

# Synthesis and Kinetic Studies of UV-Curable Urethane-Acrylates

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**ABSTRACT:** The UV-curable urethane-acrylates based on 2-hydroxyethyl methacrylate (HEMA)-terminated polyurethane (PU) for lithographic and coating applications are investigated in this study. Series of PU prepolymers were made from 4,4-diphenyl methane diisocyanate (MDI), poly(propylene oxide) glycol (PPG 400), poly(butylene adipate)glycol (PBA 500), or poly(tetramethylene oxide) glycol (PTMO 1000) and are terminated with HEMA. The 2,2-azobisisobutyronitrile (AIBN) was used as a UV-initiator under air atmosphere. The curing kinetics of HEMA-terminated PU film were studied. The curing analysis, using FTIR and reaction kinetics, indicate the reaction rate equation

correlates well with the film thickness  $[T]$ , initiator concentration  $[I]$ , unreacted double bond concentration  $[C=C]$ , and exposed energy  $[E]$  of the reaction system. The kinetic rate equation for the UV-curable reaction can be written as

$$-\frac{d[C=C]}{dt} = k[C=C][I]^{0.5}[E]^{0.5}[T]^{-1}$$

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**Key words:** FTIR; UV-curable; kinetics; AIBN initiator; monomers; urethane-acrylate

## INTRODUCTION

Polyurethanes (PU) are characteristic for their toughness, abrasion resistance, and flexibility and have been widely used for making elastomers, foams, and coatings<sup>1,2</sup> or used as biomaterials.<sup>3</sup> The block copolymer structure of the PU is made from the polycondensation reaction of the PU precursor formulation components containing isocyanate groups and hydroxy groups. Different properties of PU can be easily tailored by the variation of soft/hard segments in its structure and have been extensively discussed in the literature.<sup>4</sup> As an extension to the PU applications, an ultraviolet (UV) curable urethane formulation has recently attracted much more attention due to the advantages of reaction speed and the environmentally friendly nature. For example, Hamouly and Fayoumy<sup>5</sup> investigated the photo-crosslinking reactions of unsaturated polyether-polyurethane copolymers for wood-coating applications. Cook<sup>6</sup> studied the photo-polymerization kinetics of several commercial urethane dimethacrylate resins used in dental impression ma-

terials. Reddy et al.<sup>7</sup> and many other researchers investigated the crosslinking reaction of unsaturated acrylates.<sup>8–10</sup>

An UV curable urethane-acrylate formulation usually contains reactive urethane oligomers, reactive diluents, and photo-initiators. In this study, several urethane-acrylates were prepared, using *N,N'*-azobisisobutyronitrile (AIBN) as the initiator. The symmetric cleavage of AIBN into two radicals initiates the free radical reaction of the acrylate resin.<sup>11</sup> The air-insensitivity of the AIBN radicals makes the reaction easier to proceed in ambient atmosphere. The effects of film thickness, initiator concentration, curing time, and exposed energy of various urethane-acrylates on the curing kinetics were investigated.

## EXPERIMENTAL

### Materials

The polyols, poly(butylene adipate)glycol with MW.500 (PBA 500), poly(propylene oxide) glycol (PPG 400), and poly(tetramethylene oxide) glycol (PTMG 1000), were purchased from Acros Company and were dried under vacuum before use. 2-Hydroxyethyl methacrylate (HEMA), dibutyltin dilaurate (T-12), 4,4-diphenyl methane diisocyanate (MDI), trimethylolpropane (TMP), and AIBN were purchased from Acros Company and were used without further purification. Tetrahydrofuran (THF) was dried over sodium benzophenone ketyl and distilled prior to use.

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**TABLE I**  
Different Kinds of PU Prepolymers Used in This Study

Composition	Shrinking Ratio (%)
A (HEMA) <sub>2</sub> -MDI	7.8
B (HEMA-MDI) <sub>2</sub> -PPG 400	5.7
C (HEMA-MDI) <sub>2</sub> -PTMG 1000	6.2
D (HEMA-MDI) <sub>2</sub> -PBA 500	5.8
E (HEMA-MDI) <sub>3</sub> -TMP	12.4
F (HEMA-MDI- PPG 400-MDI) <sub>3</sub> -TMP	9.4
G (HEMA-MDI- PTMG 1000-MDI) <sub>3</sub> -TMP	8.9
H (HEMA-MDI- PBA 500-MDI) <sub>3</sub> -TMP	9.3

### Synthesis of HEMA-terminated PU prepolymer

The composition and shrinking ratios of HEMA-terminated PU prepolymers are listed in Table I. Alternative additions of hydroxy group (polyol or TMP) and isocyanate group (MDI) were used to prepare the prepolymers. The condensation reactions were monitored by following the NCO concentration at  $2,270\text{ cm}^{-1}$  with FTIR spectrometry. The reaction was nearly completed when the NCO concentration reduced to almost constant quantity, which is shown as an unchanged peak intensity at  $2,270\text{ cm}^{-1}$  in the FTIR spectrum. In example F of Table I, 2N of MDI and 1N of PPG 400 was first dissolved in dried THF at  $60^\circ\text{C}$ . Trace amount of catalyst T-12 (0.1 phr) was added to facilitate the reaction between MDI and PPG 400. Until about a half of NCO concentration in the mixture reacted with hydroxyl groups, another quantity of 1N of HEMA was added to the reaction mixture to finish the residual NCO groups. The reaction was continuously monitored by observing the IR absorption of the NCO group at  $2,270\text{ cm}^{-1}$  with a FTIR spectrometer

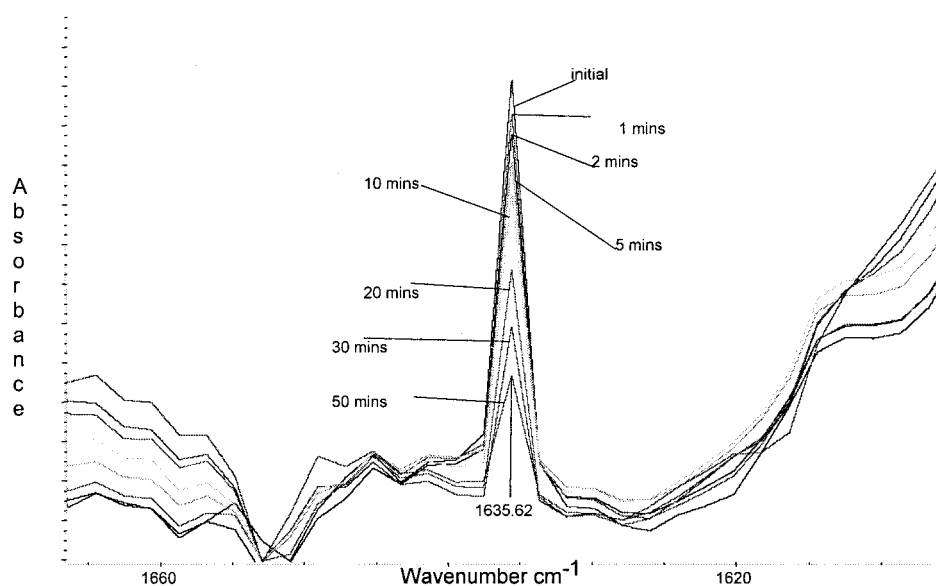
until its completion. After the reaction was completed, as shown by the disappearance of the characteristic IR absorption of the NCO group, the reaction mixture was quenched over 1.5 h to the room temperature for further use.

### Methods of measurement

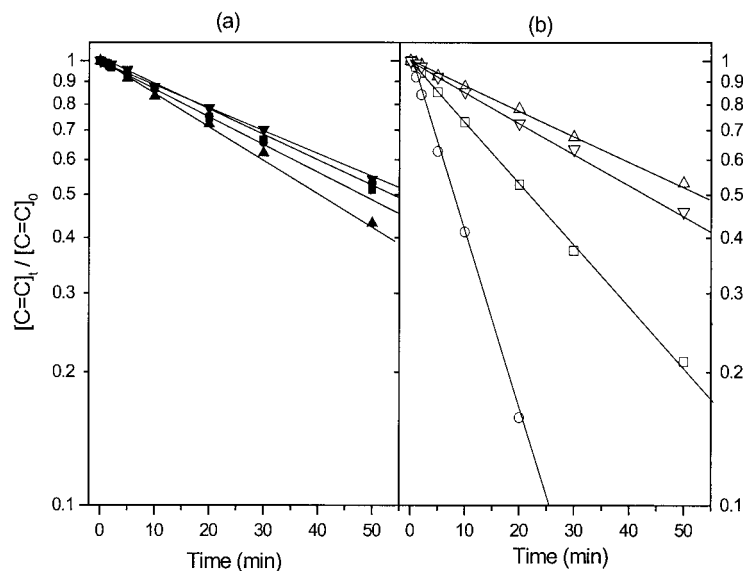
Prepolymers were coated on double-sided polished wafer by a spin coater and were then baked under a vacuum chamber at room temperature for 4 h to remove residual solvent. Oriel mercury lamp Model 68810 was used for the UV-curing of the urethane-acrylates reactions. Analyses of the functional groups of NCO of the urethane-acrylates were carried out on a Bio-Rad FTS-40.

## RESULTS AND DISCUSSION

The quantity of the unreacted double bond remaining in the urethane-acrylate was calculated from the intensity of the FTIR absorption peak. The ratio of absorption of C=C at a peak of  $1,635\text{ cm}^{-1}$  to the absorption of aromatic C-H at a peak of  $840\text{ cm}^{-1}$  was defined as the degree of reaction.<sup>12</sup> Figure 1 shows the time course of the UV-curing reaction, by following the decrease in IR absorption of the C=C bond at a peak of  $1,635\text{ cm}^{-1}$  as irradiation time increased. The reaction rate appeared to be dependent on the exposed UV-energy [E], irradiation time, the film thickness [T], and the concentration of initiator [I]. To analyze the effects of the four important parameters, [C=C], [E], [I] and [T], on UV-curing reaction rate, the four steps proceeded as follows below.



**Figure 1** IR absorption spectrum of UV-cured urethane-acrylates.



**Figure 2** Time course of the decrease of double bond of urethane-acrylates. An UV light of 200 W and AIBN of 1 phr were used for curing the reactions. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.

### Effect of reaction rate

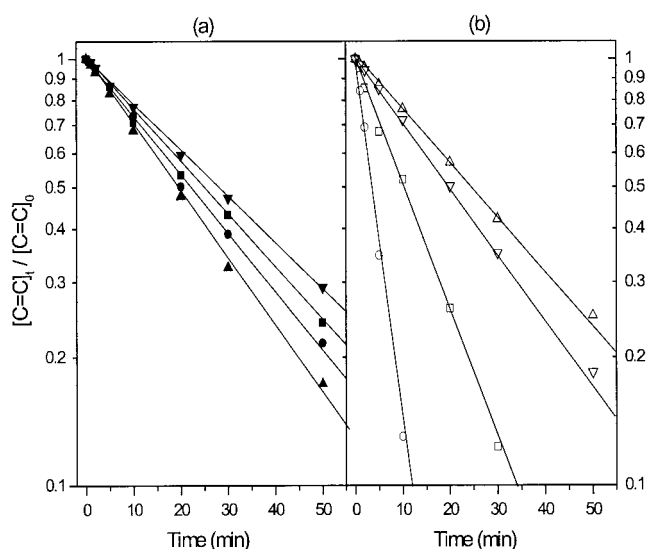
Time courses of the conversion of the unreacted double bond in the urethane-acrylates are shown in Figures 2 and 3. The reaction rate was also proportional to the quantity of residual double bond C=C. The rate of reaction can therefore be represented as follows

$$\begin{aligned} -\frac{d[\text{C}=\text{C}]}{dt} &= k[\text{C}=\text{C}][I]^a[E]^b[T]^c \\ &= k_1[\text{C}=\text{C}] \end{aligned} \quad (1)$$

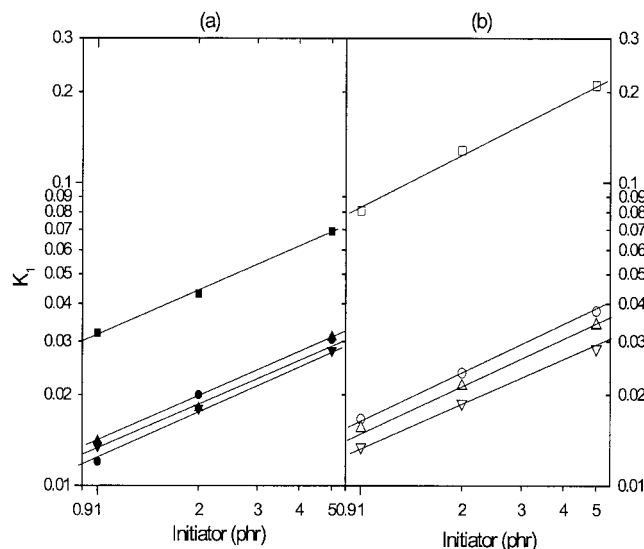
or

$$-\frac{d[\text{C}=\text{C}]}{dt} = k_1[\text{C}=\text{C}] \quad (2)$$

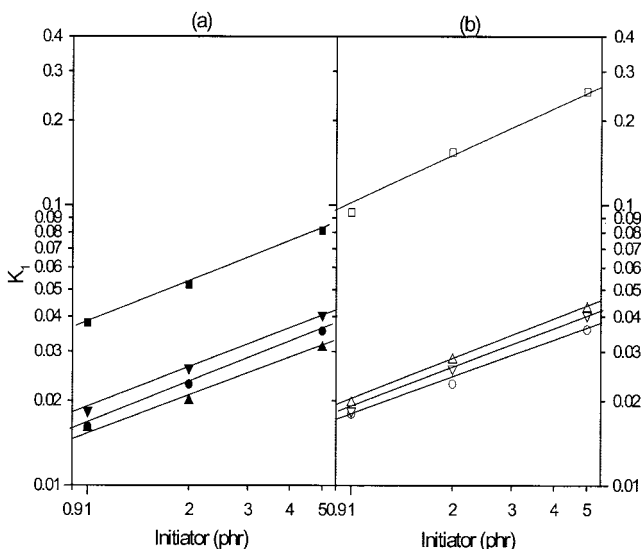
where  $k_1$  represents the slope of the reaction lines as shown in Figure 2, when the other three parameters  $[I]$ ,  $[E]$ , and  $[T]$  were kept constant.



**Figure 3** Time course of the decrease of double bond of urethane-acrylates. An UV light of 200 W and AIBN of 5 phr were used for curing the reactions. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.



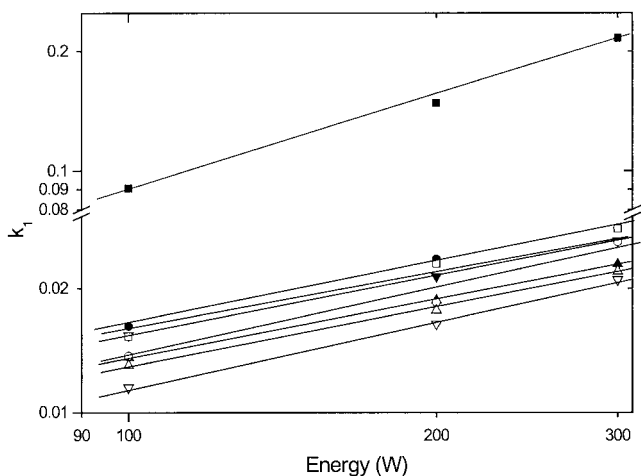
**Figure 4** Log-log plot of kinetic constant  $k_1$  versus concentration of AIBN initiator  $[I]$  for the reaction of urethane-acrylates. An UV light of 200 W was used. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.



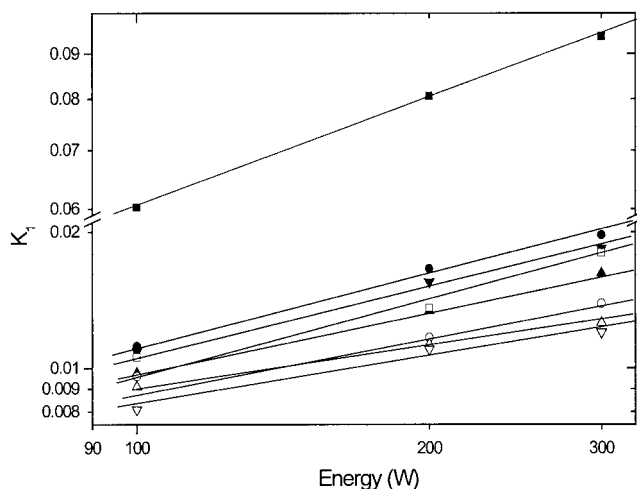
**Figure 5** Log-log plot of kinetic constant  $k_1$  versus concentration of initiator  $[I]$  for the reaction of urethane-acrylates. An UV light of 300 W was used. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.

**Effect of initiator concentration**

Various amounts of initiator used in a series of the urethane-acrylates reaction systems, and the values of  $k_1$  obtained from eq. (2) are plotted against the concentrations of the initiator. The  $k_1$  value obtained were shown in Figures 4 and 5. The regression curves are found to be parallel for all urethane-acrylates and has a slope of 0.5. The linearity of all sets of data indicated that the decreasing rate of the double bonds for the



**Figure 6** Log-log plot of kinetic constant  $k_1$  versus exposure energy for the reaction of urethane-acrylates. AIBN (1 phr) was used as initiator. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.



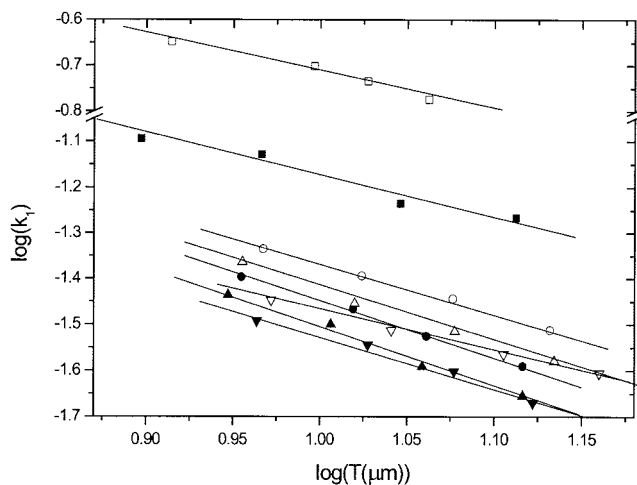
**Figure 7** Log-log plot of kinetic constant  $k_1$  versus exposure energy for the reaction of urethane-acrylates. AIBN (2 phr) was used as initiator. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.

urethane-acrylate reaction is proportional to the square root of the concentration of initiator, i.e.,

$$-\frac{d[C=C]}{dt} \propto [I]^{0.5}$$

**Effect of exposed UV energy**

The effect of the exposed UV energy on the reaction rate constant ( $k_1$ ) were shown in Figures 6 and 7. The regression curves are found to be parallel for all urethane-acrylate reactions and have a slope about 0.5. The linearity of all sets of data indicated that the decreasing rate of the double bond C=C for the ure-



**Figure 8** Log-log plot of reaction rate constant  $k_1$  versus film thickness. ■, A; ●, B; ▲, C; ▼, D; □, E; ○, F; △, G; ▽, H are the urethane-acrylate systems shown in Table 1.

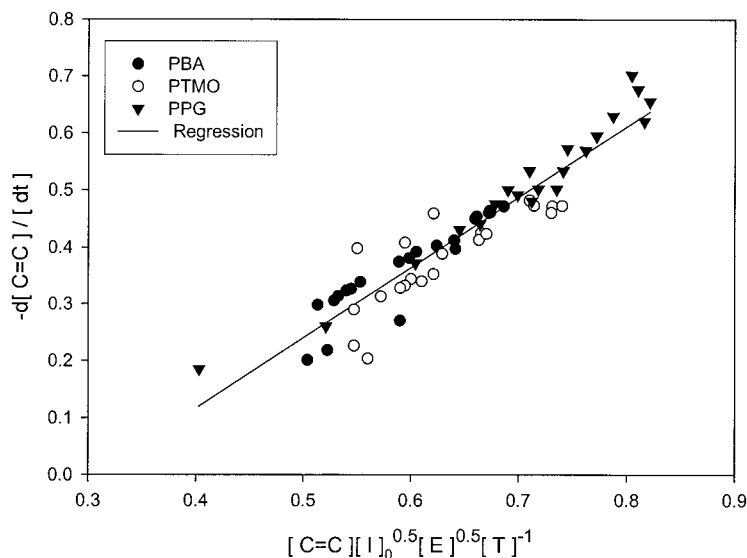


Figure 9 Plot of overall reaction rate dependence for the urethane-acrylates systems studied.

thane-acrylate reactions is proportional to the square root of the exposure energy, i.e.,

$$-\frac{d[\text{C}=\text{C}]}{dt} \propto [E]^{0.5}$$

#### Effect of film thickness

The films with different thickness were prepared by using various spin-coating rates. The effect of the film thickness on the reaction rate is shown in Figure 8. The linearity of all sets of data indicated that the decreasing rate of the double bonds for the urethane-acrylate reactions is proportional to the film thickness, i.e.

$$-\frac{d[\text{C}=\text{C}]}{dt} \propto [T]^{-1}$$

From the results obtained in the above sections, we can conclude that the rate equation is as follows

$$-\frac{d[\text{C}=\text{C}]}{dt} = k[\text{C}=\text{C}][I]^{0.5}[E]^{0.5}[T]^{-1}$$

where  $k$  relates to the intrinsic property of the urethane-acrylates. Fitting all the data of this study to eq. (1), the rate constant  $k$  was found to have a value of 1.23. The data fitting is shown in Figure 9, and the correlation coefficient is 0.95. The reaction rate of the double bond C=C was mainly contributed from those double bonds located in both ends of the urethane-acrylate molecules.

#### CONCLUSION

Various HEMA-terminated PU were synthesized. The double bonds of the urethane-acrylates can undergo crosslinking reaction upon UV exposure. The disappearing rate of the double bond in the urethane-acrylates was found to follow the rate equation:  $\frac{d[\text{C}=\text{C}]}{dt} = k[\text{C}=\text{C}] \times [I]^{0.5}[E]^{0.5}[T]^{-1}$ . The kind of polyol in urethane-acrylates has a negligible effect on the reaction rate.

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