

## Synthesis and Properties of UV-Curable Polyurethane Acrylate with Star-Shaped Structure

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Novel UV-curable polyurethane acrylate with star-shaped structure is synthesized by using trimethylolpropane as the core and polybutylene adipate as flexible arms. The chemical structure of polyurethane acrylate oligomer is identified by nuclear magnetic resonance and Fourier transform infrared spectra. Molecular weight and molecular weight distribution are measured by gel permeation chromatography. The rheological behaviour of polyurethane acrylate oligomer and mechanical properties of cured film are also investigated.

**Key Words:** Trimethylolpropane, Star-shaped polymer, Polyurethane acrylate, UV-Curing, Rheological behaviour.

### INTRODUCTION

The UV-radiation technology has been widely used for its distinct advantages since 1960s, such as instant curing, energy conservation, solvent-free and no volatile organic compounds<sup>1-3</sup>. UV-curable system consists of oligomer, monomer, photoinitiator and additive. The properties of polyurethane acrylate, such as hardness, flexibility, adhesion, optics, abrasive resistance and weatherability, mainly account on the oligomer structure and its concentration in the formulation<sup>4-7</sup>. Polyurethane acrylate is a kind of most widely applied oligomer in optics, electronics, inks, coatings and adhesives, which combines the excellent performance of polyurethane and acrylic resins.

Existing UV-curable resin is generally linear structure, with a high melting point and viscosity, but poor liquidity and stability. So looking for new structure and special property polyurethane acrylate would play a key role in the development of UV-curable chemistry. It is well known that the star-shaped polymer has a lower melt viscosity, diffusion coefficient and volume of fluid dynamics, in comparison with the linear polymer at the same molecular weight<sup>8-13</sup>.

This article describes an attempt to synthesize star-shaped UV-curable polyurethane acrylate by introducing trimethylolpropane as the core and polybutylene adipate as the soft segment. Trimethylolpropane (TMP) and polybutylene adipate (PBA) react as the hydroxyl compound while toluene-2,4-diisocyanate (TDI) and 2-hydroxypropyl methacrylate (HPMA) are chosen as diisocyanate and hydroxyalkyl acrylate. The polymerization reaction is controlled according to temperature and molar ratio of raw materials. Finally, the polyurethane acrylate with star-shaped structure would have three-functional

theoretically. The molecular weight and structure are analyzed by GPC, <sup>1</sup>H NMR, IR. Then, the synthesized oligomer is mixed with isobornyl acrylate (IBOA) and photoinitiator and the system is subjected to photoinduced free radical polymerization, which caused the polymerization of acrylate double bonds to form a network. And the rheological behaviour of polyurethane acrylate oligomer and properties of cured films are measured, respectively.

### EXPERIMENTAL

Polybutylene adipate (PBA, Mn = 2000) is distilled under reduced pressure, trimethylolpropane (TMP) is used with further purification, toluene-2,4-diisocyanate (TDI), dibutyltin dilaurate (DBTDL, Kelong Chemical Reagent Co., China), 2-hydroxypropyl methacrylate (HPMA, Beijing Chemical Co.) is dried at 35 °C for 2 h in vacuum before used, isobornyl acrylate (IBOA, Tianjin Tianjiao Material Co. Ltd., China), 1-benzoylcyclohexanol (184), 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO, Nanjing Chunghosung Technology Co. Ltd., China) are used without further purification.

**Synthesis procedure of polyurethane acrylate:** The synthesis of polyurethane acrylate is carried out in a four-necked flask reactor equipped with a stirrer, a reflux condenser, a centigrade thermometer and a constant-voltage dropping funnel. Toluene-2,4-diisocyanate and trimethylolpropane are poured into the reactor and the reaction temperature is controlled below 40 °C for about 80 min. After that dibutyltin dilaurate (DBTDL) is added into the reactor and when the temperature reaches 60 °C polybutylene adipate (PBA) is dropped into the flask slowly, until the theoretical NCO value is achieved. At the moment, HPMA is dropped immediately

into the reactor. The change of NCO value during reaction is achieved by using the dibutylamine back titration method. And after 1 h, the temperature of the reaction system is raised to 70 °C. Keep this for *ca.* 0.5 h and then the whole procedure is over.

<sup>1</sup>H NMR spectra is recorded by a Bruker AVII spectrometer operated at 400 MHz, using TMS as the internal reference and CDCl<sub>3</sub> as the solvent. Fourier transform infrared spectra (FTIR) are obtained with an FI-RT670 spectrometer in the wave frequency range of 4000-500 cm<sup>-1</sup>. The molecular weights and molecular weight distributions are measured by gel permeation chromatography (GPC) with an Agilent HPLC-1100 instrument, while THF is used as the eluent at a flow rate of 1.0 mL/min at 35 °C. An NXS-IIA rotational viscometer is employed to measure the viscosity of the polyurethane acrylate oligomer at different shear rates at 25 ± 0.2 °C.

The samples is prepared by adding photoinitiator and isobornyl acrylate as reactive diluent and coated with 0.3 mm on the glass plates, then UV-curing is performed by exposing with UV-radiation apparatus (20 mW/cm<sup>2</sup>) in the air for different lengths of time. The cross-linking density, impact resistance and pencil hardness are tested according to China national standards QJ1616-89, GB/T 1732-1993 and GB/T 6739-2006, respectively.

## RESULTS AND DISCUSSION

**Synthesis and structure characterization of polyurethane acrylate oligomer:** It is well known that TDI has two NCO groups with different reactivity, so when the temperature of reaction and the amount of catalyst are controlled, the two NCO groups can be selected and separated<sup>14</sup>. In this paper, the concentration of NCO groups is always more than the concentration of OH groups, it is expected that only one NCO group of TDI molecule would participate in the first step reaction. Then, polyols will be dropped into the flask with catalyst at a lower temperature. While the concentration of the NCO group in the reaction system is comparably low, hydroxyl acrylate is added into the flask and the temperature of the system is heated up in order to accelerate the rate of reaction. Finally, the desired

molecule is obtained by tight control of temperature. The synthetic route was shown in **Scheme-I**.

The FTIR spectra of synthesized polyurethane acrylate oligomer and cured film are shown in Fig. 1. The absorption peaks at 3346 and 1534 cm<sup>-1</sup> belonged to NH, at 2960-2850 cm<sup>-1</sup> are assigned to CH<sub>2</sub> and CH<sub>3</sub>, respectively. The strong absorption peaks at 1732 cm<sup>-1</sup> are ascribed to C=O, which come from both of ester and carbamate. NCO stretching absorption peaks disappear from 2273 cm<sup>-1</sup> and the characteristic absorption peaks at 1250-1110 cm<sup>-1</sup> indicate that the polyurethane is obtained. The absorption peaks at 815 cm<sup>-1</sup> illustrate that the C=C bond have been incorporated into the polyurethane chains and the peaks disappear from the spectra of cured film indicate that the double bonds have been converted in the process of UV-curing.

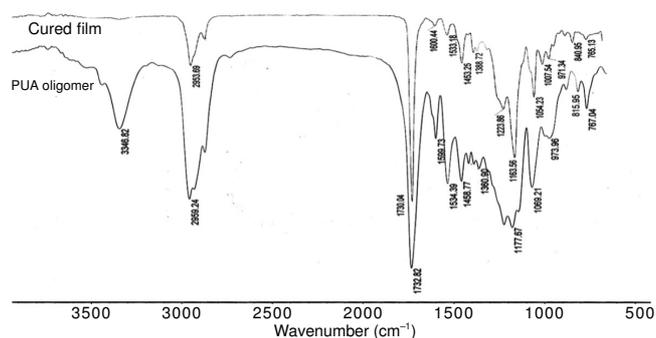
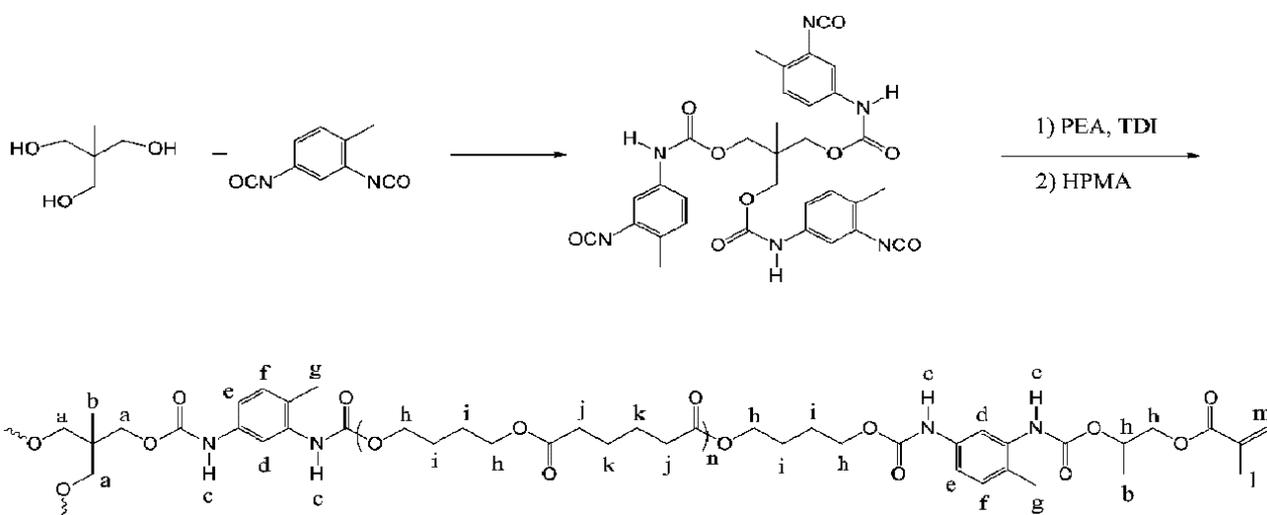


Fig. 1. IR spectra of synthesized polyurethane acrylate oligomer and cured film

The <sup>1</sup>H NMR spectra of synthesized polyurethane acrylate oligomer is shown in Fig. 2 and the data from spectra trace <sup>1</sup>H NMR is shown in Table-1, in which the letter "a, b, c, ..." accord with the same symbol in **Scheme-I**. Theoretically, the number of H atoms on the polyurethane acrylate oligomer obeys the following rules:

$$h = j = \frac{i}{2},$$

$$d + e + f = g$$



**Scheme-I:** Synthetic route and the symbol of different H atom in polyurethane acrylate oligomer

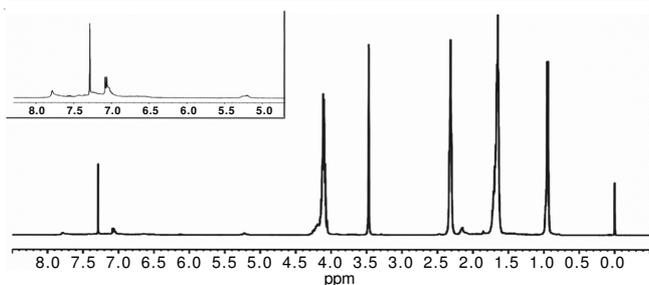


Fig. 2. NMR spectra of synthesized polyurethane acrylate oligomer

The integration of  $^1\text{H}$  NMR peak values of polyurethane acrylate oligomer in Table-1 is well in accordance with the above rules. In addition, the rule ( $c = 2 \times m$ ) should be observed, but the result is outside of the rule in fact. So the result shows that star-shaped structure of polyurethane acrylate oligomer is not perfect, because the polyester chain has not been incorporated into each arm of the star-shaped molecular evenly. This phenomenon should be the result of the steric hindrance.

TABLE-1  
NMR DATA OF SYNTHESIZED POLYURETHANE  
ACRYLATE OLIGOMER

	Chemical shift	Integration values
a + h	4.077-4.141	29.73
b + i + k + l	1.655-1.696	53.92
c	7.786	1.00
d + e + f	7.030-7.085	1.66
g	2.147-2.160	1.54
j	2.305-2.321	29.30
m	5.178-5.247	0.36

**Properties of polyurethane acrylate oligomer:** Polymer material is a mixture with different degrees of polymerization and the molecular weight generally refers to an average. The composition of polymer is important for the mechanical properties of materials and processing technology. Then the molecular weight and molecular weight distribution are measured by gel permeation chromatography, with the results shown in Table-2. The polyurethane acrylate oligomer is synthesized by the polycondensation reaction, so the polydispersity index is close to 2. Also the number average molecular weight ( $M_n$ ) is very close to the theoretical value.

TABLE-2  
PROPERTIES OF SYNTHESIZED POLYURETHANE  
ACRYLATE OLIGOMER

$M_n$ (g/mol)	$M_w$ (g/mol)	Polydispersity index (D)	Consistency factor (K)	Flow index (n)	Viscosity (25 °C, mpa s)
7.6948e3	1.8649e4	2.4235	1.14e4	0.93	1.08e4

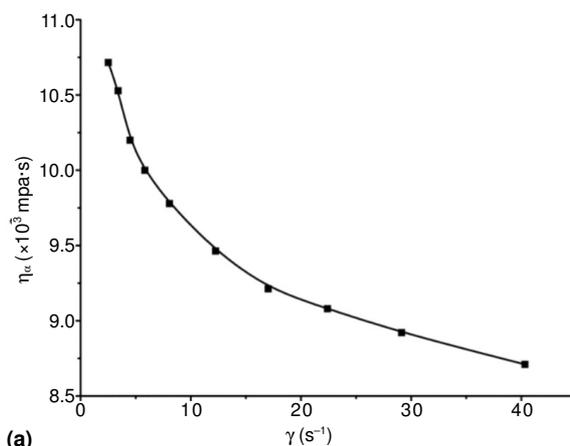
In this study, rheological behaviour of the polyurethane acrylate oligomer which is another important property of fluid is measured at  $25 \pm 0.2$  °C. Fig. 3(a) shows that the tendency of apparent viscosity ( $\eta_a$ ) decreases when the shear rate ( $\dot{\gamma}$ ) increases. This indicates that the fluidity of the polyurethane acrylate oligomer follows that of shear thinning pseudoplastic fluid. The rheological property is analyzed in a linear regress equation. According to the Oswald-de Waele power law equation<sup>15</sup>:  $\eta_a = K\dot{\gamma}^{n-1}$ , the following relationship can be derived:

$$\log \eta_a = \log K + (n - 1) \log \dot{\gamma}$$

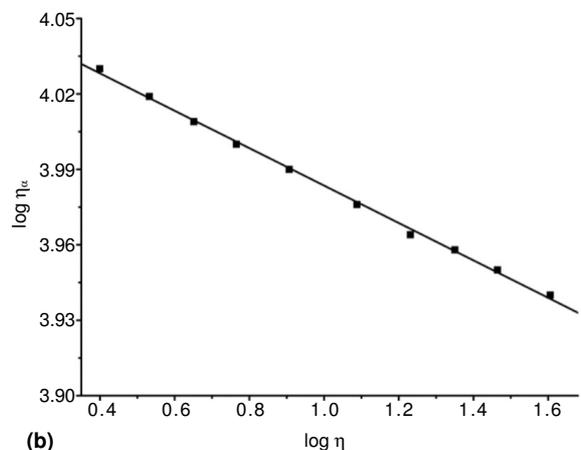
where K is the consistency factor which is proportional to the apparent viscosity, n is the flow index, when  $n < 1$ , it is for non-Newtonian fluid, when  $n = 1$ , it is for Newtonian fluid. The plots of  $\log \eta_a$  versus  $\dot{\gamma}$  are shown in Fig. 3(b). Values of K and n can be calculated based on the above equation and are shown in Table-2. When shear rate ( $\dot{\gamma}$ ) is zero, zero shear viscosity can be obtained from Cross equation<sup>16</sup>:

$$\frac{1}{\eta_a} = \frac{1}{\eta_0} + \left( \frac{\alpha}{\eta_0} \right) \dot{\gamma}^{2/3}$$

where  $\eta_0$  is the zero shear viscosity,  $\eta_0$  is calculated according to the above equation and the result is listed in Table-2.



(a)



(b)

Fig. 3. Rheological behavior of the polyurethane acrylate oligomer. Plots showing (a) dependence of  $\eta_a$  versus  $\dot{\gamma}$ ; (b) dependence of  $\log \eta_a$  versus  $\log \dot{\gamma}$

**Mechanical properties of cured film:** The tested sample is prepared at the mass ratio of PUA:IBOA: photoinitiator as 50:47:3 and cured by UV irradiation. The results of the cross-linking density, impact resistance and pencil hardness of the cured film are shown in Table-3.

TABLE-3  
CROSS-LINKING DENSITY, IMPACT RESISTANCE AND  
PENCIL HARDNESS OF CURED FILMS

Cross-linking density	Impact resistance (kg cm)	Pencil hardness
90.80 %	50	2H

The hardness of film is determined mainly by the cross-linking density. The pencil hardness and impact resistance of film depend on the chain flexibility of molecules, cross-linking density and adhesion. These are important issues that need to be concerned, especially in the application of coatings.

The density of double bonds increases, while the star-shaped structure instead of linear at the same molecular weight. And each star-shaped structure molecule will be cross-linked point, so the cured film will obtain high cross-linking density. But the rigidity of cross-linked network might result in cracking which would influence the properties of the final product. Therefore, the introducing of the flexible chain of polyester is very important.

### Conclusion

Star-shaped structure UV-curable polyurethane acrylate is synthesized by introducing trimethylolpropane and polybutylene adipate. From the FTIR and NMR spectra, it could be concluded that expected molecular structure and appropriate molecular weight are obtained by controlling temperature and reactant molar ratio. The tests of gel permeation chromatography and rheological behaviour indicate that the product is suitable for application of coating with appropriate molecular weight and fluidity. The cured film with high cross-linking density is obtained by mixing the synthesized polyurethane acrylate oligomer and isobornyl acrylate. However, the presence of the flexible chain of polybutylene adipate maintains good mechanical properties and the phenomenon of crack is avoided.

For further work, more categories and better perfect structure of star-shaped are needed to be exploited and investigated and the mechanical properties of the cured films are needed to be improved.

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