

# Synthesis and Photopolymerization of 2-(Acryloyloxy)ethyl Piperidine-1-Carboxylate and 2-(Acryloyloxy)ethyl Morpholone-4-Carboxylate

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**ABSTRACT:** Two low-viscosity monomers, 2-(acryloyloxy)ethyl piperidine-1-carboxylate (AEPC II) and 2-(acryloyloxy)ethyl morpholone-4-carboxylate (AEMC), were synthesized with a non-isocyanate route. The photopolymerization kinetics was monitored by real-time infrared spectroscopy with a horizontal sample holder. The results indicated that AEPC II and AEMC had high ultraviolet curing rates and final double-bond conversions, which could reach 90 and 95%, respectively. The glass-transition temperatures of AEPC II/urethane acrylate

resin (1/4 w/w), AEMC/urethane acrylate resin (1/4 w/w), and isobornyl acrylate/urethane acrylate resin (1/4 w/w) mixtures were 37.5, 45.6, and 57°C, respectively. The crosslink density of the AEMC/urethane acrylate resin (1/4 w/w) mixture was lower than that of the isobornyl acrylate/urethane acrylate resin (1/4 w/w) mixture. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 119: 1978–1985, 2011

**Key words:** kinetics (polym.); photopolymerization

## INTRODUCTION

Photopolymerization offers multiple advantages, including spatial and temporal control, solventless polymerization, energy savings, and resistance to swelling in a wide variety of solvents. Hence, it has been used extensively in a range of applications, including stereolithography, coatings, biomaterials, contact lenses, and adhesives.<sup>1–13</sup> Reactive diluents are very important components in photopolymerization systems because they influence the viscosity, adhesion, toughness, flexibility, abrasion resistance, pigment wetting, and cure speed.<sup>14</sup> Urethane acrylates find applications in areas such as coatings, adhesives, stereolithography, and dental restorative materials.<sup>15–17</sup>

Urethane acrylates are usually synthesized through the reaction of isocyanates with hydroxyalkyl acrylates. However, isocyanates have a pungent odor and are harmful to the environment. On the other hand, the hydrogen bonds in traditional urethane acrylates may increase the viscosity of resins and limit the applications of urethane acrylates as reactive

diluents, especially in areas requiring low-viscosity curing formulations, such as spray inks and nonsolvent coatings.<sup>18–22</sup>

Polyurethanes can be prepared with non-isocyanate methods. Thus, oligomers terminated with five-membered cyclic carbonate groups are reacted with diamines. The reaction products additionally contain hydroxyl groups in the  $\beta$  position.<sup>23–28</sup> Another non-isocyanate synthetic method leading to urethane species involves the reaction of vinyl carbonates with amines.<sup>29</sup> Five-membered ethylene carbonate, for ecological and economic reasons (ethylene carbonate is easily available from ethylene oxide and carbon dioxide), seems to be a very attractive monomer and reagent.<sup>30,31</sup>

In this study, reactive low-viscosity urethane acrylate diluents, 2-(acryloyloxy)ethyl piperidine-1-carboxylate (AEPC II) and 2-(acryloyloxy)ethyl morpholone-4-carboxylate (AEMC), were synthesized through the reaction of five-membered ethylene carbonate and secondary amines. This route without isocyanates would contribute to health and the environment. Meanwhile, there was no  $-\text{NH}$  in the synthesized urethane acrylates, so their viscosities were reduced dramatically, and they could be used as reactive diluents in ultraviolet (UV) technology. The photopolymerization kinetics was measured with real-time infrared (RTIR) spectroscopy. The glass-transition temperature was recorded with a dynamic mechanical analyzer.

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## EXPERIMENTAL

## Materials and instruments

Piperidine and morpholine (Tiantai Chemical Co., Tianjin, China), ethylene carbonate (J. T. Baker Chemical Co., Phillipsburg, NJ), acryloyl chloride (SanshengTengda Science and Technology Co., Beijing, China), triethylamine (YongDa Chemical Agent Development Center, Tianjin, China), isobornyl acrylate (IBOA), and a urethane acrylate resin (CN964, Sartomer Co., Exton, PA) were used as received. The photoinitiators 2-hydroxy-2-methyl-1-phenyl-1-propanone (1173), 2-isopropylthioxanthone (ITX), benzophenone (BP), 2-methyl-1[4-(methylthio)phenyl]-2-morpholinopropan-1-one (907), and ethyl-4-dimethylaminobenzoate (EDAB) were donated by Runtec Chemistry (Changzhou, China) and used without any purification. The structures of the photoinitiators and IBOA are shown in Figure 1.

<sup>1</sup>H-NMR spectra were (Germany) recorded on a Bruker AV600 unity spectrometer operated at 600 MHz with tetramethylsilane as the internal reference and with deuterated chloroform (CDCl<sub>3</sub>) as the solvent.

The shear viscosities of the monomers were measured at a shear rate of 2028 s<sup>-1</sup>, and the mixtures of the monomers and oligomer (CN964) were measured at a shear rate of 344 s<sup>-1</sup> with a rotational viscometer (NDJ-79, Shanghai Jichang Geology Instrument Co., Ltd., Shanghai, China) equipped with coaxial cylinders.

RTIR spectroscopy was performed on a Nicolet 5700 instrument (Nicolet Instrument, Thermo Co., United States). A series of RTIR spectra was used to determine the conversion of double bonds, and about three spectra per second were taken. RTIR samples were prepared by the sandwiching of a drop of the mixture (including the monomer, photoinitiator, and oligomer) between two pieces of KBr crystals. This sample geometry ensured uniform irradiation of the polymerization system and reduced oxygen permeation. Upon irradiation with a UV spot light source (model 100 UV, Rolence, Taiwan, China), the reduction of the =C–H absorption band accurately reflected the extent of the polymerization. The wavelength of the irradiation light was 300–500 nm. The light intensity on the surface of the samples varied from 5 to 70 mW/cm<sup>2</sup> and was detected with a light radiometer (UV-A, Beijing Normal University, Beijing, China). For each sample, the series RTIR was repeated three times. Because the IR absorbance was proportional to the monomer concentration, conversion–time profiles were directly obtained from the recorded curves. The degree of conversion (DC) can be expressed as follows:

$$DC = \frac{A_0 - A_t}{A_0} \times 100\% \quad (1)$$

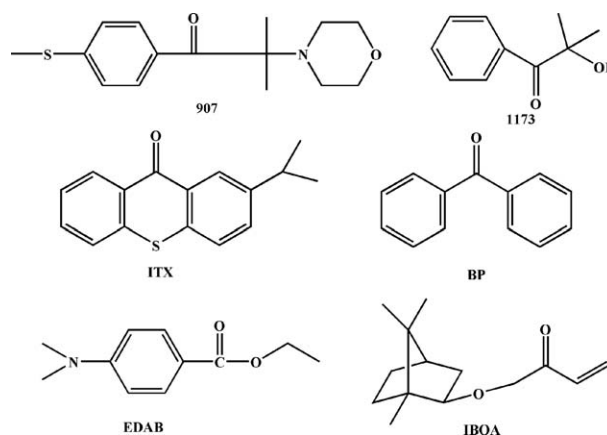


Figure 1 Structures of the photoinitiators and IBOA.

where  $A_0$  is the initial absorbance around 810 cm<sup>-1</sup> and  $A_t$  is the absorbance value at irradiation time  $t$ . The polymerization rate ( $R_p$ ) was determined from the slope of the initial linear portion of the conversion–time curves as follows:

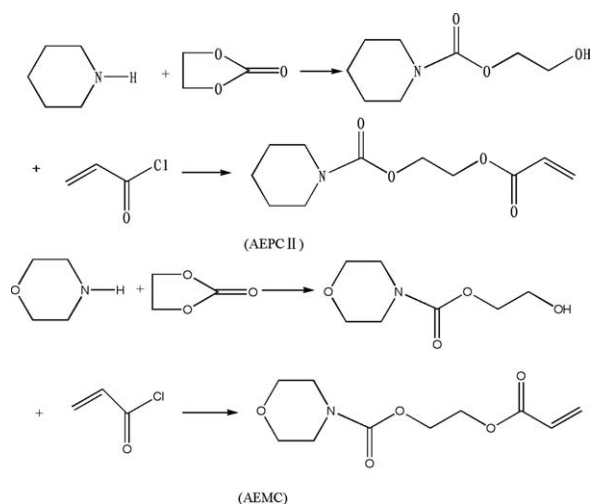
$$\frac{R_p}{[M]_0} = \frac{d(DC)}{dt} \quad (2)$$

where  $[M]_0$  is the initial concentration of C=C double bonds (mol<sup>-1</sup>).

A dynamic mechanical analyzer (DMTA-V, Rheometric, United States) was used to perform the dynamic mechanical measurements. Samples were photocured in a mold made from two glass slides and spacers approximately 1.2 mm thick with dimensions of 7 mm × 35 mm and were recorded on a Rheometric DMTA-V at 1 Hz and 0.005% strain over a temperature range of –100 to +100°C with a ramping rate of 5°C/min in a tensile rectangular mode. The storage modulus and the loss tangent (i.e., the ratio of the loss modulus to the storage modulus) were recorded as functions of temperature, and the glass-transition temperature was taken to be the maximum of the tangent–temperature curve.

## Synthesis of AEPC II and AEMC

Piperidine (34.0 g, 0.4 mol), ethylene carbonate (33.46 g, 0.38 mol), and 70 mL of toluene were added to a 250-mL, three-necked flask. Under magnetic stirring, the temperature of the mixture was slowly increased to 75°C. When the peak of cyclic –C=O at 1805.0 cm<sup>-1</sup> in the Fourier transform infrared spectrum disappeared, the first step reaction was finished. Then, the resultant mixture was cooled to room temperature. Subsequently, 42.50 g of triethylamine (0.42 mol) was added to the mixture, and 38.00 g of acryloyl chloride (0.42 mol) was



**Figure 2** Synthesis processes of AEPC II and AEMC.

dropped slowly into the three-necked flask with a mechanical stirrer. An ice-water bath was used to cool the reaction to 0°C to keep the reaction going smoothly. After the acryloyl chloride was added, the temperature of the reaction mixture gradually rose to room temperature, and the reaction lasted 1–2 h. The reaction mixtures were filtered to remove the solid, were washed with 1 mol/L hydrochloric acid, a saturated NaHCO<sub>3</sub> solution, and distilled water three times, and were dried overnight with anhydrous sodium sulfate. The liquid phases were evaporated with rotary evaporation. A slightly yellow liquid was obtained. The crude products were purified by column chromatography (200–300-mesh silica gel) with hexane/ethyl acetate (3/5 v/v) as the eluent. The yield was 51%, and the purity was 96%. The final products were identified with <sup>1</sup>H-NMR.

When morpholine was used to replace the piperidine, with the same reaction procedure, AEMC was obtained. The yield was 56%, and the purity was 93%. The synthesis processes are shown in Figure 2.

<sup>1</sup>H-NMR of AEPC II (500 MHz, CDCl<sub>3</sub>, ppm, δ): 1.48 (m, 4H, –NH–CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–), 1.54 (m, 2H, –CH<sub>2</sub>–CH<sub>2</sub>–CH<sub>2</sub>–), 3.36 (m, 4H, –CH<sub>2</sub>–CH<sub>2</sub>–NH–), 4.27 (m, 2H, –O–CH<sub>2</sub>–CH<sub>2</sub>–O–), 4.33 (m, 2H, –O–CH<sub>2</sub>–CH<sub>2</sub>–O–), 5.8 (m, 1H, CH<sub>2</sub>=CH–), 6.1 (m, 1H, CH<sub>2</sub>=CH–), 6.4 (m, 1H, CH<sub>2</sub>=CH–).

<sup>1</sup>H-NMR of AEMC (500 MHz, CDCl<sub>3</sub>, ppm, δ): 3.45 (m, 4H, –CH<sub>2</sub>–CH<sub>2</sub>–NH–), 3.64 (m, 4H, –O–CH<sub>2</sub>–CH<sub>2</sub>–), 4.33 (m, 2H, –O–CH<sub>2</sub>–CH<sub>2</sub>–O–), 4.37 (m, 2H, –O–CH<sub>2</sub>–CH<sub>2</sub>–O–), 5.81 (m, 1H,

CH<sub>2</sub>=CH–), 6.1 (m, 1H, CH<sub>2</sub>=CH–), 6.4 (m, 1H, CH<sub>2</sub>=CH–).

## RESULTS AND DISCUSSION

### Viscosity

The viscosity of the curing formulations is an important parameter that influences the flow ability, air-release rate, curing rate of photopolymerization, and performances of cured films. The viscosities of oligomer CN 964, AEPC II, AEMC, IBOA, and the mixtures of the monomers and oligomer are shown in Table I. The table indicates that the viscosities of AEPC II and AEMC were lower than that of IBOA, and when AEPC II and AEMC acted as diluent mixes with CN964, the ability to reduce the viscosity of AEPC II and AEMC was better than that of IBOA.

### Photopolymerization of the monomers

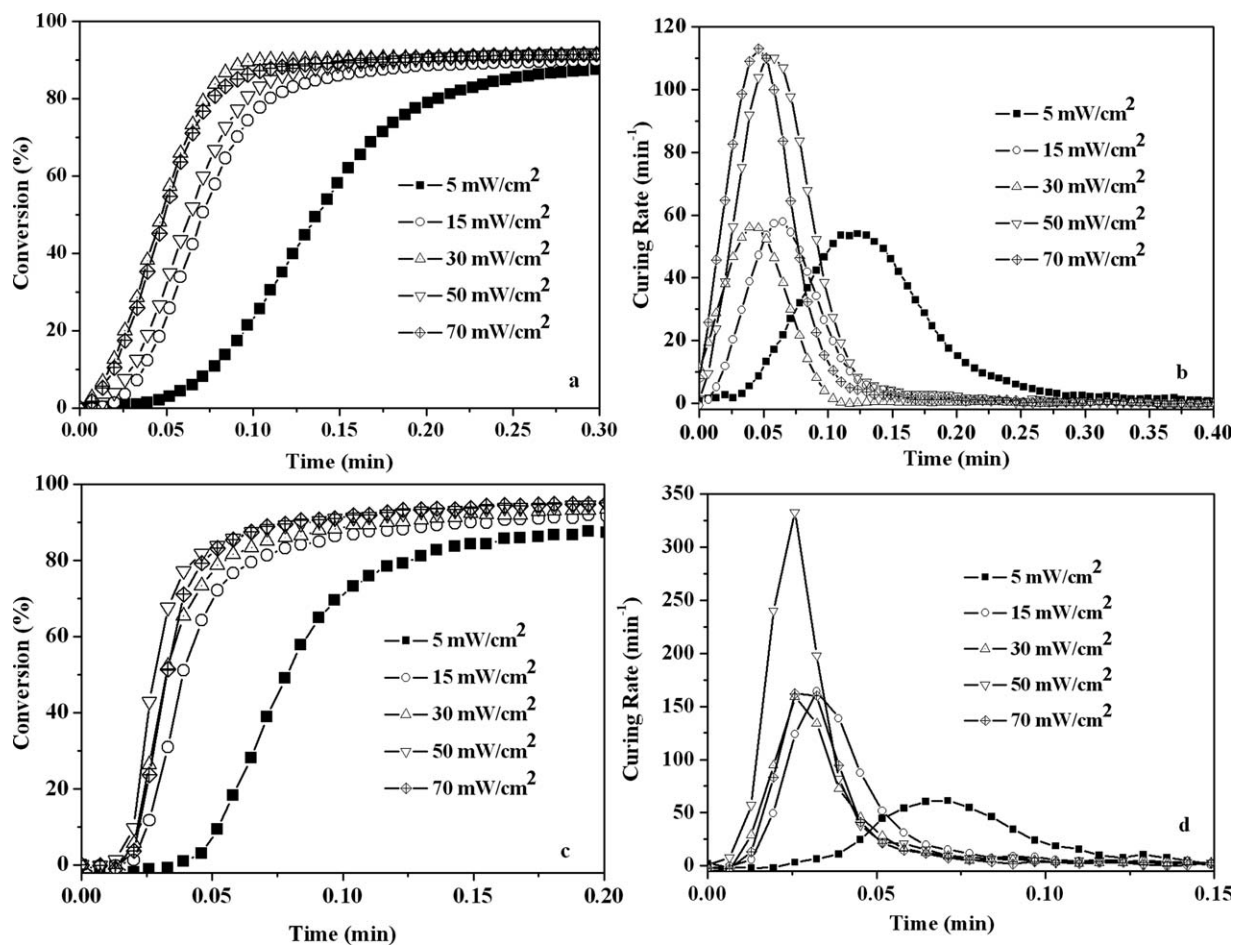
For photopolymerization, upon light irradiation, the photoinitiator absorbs the light energy to induce a series of photochemical and photophysical processes and finally to form reactive species. Therefore, the light intensity, photoinitiator concentration, and photoinitiator structure have great effects on the polymerization process.<sup>32</sup>

Figure 3 shows the effect of the light intensity on the conversion and curing rate of AEPC II and AEMC when 0.5 wt % 1173 was used as the initiator. Table II summarizes some key results. The table indicates that the light intensity had no obvious influence on the final conversion of AEPC II and AEMC. However, the time to reach the highest curing rate was shortened as the light intensity increased. For AEPC II, the highest curing rate of 5–30 mW/cm<sup>2</sup> was almost the same (ca. 55 min<sup>–1</sup>), but the times to reach the maximum polymerization rates of 5, 15, and 30 mW/cm<sup>2</sup> were different. The time to reach the maximum polymerization was reduced with the light intensity increasing. When the light intensity reached 50 mW/cm<sup>2</sup>, the increase in the intensity led to the higher maximum polymerization rate.

However, for AEMC, the highest curing rates were 61, 164, 159, 333, and 162 min<sup>–1</sup>, respectively, when the light intensity increased from 5 to 70 mW/cm<sup>2</sup>. A high light intensity induced more photons, which could produce more free radicals. The free

**TABLE I**  
Viscosity of the Monomers and Monomer–Oligomer Mixtures

	CN964	AEPC II	AEMC	IBOA	AEPC II/ CN964 (1/4)	AEMC/ CN964 (1/4)	IBOA/ CN964 (1/4)
Viscosity at 25°C (cP)	3.4 × 10 <sup>6</sup>	5.0	6.5	9	2.5 × 10 <sup>5</sup>	7.0 × 10 <sup>4</sup>	3.4 × 10 <sup>5</sup>



**Figure 3** Effect of the light intensity on the photopolymerization of the monomers: (a) the AEPC II conversion versus time, (b) the AEPC II curing rate versus time, (c) the AEMC conversion versus time, and (d) the AEMC curing rate versus time ([1173] = 0.5 wt %).

radicals reacted with the monomer to initiate the polymerization, so increasing the light intensity could lead to a high curing rate. However, when the light intensity was high enough, increasing the light intensity decreased the rate. The reason was that when the concentration of free radicals was too high, they reacted with one another, and the termination reaction became dominant.<sup>32–34</sup> On the other hand, the formation of primary radicals became fast with the light intensity increasing; then, these

primary radicals reacted with macroradicals, and the polymerization was retarded by the primary termination.

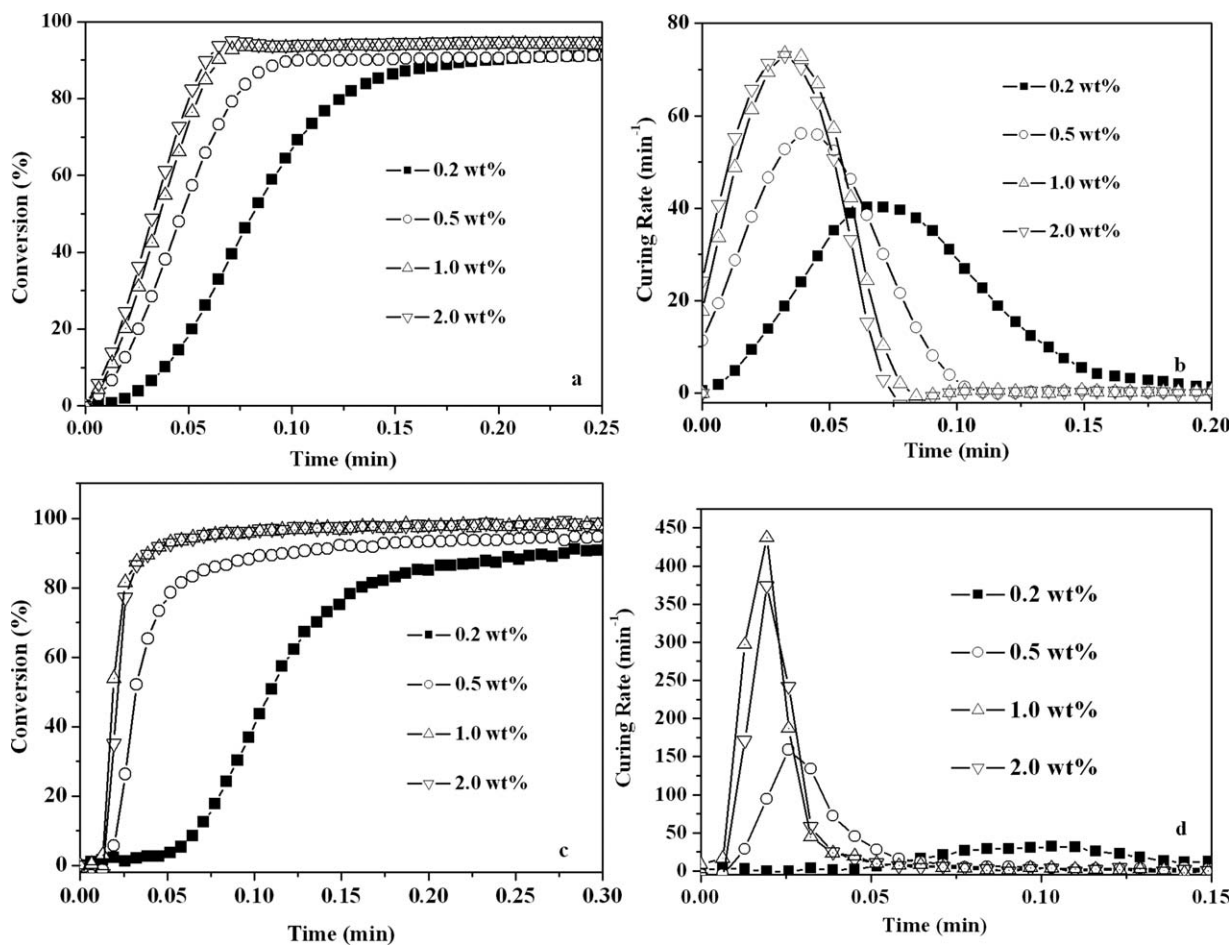
The concentration of the photoinitiator is another important factor influencing the final conversion and curing rate. Normally, at low initiator concentrations, the photopolymerization rate tends to increase as the amount of the photoinitiator increases. Increasing the photoinitiator concentration does not always lead to an increase in the cure rate.

**TABLE II**  
Summary of the Kinetic Results for the Polymerization of AEPC II and AEMC with Various Light Intensities

Light intensity (mW/cm <sup>2</sup> )	Monomer	Time to reach R <sub>p,max</sub> (min)	R <sub>p,max</sub> (min <sup>-1</sup> )	Final conversion (%)	Monomer	Time to reach R <sub>p,max</sub> (min)	R <sub>p,max</sub> (min <sup>-1</sup> )	Final conversion (%)
5	AEPC II	0.124	54.5	91.2	AEMC	0.071	61.4	96.0
15		0.094	57.3	90.8		0.032	164.0	97.7
30		0.056	56.5	91.0		0.026	159.0	97.4
50		0.075	110.6	92.4		0.026	333.0	98.2
70		0.051	113.4	91.9		0.026	162.0	98.2

R<sub>p,max</sub> = maximum polymerization rate.





**Figure 4** Effect of the 1173 concentration on the photopolymerization of the monomers: (a) the AEPC II conversion versus time, (b) the AEPC II curing rate versus time, (c) the AEMC conversion versus time, and (d) the AEMC curing rate versus time (light intensity = 30 mW/cm<sup>2</sup>).

Figure 4 shows the results of the photopolymerization of AEPC II and AEMC initiated by 1173 when the light intensity was 30 mW/cm<sup>2</sup>. Some key results are shown in Table III. For AEPC II, the final conversion increased gradually from 92.8 to 95.3% when the 1173 concentration increased from 0.2 to 2 wt % [Fig. 4(a)]. Figure 4(b) shows that the highest curing rate increased from 40 to 73 min<sup>-1</sup> as the 1173 concentration increased from 0.2 to 1 wt %, and the time to reach the highest curing rate was shortened obviously (from 0.071 to 0.045 min). Formulations of 1 and 2 wt % 1173 had the same highest cur-

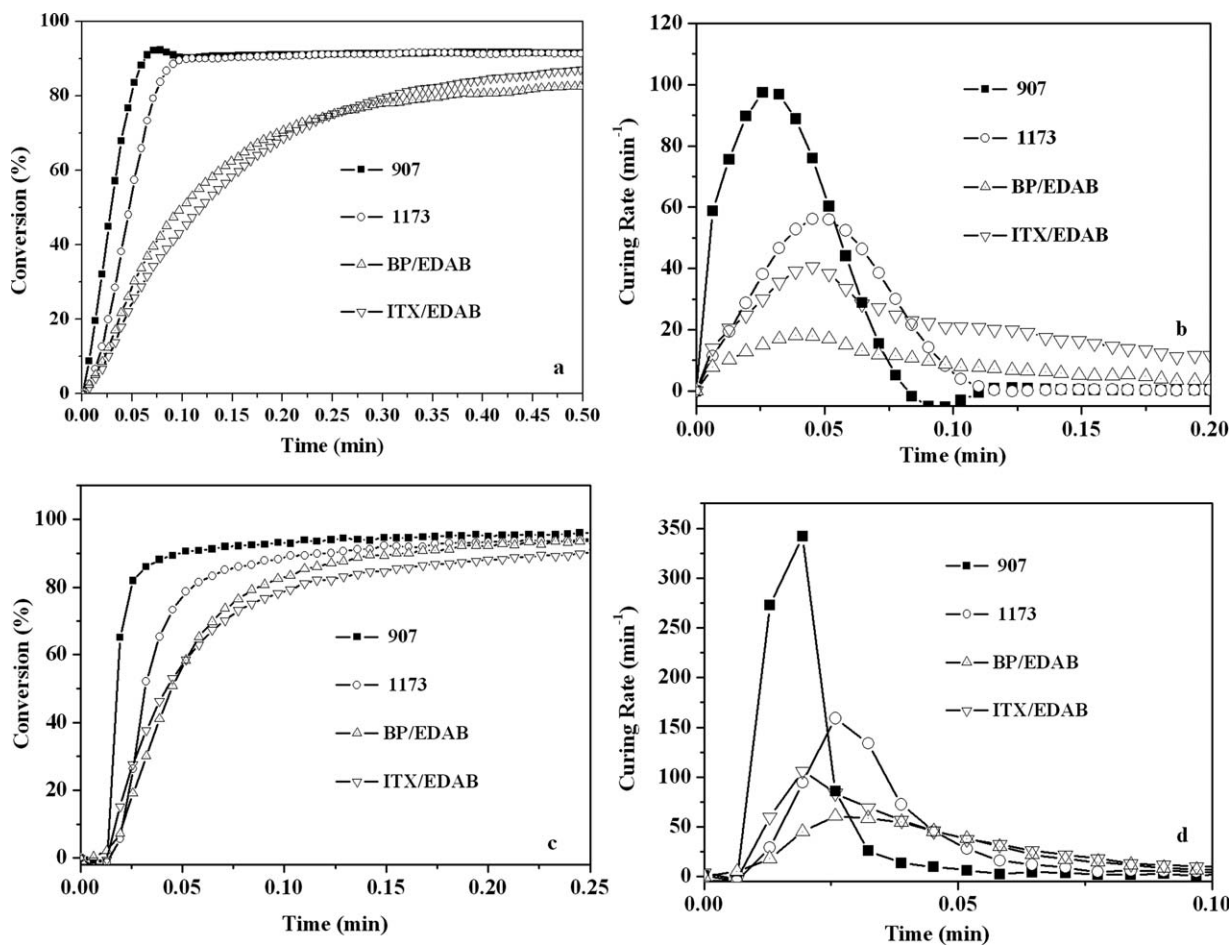
ing rate, and the time to reach the highest rate was almost the same as well. For AEMC, the final conversion increased gradually and could reach about 100% in only 0.3 min when the 1173 concentration was 1 or 2 wt %. For 1173 concentrations of 0.2, 0.5, 1, and 2 wt %, the highest curing rates were 31, 342, 437, and 374 min<sup>-1</sup>, respectively.

When the photoinitiator concentration was very low, the number of radicals produced was low in comparison with the number of reactive sites available. As the initiator concentration increased, the number of radicals produced per unit of volume

**TABLE III**  
Summary of the Kinetic Results for the Polymerization of AEPC II and AEMC with Various Initiator Concentrations

Photoinitiator (wt %)	Monomer	Time to reach $R_{p,max}$ (min)	$R_{p,max}$ (min <sup>-1</sup> )	Final conversion (%)	Monomer	Time to reach $R_{p,max}$ (min)	$R_{p,max}$ (min <sup>-1</sup> )	Final conversion (%)
0.2	AEPC II	0.071	40.2	92.8	AEMC	0.103	31.7	97.2
0.5	AEPC II	0.052	56.1	91.0	AEMC	0.019	342	97.4
1.0	AEPC II	0.045	73.4	94.4	AEMC	0.019	437	98.9
2.0	AEPC II	0.045	73.0	95.2	AEMC	0.019	374	99.5

$R_{p,max}$  = maximum polymerization rate.



**Figure 5** Effects of the different kinds of photoinitiators on the photopolymerization of the monomers: (a) the AEPC II conversion versus time, (b) the AEPC II curing rate versus time, (c) the AEMC conversion versus time, and (d) the AEMC curing rate versus time (initiator concentration = 0.5 wt %, light intensity = 30 mW/cm<sup>2</sup>).

increased, and the cure rate increased as well. Above a certain concentration, there was an excess of initiating radicals in comparison with the reactive sites available, the produced free radicals quenched one another, and the rate of curing remained stable. The reaction could even be retarded if the termination step became dominant because of a high concentration of free radicals.<sup>34–36</sup>

Radical photoinitiators are generally divided into two classes according to the process by which the initiating radicals are formed. Compounds that undergo unimolecular bond cleavage upon irradiation are termed type I photoinitiators. If the excited-state photoinitiator interacts with a second molecule (a coinitiator) to generate radicals in a bimolecular reaction, the initiating system is termed a type II photoinitiator. The effects of different photoinitiators on the photocuring of urethane acrylate are shown in Figure 5. Four photoinitiator systems were investigated. The concentration of the photoinitiator was 0.5 wt %, and the light intensity was 30 mW/cm<sup>2</sup>; EDAB was used as a coinitiator for BP and ITX ([BP] = [EDAB] = [ITX]). 1173 and 907 were the

type I photoinitiators. BP/EDAB and ITX/EDAB were the type II photoinitiator systems.

The results in Figure 5(a,b) indicate that for AEPC II, the final conversions with 907, 1173, BP/EDAB, and ITX/EDAB as the initiators were 93, 91.6, 85.4, and 88.5%, respectively, and the highest curing rates were 97.4, 56.1, 18.1, and 40.6 min<sup>-1</sup>. Figure 5(c,d) shows that for AEMC, the final conversion was almost the same (ca. 98.5%), and the highest curing rates were 342, 159, 60.6, and 106 min<sup>-1</sup>, respectively. The results in Figure 5 indicate that both AEPC and AEMC had the highest curing rate when 907 was used as the initiator, whereas when BP/EDAB was used as the initiator, the curing rate was the lowest. Unimolecular type I initiators are inherently more efficient than type II initiators in a coinitiator/photoinitiation system because no bimolecular processes, which are usually rate-determining, are involved.<sup>37</sup>

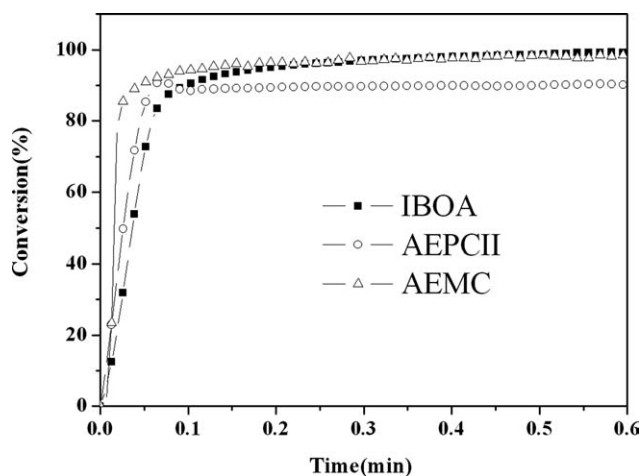
Thioxanones react in the same way as BP with tertiary amines. Essential differences with the former compounds are the absorption characteristics, which exhibit maxima in the range of 380–420 nm. The

extinction coefficient of ITX was higher than that of BP, and it could absorb the irradiation light efficiently. Therefore, the curing rates of the ITX/EDAB systems were higher than those of the BP/EDAB systems.<sup>38</sup>

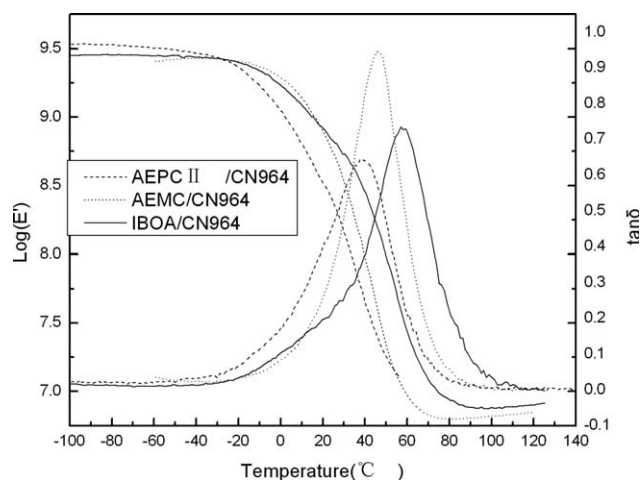
Figure 6 presents the photopolymerization behaviors of the two synthesized monomers (AEMC and AEPC II) and the common monomer IBOA. The double-bond conversions and polymerization rates of the synthesized monomers (AEPC II and AEMC) were similar to those of the commonly used reactive diluent IBOA. Meanwhile, the polymerization rate of AEMC was higher than that of AEPC II. This might have been due to the strong hydrogen-donor character.<sup>39–42</sup> It would enhance chain-transfer reactions and make these compounds act as crosslinking agents. Moreover, the increase in the viscosity due to the buildup of a three-dimensional polymer network would favor propagation over termination and thus would be a key factor in the increase in the monomer reactivity. Indeed, the termination rate constant for monoacrylates containing heterocyclic structures was found to be 5 times lower than that of conventional monoacrylate monomers.

#### Dynamic mechanical analysis (DMA)

The mechanical properties of the photopolymers were measured by DMA.<sup>43–46</sup> Figure 7 shows typical profiles recorded by DMA for UV-cured samples through the monitoring of the variation of the storage modulus and the tensile loss factor with an increase in the temperature. The glass-transition temperatures and storage moduli of the photocured samples of AEPC II/CN964 and AEMC/CN964 were lower than those of IBOA/CN964 (37.5 and



**Figure 6** Double-bond conversion versus the irradiation time for IBOA, AEPC II, and AEMC ( $[907] = 0.3$  wt %, light intensity =  $30$  mW/cm<sup>2</sup>).



**Figure 7** Influence of the different monomers on the elastic modulus ( $E'$ ) and loss tangent ( $\tan \delta$ ) profile recorded by DMA.

45.6 versus  $57^\circ\text{C}$ ). The rigid structure of IBOA may be the major reason.

The behavior of the storage modulus as a function of temperature provides clues regarding the nature of the polymer network being evaluated. Specifically, the modulus in the rubbery plateau region, when such a region was present, was used to estimate the molar number of elastically effective network chains per cubic centimeter ( $V_e$ )<sup>47</sup>:

$$V_e = E'/3RT \quad (3)$$

where  $E'$  is the storage modulus in the rubbery plateau,  $R$  is the gas constant, and  $T$  is the temperature (K). When the temperature was  $94^\circ\text{C}$ ,  $V_e$  of AEMC/CN964 was about  $0.71$  mmol/cm<sup>3</sup>, whereas for IBOA/CN964, it was about  $0.82$  mmol/cm<sup>3</sup>. However, the sample of AEPC II/CN964 ruptured before the rubbery plateau region, so we could not determine  $V_e$ . The higher crosslink density made the chains more restricted, resulting in chain motion being possible only at higher temperatures,<sup>48</sup> and hard, less flexible, even brittle films, which usually had poor adhesion with most substrates because of the high crosslink density, were produced.

#### CONCLUSIONS

The monomers AEPC II and AEMC were synthesized through a non-isocyanate route. Because of the absence of hydrogen bonds, they had low viscosities and a good ability to reduce the viscosity of the oligomer. As the initiator concentration and the light intensity increased, the curing rate increased, and the final double-bond conversions of AEPC II and AEMC could reach about 90 and 95%, respectively.

The AEPC II/CN964 (1/4 w/w) and AEMC/CN964 (1/4 w/w) mixtures had lower viscosities, glass-transition temperatures, and storage moduli than IBOA/CN964 (1/4 w/w). The crosslink density of AEMC/CN964 was lower than that of IBOA/CN964 (1/4 w/w).

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