Polym. Bull. (2012) 68:1009–1022
DOI 10.1007/s00289-011-0597-6

ORIGINAL PAPER

Synthesis and properties of UV-curable hyperbranched polyurethane acrylate oligomers containing carboxyl groups

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Received: 7 April 2011 / Revised: 2 August 2011 / Accepted: 8 August 2011 /

Abstract Using step by step polymerization process, the first- and second-generation hyperbranched polyesters were synthesized with *N*,*N*-diethylol-3-amine methylpropionate as branched monomer and pentaerythrite as a core molecule. The second-generation hyperbranched polyurethane acrylate oligomers containing carboxyl groups were obtained by further reacting with semiadduct urethane monoacrylate and maleic anhydride. The structures of the oligomers were investigated with elemental analysis, FT–IR, and NMR. UV–Vis spectra results showed that the oligomers had sharp absorption bands at about 207 nm. The glass transition temperatures were investigated by differential scanning calorimetry and showed in the range of −44.96 to −19.83 °C. Gel permeation chromatograph was used to observe the molecular weights and polydispersities of the oligomers. UV-curing properties were characterized by FT–IR with different curing time. In addition, the solubilities and viscosity of the oligomers were also examined.

Keywords Hyperbranched urethane acrylate · Modification · Synthesis · UV curable

Introduction

In recent years, UV-curing technologies are developing very fast due to their high curing speed, low solvent emission, reduced energy consumption, and high-speed processing. They have been widely used in the fields of coatings, printing, electronic devices, adhesives, and inks [1, 2]. UV-curable system is typically composed of photosensitive resin oligomers, reactive diluents, and photoinitiator, etc.

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The photosensitive resin oligomer is the most important component of UV-curable system, which determines the physical properties of UV-cured coatings [3]. In general, unsaturated polyesters, epoxy acrylates, and polyurethane acrylates are the three dominant prepolymers in UV-curable system. Most of the structures of these prepolymers are linear which, however, have some disadvantages, such as high viscosity, requiring more reactive diluents and low reactivity. Thus, it is highly desirable to synthesis novel oligomers with low viscosity and high functionality.

Hyperbranched polyesters recently have recently attracted many attentions since they could bring benefits of low viscosity, good solubility and highly branching molecular structures, which contain a large number of functional end groups and are facile for chemical modifications [1, 4, 5]. Introduction of hyperbranched polyesters into UV-curable system has drawn polymer scientists' considerable attentions. Lin et al. [6] synthesized the UV-curable hyperbranched urethane acrylate (HBUA) with a multi-hydroxyl functional hyperbranched polyester core via a two-step procedure. Wang et al. [7] used a second-generation of hyperbranched polyester and maleic anhydride to synthesize a water-soluble hyperbranched polymer. Asif et al. [8] synthesized three series of novel waterborne hyperbranched polyurethane acrylates based on hydroxyl-functionalized hyperbranched aliphatic polyesters Boltorne™ of varying generation number, and their physical and thermal properties were also studied. Although a lot of efforts have been performed, the hyperbranched polyurethane acrylate oligomer containing carboxyl groups which can improve alkaline solubility has never been reported to our knowledge.

In this manuscript, a series of hyperbranched polyurethane acrylate oligomers containing carboxyl groups were synthesized by modifying the second-generation hyperbranched polyester with semiadduct urethane monoacrylate (IPDI–HEA) and maleic anhydride (MAH) at different feed ratios. The chemical structures of these oligomers were confirmed by FT–IR, ^{1}H-NMR, and gel permeation chromatography (GPC). Furthermore, the UV–Vis absorption spectrum, viscosity, solubility, UV curing, and thermal properties of these hyperbranched polyurethane acrylate oligomers containing carboxyl groups were also studied.

Experimental

Materials

2-Hydroxyethyl acrylate (HEA) and isophorone diisocyanate (IPDI) were obtained from Aladdin Reagent Co. (Shanghai, China). 2-Hydroxy-2-methylpropiophenone was provided by TCI-EP (Tokyo Kasei, Japan). Pentaerythritol (PE), methyl acrylate, diethanolamine, 1,4-dioxane, dibutylamine, MAH, and dibutyltin dilaurate (DBTDL) were purchased from Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Methanol, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMAC), ethyl ether, acetone, and methylbenzene were obtained from Sinopharm Chemical Reagent Co. Ltd, China. All other common chemical reagents were all analytical grade and used as received.

Preparation of first-generation hyperbranched poly(amine-ester) (HBPE1)

First-generation hyperbranched poly(amine-ester) was synthesized according to a three-step procedure: *N*,*N*-diethylol-3-amine methylpropionate was synthesized according to the previously reported literature at the first step [9] and the structure was characterized by FT–IR and ^{1}H-NMR. At the second step, PE (1.362 g, 0.01 mol) was dissolved by DMF and *N*,*N*-diethylol-3-amine methylpropionate (7.649 g, 0.04 mol) was added dropwise to a 250 mL four-neck flask, which was equipped with a magnetic stirrer, nitrogen inlet, a theromometer and a water separator. After the mixture was stirred for 4 h at 120 °C in the presence of *p*-toluene sulfonic acid (*p*-TSA) as catalyst, it was distilled to remove DMF under vacuum. The HBPE1 was obtained. Finally, the HBPE1 refined by fractional precipitation method. The procedure was described as follows: First, the HBPE1 was dried in a vacuum oven to remove the water, and then it was redissolved into dried 1,4-dioxane at room temperature. The solution was dropwise added into ethyl ether. The precipitate was collected, washed with the mixture of acetone and ethyl ether (1:1) and dried in a vacuum oven. The fractionalized HBPE1 was obtained.

IR (KBr, cm^{-1}): 3391.5 cm^{-1} (–OH), 2949.5 cm^{-1} (–CH_3), 2882.2 cm^{-1} (–C–H stretching vibration), 874.0 cm^{-1} (–C–H deformation vibration), 1729.2 cm^{-1} (–C=O), 1187.9 cm^{-1} (–C–O), 1460.1 cm^{-1} (–C–N–), 1623.5 cm^{-1} (–C=NH). ^{1}H-NMR (500 Hz, DMSO-d_6): 3.92–4.02 (–C–CH_2–O–), 2.09 (–OOC–CH_2), 2.32–2.76 (–CH_2–N<), 3.32–3.57 (–CH_2–OH), 3.45 (–OH).

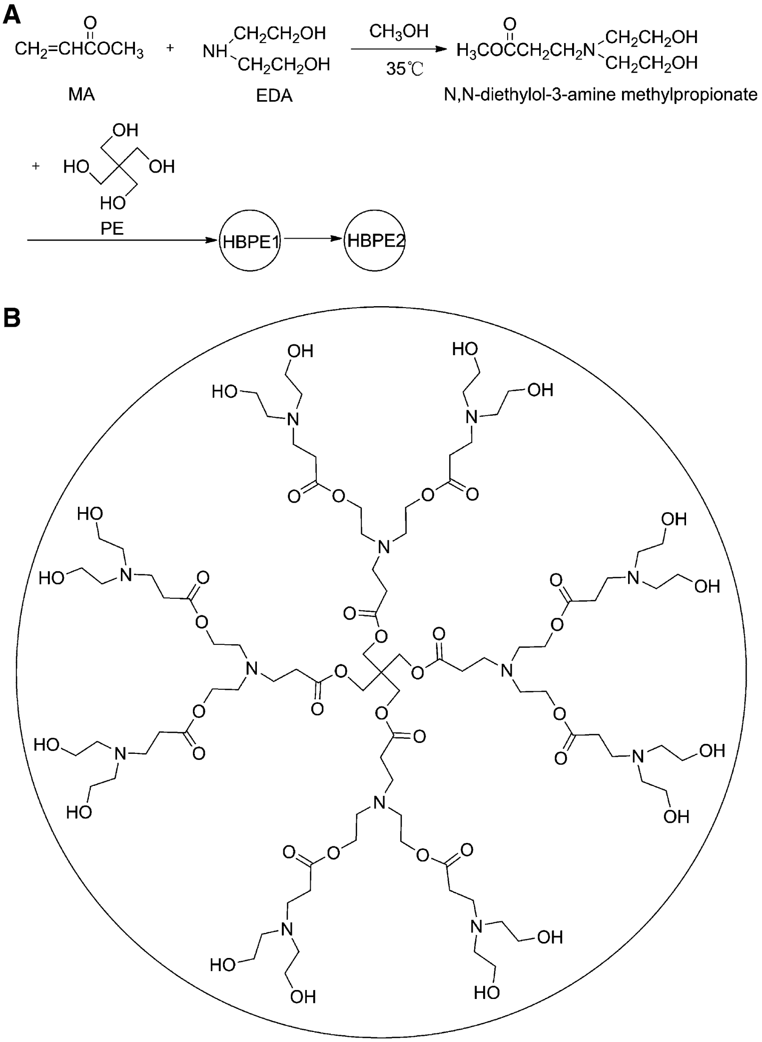
Preparation of second-generation hyperbranched poly (amine-ester) (HBPE2)

HBPE2 was synthesized based on HBPE1, and the process was described as follows: HBPE1 (7.73 g, 0.01 mol) was added to a 250-mL four-neck flask, which was equipped with a magnetic stirrer, nitrogen inlet, a theromometer, and a water separator. To the stirring mixture *N*,*N*-diethylol-3-amine methylpropionate (15.29 g, 0.08 mol) was added dropwise. The mixture was stirred for 4 h at 120 °C in the presence of p-TSA as catalyst, which stripped off most of the methanol to the system. Then the HBPE2 was obtained. Finally, the HBPE2 refined by fractional precipitation method and the procedure was similar to that of HBPE1. The synthesis process is described in Scheme 1.

IR (KBr, cm^{-1}): 3324.2 cm^{-1} (–OH), 2946.3 cm^{-1} (–CH_2), 1722.8 cm^{-1} (–C=O), 1191.1 cm^{-1} (–C–O), 1456.9 cm^{-1} (–C–N–), 1613.9 cm^{-1} (–C=NH). ^{1}H-NMR (500 Hz, DMSO-d_6): 2.58–2.61 (–N–CH_2–), 2.73–2.81 (O=C–CH_2–), 3.44 (–OH), 3.53–3.59 (–CH_2–OH), 4.20 (–CH_2–OOC–).

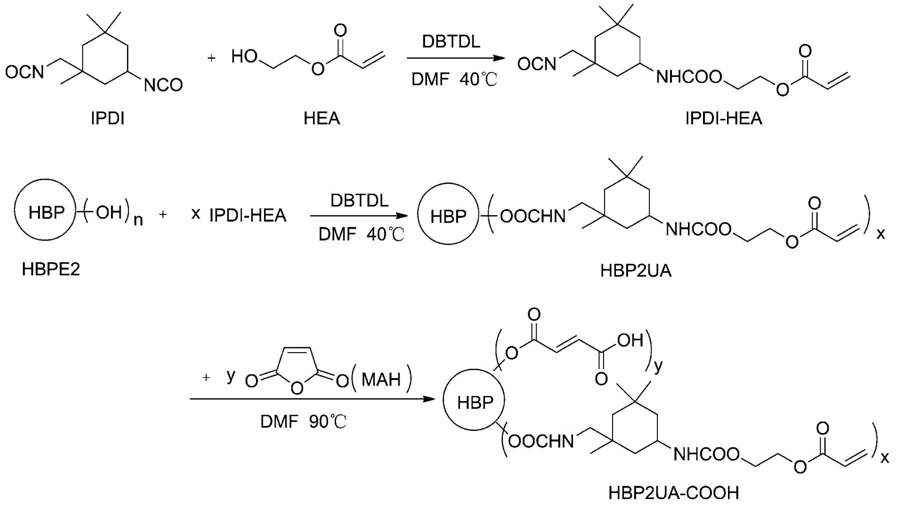
Synthesis of second-generation hyperbranched urethane acrylate containing carboxyl groups (HBP2UA-COOH)

The HBP2UA-COOH was synthesized via a two-step procedure. One typical process for synthesizing HBP2UA-COOH (0.5:0.5) was described as follows: First, the IPDI-HEA was synthesized by IPDI/HEA. IPDI (1.778 g, 8 mmol), hydroquinone (0.051 g), DBTDL (0.126 g) were mixed in a three-neck flask equipped with



Scheme 1 **a** Preparation of hyperbranched poly(amine-ester)s. **b** Idealized structures of HBPE2

a magnetic stirrer, a reflux condenser, and a separatory funnel. The HEA (0.928 g, 8 mmol) was slowly dropped into the mixture and stirred for about 12 h at 50 °C until the content of isocyanate reached the theoretical value of mono-isocyanate (IPDI-HEA) by titration. Second, the HBPE2 (2.046 g, 1 mmol) dissolved in DMF was added to the IPDI-HEA and stirred for an additional 9 h at 70 °C, then the heat was increased to 90 °C and MAH (0.784 g, 8 mmol) dissolved in DMF was added to the solution for another 9 h. Finally, the HBP2UA-COOH (0.5:0.5) was obtained after the DMF was evaporated. The synthesis process is described in Scheme 2. The HBP2UA-COOH synthesized form IPDI-HEA (*x*) and MAH (*y*) with a mole ratio of 1.0:0, 0.7:0.3, and 0.5:0.5 was designated HBP2UA, HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5), respectively.



Scheme 2 Synthesis of second-generation hyperbranched urethane acrylate containing carboxyl groups

IR (KBr, cm^{-1}): 3346.0 and 2949.5 cm^{-1} (–NH stretching and deformation vibration), 2949.5 cm^{-1} (–CH stretching), 1635, 1408, and 810 cm^{-1} (acrylate unsaturation), 1722.1 cm^{-1} (C=O), 1661.9 cm^{-1} (–COOH). ^{1}H-NMR (500 Hz, DMSO-d_6): 10.5–11.5 (–COOH), 8.00 (–NH), 5.95–6.36 ($-COCH=CH_2$), 4.04–4.26 ($-CH_2CH_2OC=O$) 6.28–6.33 (–CO–C*H*=C*H*–COOH), 0.7–1.9 ($-CH_2$ and $-CH_3$ of IPDI).

Measurements

Infrared absorption spectra (IR) were measured on a Nicolet Magna IR650 (Madison, WI). The ^{1}H-NMR spectrums were carried out on a Bruker 500 MHz spectrometer (Karlsruhe, Germany) in DMSO-d_6 with Me_4Si (TMS) as an internal standard. The UV spectra were measured with UV–Vis spectrophotometer (Simadzu UV-2450, Japan). Elemental analysis was performed with a Leeman CE440 instrument.

Intrinsic viscosity measurements were carried out with an Ubbelohde viscometer in DMF at 30 ± 0.1 °C. Differential scanning calorimetry (DSC) spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen purge at a heating rate of 10 °C/min from −90 to 90 °C. The molecular weight and molecular weight distribution (M_w/M_n) of the oligomers were estimated by Water 515–2410 gel permeation chromatography (GPC, Water, USA), tetrahydrofuran (1.0 mL min^{-1}), was used as the mobile phase. Calibration was carried out by linear polystyrene of known molecular weight and dispersity. The UV-curing properties of the oligomers were monitored by FT–IR. The oligomers were exposed to 365 nm UV-light of 23 mw/cm^2 in the absence of photoinitiator, and the distance of the sample to the focal point of UV-lamp was 10 cm. Hydroxyl value was determined according to GB/T 12008.3-1989. The content of isocyano (–NCO%) was determined according to GB/T 12009.4-1989. The solubility of the oligomers was determined by the observation of the soluble process in different solvents at room temperature.

Results and discussion

Characteristics of HBPE1, HBPE2, and synthesis of IPDI-HEA

Hydroxyl value and element analysis of HBPE1 and HBPE2 are summarized in Table 1. The hydroxyl value is an important parameter for the modification of HBPE [10]. It is evident that the hydroxyl value of HBPE1 and HBPE2 is 10.4 and 8.0, respectively. Although the hydroxyl number and molecular weights increase with increasing generation number, the hydroxyl value decreases with increasing generation number. This can be attributed to the fact that the increasing extent of molecular weights was greater than that of hydroxyl number. The results of element analysis of N, C, and H in HBPE1 and HBPE2 were also shown in Table 1. It shows that the measured results are closed to their theoretical ones. The element contents of N, C and H in HBPE1 are 7.12, 51.16, and 8.25%, and the corresponding values of HBPE2 are 8.16, 52.04, and 8.20%, respectively. It also illustrates that the synthesized hyperbranched oligomers have well-defined structures. In the process of synthesizing IPDI-HEA, temperature control is very important. IPDI is cycloaliphatic diisocyanate, which possesses two NCO groups of unequal reactivity. At 50 °C, the secondary cycloaliphatic NCO group is more reactive than the primary aliphatic NCO group [11]. During the adduct synthesis of IPDI-HEA, the secondary cycloaliphatic NCO group reacted with HEA at 50 °C. The unreacted aliphatic NCO group reacted with HBPE2 at 70 °C. The progress of the reaction was monitored by titration.

FT–IR and ^{1}H-NMR spectra of the oligomers

The FT–IR spectra of HBPE2, HBP2UA, and HBP2UA-COOH are shown in Fig. 1. Three absorption peaks are observed at around 1635, 1408, and 810 cm^{-1} which indicates the double bonds of the acryl groups. The strong peak at 1722.1 cm^{-1} is assigned to the carbonyl bonds of the acryl groups [12]. These peaks indicate that the HEA was successfully introduced into the prepolymers. The peaks at 3346.0 and

Table 1 Characteristics of the HBPE1 and HBPE2

Sample	Generation number	Theoretical functionality	Hydroxyl value (mmol/g)		Element analysis (%)					
					Theoretical			Measured		
			Theoretical	Measured	N	C	H	N	C	H
HBPE1	1	8	10.4	10.4	7.25	51.28	8.35	7.12	51.16	8.25
HBPE2	2	16	7.8	8.0	8.21	52.24	8.27	8.16	52.04	8.20

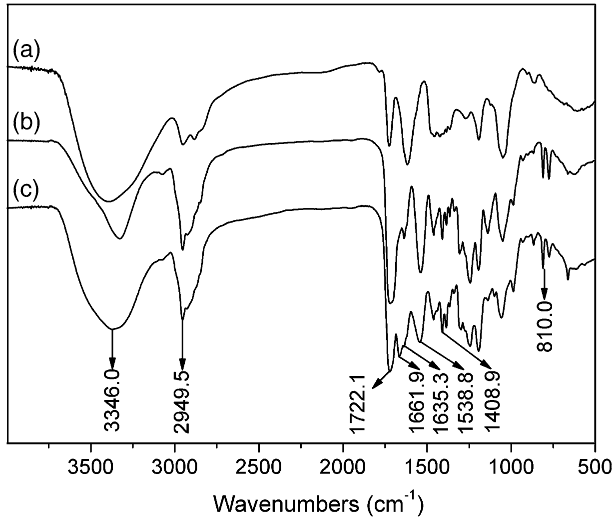


Fig. 1 FT–IR spectra of (*a*) HBPE2, (*b*) HBP2UA, and (*c*) HBP2UA-COOH

1538.8 cm^{-1} are assigned to the N–H stretching vibration and deformation vibration. The peak at 1661.9 cm^{-1} of HBP2UA-COOH indicates the existence of –COOH. It shows that the MAH was reacted with HBPE2.

Figure 2 shows the ^{1}H-NMR spectra of the HBP2UA. Three groups of characteristic peaks at 5.95–6.36 ppm are obviously observed, which prove the existence of acrylic group in the molecular structure of HBP2UA. The peak at 8.00 ppm is assigned to the hydrogen atom of amide group. The peaks at 4.04–4.26 ppm are assigned to the hydrogen atom of methylene connected to ester group. The peaks below 2.0 ppm are assigned to the hydrogen atom of IPDI [13]. Figure 3 is the ^{1}H-NMR spectra of the HBP2UA-COOH (0.7:0.3) which is similar to that of HBP2UA. Some of the characteristic peaks in HBP2UA can also be observed in the spectra of HBP2UA-COOH (0.7:0.3). The peak at 10.5–11.5 is assigned to the carboxyl groups of HBP2UA-COOH (0.7:0.3).

Through the FT–IR and ^{1}H-NMR analysis, it is confirmed that the acrylic groups and carboxyl groups are both introduced into the molecular structure of HBPE2.

Viscosity and physical state

The intrinsic viscosity ([η]) of an oligomer is considered as one of the most important parameters as it is a measure of hydrodynamic volume and depends on molecular weight. The [η] of the synthesized oligomers have been analyzed by Ubbelohde viscometer in DMF at 30 °C and the results are shown in Table 2. It is observed that the HBP2UA exhibited higher intrinsic viscosity and its value is 7.45 mL/g while the [η] of the HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5) is 5.82 and 4.00 mL/g, respectively. It can be interpreted that the HBP2UA has higher molecular weight, when introducing carboxyl groups into the HBP2UA,

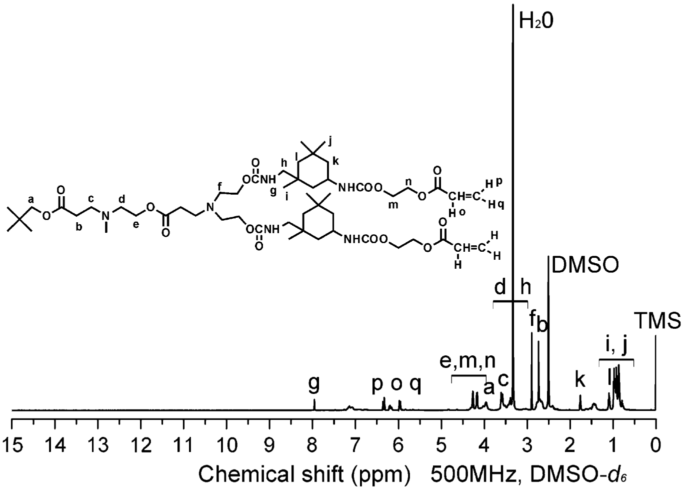


Fig. 2 ^{1}H-NMR spectrum of HBP2UA

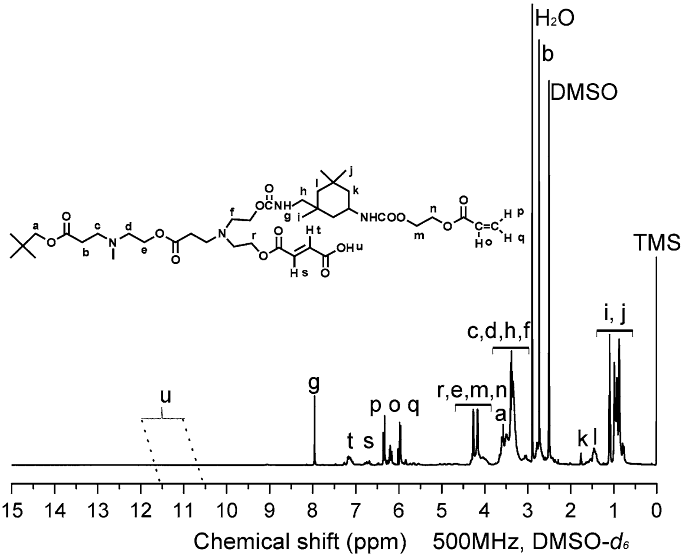


Fig. 3 ^{1}H-NMR spectrum of HBP2UA-COOH (0.7:0.3)

the molecular weight decreased, so the intrinsic viscosity went down. It can also be seen that all the synthesized oligomers have low intrinsic viscosity and changed little. This may be explained that all the synthesized oligomers have similar hyperbranched structures and there will be little entanglement among molecular chains. The physical states of the oligomers at room temperature are also list in Table 2.

Table 2 Intrinsic viscosity and physical state of synthesed oligomers

Sample	$[\eta]_{\mathrm{DMF,\ 30\ ^\circ C}}$ (mL/g)	Physical state (room temperature)
HBP2UA	7.45	Soft solid
HBP2UA-COOH (0.7:0.3)	5.82	Yellow viscous fluids
HBP2UA-COOH (0.5:0.5)	4.00	Yellow viscous fluids

Table 3 Molecular weight distributions of HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5)

Samples	M_n	M_w	M_w/M_n
HBP2UA	1059	1408	1.33
HBP2UA-COOH (0.7:0.3)	1328	1593	1.20
HBP2UA-COOH (0.5:0.5)	926	1079	1.17

GPC

The molecular weights and polydispersity indexes of the HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5) have been analyzed by GPC and the results are shown in Table 3. The GPC instrument was calibrated using linear polystyrene standard. The number molecular weight, weight molecular weight, and molecular weight distribution of HBP2UA-COOH (0.7:0.3) are 1328, 1593 g/mol, and 1.20, and the corresponding values of HBP2UA-COOH (0.5:0.5) are 926, 1079 g/mol, and 1.17, respectively. The results are much lower than their theoretical values because the hyperbranched polyesters have smaller molecular sizes than the linear polystyrene with the same molecular weights. Thus, it is difficult to obtain exact molecular weight of hyperbranched polymers by GPC [14]. Meanwhile the molecular weight distributions of HBP2UA are higher than those of HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5). It can be explained that the IPDI-HEA has much larger steric hindrance than MAH does and some of the hydroxyl terminal groups of HBPE2 did not react completely with the IPDI-HEA [15, 16].

UV–Vis absorption spectrum

The photosensitive groups of the oligomers were characterized with UV–Vis spectra in the range of 190–400 nm. The samples were diluted to 0.01 mmol/L in ethanol before analysis. The UV–Vis absorbance spectra of HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5) are shown in Fig. 4. These spectra are very similar and all show a sharp absorption bands around 207 nm. The molecular structures of oligomers contain acrylate groups which have conjugate carbon–carbon double bond (C=C) and carbon–oxygen double bond (C=O). They can produce π^*–π^* electronic transitions and can show absorption bands around 200 nm [17–19]. It can be expected that the oligomers can photopolymerize by photoinitiator under UV illumination.

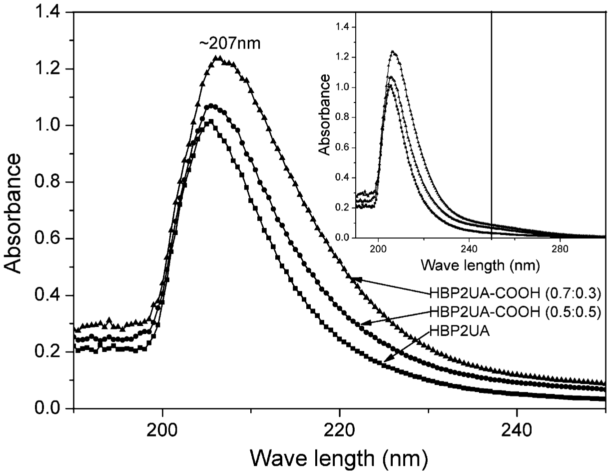


Fig. 4 UV–Vis absorbance spectra of HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5) in C_2H_5OH

UV curing

The synthesized hyperbranched polyurethane acrylate oligomers containing carboxyl groups can be cured under UV irradiation. The oligomers were exposed to 23 mW/cm^2 of 365 nm light for increasing amounts of time and the UV-curing process was monitored by FT–IR. Figure 5 shows the FT–IR spectra of HBP2UA (0.7:0.3) with different curing time (30, 90, 120, 150, and 200 s) in the absence of photoinitiator.

The change in acrylate absorption at 810 cm^{-1} which is related to the C–H out of plane deformation vibration of the acrylate double bond was monitored. The variation in film thickness (due to shrinkage) was compensated by normalizing the acrylate band to a band at 2951 cm^{-1} which is related to the C–H stretching band. The double bond conversion was measured using the following equation:

$$\text{Double bond conversion (\%)} = \frac{[(A810/A2951)t - (A810/A2951)0]}{(A810/A2951)0} \times 100$$

where $(A810/A2951)t$ is the peak area at 810 cm^{-1} after irradiation for t in seconds, $(A810/A2951)0$ is the peak area at 810 cm^{-1} before irradiation [20].

Figure 6 shows the relationships between the double bond conversion and irradiation time in the absence of photoinitiator. It can be seen that all the oligomers have lower conversions, and the conversions of HBP2UA, HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5) were 42.6, 32.4, and 22.8% at 150 s, respectively. HBP2UA shows higher photo-reactivity than HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5). This may be explained since HBP2UA has more IPDI-HEA groups than HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5). Furthermore, the hyperbranched polyurethane acrylate containing carboxyl groups have lower viscosities than HBP2UA, so that oxygen can easily

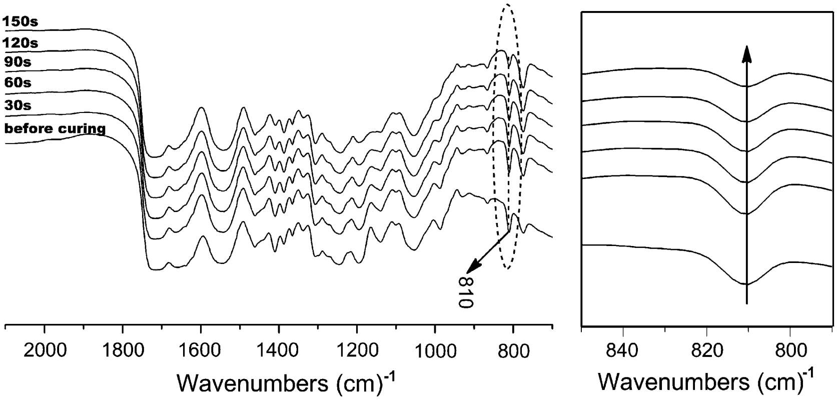


Fig. 5 FT–IR spectra of the course of UV curing (HBP2UA-COOH (0.7:0.3))

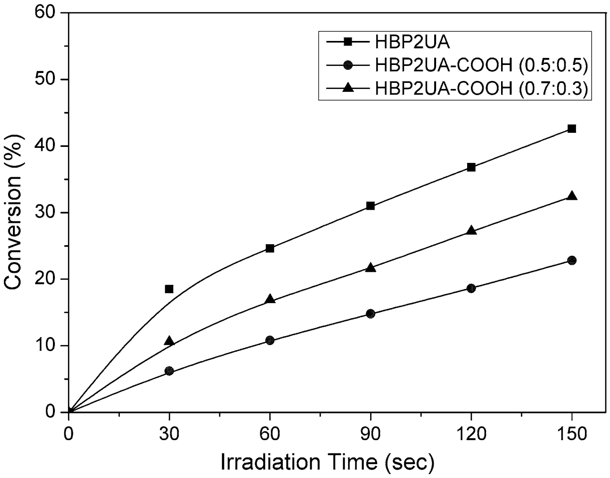


Fig. 6 The relationships between the double bond conversion (%) and reaction time (s)

penetrate into the surface layers which can inhibit the polymerization. So the HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5) have lower conversions than HBP2UA [21, 22].

Differential scanning calorimetry (DSC)

Thermal properties of the HBP2UA, HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5) were investigated using DSC by heating the samples from −90 to 90 °C at 10 °C min^{-1}. The DSC curves of the oligomers are presented in Fig. 7. For each of the oligomers, a strong single endothermic peak was obtained at 53.87, 33.17, and 32.80 °C, respectively. These peaks could be due to the molten of microcrystalline domains formed by ordered hard segments (IPDI-HEA) in

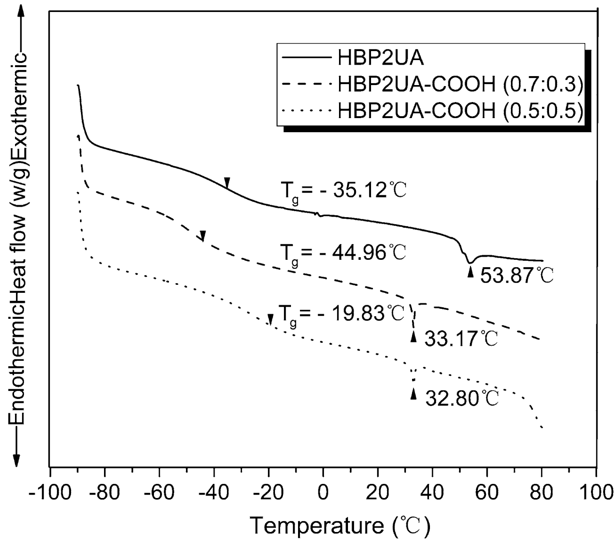


Fig. 7 DSC curves of HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5) over the range temperature from −90 to 90 °C

hyperbranched polyurethane acrylate [23, 24]. The melting points of hard segments decrease with the increase of the carboxyl groups. This decrease in melting temperature is mainly due to the decreased hard segments of hyperbranched polyurethane acrylate. The glass transition temperatures (T_g) were determined from the middle point of the heat capacity change and the T_g of HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5) are −35.12, −44.96, and −19.83 °C, respectively. Many factors affect the T_g, including polymer structure, side groups, molecular weight, structural rigidity, and so on. In the case of HBP2UA-COOH (0.5:0.5), the structure has more carboxyl groups, which are more polar than that of HBP2UA-COOH (0.7:0.3). With the increase of the polar groups, the intermolecular forces increase. Thus, the T_g of HBP2UA-COOH (0.5:0.5) is higher than that of HBP2UA-COOH (0.7:0.3). HBP2UA has more hard segments than that of HBP2UA-COOH (0.7:0.3). Thus, the T_g of HBP2UA is higher than that of HBP2UA-COOH (0.7:0.3). So the T_g of the oligomers is varied in the increasing order: HBP2UA-COOH (0.5:0.5) > HBP2UA > HBP2UA-COOH (0.7:0.3) [25, 26].

Solubility

The solubilities of the HBPE1, HBPE2, HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5) were examined at room temperature. These results are summarized in Table 4. It can be seen that the samples are well soluble in DMF, DMAC, and DMSO, and partially soluble in methanol, acetone, THF, and 1,4-dioxane. Although the HBPE1 and HBPE2 have a large number of hydroxyl terminal groups, it can not be well dissolved in water. This may be because some of

Table 4 Solubilities of the HBPE1, HBPE2, HBP2UA, HBP2UA-COOH (0.7:0.3), and HBP2UA-COOH (0.5:0.5)

Solvent	HBPE1	HBPE2	HBP2UA	HBP2UA-COOH (0.7:0.3)	HBP2UA-COOH (0.5:0.5)
Water	+	+	+	++	++
Methanol	+	+	+	+	+
Acetone	+	+	+	+	+
DMAC	++	++	++	++	++
DMF	++	++	++	++	++
THF	+	+	+	+	+
DMSO	++	++	++	++	++
1,4-dioxane	+	+	+	++	++

++ soluble at room temperature, + partially soluble

the hydroxyl terminal groups are embedded into the HBUA oligomers. HBP2UA-COOH (0.7:0.3) and HBP2UA-COOH (0.5:0.5) can be well dissolved in water. This means that the solubility of HBPE2 changes by the introduction of carboxyl groups into the end of hyperbranched polyester [27].

Conclusions

A series of hyperbranched polyurethane acrylate oligomers containing carboxyl groups were successfully synthesized by modifying the hyperbranched polyesters with IPDI-HEA and MAH at different feed ratios and characterized by FT–IR, ^{1}H-NMR, GPC, and elemental analysis. The obtained oligomers showed sharp absorption bands around 207 nm and had lower conversions in the absence of photoinitiator. The T_g values of the oligomers were in the range of -53.95 to -31.60 °C. Moreover, all the oligomers have good solubilities in strong polar solvents (e.g., DMF, DMAC, and DMSO). Our synthesized hyperbranched polyurethane acrylate oligomers containing carboxyl groups have potential application in photoresists. This part of result will be the subject of a future publication.

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