UV Photopolymerization Behavior of Dimethacrylate Oligomers With Camphorquinone/Amine Initiator System

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ABSTRACT: Ultraviolet (UV)-initiated polymerization of dimethacrylate oligomers with camphorquinone (CQ) and a tertiary amine as a radical photoinitiator system was studied using differential scanning calorimetry. Polymerization behavior of two curing systems, one glass-forming and the other elastomer-forming, were compared, based on the rate of polymerization and the double bond conversion. The radical termination in the glass-forming system (E-bis-A DMA-1) became diffusion controlled immediately upon exposure to UV radiation, with the reaction rate quickly reaching its maximum. The elastomer-forming system (E-bis-A DMA-2) polymerized at a much lower rate than E-bis-A DMA-1 because of its lower methacrylate group content. The two systems introduced a different temperature dependence on the rate of polymerization. Increasing the temperature reduced the viscosity and enhanced chain segmental mobility. This delayed the autoacceleration in the glass-forming system. Polymerization rates for both the curing systems increased with initiator concentration, but the dependence on CQ was only characterized by an exponential factor of <0.5. Presumably, this was due to primary radical recombination. The vinyl group conversion and gel fraction of E-bis-A DMA-1 increased with the increase in CQ concentration and/or curing temperature, while the extent of reaction for E-bis-A DMA-2 was relatively insensitive to the latter two factors. A large number of radicals were trapped inside the network of E-bis-A DMA-1 after photocuring and they decayed slowly. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 82: 1107–1117, 2001

Key words: dimethacrylate oligomer; UV curing; photopolymerization; radical decay; DSC

INTRODUCTION

Photoinitiated radical polymerization of multifunctional monomers offers a convenient path for producing highly crosslinked polymer networks.

With its unique advantage of fast reaction rates, solvent-free formulation, and excellent physical properties introduced into the products, the photopolymerization of multifunctional monomers has found a wide variety of applications in many areas, such as the production of aspherical lenses and optical discs, in-line coating of optical fibers, elastomeric impression and restoration materials, and microelectronics.[1–7]
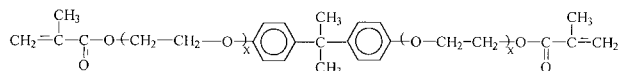
Figure 1 General structure of ethoxylated bisphenol A dimethacrylate.

The importance of the polymerization kinetics of multifunctional monomers in determining the structures and physical properties of final polymer networks has made it the subject of many investigations.[8–19] Extensive studies have shown that the photopolymerization of multifunctional monomers can exhibit unique reaction behavior. This behavior includes unequal functional group reactivity,[5,20,21,26] autoacceleration, and autodeceleration induced by diffusion-controlled propagation and termination.[5,10,22] Physical and structural changes, such as structural heterogeneity[23,24] and delay in volume shrinkage with respect to equilibrium, are involved in the process.[5,25,26]

Camphorquinone (CQ) is often selected as a photoinitiator for visible light initiation systems.[7] The combination of CQ with a tertiary amine effectively produces free radicals to start the polymerization upon exposure to radiation at a wavelength of 450–500 nm. However, CQ also absorbs light in the region of 200–300 nm, where the molar absorption coefficient of CQ is much higher than that of the visible light region. This makes CQ an effective photoinitiator for UV curing. However, to date only a few comprehensive studies have reported on the UV photocuring behavior of this photoinitiator system.

High monomer conversions and high gel fractions are essential for many applications of dimethacrylate polymer networks, especially for dental materials, for which residual monomers may produce allergic and toxic effects. It should be pointed out that visible light curing in the dental area must progress to high monomer con-

versions in <1 min. Unfortunately, significant residual monomers always remain when a glass-forming dimethacrylate is cured at an ambient temperature. The introduction of a rubber-forming monomer into the glass-forming system could increase the extent of crosslinking.

In the present work, we report the results of an experimental study on UV-initiated polymerization of dimethacrylate oligomers with a CQ/amine initiator system, using differential scanning calorimetry (DSC). The polymerization behavior of two curing systems, one glassy and the other elastomeric, were studied and compared on the basis of polymerization rate, double bond conversion, and gel formation. The effects of reaction temperature and photoinitiator concentration on the reaction were also discussed. The radical decay profiles of photocured samples were monitored by electron spin resonance (ESR) in an attempt to elucidate the effect of crosslinking density and segmental mobility on the postcuring reaction.

EXPERIMENTAL

Materials

The dimethacrylates used in this study were ethoxylated bisphenol A dimethacrylate oligomer (supplied by Aldrich, Oakville, ON). Two dimethacrylate oligomers had similar chemical structures (Fig. 1) but different chain lengths; their nomenclatures were E-bis-A DMA-1 and E-bis-A DMA-2. The average number of oxyethyl units in the two oligomers was determined by [1]H-nuclear magnetic resonance (NMR) analysis. The glass-transition temperatures (T_g) for the oligomers and fully cured materials were measured by DSC. When T_g measurement by DSC was hampered by broadening of the transition, dynamic mechanical analysis (DMA) was intro-

Table I Properties of the Dimethacrylate Oligomers

Code Name	Average No. of Oxyethyl Unit	M_r	Viscosity (cp, 25°C)	$T_{g(monomer)}$ (°C)	$T_{g(network)}$ (°C)
E-bis-A DMA-1	4.6	566	555	−45	116
E-bis-A DMA-2	30	1684	610	−60	−40

E-bis-A, ethoxylated bisphenol A; DMA-1, dimethacrylate-1 (glass-forming system); DMA-2, dimethacrylate-2 (elastomer-forming system); T_g, glass-transition temperature.

duced as a second means for T_g values. These parameters are presented in Table I.

The photoinitiator system consisted of camphorquinone (CQ; Aldrich, Oakville, ON) and ethyl-4-dimethylaminobenzoate (DMABE; Aldrich, Oakville, NO). The chemicals were used as received. CQ and DMABE were dissolved in the oligomers in darkness and at room temperature for 5 h. For a standard formulation, 0.02 mol CQ and 0.04 mol DMABE per 1000-g monomer were used. In studying the photoinitiator concentration, the content of CQ and DMABE varied within the range of 0.005–0.04 mol and 0.01–0.08 mol per 1000-g monomer, respectively.

Measurements

The photopolymerization was carried out by DSC attached to an irradiation unit (DSC 2910, TA Instruments). The light source consisted of a 200-W medium-pressure mercury lamp and a series of optical lenses, which emitted radiation predominantly within the UV light range. Light intensity of 71 mw/cm^2 was measured at the sample level by a radiometer. Approximately 8 mg of sample mixture was placed as a thin layer in an open aluminum pan of 4.5-mm diameter, to avoid optical disturbance and temperature fluctuation during the photocuring process. To minimize the effect of dissolved oxygen on the polymerization, the DSC cell was purged with ultra-high-purity nitrogen gas for 10 min before the sample pan was exposed to radiation.

Heat flow versus time (DSC thermogram) was recorded in an isothermal mode under a nitrogen flow of 50 mL/min. The reaction heat liberated in the polymerization was directly proportional to the number of vinyl groups reacted in the system. By integrating the area under the exothermic peak, the conversion of the vinyl groups (C) or the extent of reaction could be determined according to:

$$C = \Delta H_t / \Delta H_o^{\text{theor}} \qquad (1)$$

where ΔH_t is the reaction heat evolved at time t, and $\Delta H_o^{\text{theor}}$ is the theoretical heat for complete conversion. For a methacrylate double bond, $\Delta H_o^{\text{theor}} = 13.1$ kcal/mol.[13] The rate of polymerization (R_p) is directly related to the heat flow (dH/dt) by the following equation:

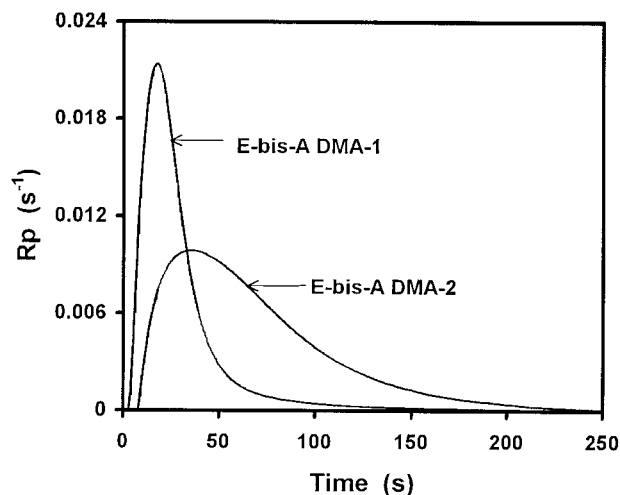$$R_p = dC/dt = (dH/dt)/\Delta H_o^{\text{theor}} \qquad (2)$$

Figure 2 Rate of polymerization profiles for E-bis-A DMA-1 and E-bis-A DMA-2 oligomers, cured at 30°C by UV light with an intensity of 71 mW/cm^2.

After photopolymerization, the cured sample was immediately placed into acetone for extraction of unreacted monomers and sol polymers. The extraction was conducted at 25°C for 72 h. The percentage of insoluble materials was defined as the gel fraction. The weight of swollen gel divided by the weight of dried gel gave the swelling ratio.

ESR measurements were carried out with a Bruker EPR spectrometer (EP072) at a modulation frequency of 100 kHz. The spectrometer was operated at 1.27-mW power. Liquid oligomer mixture was put into a glass ampoule with an inner diameter of 3 mm and 150 mm in length. After being photocured with a 75-W halogen lamp at 30°C for 40 min, the cured samples were stored in darkness for radical decay studies. The spectra were recorded at different time intervals of sample storage in order to follow the free radical decay. Radical concentrations were calculated by double integration of the ESR signal and 4-hydroxy-2,2,6,6-tetramethylpipieridine-1-oxyl (Tempo) was used as a reference for radical concentration calibration.

RESULTS AND DISCUSSION

Polymerization Rate

The rate of polymerization profiles for the two photocuring systems are shown in Figure 2. Their polymerization behavior appears similar to that

of other dimethacrylate systems reported in the literature.[9,13,14] Both systems demonstrated diffusion-controlled kinetics. In the photopolymerization of multifunctional monomers, gelation often occurs at an early stage of the reaction (normally less than a few percentage conversion). The formation of a three-dimensional (3-D) gel structure restricts the diffusion and mobility of both macroradicals and pendant double bonds, slowing down the radical termination rate. This results in a buildup of radical species, promoting the rate of polymerization, leading to autoacceleration. However, when the reaction continues, the increased crosslinking level eventually limits the monomer mobility; the propagation reaction then also becomes diffusion controlled along with radical termination. Thus, the overall polymerization rate begins to decrease. As the mobility of the reaction system is further reduced, the reactive species become trapped, and the reaction eventually stops.

The major difference between the two curing systems was that E-bis-A DMA-1 was polymerized below the T_g of poly(E-bis-A DMA-1), whereas E-bis-A DMA-2 was cured above the T_g of poly(E-bis-A DMA-2). Although two oligomers exhibited similar polymerization behaviors at ambient temperature, certain discrepancies were apparent in their polymerization rate profiles. The autoacceleration of E-bis-A DMA-1 began at an earlier stage and was more pronounced than that of E-bis-A DMA-2. The rate of polymerization decreased dramatically after propagation became diffusion controlled, and the reaction was subsequently stopped by vitrification. In contrast, the E-bis-A DMA-2 system continued to undergo reaction up to high conversions.

Figure 2 shows that E-bis-A DMA-1 polymerized much more quickly than E-bis-A DMA-2. In studying the photopolymerization kinetics of a series of bisphenol A-based dimethacrylate monomers, Cook[9] found that the polymerization rate increased with the length of spacer group between the methacrylate and the bisphenol A moiety. This dependence was attributed to the reduced mobility of pendant double bonds and to the steric shield by the close proximity of the bulky bisphenol-A as the spacer group length was shortened. The experimental results presented in Figure 2 show that the shorter spacer oligomer (E-bis-A DMA-1) had a higher rate than the longer one (E-bis-A DMA-2). However, an opposite conclusion regarding the spacer length dependence of pendant double bond mobility (and reactivity) cannot be drawn, considering the different functional group concentrations in the two systems. Although the chemical reactivity of the pendant double bonds in the E-bis-A DMA-2 system may be higher than that in E-bis-A DMA-1, its lower methacrylate group content would make E-bis-A DMA-2 to polymerize in a lower rate.

Effect of Initiator Concentration

Figure 3 (a) and (b) shows the polymerization rate (R_p) as a function of double bond conversion at various CQ concentrations for the two photocuring systems. The initial (at 1% conversion) and maximum polymerization rates increased with an increase in CQ concentration. For a photoinitiated radical polymerization, the rate is often expressed as[29]

$$R_p = -d[M]/dt = k_p/k_t^{1/2}[M](\phi\epsilon I_o[A])^{1/2} \quad (3)$$

where k_p and k_t are the propagation and termination rate constants, [M] is the molar concentration of the methacrylate group, ϕ is the initiator efficiency, ϵ is the absorption coefficient, I_o is the incident light intensity, and [A] is the photoinitiator concentration. According to eq. (1), the photopolymerization rate is proportional to $[A]^{1/2}$.

However, instead of the 0.5 power from the bimolecular termination mechanism, the exponent for E-bis-A DMA-1 was 0.4 and that of E-bis-A DMA-2 was 0.3 from Figure 4(a) and (b). It is believed that the deviation from the theoretical exponential relationship is caused by primary radical recombination, which is more likely to occur at high initiation rates (also at high light intensities). At high CQ concentrations, the recombination of primary radicals is so great that the initiator efficiency, ϕ, decreases. The reduced ϕ limits further increase of polymerization rate with CQ. Figure 4(a) and (b) clearly shows that the rate dependence on the CQ concentration deviated from the linearity at high CQ concentrations.

In a glass-forming crosslinking system, although gelation reduces the mobility of reactive species, polymerization stops by vitrification when the T_g of the polymerizing system approaches the curing temperature. This gives rise to an incomplete conversion of the functional groups. The incomplete conversion can be improved by changing the initiator concentration,
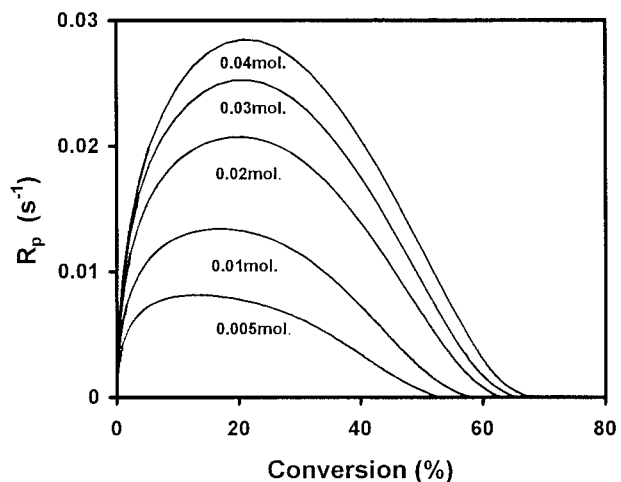
(a)
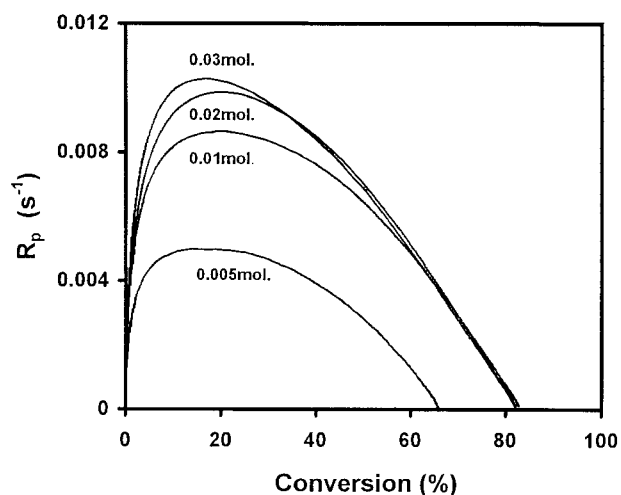
(b)

Figure 3 (a) Polymerization rate as a function of double bond conversion for E-bis-A DMA-1 at different CQ concentration, cured at 30°C by UV light with an intensity of 71 mW/cm^2. (b) Polymerization rate as a function of double bond conversion for E-bis-A DMA-2 at different CQ concentration, cured at 30°C by UV light with an intensity of 71 mW/cm^2.

which is caused by the delay in the volume shrinkage rate.[5,25,26] Because of the fast polymerization rate, the system cannot maintain its equilibrium volume. Accordingly, the delay in volume shrinkage will generate an excess free volume, enhancing the mobility of the reactive species and allowing the reaction to yield higher conversions.

Both the gel fraction and the final conversion values for the E-bis-A DMA-2 system showed a weak dependence on the initiator concentration after an initial rise at the low CQ concentration.
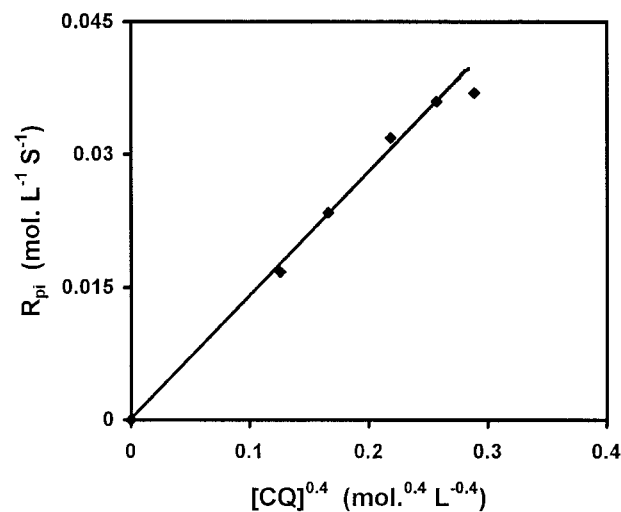
(a)

(b)

Figure 4 (a) Initial polymerization rate (at 1% conversion) vs.[CQ]$^{0.4}$ for E-bis-A DMA-1. (b) Initial polymerization rate (at 1% conversion) vs.[CQ]$^{0.3}$ for E-bis-A DMA-2.
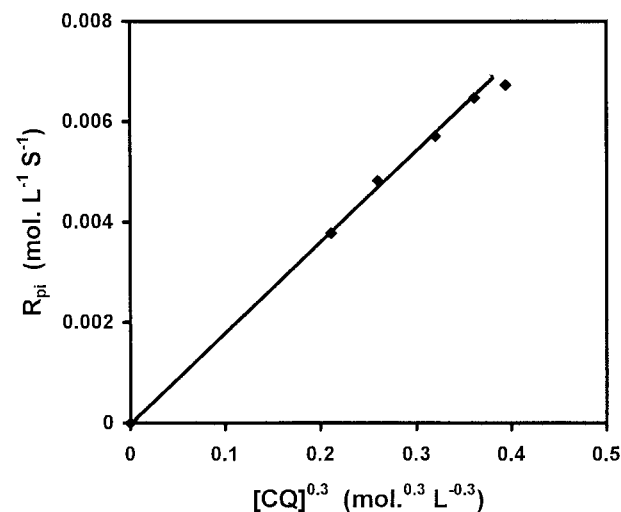
light intensity, and reaction temperature. The influence of CQ concentration on the extent of crosslinking for the two curing systems is shown in Figure 5. The final conversion and gel fraction for E-bis-A DMA-1 were found to be much lower than those for E-bis-A DMA-2 but to increase with CQ concentration. This increase in the extent of reaction with initiator concentration has been observed in many photocuring systems and is widely attributed to the free volume effect,
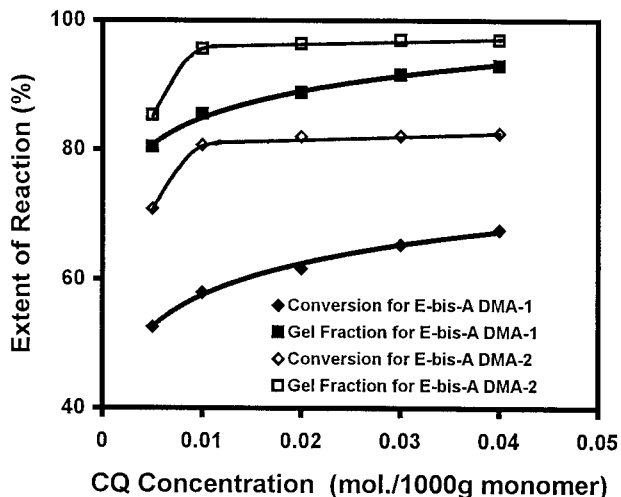
Figure 5 Dependence of reaction extent of the two curing systems on CQ concentration, cured at 30°C for 5 min with UV light intensity of 71 mW/cm^2.

This may be related to its flexible chain and good segmental mobility, which renders volume relaxation almost instantaneous. Considering the character of an elastomeric and loosely crosslinked network, a complete conversion of functional groups in E-bis-A DMA-2 should be expected. However, after photocuring, about 20% of original methacrylate groups still remained unreacted. Clearly, the glass temperature was not the limiting factor. Hence, the presence of the residual unreacted groups was attributed to the higher molecular weight (lower vinyl group content) for E-bis-A DMA-2 and the limited reaction period.

Assuming that the sol portion of the cured sample consists mainly of the unreacted monomers, the comparison between gel fraction and ultimate conversion values gives the amount of pendant double bonds in the polymer networks. These data are provided in Table II. Among the unreacted methacrylate groups, at least one-half of them were pendant double bonds attached to the

network. Whereas the total amount of unreacted vinyl groups decreased as CQ concentration increased, the fraction of pendant double bonds increased, indicating that the reactivity of the monomeric double bonds was higher than that of the pendant double bonds in the later stage of reaction. This is not surprising, as the mobility of the monomers will be greater than that of the pendant double bonds. It should also be noted that despite the high percentage of the pendant double bonds trapped in the network, the absolute level of these double bonds in the E-bis-A DMA-2 cured sample was much lower than in the E-bis-A DMA-1 system.

Effect of Curing Temperature

For crosslinking polymerizations, the radical termination is always diffusion-controlled. Particularly in the late stage, radicals are terminated by a reaction diffusion mechanism.[9,13,33] An increase in the curing temperature should improve the diffusion of the reactive species, as well as increasing the propagation and termination rate constants, k_p and k_t. Polymerization rate profiles at various curing temperatures for both the E-bis-A DMA-1 and E-bis-A DMA-2 systems are shown in Figure 6(a) and (b). The dependence of the peak polymerization rate on curing temperature is given in Figure 7. Interestingly, the two oligomers exhibited completely different behavior as a function of temperature. Whereas the polymerization rate of E-bis-A DMA-2 increased with an increase in curing temperature, consistent with other reported dimethacrylate systems,[9,13,14] the reaction rate of E-bis-A DMA-1 decreased with temperature.

Two major factors determine the temperature–rate relationship. High temperatures always favor the activation of a chemical reaction, but they also reduce viscosity, which enhances the mobility of reacting species, lessening the "gel effect."

Table II   Percentage of Pendant Double Bonds Relative to Total Amount of Unreacted Functional Groups

Sample	0.005 mol CQ	0.01 mol CQ	0.02 mol CQ	0.03 mol CQ	0.04 mol CQ
E-bis-A DMA-1	58.6	65.6	70.8	75.7	78.3
E-bis-A DMA-2	50.5	77.2	79.8	82.2	83.7

E-bis-A, ethoxylated bisphenol A; DMA-1, dimethylacrylate-1 (glass-forming system); DMA-2, dimethylacrylate-2 (elastomer-forming system); CQ, camphorquinone.

The polymerization of the E-bis-A DMA-1 system became diffusion controlled immediately upon exposure to UV radiation when cured at 30°C because of the elevated viscosity. A remarkable autoacceleration occurred as result of the restriction in radical mobility, which was caused by an increase in viscosity and network formation. The reaction quickly reached its maximum rate of 0.0214 s^{-1} at a conversion of 17.5%, [Fig. 6(a)]. Increasing the temperature decreased the maxi-
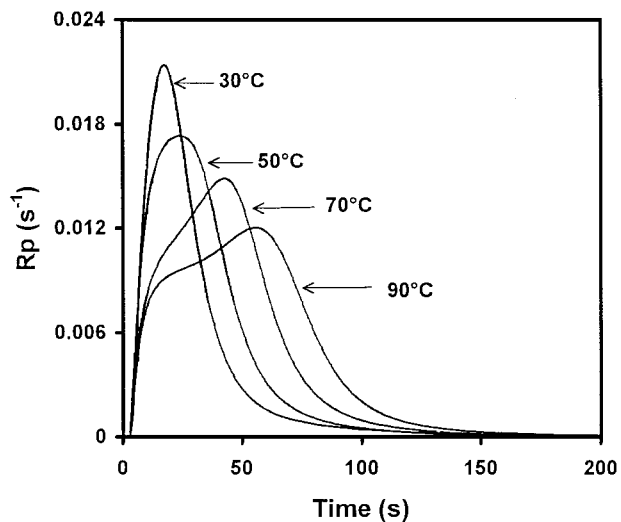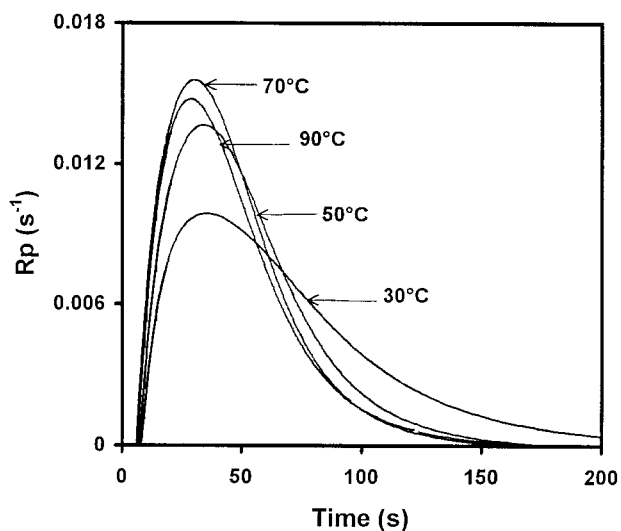
Figure 7 Dependence of maximum polymerization rate on curing temperature, CQ = 0.02 mol/1000-g resin, DMABE/CQ = 2.

mum rate: 0.0174 s^{-1} at 24% (50°C), 0.0149 s^{-1} at 43.4% (70°C), and 0.0092 s^{-1} at 56.1% (90°C), respectively.

There are two peaks in E-bis-A DMA-1 rate curves at elevated temperatures [Fig. 6(a)]. Similar behavior was also observed by other investigators for an ethylene glycol dimethacrylate/methyl methacrylate system.[28,31] The latter work suggested that the second peak in the later stage of the polymerization was related to microgel formation. Microgels are highly crosslinked domains with extremely restricted segmental mobility. They are often formed by intramolecular reaction of pendant double bonds. This heterogeneous characteristic has a significant effect on the mechanical and optical properties of crosslinked materials.

As a result of the microgel formation, some pendant double bonds are shielded inside the microgel domains. The accessibility and thus reactivity of these pendant double bonds towards the macroradicals is lower than that of the monomeric double bonds.[28,32] Therefore, as the polymerization proceeds, the shielded pendant double bonds remain almost unreacted. When these shielded pendant double bonds regain their reactivity in the propagation under certain conditions (e.g., high curing temperature), the reaction will experience an autoacceleration. In this case, the reaction inside the microgel region becomes dominant over intermolecular crosslinking, resulting in the appearance of the second peak in the polymerization rate curve.

(a)

(b)

Figure 6 (a) Polymerization rate profiles for E-bis-A DMA-1 at various curing temperatures. (b) Polymerization rate profiles for E-bis-A DMA-2 at various curing temperatures, cured with UV light intensity of 71 mW/cm^2 (CQ = 0.02 mol/1000-g resin, DMABE/CQ = 2).

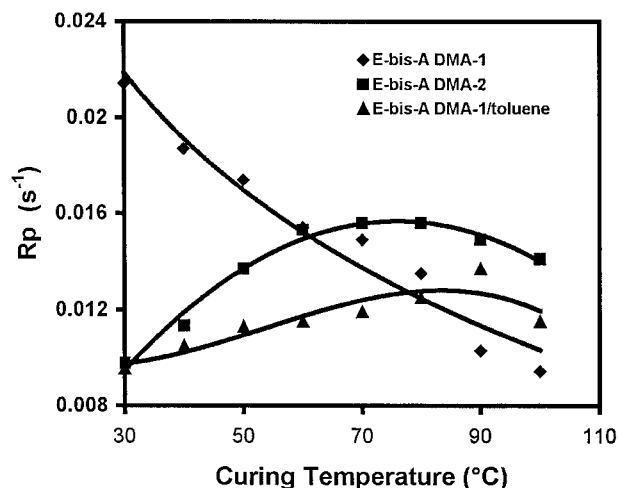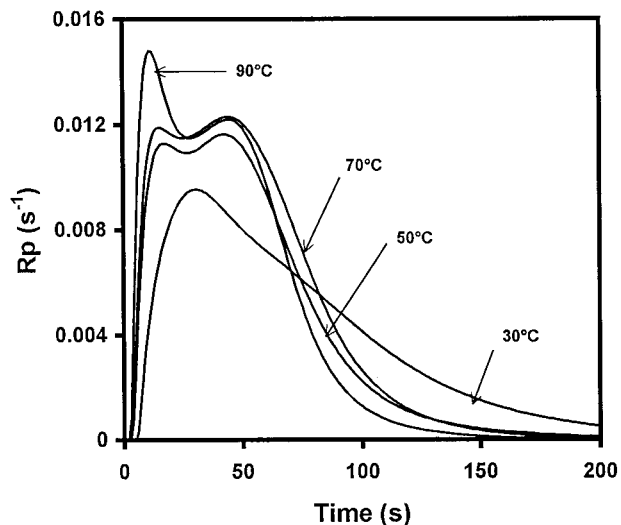**Figure 8** Polymerization rate profiles for E-bis-A DMA-1/toluene system at various curing temperatures, same curing conditions as in Figure 6.

To support the explanation of the influence of viscosity on the polymerization rate in the E-bis-A DMA-1 curing system, a solution of E-bis-A DMA-1 in 20% (wt) toluene was photopolymerized under the same reaction conditions as was carried out with the pure monomers. Figure 8 shows the polymerization rate profiles. Because of the dilution effect of toluene, the viscosity of the reaction system was significantly reduced, allowing the polymerization to proceed in a less restricted environment. In this case, the diffusion controlled reaction was delayed and the "gel effect" was partially suppressed. Hence, the reaction was kinetically controlled in the early stage and the peak polymerization rate increased with curing temperature as seen in Figure 7. As well, the two rate peaks for E-bis-A DMA-1 appeared at lower curing temperatures in solution than in bulk (Fig. 6a vs Fig. 8). This behavior is readily explained by the increased mobility (and thus reactivity) of the pendant double bonds, which permitted the more rapid motion of microgel at lower temperature.

Figure 9 shows the temperature dependence of the final conversion for the two systems. The conversion in the E-bis-A DMA-1 system increased with curing temperature, while the extent of reaction for the E-bis-A DMA-2 system remained almost unchanged. It is widely accepted[9,14,28] that the conversion increase is mainly due to the increased mobility of the reactive species. Since increasing temperature lifts the limitation of the T_g

on the polymerization, the reaction system can further polymerize and reach a higher level of conversion before the network T_g reaches the curing temperature.

Radical Decay

ESR can provide further information regarding the nature of the trapped radicals within each of the polymer networks, and the effect of radical decay on the post reaction for the two curing systems. ESR measurement was conducted immediately after undergoing photocuring at 30°C. Both samples showed the same ESR features, with a 9-line hyperfine structure (Fig. 10). This spectrum is typical of methacrylate radicals residing in the solid phase.[32] The E-bis-A DMA-1 showed a very strong ESR signal, indicating that a large number of radicals were trapped inside the polymer network. These radicals are still slowly reactive toward vinyl groups and are responsible for the postcuring or dark reaction. After calibrating the spectrum with a Tempo/toluene solution, the calculated radical concentration of E-bis-A DMA-1 was found to be equal to 2.7 $\times$ 10^{-4} mol/L. As a result of the loosely crosslinked network and high segmental mobility for E-bis-A DMA-2, the number of trapped radicals was found to be much lower (4.8×10^{-6} mol/L). It should be mentioned that even in the E-bis-A DMA-2 network, the concentration of trapped rad-
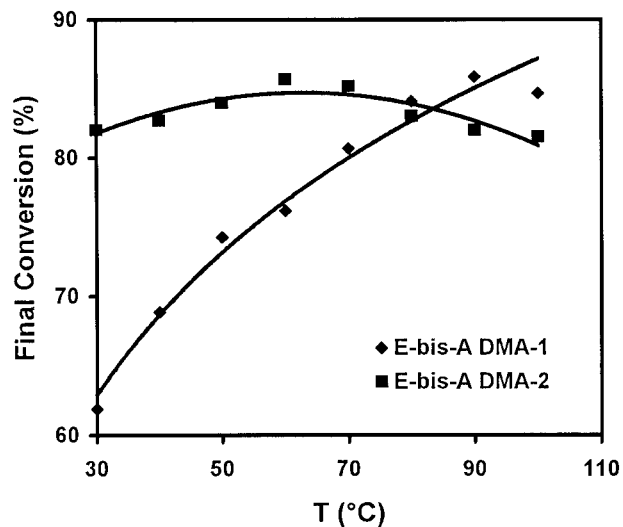

Figure 9 Dependence of final conversion on curing temperature, CQ = 0.02 mol/1000-g resin, DMABE/CQ = 2.

icals is still much higher than that found in conventional linear polymerization systems.

ESR peak intensities for both cured samples decreased, but with different rates during sample storage under dark conditions. The radical decay curves were biexponential, indicating that two radical populations were involved in the process. This further rationalized the previous discussion on the existence of microgels. The environment in which the radicals reside is believed to govern the radical activity. For the free radicals residing in the microgel region the active centers were shielded by the densely crosslinked network, and therefore had long lifetimes in the decay.

The decay rate constants and the half-life times for the two radical types are listed in Table III. Radical decay in crosslinked polymer networks has been the subject of extensive studies.[30,33–35] It has been found that the decay rate of trapped radicals mainly depends on the crosslinking density, storage temperature, and atmosphere. Obviously, the T_g of the network and the chain flexibility also strongly affect the radical decay. In the E-bis-A DMA-2 cured sample, the flexible chains accelerate the segmental mobility in the network and result in more than a 10-fold increase in radical decay. Increasing storage temperature could also improve the segmental mobility of the network and thus favor the radical decay. In this study, the trapped radicals completely disappeared after only 30 min in storage at 90 °C, whereas radicals remained for 3 h when stored at 60 °C.
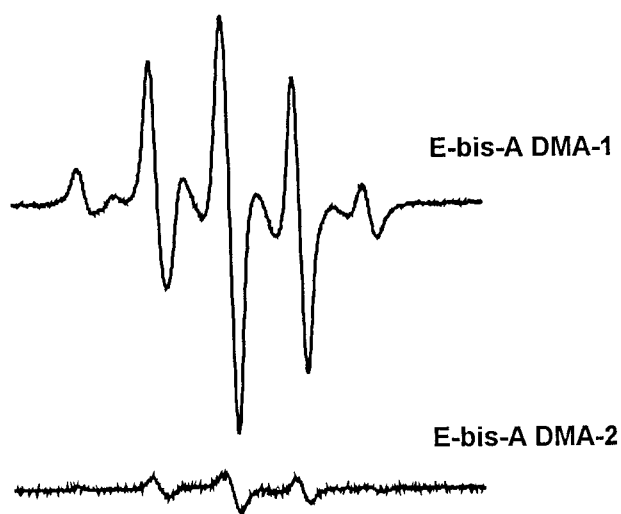

Figure 10 Electron spin resonance spectrum of the photocured samples.

Table III Radical Decay Rate Constants and Half-Lives for Samples Stored at 30°C

Sample	k_1 (h^{-1})	$t_{1/2}$ (h)	k_2 (h^{-1})	$t_{1/2}$ (h)
E-bis-A DMA-1	0.312	2.224	0.043	16.012
E-bis-A DMA-2	3.060	0.227	0.355	1.953

E-bis-A, ethoxylated bisphenol A; DMA-1, dimethylacrylate-1 (glass-forming system); DMA-2, dimethylacrylate-2 (elastomer-forming system).

Radicals can be consumed either by bimolecular termination via propagating reaction with the surrounding unreacted vinyl groups or by terminating with atmospheric oxygen that has diffused into the matrix, or both.[11,27,30,34,35] To determine which of these reactions was dominant in the studied systems, the gel fraction and swelling ratio in acetone was measured immediately after photocuring and was then measured again after the samples were stored at different temperatures for a defined period of time until trapped radicals disappeared. These data are given in Table IV.

At a low storage temperature, although a large number of trapped radicals existed in the E-bis-A DMA-1 network, they were firmly bound by the rigid segments. Most of the radicals were consumed by penetration of oxygen into the materials. Only a small fraction of the radicals could react with unreacted vinyl groups, giving rise to a small increase in the gel fraction. By contrast, the flexible chains of E-bis-A DMA-2 accelerated the segmental mobility of the network. The trapped radicals had more opportunity to react with the unreacted vinyl groups. Therefore, an increase in the gel fraction was observed. At an elevated storage temperature, the segmental mobility was improved, especially in E-bis-A DMA-1 networks. The radicals propagate relatively well with unreacted monomers.

CONCLUSIONS

The following conclusions are based on the experimental results:

1. E-bis-A DMA-1 and E-bis-A DMA-2 UV photocuring systems showed clear differences in their polymerization profiles. The radical termination in E-bis-A DMA-1

Table IV   Variation in Crosslinking Extent After Radical Decay at Different Storage Temperatures

Sample	Immediately After Photocuring at 30°C		After Storage at 30°C for 1 wk		After Storage at 60°C for 4 h		After Storage at 90°C for 1 h	
	Gel (%)	Swelling Ratio	Gel (%)	Swelling Ratio	Gel (%)	Swelling Ratio	Gel (%)	Swelling Ratio
E-bis-A DMA-1	86.7	0.2724	88.2	0.2616	92.2	0.2266	95.3	0.2084
E-bis-A DMA-2	91.3	0.4243	96.8	0.4084	97.0	0.4060	96.8	0.4023

E-bis-A, ethoxylated bisphenol A; DMA-1, DMA-2, dimethacrylate-1 (glass-forming system), dimethylacrylate-2 (elastomer-forming system).

became diffusion controlled immediately upon exposure to UV radiation, giving rise to a fast increase then followed by a quick drop in the rate of polymerization. E-bis-A DMA-2 polymerized at a much slower rate because of its lower vinyl group concentration and the rubbery nature of the resulting network.

2. The two oligomers exhibited opposite character in the temperature dependence of polymerization rates. While the polymerization rate of E-bis-A DMA-2 increased with an increase in curing temperature, the reaction rate of E-bis-A DMA-1 decreased with temperature because the reduced viscosity and improved segmental mobility postponed the autoacceleration.

3. Polymerization rates in both curing systems increased with initiator concentration and the exponents in the relationship between the rates and CQ concentration were <0.5. The final conversion and gel fraction in the E-bis-A DMA-1 system increased with an increase in CQ concentration and curing temperature. However, the extent of reaction for E-bis-A DMA-2 was showed to be insensitive to the two factors.

4. A large number of radicals were trapped inside the networks. These radicals were responsible for the increase in conversion in the postcuring stage. High storage temperatures and flexible segments favored the reaction between trapped radicals and unreacted vinyl groups.

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