

Synthesis and Photopolymerization Kinetics of Multifunctional Aliphatic Urethane Acrylates Containing the Tertiary Amine Group

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ABSTRACT: Two multifunctional aliphatic urethane acrylates, based on isophorone diisocyanate (IPDI), β -hydroxyethyl acrylate (HEA), and synthetic multifunctional hydroxyl compounds, were synthesized by classical condensation reaction. FTIR was used to monitor the process of the reaction. The photopolymerization kinetics of the urethane acrylates with different photoinitiators was studied by real-time infrared spectroscopy. The results indicated that compared with the commercial hexa-func-

tional urethane acrylate CN 9010, the synthetic multifunctional urethane acrylates could be initiated by benzophenone more efficiently without the addition of any coinitiators because they have tertiary amine structures. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 896–900, 2009

Key words: multifunctional urethane acrylate; tertiary amine; FTIR; kinetics; photopolymerization

INTRODUCTION

Photopolymerization has become a well-accepted technology in the fields of coatings on various materials, adhesives, printing inks, photoresists, and biomaterials because of its high curing speed, energy conservation, pollution reduction, and cost-effectiveness.^{1–5} In photopolymerization, a typical formulation consists of a mixture of a photoinitiator, a functionalized oligomer, and a low-viscosity monomer serving as a reactive diluent to meet the formulation viscosity requirements.⁶

It is well known that urethane acrylate resins are often used as oligomers to produce three-dimensional networks, which give the final product high performance in terms of hardness, flexibility, and abrasive resistance. This behavior is in keeping with the material requirements for various industrial sectors such as automobile, aeronautic, composite devices, and coating.^{7,8}

Tertiary amines are necessary during the photopolymerization of conventional urethane acrylates initiated by benzophenone (BP). However, low-molecular-weight tertiary amines have some drawbacks, such as odor and migration in the postcured materials. If the tertiary amine group is introduced

into urethane acrylates, it is expected to be attached with postcured materials through the polymerization of acrylate double bond during the curing process, which limits the tendency to migrate.

In this research, two multifunctional aliphatic urethane acrylates containing the tertiary amine group were synthesized, and then the photopolymerization kinetics of the urethane acrylates was studied in different conditions by real-time infrared spectroscopy (RTIR). The results showed that the synthetic multifunctional urethane acrylates could be initiated by BP more efficiently than the commercial urethane acrylate CN 9010 with or without the addition of coinitiators because of the existence of the tertiary amine group in them.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) was obtained from JiangSu Sanmu Group (Yixing, China). Dibutyltin dilaurate (DBTDL) was purchased from Beijing Chemical (Beijing, China). Ethoxylated trimethylolpropane triacrylate (SR 454), ethoxylated pentaerythritol tetraacrylate (SR 494), tripropylene glycol diacrylate (SR 306), and hexa-functional aliphatic urethane acrylate (CN 9010) were obtained from Sartomer Company (Warrington, PA). Diethanolamine (DEOHA) and hydroxyethyl acrylate (HEA) were

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purchased from Sinopharm Group Chemical Reagent, Beijing, China. BP and 1-phenyl-2-hydroxy-2-methylpropan-1-one (RUNTECURE 1103) were obtained from Runtec (Jintan, Jiangsu, China) and used as received. Ethyl acetate was dried and purified according to standard laboratory methods. All other reagents were of analytical grade and used as received unless otherwise specified.

Instrumentation

FTIR spectra were recorded on a Nicolet 5700 instrument (Thermo Electron Corporation, Waltham, MA, USA) with the resolution of 4 cm^{-1} at room temperature.

UV spot source (EFOS Lite, 50-W miniature arc lamp, with 5-mm crystal optical fiber, Canada) was used as light source.

Light intensity was measured by the UV Light Radiometer (Photoelectric Instrument Factory, Beijing Normal University, China).

Synthesis of multifunctional aliphatic urethane acrylate

Synthesis of HEA-IPDI

IPDI (40.0 g, 180 mmol), 0.2 mL DBTDL, and 150 mL ethyl acetate were added into a 500-mL, four-necked, round-bottom flask fitted with a condenser, an overhead stirrer, a thermometer, and an addition funnel. The solution was stirred and heated to 50°C , and then a mixture of HEA (20.9 g, 180 mmol) and 120 mL ethyl acetate was dropped into the flask. Once all the HEA solution was added, the temperature was maintained at 50°C for about 3 h. Infrared spectroscopy was used to monitor the disappearance of $-\text{OH}$ peak at about 3420 cm^{-1} and appearance of $-\text{NH}$ peak at about 3340 cm^{-1} . The absence of the peak at about 3420 cm^{-1} indicated a level of residual $-\text{OH}$ below the detection limits of the spectrophotometer, and the first step reaction was completed.

Synthesis of SR454-DEOHA and SR494-DEOHA

The procedure for SR454-DEOHA was as follows: DEOHA (6.3 g, 60 mmol) dissolved in 30 mL of ethyl acetate was added into a round-bottom flask. To this mixture, SR454 (8.6 g, 20 mmol) dissolved in 20 mL ethyl acetate was dropped under magnetic stirring in an N_2 purge. The mixture was kept at 38°C for 48 h. FTIR was used to monitor the process of the reaction. When the $\text{C}=\text{C}$ peak at about 1640 cm^{-1} disappeared, the reaction was cooled to room temperature.

By replacing SR 454 with 7.9 g SR 494, following the above procedure, SR494-DEOHA was obtained.

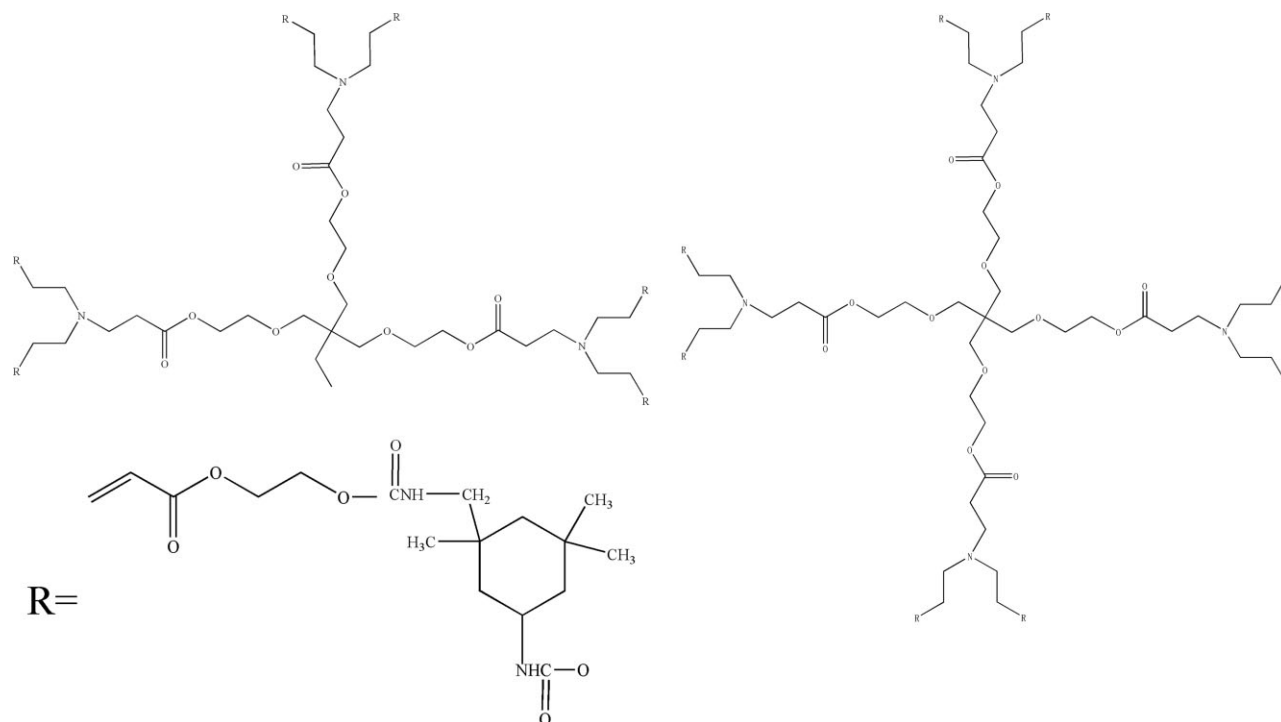
Synthesis of hexa-functional and octa-functional aliphatic urethane acrylate

The procedure for hexa-functional aliphatic urethane acrylate was as follows: SR454-DEOHA (11.2 g, 15 mmol), 0.2 mL DBTDL, and 120 mL ethyl acetate were added into a 500-mL, four-necked, round-bottom flask fitted with a condenser, an overhead stirrer, a thermometer, and an addition funnel. The above mixture was stirred and heated to 60°C , and then the mixture of HEA-IPDI (30.4 g, 90 mmol) and ethyl acetate (100 mL) was dropped into the flask. Once all the HEA-IPDI solution was added, the temperature was heated to 78°C and maintained for about 3 h. Infrared spectroscopy was used to monitor disappearance of $-\text{NCO}$ peak at about 2270 cm^{-1} . The absence of this peak indicates the completion of the reaction. When the peak disappeared completely, the organic layer was washed with 10% aqueous NaOH solution twice, followed by washes with deionized water twice, and then dried overnight with sodium sulfate. Finally, the solvent was removed by vacuum distillation to obtain hexa-functional aliphatic urethane acrylate (HFAUA).

The procedure for octa-functional aliphatic urethane acrylate (OFAUA) preparation was the same as for HFAUA, only using SR494-DEOHA (9.5 g, 10 mmol) to replace SR454-DEOHA, and HEA-IPDI (27.1 g, 80 mmol) was used for the reaction.

Real-time infrared spectroscopy

The photopolymerization kinetics of multifunctional aliphatic urethane acrylates were studied by RTIR, which had become an important method for obtaining kinetics data.⁹ The basic principle of RTIR spectroscopy consists of exposing the sample simultaneously to the UV light, which induces the polymerization, and to the infrared beam, which serves to measure the monomer concentration at any given time. The resulting decrease in the IR absorption band characteristic of that monomer is monitored continuously on a transient memory recorder. Since the absorbance increment ($A_0 - A_t$) is always proportional to the amount of monomer that has polymerized after a given exposure and thus to the degree of conversion, the recorded RTIR trace actually corresponds to a conversion versus time curve.^{9,10} Conversion data were obtained by monitoring the decay of the acrylate double bond $=\text{C}-\text{H}$ peak at about 6165 cm^{-1} . Upon irradiation, the decrease of the $=\text{C}-\text{H}$ absorption peak area from 6101.84 to 6247.95 cm^{-1} accurately reflects the extent of the polymerization since the change of the absorption peak area was directly proportional to the number of the acrylate that had polymerized. After baseline correction, conversion of the functional



Scheme 1 Structures of HFAUA and OFAUA.

groups could be calculated by measuring the peak area at each time of the reaction and determined as follows:

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

where DC is the degree of acrylate double bond conversion at t time, A_0 is the initial peak area before irradiation, and A_t is the peak area of the double bonds at t time.

All samples were photocured in 1.6-mm-thick plastic molds with an 11-mm diameter central. The molds were clamped between two glass slides with spring-loaded binder clips.¹¹ The samples were irradiated with a UV spot source. Each spectrum was a signal of 1 scan with the resolution of 4 cm^{-1} at room temperature. For each sample, the series RTIR runs were repeated three times.

RESULTS AND DISCUSSION

Synthesis

Multifunctional aliphatic urethane acrylates were synthesized in a three-step reaction. The structures of HFAUA and OFAUA are shown in Scheme 1. In the first step, IPDI reacted with an equimolar amount of HEA at 50°C , and the obtained precursor was named HEA-IPDI. During the synthesis of HEA-IPDI, there is an inevitable side reaction, though the reactivity of the primary cycloaliphatic NCO group is up to 10 times more reactive than the

secondary aliphatic NCO group in urethane reaction (with DBTDL as the most selective catalyst).¹² This side reaction alters stoichiometry, and some unreacted IPDI remains in the adduct. This unreacted IPDI can react with polyol in the third step, giving high-molecular-weight products. Side products obtained by reaction of two HEA molecules with IPDI serve as reactive diluent. The consumption of hydroxyl groups of HEA was confirmed by the disappearance of the IR absorption at 3420 cm^{-1} , which indicated the completion of the reaction [Fig. 1(a)]. In the second step, DEOHA reacted with commercial multifunctional acrylate through the Michael addition reaction. The rates of Michael addition of primary amines are higher than that of secondary amines,¹³ therefore, Michael addition of the secondary amine (DEOHA) to multifunctional acrylate was proceeded for 48 h at 38°C to ensure the completion of the reaction. The disappearance at about 1640 cm^{-1} of $\text{C}=\text{C}$ peak in FTIR spectra allowed us to monitor the course of the reaction [Fig. 1(b)]. In the third step, HEA-IPDI reacted with the Michael adduct at 78°C . The progress of the reaction was monitored through the disappearance of the NCO band at 2270 cm^{-1} [Fig. 1(c)].

Photopolymerization kinetics

The photopolymerization kinetics of the synthetic multifunctional aliphatic urethane acrylates were

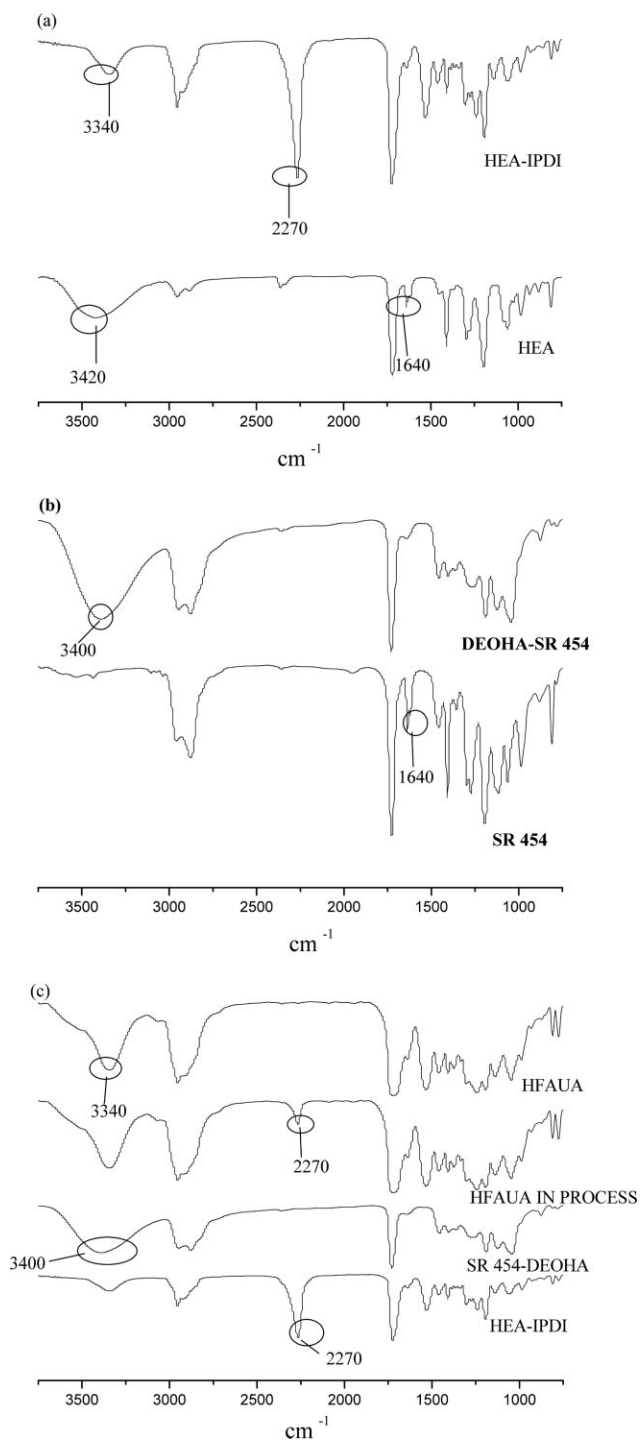


Figure 1 Using FTIR to monitor the process of reactions.

studied by RTIR. All urethane acrylates were diluted with SR 306 (40 wt %) and mixed with 3 wt % of photoinitiator.

Photoinitiators play a key role in UV-radiation curing because they are suited to absorb a light radiation of the appropriate wavelength and to produce primary radical species to convert a multifunctional acrylate into a cross-linked network. All photoinitiators for free-radical polymerization proceed by either

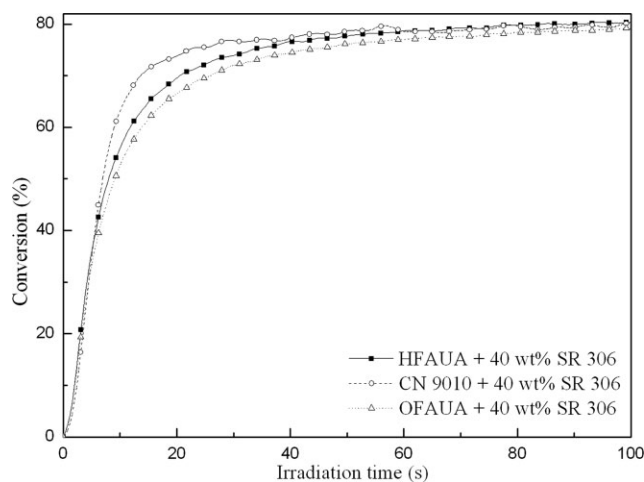


Figure 2 Conversion vs. irradiation time plot for different urethane acrylates (RUNTECURE 1103 = 3.0 wt %, $I = 50 \text{ mW/cm}^2$).

a cleavage mechanism (Type I photoinitiator) or a hydrogen abstraction mechanism (Type II photoinitiator).⁴

The chemical structure of the acrylate-functionalized oligomer may affect the photopolymerization kinetics as well. The kinetic behavior of two synthetic urethane acrylates/SR 306 system and commercial hexa-functional aliphatic urethane acrylate CN 9010/SR 306 system containing 3.0 wt % RUNTECURE 1103 has been studied by RTIR spectroscopy. The most important parameters characterizing the photopolymerization behavior of a multifunctional oligomers are the maximum rate of polymerization ($R_{p,\text{max}}$), the time to reach the maximum rate of polymerization (t_{max}), and final double-bond conversion (C).

In Figure 2 and Table I, the OFAUA/SR 306 system exhibited lower final conversion (81.9%) than did the HFAUA/SR 306 system (82.9%). This is because OFAUA has higher acrylate functionalities, which had a strong influence on both the polymerization rate and the residual acrylates content. With the increase of acrylate functionality, the content of residual unsaturations rose. An increase in the functionality leads to a higher concentration of polymerizable groups, but the extent of reaction decreases because of mobility restrictions of the reactive sites

TABLE I
Photopolymerization Kinetics Data of Different Urethane Acrylates Initiated by 3.0 wt % RUNTECURE 1103

Urethane acrylates	t_{max} (s)	DC (%)	$R_{p,\text{max}} \times 10^3$ (s ⁻¹)
HFAUA + 40 wt % SR 306	2.7	82.9	104.0
OFAUA + 40 wt % SR 306	2.7	81.9	95.4
CN 9010 + 40 wt % SR 306	3.8	83.0	100.2

in the highly cross-linked and stiff polymer formed.¹⁴ Compared with the commercial urethane acrylate CN 9010, which has six-acrylate functionality, the HFAUA/SR 306 system exhibited shorter t_{\max} (2.7 s), higher $R_{p,\max}$ (0.104 s^{-1}), and almost the same final conversion.

When initiated by RUNTECURE 1103, acrylates could reach high conversion at very early stages of polymerization. Because the initiation is based on a unimolecular reaction, the generation of free radicals by Type I photoinitiator RUNTECURE 1103 is generally faster than Type II photoinitiator BP, which is based on bimolecular formation of radicals. Figure 3 and Table II show the kinetic behavior and data of two synthetic urethane acrylates and commercial hexa-functional aliphatic urethane acrylate CN 9010 containing 3.0 wt % BP.

As shown in Figure 3 and Table II, the synthetic urethane acrylates systems could be initiated by BP without the addition of coinitiators because they contain tertiary amine structures acting as coinitiators. The HFAUA/SR 306 system exhibited higher final conversion (63.4%) than did the OFAUA/SR 306 system (57.0%) because HFAUA has fewer functionalities. Compared with the commercial urethane acrylate CN 9010, which has six functionalities, the HFAUA/SR 306 system could reach much higher final conversion (63.4%) than did the CN 9010/SR 306 system (35.9%) because of the absence of a coinitiator in the CN 9010/SR 306 system. The HFAUA/SR 306 system exhibited shorter t_{\max} (5.4 s) and higher $R_{p,\max}$ ($25.9 \times 10^{-3} \text{ s}^{-1}$) conversions than did the CN 9010/SR 306 system. When 3.0 wt % DEOHA was added to the CN 9010/SR 306 system as a coinitiator, the conversion (55.0%) was still lower than that in the HFAUA/SR 306 system. This indicates that the synthetic hexa-functional aliphatic urethane acrylate can be cured more effectively by BP.

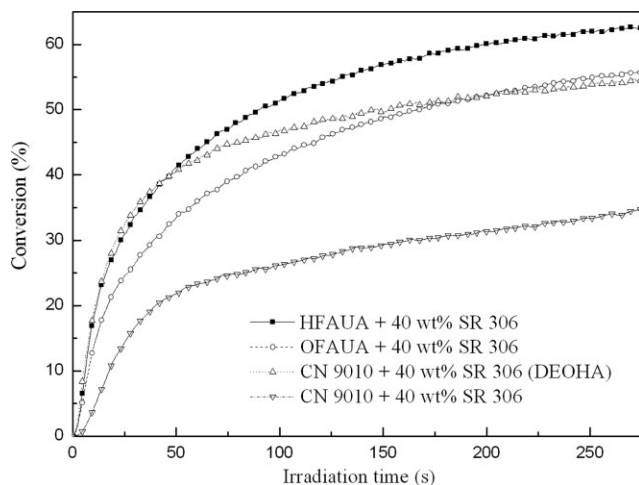


Figure 3 Conversion vs. irradiation time plot for different urethane acrylates (BP = 3.0 wt %, $I = 50 \text{ mW/cm}^2$).

TABLE II
Photopolymerization Kinetics Data of Different Urethane Acrylates Initiated by 3.0 wt % BP

Urethane acrylates	t_{\max} (s)	DC (%)	$R_{p,\max} \times 10^3$ (s^{-1})
HFAUA + 40 wt % SR 306	5.4	63.4	25.9
OFAUA + 40 wt % SR 306	5.4	57.0	19.1
CN 9010 + 40 wt % SR 306 (3.0 wt % DEOHA)	4.6	55.0	28.6
CN 9010 + 40 wt % SR 306	10.9	35.9	8.2

CONCLUSIONS

In this research, two multifunctional aliphatic urethane acrylates, HFAUA and OFAUA, were synthesized. Their photopolymerization kinetics were studied by RTIR. Compared with BP, acrylates could reach higher conversion at early stages of polymerization when initiated by RUNTECURE 1103. Different from the commercial urethane acrylate CN 9010, which has the same acrylate functionalities as HFAUA, the HFAUA/SR 306 system and the OFAUA/SR 306 system could be efficiently initiated by BP without the addition of any coinitiators because they have tertiary amine structures. The HFAUA/SR 306 system exhibited higher final conversion than did the OFAUA/SR 306 system and commercial urethane acrylate CN 9010, even with the addition of 3.0 wt % DEOHA.

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