. In addition, neutral density filters (Melles Griot, Irvine, CA) were used to control the light intensity by placing them between the light source and the sample. The subsequent light intensity was experimentally verified by monitoring, with the DSC, the amount of heat absorbed by carbon disks (Perkin–Elmer, Norwalk CT) which were placed in the sample holder. Acetone was used to deliver the proper amount of initiator and disulfide into the TEGDMA monomer. Approximately 8 wt% acetone was initially added. After a thorough mixing of the solution, all of the acetone was evaporated off before the monomers were cured. Finally, several photopolymerizations of each reaction condition were performed to ensure repeatability of the results.

2.4. FTIR experiments

In addition to the experiments performed in the DSC apparatus, FTIR spectroscopy (Fourier Transform Infrared, Magna-IR 750, Series II, Nicolet Instruments, Madison, WI) was used to verify the kinetic results. A horizontal-mounting unit, which redirects the IR beam vertically, was used in conjunction with an ultraviolet light source (Efos Ultracure, EIT, Sterling, VA) to allow for curing of the monomer samples within the IR unit. Series scans (DTGS detector, NaCl crystals) were performed to monitor the conversion of the C=C bond (1637 cm^{-1}) as a function of time. In addition, spectra were collected at the beginning and end of the polymerization to determine the conversion using the C=O (1720 cm^{-1}) bond as an internal reference. The samples were then left in a dessicator for 50 h and the IR spectrum was obtained again to determine the final conversion of the samples at room temperature. Then, the samples were heated in an oven at 70 and 90°C for 30 min each. The IR spectrum was taken after each heating to determine if additional post-cure occurred. A similar procedure was used with a 290 nm light source (DSC photo accessory) except the series scans were omitted.

3. Results and discussion

3.1. Full cure results

Once the UV–Vis spectra of DMPA and TED were obtained, the ratios of molar absorbtivities were calculated as a function of wavelength. As shown in Fig. 2, the molar absorptivity of TED is significantly higher than DMPA for the wavelengths between 280 and 330 nm. This result suggests that TED initiation may be more energetic between these wavelengths and less responsive at higher wavelengths such as 365 nm (the dominant spectral line in

Table 1
Wavelength of light, molar absorptivities (ϵ) of TED and DMPA, and light intensity

Wavelength (nm)	ϵ (mol l^{-1} cm^{-1})		Light intensity (mW cm^{-2})
	TED	DMPA	
290	14 000	1240	0.5
310	4450	200	2.8
324	1370	260	2.1
365	210	160	3.1

most UV light sources). However, for DMPA it is known that the peak of lesser intensity (332 nm) actually has a greater efficiency in generating radicals by an $n \rightarrow \pi^*$ excitation [19]. Four wavelengths were chosen to determine if the efficiency of DTC radical generation and, hence, the dominance of carbon–sulfur termination were affected by the wavelength of irradiating light. The wavelengths of 290, 310 (peak maximum), 324 and 365 nm were used and the calculated molar absorbtivities (ϵ) are given in Table 1. To ensure that the results were not masked by the effect of wavelength on the DMPA initiation, the light intensity at each wavelength was varied so that the rates of initiation by DMPA were the same at each wavelength assuming an efficiency of 1 (initiation rate is 1.3×10^{-5} mol l^{-1} s^{-1}). In other words, the light intensity was controlled so that the moles of photons absorbed by the DMPA was constant for all the wavelengths studied. Unfortunately, the efficiency of DMPA in our monomer system as a function of wavelength has not been characterized so the rates of initiation could not be matched exactly. The light intensities used at the chosen wavelengths are also given in Table 1. By using varying amounts of TED (0.001, 0.005, 0.01 wt%) in the photopolymerization of TEGDMA (with 0.01 wt% DMPA), one is able to monitor the effect of TED as a function of wavelength and concentration.

Fig. 3a–d gives the polymerization rate normalized by the initial monomer concentration (in units of inverse time) as a function of double bond conversion for all four wavelengths that were studied. The highest curve in each plot corresponds to the reaction with only DMPA and monomer. All four of these curves are similar and reach approximately the same final conversion (48–54%); however, the maximum rate of polymerization does change as a function of wavelength. Higher polymerization rates are measured at 310 and 324 nm than at 290 and 365 nm. If one assumes a polymerization efficiency at 310 nm to be 1, all of the other rate curves can be scaled to give a relative efficiency at the other wavelengths. This procedure was implemented and the results are shown in Table 2. The lowest relative efficiencies, 0.35 and 0.46, were calculated at 290 and 365 nm, respectively.

Even though there were no significant differences in the polymerization behavior with only DMPA present, the same is not case for the systems that contain both DMPA and TED. As one increases the wavelength of irradiating light, pronounced differences in the polymerization rates arise. At 290 nm (Fig. 3a), the rate maxima does not shift as more

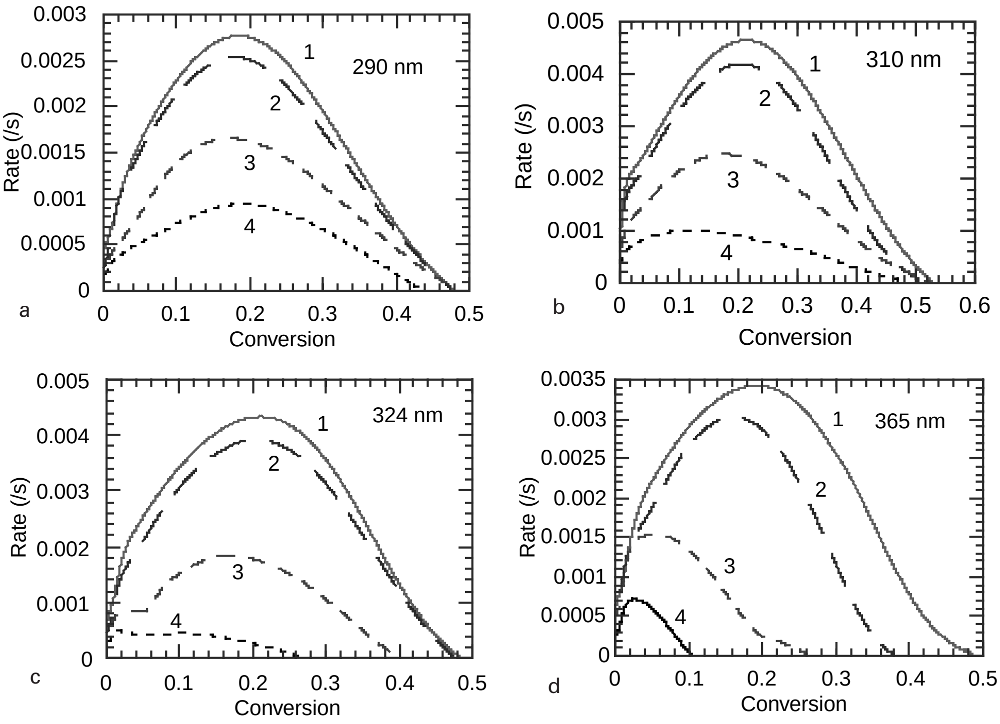


Fig. 3. Photopolymerizations of TEGDMA cured with 0.01 wt% DMPA using light from the four wavelengths (a) 290 nm; (b) 310 nm; (c) 324 nm; and (d) 365 nm. The samples were cured with (1) no TED; (2) 0.001 wt% TED; (3) 0.005 wt% TED; and (4) 0.01 wt% TED.

Table 2
Efficiency of radical formation (ϕ) and kinetic parameters used for model fitting

	Wavelength (nm)			
	290	310	324	365
ϕ (DMPA)	0.35	1	0.85	0.46
ϕ (TED)	0	0.03	0.16	0.33
k_p	400	400	400	400
k_t	6000	6000	6000	6000
k_{ti}	215	215	215	215

TED is added and the final conversion is only slightly affected when 0.01 wt% TED is present (44% compared to 48% for the other concentrations). Similar behavior is evident for the polymerization performed at 310 nm, except the maximum polymerization rate does begin to shift to earlier conversions as the concentration of TED is increased. When 324 nm light is used, the polymerization behavior changes more dramatically than for those initiated at 290 and 310 nm. The rate maximum is shifted to earlier conversions and at the highest concentration of TED (0.01 wt%) auto-acceleration is almost completely suppressed. Furthermore, the final conversion dramatically decreases from 48 to 25% when more TED is added. The polymerizations in which 365 nm light was used to initiate the DMPA and TED are quite different from the other wavelengths. The effect of TED during the latter half of the polymerization is quite pronounced; however, during the initial stages, autoacceleration is more evident than in the experiments using 324 nm light and very little difference exists in the initial polymerization rate. The high polymerization rate in the beginning of the reaction suggests that carbon–carbon termination is dominant and the addition of disulfide only becomes important in the kinetics as the reaction progresses. Presumably, carbon–sulfur termination is only significant when carbon–carbon termination is diffusion limited. The final conversion is significantly affected when the TED concentration is increased. Even when only 0.001 wt% TED is added, the final conversion decreases 10% from the polymerization with only DMPA. Once 0.01 wt% TED has been added, the final conversion is only 10% and the maximum rate occurs by 4% conversion. The addition of TED into the reaction mixture has a strong hindering effect on the reaction kinetics, and the polymerization rate falls below the monitoring capacity of the DSC.

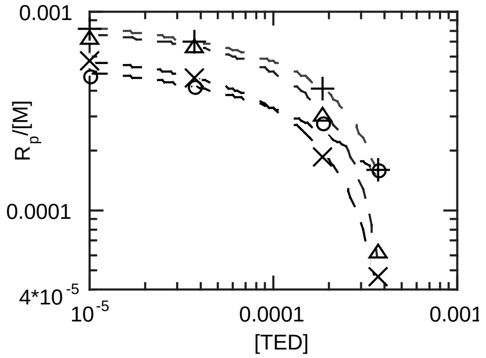


Fig. 4. Experimental data (points) versus model fit (lines) for R_p/[M] at 5% conversion past the maximum rate. The data points correspond to (○) 290 nm; (+) 310 nm; (△) 324 nm; and (×) 365 nm. The points on the left axis are provided as a reference and represent data points with no TED added to the polymerizing system.

3.2. Model

To probe the polymerization mechanism further, a model was developed that accounted for the various modes of free radical termination. As discussed in the introduction, the growing carbon radical can react with another carbon radical (M·), a dithiocarbamyl radical (DTC·), or TED in a chain transfer reaction. These three reactions are given in Eqs. (1)–(3). Taking into account the formation of carbon and dithiocarbamyl radicals through initiation reactions and the three termination reactions presented in Eqs. (1)–(3), species balances on the two radical types were derived (4 and 5). The pseudo-steady state assumption was then applied and the concentration of carbon radicals [M·] was deduced (6). This expression was used in conjunction with the classical rate expression for free radical polymerizations ($R_p = k_p[\mathrm{M}][\mathrm{M}\cdot]$) to give the rate of polymerization as a function of TED concentration (7). As discussed in the introduction, this model neglects all other modes of termination except those detailed in Eqs. (1)–(3) and assumes that DTC radicals do not initiate the polymerization to a significant extent.

$$\frac{\mathrm{d}[\mathrm{M}\cdot]}{\mathrm{d}t} = R_{ic} - k_t[\mathrm{M}\cdot]^2 - k_{ti}[\mathrm{M}\cdot][\mathrm{TED}] - k_{tx}[\mathrm{M}\cdot][\mathrm{DTC}\cdot] \tag{4}$$

$$\frac{\mathrm{d}[\mathrm{DTC}\cdot]}{\mathrm{d}t} = R_{is} + k_{ti}[\mathrm{M}\cdot][\mathrm{TED}] - k_{tx}[\mathrm{M}\cdot][\mathrm{DTC}\cdot] \tag{5}$$

$$[\mathrm{M}\cdot] = -2k_{ti}[\mathrm{TED}]] + \frac{\sqrt{(2k_{ti}[\mathrm{TED}])^2 - 4k_t(R_{is} - R_{ic})}}{2k_t} \tag{6}$$

$$R_p = [\mathrm{M}]k_p\left(\frac{-2k_{ti}[\mathrm{TED}] + \sqrt{(2k_{ti}[\mathrm{TED}])^2 - 4k_t(R_{is} - R_{ic})}}{2k_t}\right) \tag{7}$$

R_{is} is the rate of initiation of sulfur (DTC) radicals and R_{ic} is the rate of initiation of carbon radicals. k_p and k_t are, respectively, the propagation and termination rate constants for TEGDMA polymerized without TED. These two parameters were determined by analyzing the reaction rate data without TED. The sulfur radical generation efficiency at each wavelength and the rate constant for the chain transfer reaction (k_{ti}) were calculated from data for reactions performed with TED. Since varying the energy of the irradiating light only affects the efficiency of DTC radical generation, the value for the chain transfer rate constant

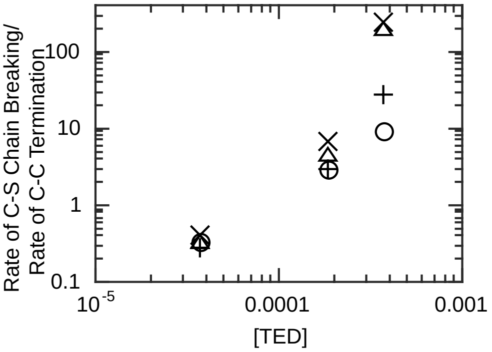


Fig. 5. Rate of carbon–sulfur chain breaking reactions divided by rate of carbon–carbon termination as predicted by the model for the wavelengths (○) 290 nm; (+) 310 nm; (△) 324 nm; and (×) 365 nm.

was not changed as a function of wavelength. The cross termination rate constant (k_{tx}) is not present in the final rate expression (7), so its value was not determined. The model was fit to the experimental data at 5% conversion past the maximum rate since the kinetic constants should all have similar values at this point.

The approach to determine the parameters involved a minimization of sum of squares error (SSE) between the data and model prediction. The parameters determined from the data fitting procedure are given in Table 2. In Fig. 4, the rates of polymerization, normalized by the monomer concentration, are given as a function of TED concentration. The curves represent the model fit whereas the data are given as points. With the available data, the model predicts the effect of TED on the system quite well. However, since only three concentrations of TED were examined, one is not able to include DTC radical-DTC radical recombination in the model. The introduction of a recombination term leads to a fourth-order polynomial that would require at least five data points to fit. The recombination of sulfur radicals is less important in our analysis since we are concerned with the termination reactions that include carbon radicals, but its exclusion should be noted since several other researchers have discussed it [5,22].

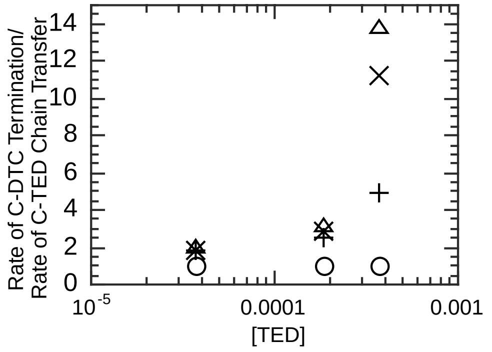


Fig. 6. Rate of carbon–DTC radical termination to the rate of carbon radical–TED chain transfer reactions as predicted by the model for the wavelengths (○) 290 nm; (+) 310 nm; (△) 324 nm; and (×) 365 nm.

Once the parameters were obtained, several tests were performed to verify the model. For example, the model predicts no polymerization to occur in samples cured using 310, 324, and 365 nm light once 0.0005 mol l^{-1} of TED have been added to the mixture. On the other hand, with a 290 nm light source, a measurable rate persists even when 0.1 mol l^{-1} of TED is added to the mixture. This difference occurs because the best fit of the experimental data at 290 nm occurs when the efficiency of sulfur radical initiation is approximately 0. To test the validity of this parameter value, polymerizations were carried out at 310 and 290 nm with 0.032 wt% TED. At this concentration (0.0012 mol l^{-1}), the model predicts no polymerization when 310 nm light is used; however, with a 290 nm light source, a measurable rate should still exist. When the experiments were carried out, this effect was quite evident. Polymerization was measurable with a 290 nm light source and not a 310 nm light source. Based on these findings, it appears that the generation of DTC at 290 nm is significantly lower than at the other wavelengths studied.

In an additional test of the model parameters, a comparison was made between our values for TEGDMA and model results reported for methyl methacrylate [5]. In their work, Kysela and Staudner modeled the thermal polymerization of styrene and methyl methacrylate with TED and reported values for several lumped kinetic parameters. Using this information, the k_p and k_t values for methyl methacrylate from the Polymer Handbook [22], and our value for the termination kinetic constant for the chain transfer reaction ($k_{ti} = 215$ l mol^{-1} s^{-1}), we were able to calculate a DTC radical concentration for TEGDMA cured with 365 nm light and 0.01 wt% TED. The DTC radical concentration predicted is on the order of 10^{-5} mol l^{-1}, which is two orders of magnitude higher than the carbon radical concentration (10^{-7} mol l^{-1}). These concentrations are reasonable since one would expect a significantly larger concentration of sulfur radicals to exist when the rate of polymerization is strongly hindered (like it is at these experimental conditions).

Even though this model involves several assumptions and a limited data set, it gives a credible description of the variation in the dominant mode of chain breaking as a function of wavelength of irradiating light and concentration of TED. The parameters gleaned from the model can be used to predict the rate of chain breaking for the three different modes discussed previously. Fig. 5 is the ratio of carbon–sulfur chain breaking (both cross-termination and chain transfer) to traditional carbon–carbon termination as a function of wavelength and TED concentration. Two results are quite apparent from the figure. For one, carbon–carbon termination dominates over carbon–sulfur termination when only 0.001 wt% TED is used in the polymerization. Therefore, higher concentrations of TED are needed to ensure carbon–sulfur chain breaking and prevent the presence of trapped carbon radicals. The second point is that the dominance of carbon–sulfur chain breaking

Table 3
Double bond conversion (%) of TEGDMA from FTIR spectra

	Wavelength (nm)	Double bond conversion (%)			
		Immediately after curing	After being at room temperature for 50 h	Following heating to 70°C	Following heating to 90°C
0.1 wt% DMPA	290	46	52	52	77
	365	47	57	73	81
0.1 wt% DMPA/0.01 wt% TED	290	50	66	73	80
	365	51	69	71	81
0.1 wt% DMPA/0.05 wt% TED	290	47	56	56	56
	365	30	35	35	35
0.1 wt% DMPA/0.1 wt% TED	290	40	40	40	40
	365	49	55	55	55
0.1 wt% XDT	365	45	45	45	45

increases with wavelength. At 324 and 365 nm, the rate of carbon–sulfur termination is about 200 times greater than carbon–carbon termination (0.01 wt% TED). However, at 290 nm, the value is only 10.

Fig. 6 illustrates the effect wavelength has on the type of sulfur–carbon chain breaking that is occurring. As more TED is added to the system, it is apparent that cross-termination (DTC radical reacting with a carbon radical) is more pronounced at 324 and 365 nm than the other wavelengths (290 and 310 nm). At 290 nm, little cross-termination occurs since the model predicts a very slow generation of DTC radicals.

3.3. IR data

By using TED in conjunction with DMPA, one should be able to create polymer samples that do not contain any trapped radicals and can be heated to determine the glass transition temperature (T_g) and rubbery modulus without increasing the conversion of the sample. To determine whether TED is effective at capping trapped radicals that exist in the cured polymers, FTIR studies were completed to determine if post-curing of the samples occurred. Thin monomer samples with 0.1 wt% DMPA and the same relative concentrations of TED (0, 0.01, 0.05, 0.1 wt%) were studied along with a sample only cured with XDT (an iniferter, 0.1 wt%). The samples were cured using either 290 or 365 nm light and the double bond conversions were determined by FTIR immediately after cure. Then, the samples were left at room temperature for 50 h to ensure that the sulfur–carbon termination was complete, and the conversion was determined a second time. Finally, spectra of the samples were obtained immediately after heating the samples at 70–80°C (close to the T_g of TEGDMA at these conversions) for 30 min and immediately after heating the samples a second time between 90 and 100°C for 30 min (above the T_g of TEGDMA).

Table 3 provides the double bond conversions for the sequence outlined above. Samples cured with 290 and 365 nm light exhibit similar trends in residual cure as the concentration of TED is increased. The samples without TED and those with only 10:1 ratio of DMPA:TED showed an increase in the double bond conversion (from 50 to 80%) as the samples were heated above 90°C. The similarity in the runs with no TED and 10:1 ratio (DMPA:TED) suggests that the presence of TED has very little effect in reducing the number of trapped radicals that remain in the system after curing. When more TED is added to the system (2:1 and 1:1 wt% DMPA:TED), the TED is effective in eliminating trapped radicals. Some of the samples showed an increase in conversion during storage, but no residual cure occurred upon heating. This result suggests that the rate of sulfur–carbon termination need not be dramatically larger than carbon–carbon termination to prevent post cure (i.e. 200 times greater as was predicted for samples with 1:1 relative concentrations of DMPA:TED at 365 nm). Samples in which the model only predicts an equal amount of carbon–sulfur and carbon–carbon termination (i.e. 2:1 relative concentration at 290 nm), still exhibit a lack of trapped carbon radicals and post-cure. Based on the model and FTIR results, samples that contain a 2:1 relative concentration of TED:DMPA undergo enough sulfur–carbon termination to prevent trapped radicals from existing for extended time periods. The effect of wavelength has much greater influence on the polymerization rate since the relative rates of sulfur–carbon chain breaking (either cross-termination or chain transfer) changes as a function of wavelength.

4. Conclusions

In this work, a dimethacrylate monomer (TEGDMA) was photopolymerized with DMPA as the initiator and TED as the disulfide to determine what effect the disulfide had on the termination kinetics as a function of wavelength. The results suggest that several modes of chain breaking occur in the polymerizing system. Carbon–dithiocarbamyl radical termination is occurring along with carbon radical–TED molecule chain transfer reactions. Interestingly, changing the wavelength of the irradiating light had a significant effect on the polymerization rate. The rate is suppressed more as the wavelength of irradiating light increases.

A model of the polymerization kinetics, which included the three modes of chain stoppage just discussed, was deduced and found to fit the experimental data well. The model confirmed that carbon–sulfur chain breaking events dominated the termination process. Increasing the concentration of TED led to a higher rate of DTC radical generation as well a higher rate of chain transfer between the carbon radical and TED molecule. Increasing the wavelength of irradiating light promoted more cross-termination between the DTC and carbon radicals. Furthermore, the model predicted that dithiocarbamyl radicals were not readily created at 290 nm, thus accounting for the diminutive effects of TED on the polymerization rate at that wavelength. A set of polymer samples was heated to see if trapped radicals persisted in the network and if additional cure could be induced. The samples that contained less TED than the 2:1 ratio of DMPA:TED did show an increase in double bond conversion with heating. These findings verify the model results and suggest that DMPA:TED combinations can be used as an alternative to traditional iniferters (when one desires cross-linked polymers without trapped radicals) when enough TED has been added to the system to cause carbon–sulfur chain breaking reactions to dominate.

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