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

Wensong Han · Baoping Lin · Yidan Zhou · Jiangang Song

Abstract The hyperbranched polyurethane acrylate oligomers containing photo-initiator were synthesized by modifying the second-generation hyperbranched poly(amine-ester) with isophorone diisocyanate-2-hydroxyethylacrylate and isophorone diisocyanate-2-hydroxy-2-methylpropiophenone at different feed ratio. The elemental analysis, FT-IR and NMR methods are used for structural characterization, molecular weights, and polydispersities, photosensitive groups and thermal properties of the oligomers were analyzed by gel permeation chromatography, UV–Vis spectra and thermogravimetric analysis, respectively. UV-curing properties were characterized by FT-IR at different curing time. In addition, the solubilities of the oligomers were also examined.

Keywords Hyperbranched polyurethane acrylate · Modification · Synthesis · UV-curing

Introduction

In recent decades, UV-curing technologies have received great attention, since they offer numerous benefits, such as instant drying, high productivities, reduced energy consumption, and environmental protection, etc. These technologies have been widely used in the field of coating, electronic materials, adhesives, and inks [1–5]. Generally, photoinitiator is one of the most important components for these systems, which absorbs the UV light and generate initial species to start photopolymerization.

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However, the addition of photoinitiator leads to several problems in applications. Some photoinitiators can not be compatible with the UV-curing system and the migration of photolysis fragments out of the coating may cause yellowing and unpleasant odor. To overcome these problems, macrophotoinitiators have attracted people's attention. Wen et al. [6] have introduced thioxanthone and polyethylene glycol monoethylether glycidyl ether, which contained short poly(ethylene oxide) chain, into periphery of hyperbranched poly(ethylene imine) to obtain amphipathic hyperbranched polymeric thioxanthone photoinitiators. Gacal et al. [7] have synthesized macrophotoinitiators containing thioxanthone moieties as side chains via double click chemistry strategy. These macrophotoinitiators have good solubility and high performance in photoinitiated polymerization of monomer in comparison with their low-molecular weight analogs.

Hyperbranched polymers have gained widespread attention due to their remarkable properties such as low viscosity, good solubility, and large number of end groups. These end groups can be easily modified by acrylic groups and other functional groups to obtain UV-curable oligomers [8–10]. Hyperbranched urethane acrylate exhibit excellent physical and mechanical properties and has attracted polymer scientists' considerable attention. Bao et al. [11] have synthesized hyperbranched polyurethane acrylate by modifying hyperbranched polyurethane endcapped by hydroxyl groups (HPU-OH) with the semiadduct urethane monoacrylate isophorone diisocyanate-2-hydroxyethylacrylate (IPDI-HEA). Dzunuzovic et al. [12] synthesized photoreactive hyperbranched urethane acrylates modified with a branched saturated fatty acid and investigated their properties. Although, a lot of efforts have been made, the hyperbranched polyurethane acrylate oligomers containing photoinitiator has never been reported to our knowledge.

In this study, the hyperbranched polyurethane acrylate oligomers containing photoinitiator were synthesized by modifying the second-generation hyperbranched poly(amine-ester)s with IPDI-HEA and isophorone diisocyanate-2-hydroxy-2-methylpropiophenone (IPDI-HMPP) at different feed ration. The chemical structures of the oligomers were characterized by FT-IR, ^{1}H-NMR, and elemental analysis. The molecular weights and polydispersity indices were measured by gel permeation chromatography (GPC). Furthermore, the UV–Vis absorption spectrum, photosensitivity, thermal properties, and solubilities of the oligomers were also examined.

Experimental

Materials

Pentaerythritol tetraacrylate (PETEA) was purchased from Aldrich, USA. 2-Hydroxyethyl acrylate (HEA) and isophorone diisocyanate (IPDI) were obtained from Aladdin Reagent Co. (Shanghai, China). 2-Hydroxy-2-methylpropiophenone (HMPP) was provided by TCI-EP (Tokyo Kasei, Japan). Diethanolamine (EDA), dibutylamine and dibutyltin dilaurate (DBTDL) were purchased from Lingfeng Chemical Reagent Co. Ltd., (Shanghai, China). Methanol was obtained from

Sinopharm Chemical Reagent Co. Ltd., China. All other common chemical reagents were all analytical grade and used as received.

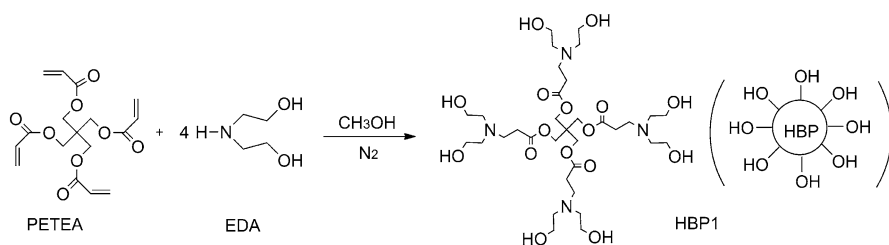Preparation of first-generation hyperbranched poly(amine-ester) (HBPE1)

PETEA (7.05 g, 0.02 mol), diethanolamine (8.41 g, 0.08 mol), and methanol as solvent were added to a 250-mL three-neck flask, which was equipped with a magnetic stirrer, nitrogen inlet, and a cooler. The mixture was stirred for 36 h at 35 °C under nitrogen atmosphere (Scheme 1). Then methanol was removed under vacuum. The first-generation hyperbranched poly(amine-ester) was obtained, named HBPE1. Finally, the HBPE1 was 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 ethanol at room temperature. The solution was dropwise added into ethyl ether. The precipitate was collected, washed with the mixture of ethanol and ethyl ether (1:1), and dried in a vacuum oven. The yield of HBPE1 was 11.75 g (76%).

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 (300 Hz, DMSO-d_6): 4.16–4.32 (–C–CH$_2$–O–), 2.41–2.75 (–OOC–CH$_2$), 3.57 (–CH$_2$–N<), 3.16–3.36 (–C$\underline{H}_2$–O$\underline{H}$).
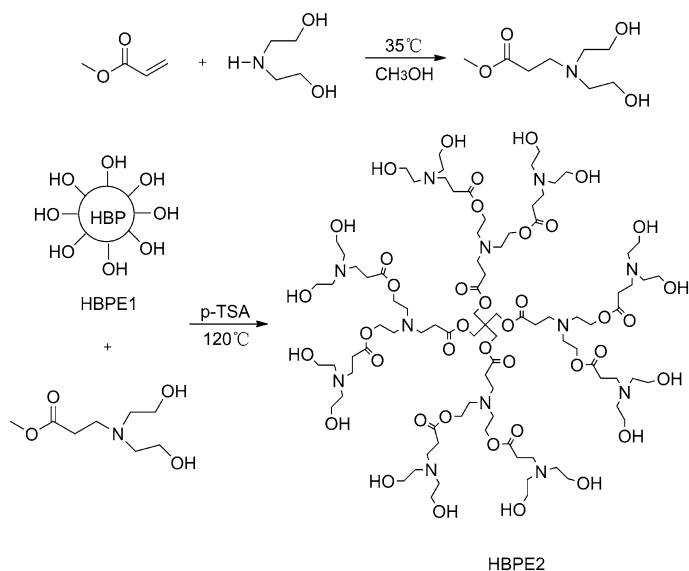
Preparation of second-generation hyperbranched poly(amine-ester) (HBPE2)

HBPE2 was synthesized according to a two-step procedure:

N,N-diethylol-3-amine methylpropionate was synthesized via Michael addition of methyl acrylate and diethanolamine according to the previously reported literature at the first step [13]. At the second step, the HBPE2 was synthesized based on HBPE1 and N,N-diethylol-3-amine methylpropionate 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 6 h at 120 °C in the presence of p-toluene sulphonic acid (p-TSA) as catalyst, which stripped off most of the methanol to the system. Then the HBPE2 was obtained

**Scheme 1** Preparation of first-generation hyperbranched poly(amine-ester) (HBPE1)

Scheme 2 Preparation of second-generation hyperbranched poly(amine-ester) (HBPE2)

(Scheme 2). Finally, the HBPE2 refined by fractional precipitation method and the procedure was similar to that of HBPE1. The yield of HBPE2 was 19.57 g (85%).

IR (KBr, cm^{-1}): 3383.3 cm^{-1} (–OH), 2949.5 cm^{-1} (–CH$_2$), 1722.8 cm^{-1} (–C=O), 1191.1 cm^{-1} (–C–O), 1456.9 cm^{-1} (–C–N–). ^{1}H-NMR (300 Hz, DMSO-d_6): 2.09 (–OOC–CH$_2$), 2.62–2.69 (–N–CH$_2$–), 3.51–3.53 (–C$\underline{H}_2$–OH), 3.57–3.61 (–CH$_2$–O$\underline{H}$), 3.93–4.01 (–CH$_2$–N–), 4.02–4.07 (–CH$_2$–OOC–), 4.14–4.15 (C–CH$_2$–O–).

Synthesis of second-generation hyperbranched polyurethane acrylate oligomers containing photoinitiator (HBP2UA-HMPP)

The HBP2UA-HMPP was synthesized via a three-step procedure. The synthesis of HBP2UA-HMPP (0.2:0.8) was described as follows: first, the IPDI-HEA was synthesized by IPDI/HEA. IPDI (28.45 g, 0.128 mol), hydroquinone (0.09 g), DBTDL (0.23 g) were mixed in a three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a separatory funnel. The HEA (21.02 g, 0.128 mol) 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 IPDI-HMPP was synthesized by IPDI/HMPP. IPDI (7.11 g, 0.032 mol), DBTDL (0.058 g) were mixed in a three-neck flask equipped with a magnetic stirrer, a reflux condenser, and a separatory funnel. The HMPP (5.25 g, 0.032 mol) 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/HMPP) by titration. Finally, the synthesized IPDI-HEA and IPDI-HMPP were added to the HBPE2 (0.01 mol, 20.46 g) dissolved in THF, and stirred for
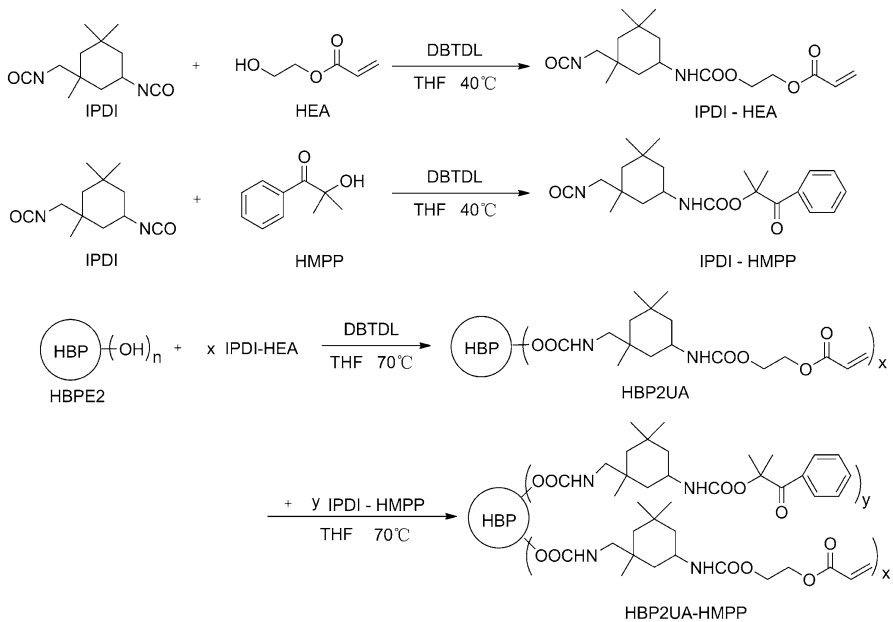
Scheme 3 Synthesis of HBP2UA-HMPP

about 9 h at 70 °C, then the HBP2UA-HMPP was obtained after the THF was evaporated. The synthesis process is described in Scheme 3. The HBP2UA-HMPP synthesized from IPDI-HEA (x) and IPDI-HMPP (y) with a mole ratio of 1.0:0, 0.8:0.2, and 0.9:0.1 was designated as HBP2UA, HBP2UA-HMPP (0.8:0.2), and HBP2UA-HMPP (0.1:0.9), respectively.

IR (KBr, cm^{-1}): 3324.2 cm^{-1}, 1537.0 cm^{-1} (N–H), 2949.5 cm^{-1} (C–H), 1713.2 cm^{-1} (C=O), 1191.1 cm^{-1} (–C–O), 1661.9 cm^{-1}, 810.0 cm^{-1} (C=C), 3068.0 cm^{-1} (benzene ring stretching vibration). ^{1}H-NMR (500 Hz, DMSO-d_6): 7.95 (–NH), 7.01-7.48 (–C–H of benzene ring), 5.95–6.36 (–COCH=CH$_2$), 3.97–4.27 (–CH$_2$CH$_2$OC=O), 1.41–1.61 (–CH$_2$–CH$_2$–), 0.83–1.76 (–CH$_2$ and –CH$_3$ of IPDI).

Measurements

The chemical structures of the oligomers were measured by FT-IR (Nicolet Magna IR650; Nicolet Analytical Instruments, Madison, WI) and by ^{1}H-NMR with a Bruker 500 MHz spectrometer (Karlsruhe, Germany). The elemental analysis was performed with a Leeman CE440 instrument. UV–Visible spectra of the oligomers were measured with UV–Vis spectrophotometer (Simadzu UV-2450, Japan). The molecular weight and polydispersity indices of the oligomers were estimated by Water 515-2410 GPC (Water, USA). Linear polystyrene standards were used for calibration and tetrahydrofuran (THF) as a solvent. 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 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 thermal stabilities of the oligomers were characterized by thermogravimetric analysis (TGA). TGA spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under air purge at a heating rate of 20 °C/min. The solubilities of the oligomers were determined by the observation of the soluble process in different solvents at room temperature.

Results and discussion

Preparation of HBPE1 and HBPE2

The HBPE1 was synthesized via Michael addition of PETEA and diethanolamine. The HBPE2 was synthesized by step by step polymerization process with HBPE1 as core molecule and N,N-diethylol-3-amine methylpropionate as branched monomer, which was synthesized via addition of methyl acrylate and diethanolamine. In order to obtain a hyperbranched poly(amine-ester) with more regular structure, the N,N-diethylol-3-amine methylpropionate was slowly added [14]. Hydroxyl value and element analysis of HBPE1 and HBPE2 are summarized in Table 1. The hydroxyl value of HBPE1 and HBPE2 is 10.4 and 8.1, respectively. It is evident that the hydroxyl value of hyperbranched polyesters close to their theoretical ones. The element contents of N, C, and H in HBPE1 are 7.14, 48.97, and 8.27%, and the corresponding values of HBPE2 are 7.31, 49.21, and 8.22%, respectively. It can also been seen that the structures of HBPE1 and HBPE2 are not well defined and there are some side reaction in the synthesis process.

FT-IR and ^{1}H-NMR

The FT-IR spectra of HBPE2, HBP2UA, and HBP2UA-HMPP are shown in Fig. 1. In Fig. 1, the characteristic peaks of HBP2UA-HMPP were marked. The peak at 3324.2 cm^{-1} is assigned to N–H stretching vibration of HBP2UA-HMPP. There are three peaks at 1661.9, 1407.0, and 810.0 cm^{-1} assigned to the double bonds of the acryl groups, indicating that the IPDI-HEA groups were successfully introduced into the HBPE2 [15]. The band at 3068.0 cm^{-1} is assigned to benzene ring stretching vibration. The peaks at 1713.2, 1191.1, and 1537.0 cm^{-1} are assigned to C=O, –C–O, and N–H, respectively. It shows the HMPP was reacted with HBPE2. Figure 2 shows the ^{1}H-NMR spectra of the HBP2UA and HBP2UA-HMPP. From the ^{1}H-NMR spectrum of HBP2UA-HMPP, the peak at 7.95 is assigned to the hydrogen atom of amide group, and those at 5.95–6.36 ppm are the acrylic group in the molecular structure of HBP2UA-HMPP. The peaks at 7.01–7.48 ppm are assigned to the hydrogen atom of benzene ring and the peaks below 2.0 ppm are assigned to the hydrogen atom of IPDI. The ^{1}H-NMR spectrum of HBP2UA is similar to that of HBP2UA-HMPP. Some of the characteristic peaks in HBP2UA-HMPP can also be observed in the spectrum of HBP2UA [16]. From the above analysis, it is confirmed that the hyperbranched polyurethane acrylate oligomers containing photoinitiator are successfully synthesized.

Table 1 Characteristics of the HBPE1 and HBPE2

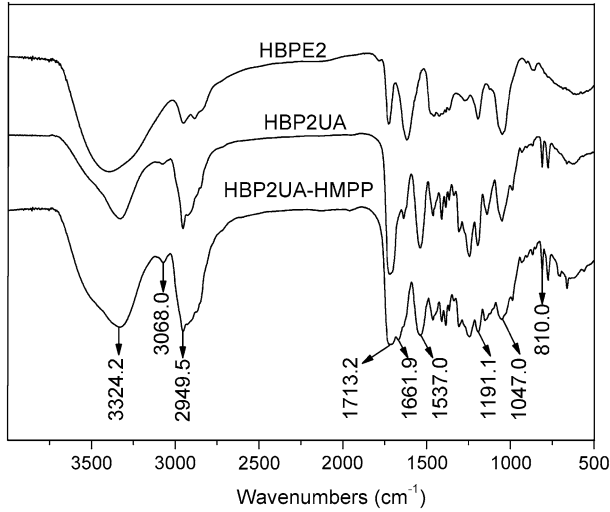| Sample | Generation number | Theoretical functionality | Hydroxyl value (mmol/g) | | Element analysis (%) | | | | | |
			Theoretical	Measured	Theoretical			Measured		
					N	C	H	N	C	H
HBPE1	1	8	10.4	10.4	7.25	51.28	8.35	7.14	48.97	8.27
HBPE2	2	16	7.8	8.1	8.21	52.24	8.27	7.31	49.21	8.22

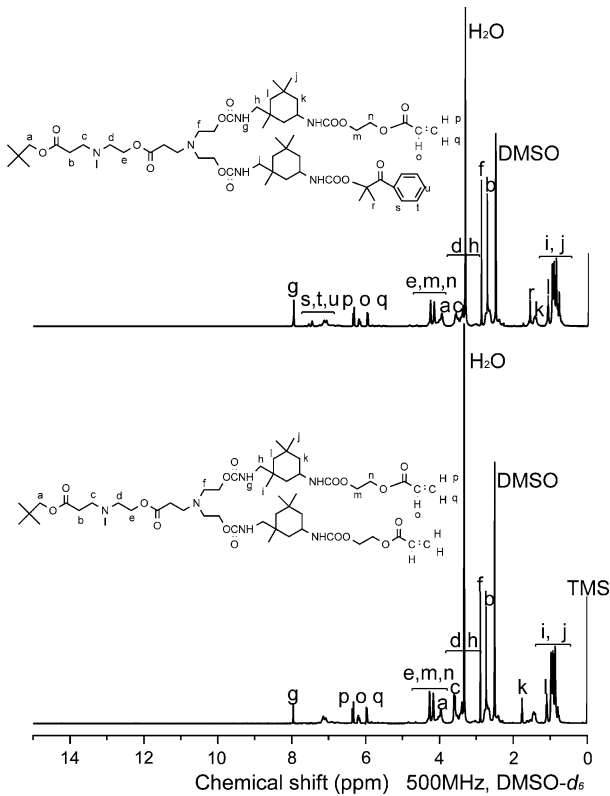**Fig. 1** FT-IR spectra of HBPE2, HBP2UA, and HBP2UA-HMPP (0.2:0.8)

Fig. 2 ^{1}H-NMR spectra of HBP2UA-HMPP (0.2:0.8) and HBP2UA

Preparation of IPDI-HEA and IPDI-HMPP

The IPDI-HEA and IPDI-HMPP were synthesized by the reaction of IPDI with HEA and HMPP in the presence of DBTDL as catalyst under N_2 atmosphere. The mixture was stirred at 50 °C and the content of isocyanate was measured by titration. It is known that the IPDI has two –NCO groups of unequal reactivity. The cycloaliphatic –NCO group is more reactive than the aliphatic –NCO group in the urethane reaction at 50 °C [17]. Figure 3 shows the variation of [–NCO] of IPDI-HEA and IPDI-HMPP with time. At the beginning, the [–NCO] of IPDI-HEA and IPDI-HMPP was 6.32 and 5.49 mmol/cm³, respectively. The [–NCO] was decreased with time. When reaction for 6 h, the [–NCO] was 3.82 mmol/cm³ for IPDI-HEA and 4.09 mmol/cm³ for IPDI-HMPP. The [–NCO] of IPDI-HMPP was higher than that of IPDI-HEA. This may be explained that the HMPP has much larger steric hindrance than HEA. After 12 h, the [–NCO] was all arrived at half their initial concentration, so the reaction time should be 12 h at 50 °C.

GPC

The molecular weights and polydispersity index of the HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) were analyzed by GPC in THF, using a linear polystyrene (PS) standard. As can be seen from Table 2, the number average
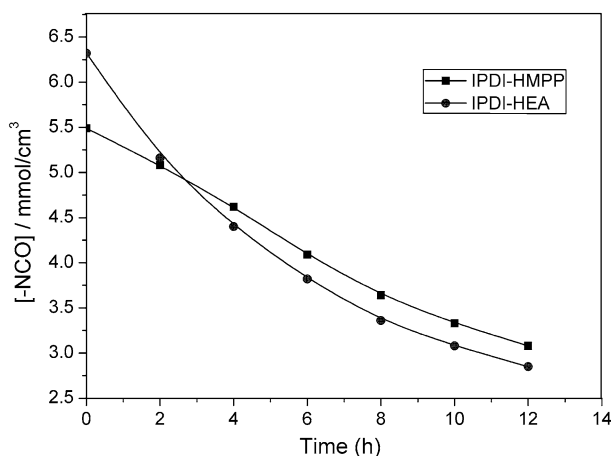

Fig. 3 Variation of [–NCO] with time (h)

Table 2 Molecular weight distributions of HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9)

Samples	M_n	M_w	M_w/M_n
HBP2UA	1059	1408	1.33
HBP2UA-HMPP (0.2:0.8)	1083	1332	1.23
HBP2UA-HMPP (0.1:0.9)	1360	1768	1.30

molecular weight, molecular weight, and polydispersity index of HBP2UA-HMPP (0.2:0.8) are 1083, 1332, and 1.23, and the corresponding values of HBP2UA-HMPP (0.1:0.9) are 1360, 1768, and 1.30, respectively. It is known that the hydrodynamic volumes of hyperbranched polymer are much lower than that of linear PS used for calibration. As no appropriate hyperbranched polymer standards are available for calibration, the results are much lower than theoretical values, and are not absolute values [18, 19]. The polydispersity index of the HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) are similar, implying that they have similar structure.

UV/Vis absorption spectrum

The HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) were dissolved in ethanol and diluted to 0.01 mmol/L. The solution was put into quartz glass cell and characterized with UV–Vis spectrum analyzer. The UV–Vis absorbance spectra of the oligomers are shown in Fig. 4 and the cutoff wavelengths of the samples are in the range of 180–400 nm. It can be seen that the spectra of HBP2UA-HMPP (0.2:0.8) and HBP2UA-HMPP (0.1:0.9) are similar and the miscellaneous absorption peaks are the ultraviolet absorption of benzene ring. These mean that the HMPP were successfully introduced into the hyperbranched urethane acrylate. The maximum absorption band of HMPP is at around 320 nm. After grafting HMPP into the hyperbranched polyurethane acrylate oligomers, about 10 nm red shift can be observed (from 320 to 330 nm). The molecular structures of HBP2UA-HMPP (0.2:0.8) and HBP2UA-HMPP (0.1:0.9) contain conjugated carbon–carbon double bond (C=C) and carbon–oxygen double bond (C=O). They can produce n–π^* electronic transitions [20, 21]. It can also be seen that the
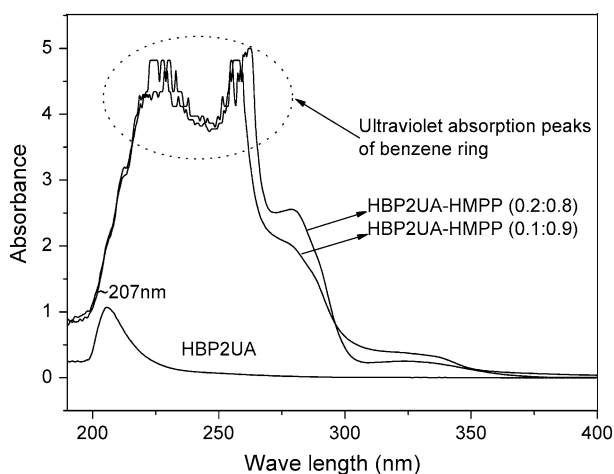

Fig. 4 UV–Vis absorbance spectra of HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) in C₂H₅OH

HBP2UA have a sharp absorption bands around 207 nm. This may be the $\pi^*-\pi^*$ electronic transitions of conjugate carbon–carbon double bond (C=C) and carbon–oxygen double bond (C=O) of HBP2UA. From above analysis, it can be expected that the oligomers can photopolymerize under UV illumination.

UV curing

The UV-curing properties of synthesized HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) were measured by FT-IR. The oligomers were dissolved in ethanol. The obtained solution was cast on a NaCl plate and dried to make film on the plate. In order to better match the photoinitiator, the film was exposed to 23 mW/cm^2 of 365 nm light for increasing amount of time. Figure 5 shows the FT-IR spectra of HBP2UA-HMPP (0.2:0.8) at various curing time (s) (20, 40, 60, 80, and 100).

The change in the C–H out of plane deformation vibration of the acrylate double bond near 810 cm^{-1} 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 conversion of double bond is calculated as:

$$\text{Double bond conversion } (\%) = \frac{[(H_{810}/H_{2951})t - (H_{810}/H_{2951})0]}{(H_{810}/H_{2951})0} \times 100,$$

where $(H_{810}/H_{2951})t$ is the peak height at 810 cm^{-1} after irradiation for t seconds, $(H_{810}/H_{2951})0$ is the peak height at 810 cm^{-1} before irradiation [22].

Figure 6 illustrates the relationships between the double bond conversion (%) and irradiation time (s). It is observed that the oligomers containing photoinitiator have higher conversions, and the conversion of HBP2UA-HMPP (0.2:0.8) and
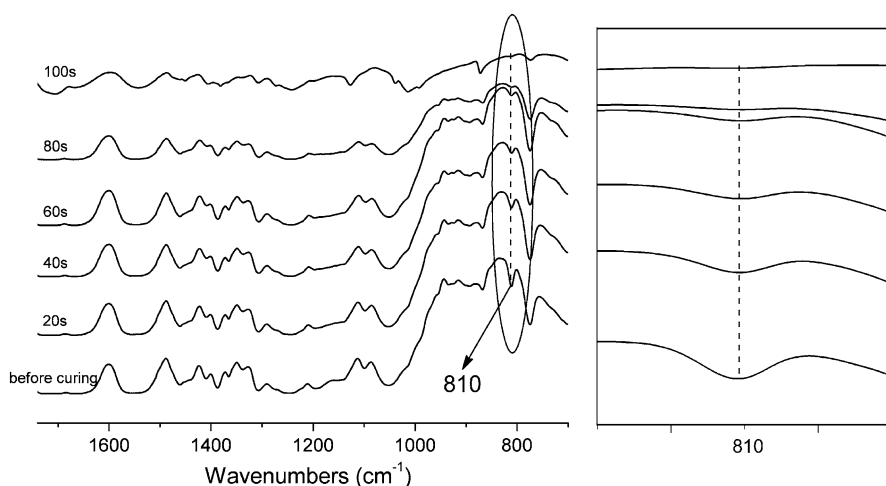

Fig. 5 The FT-IR spectra of HBP2UA-HMPP (0.2:0.8) at various curing time (s)
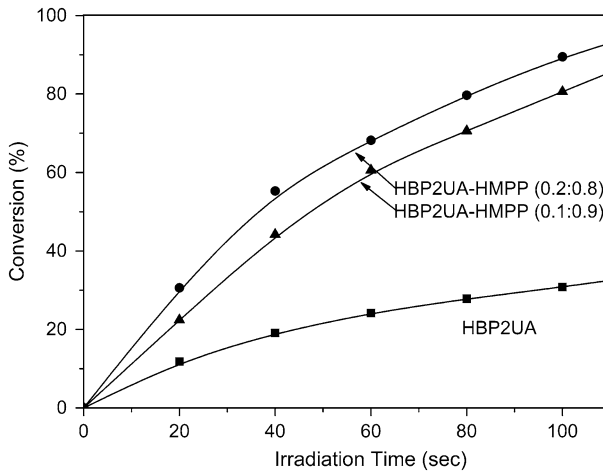
Fig. 6 The relationships between the double bond conversion (%) and irradiation time (s)

HBP2UA-HMPP (0.1:0.9) reached at 68.2 and 60.4% after 60 s. The HBP2UA-HMPP (0.2:0.8) showed higher conversion than HBP2UA-HMPP (0.1:0.9). This result indicates that the photosensitivity of HBP2UA-HMPP (0.2:0.8) is higher than that of HBP2UA-HMPP (0.1:0.9) due to the HBP2UA-HMPP (0.2:0.8) has many photoinitiator groups (HMPP) at the ends [23, 24]. However, the HBP2UA shows lower conversions in the absence of photoinitiator. So the photoinitiator is one of the most important components for UV-curing materials.
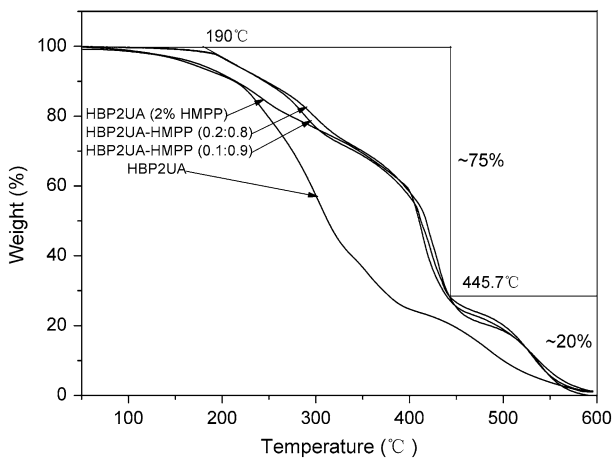

Fig. 7 TG curves of UV-cured HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) in an air atmosphere

Thermal properties of the cured film

The HBP2UA, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) were diluted with ethanol, for HBP2UA 2% Dorocure 1173 was added. The mixture was painted on the glass plate and dried in an oven for 30 min to remove the solvent, and then it was exposed to 23 mW/cm^2 of 365 nm UV lamp for 200 s. After UV exposure, the UV-cured films ($\sim$ 10 mg) were investigated by TGA at a constant heating rate of 20 °C min^{-1} in air [25, 26]. The TG curves of UV-cured oligomers are shown in Fig. 7. It can be seen that the TG curves of UV-cured HBP2UA-HMPP (0.2:0.8) are analogous to that of HBP2UA-HMPP (0.1:0.9). The onset temperature of decomposition was 190.0 °C. In the temperature ranging from 190.0 to 445.7 °C, about 75% weight loss was observed. These were due to the decomposition of crosslinked urethane–acrylate terminal groups. From 457.2 to 600 °C, about 20% weight loss. This may be attribute to the core of the HBP2UA-HMPP begin to decompose. The onset decomposition temperature of HBP2UA (2% HMPP) is lower than that of HBP2UA-HMPP (0.2:0.8) and HBP2UA-HMPP (0.1:0.9). It can be explained that the photoinitiators do not be compatible with the HBP2UA. Some of the HBP2UA have not fully cured. In order to compare to the thermal stability of the oligomers, the TG curves of HBP2UA in the absence of HMPP was also investigated. It can be seen that the HBP2UA-HMPP (0.2:0.8), HBP2UA-HMPP (0.1:0.9), and HBP2UA (2% HMPP) are more thermally stable than the HBP2UA in the absence of HMPP. From the above analysis, it can be concluded that the oligomers containing photoinitiator have good thermal stability [27].

Solubility

The solubilities of the HBPE2, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9) were examined at room temperature. These results are summarized in Table 3. All the samples were easily dissolved in strong polar organic solvents, such

Table 3 Solubility of the HBPE2, HBP2UA-HMPP (0.2:0.8), and HBP2UA-HMPP (0.1:0.9)

Solvent	HBPE2	HBP2UA	HBP2UA-HMPP (0.2:0.8)	HBP2UA-HMPP (0.1:0.9)
Water	++	++	++	++
Methanol	+	+	+	+
Acetone	+	+	+	+
DMAC	++	++	++	++
DMF	++	++	++	++
THF	+	+	+	+
DMSO	++	++	++	++
1,4-Dioxane	+	+	+	+
Ethylether	−	−	−	−
Cyclohexane	−	−	−	−

++ soluble at room temperature, + partially soluble, − insoluble

as water, DMAC, DMF, and DMSO, and partially soluble in methanol, acetone, THF, and 1,4-dioxane. The samples could hardly be dissolved in ethylether and cyclohexane. This may be explained that the HBPE2 have many hydroxyl groups, which are polar groups while the molecular structure of HBP2UA-HMPP (0.2:0.8) and HBP2UA-HMPP (0.1:0.9) has rigid benzene ring groups. Therefore, the oligomers can be only dissolved in strong polar organic solvents [28].

Conclusions

In conclusion, we successfully synthesized the second-generation hyperbranched polyurethane acrylate oligomers containing photoinitiator by introducing IPDI-HEA and IPDI-HMPP into periphery of hyperbranched poly(amine-ester)s at different feed ration. The obtained oligomers have UV absorption peaks at about 230 nm and have high double bond conversion under UV irradiation. Moreover, the oligomers have excellent solubility in strong polar organic solvents (e.g., DMF, DMAC, DMSO) and its UV-cured films have good thermal stability. These results mean that our synthesized hyperbranched polyurethane acrylate oligomers containing photo-initiator can be used for UV-curing materials.

References

 1. Hwang JS, Kim MH, Seo DS, Won JW, Moon DK, Kim DP (2009) Synthesis and characterization of polyurethane acrylate oligomers for electrodes protection adhesives of plasma display panel (PDP). Mol Cryst Liq Cryst 514:632–639
 2. Ates S, Aydogan B, Torun L, Yagci Y (2010) Synthesis and characterization of triptycene type cross-linker and its use in photoinduced curing applications. Polymer 51:825–831
 3. Wang SJ, Liu X, Kong J, Tian W, Fan XD, Xu H, Lu JR (2010) Synthesis and UV curing kinetics of rapidly UV-curable hyperbranched polycarbosiloxanes. Polym Int 59:1323–1330
 4. Bauer F, Decker U, Czihal K, Mehnert R, Riedel C, Riemschneider M, Schubert R, Buchmeiser MR (2009) UV curing and matting of acrylate nanocomposite coatings by 172 nm excimer irradiation. Prog Org Coat 64:474–481
 5. Wang SJ, Fan XD, Kong J, Lu JR (2009) Synthesis, characterization and UV curing kinetics of hyperbranched polysiloxysilanes from A(2) and CB2 type monomers. Polymer 50:3587–3594
 6. Wen YN, Jiang XS, Liu R, Yin J (2009) Amphipathic hyperbranched polymeric thioxanthone photoinitiators (AHPTXs): synthesis, characterization and photoinitiated polymerization. Polymer 50:3917–3923
 7. Gacal B, Akat H, Balta DK, Arsu N, Yagci Y (2008) Synthesis and characterization of polymeric thioxanthone photoinitiatiors via double click reactions. Macromolecules 41:2401–2405
 8. Zhao XF, Liu LX, Dai HX, Ma CX, Tan XH, Yu RH (2009) Synthesis and application of water-soluble hyperbranched poly(ester)s from maleic anhydride and glycerol. J Appl Polym Sci 113:3376–3381
 9. Morgan S, Ye ZB, Zhang KJ, Subramanian R (2008) One-pot synthesis of hyperbranched polyeth-ylenes tethered with pendant acryloyl functionalities by chain walking copolymerizations. Macromol Chem Phys 209:2232–2240
10. Mallepally RR, Smirnova I, Arlt W, Seiler M, Klee-Laquai SK, Hills G (2009) Enzymatic degra-dation of hyperbranched polyesters. J Appl Polym Sci 112:1873–1881
11. Bao FF, Shi WF (2010) Synthesis and properties of hyperbranched polyurethane acrylate used for UV curing coatings. Prog Org Coat 68:334–339

12. Dzunuzovic E, Tasic S, Bozic B, Jeremic K, Dunjic B (2006) Photoreactive hyperbranched urethane acrylates modified with a branched saturated fatty acid. React Funct Polym 66:1097–1105
13. Sun F, Shi J, Du HG, Nie J (2009) Synthesis and characterization of hyperbranched photosensitive polysiloxane urethane acrylate. Prog Org Coat 66:412–419
14. Murillo EA, Vallejo PP, Sierra L, Lopez BL (2009) Characterization of hyperbranched polyol polyesters based on 2,2-bis(methylol propionic acid) and pentaerythritol. J Appl Polym Sci 112: 200–207
15. Kim HD, Kim TW (1998) Preparation and properties of UV-curable polyurethane acrylate ionomers. J Appl Polym Sci 67:2153–2162
16. Huang L, Li YM, Yang JW, Zeng ZH, Chen YL (2009) Self-initiated photopolymerization of hyperbranched acrylates. Polymer 50:4325–4333
17. Cheng XE, Huang ZG, Liu JH, Shi WF (2007) Synthesis and properties of semi-crystalline hyperbranched poly(ester-amide) grafted with long alkyl chains used for UV-curable powder coatings. Prog Org Coat 59:284–290
18. Fu Q, Cheng LL, Zhang Y, Shi WF (2008) Preparation and reversible photo-crosslinking/photocleavage behavior of 4-methylcoumarin functionalized hyperbranched polyester. Polymer 49: 4981–4988
19. Vukovic J, Jovanovic S, Lechner MD, Vodnik V (2009) Melt rheology of aliphatic hyperbranched polyesters. J Appl Polym Sci 112:2925–2934
20. Lu WH, Xu WJ, Wu YM, Zhou X, Lu YB, Xiong YQ (2006) Synthesis of dendritic poly(urethane acrylate) used for UV-curable coatings. Prog Org Coat 56:252–255
21. Liu JH, Shih JC (2001) Preparation and lithographic performance of novel copolymers having acid labile pendant alicyclic ether moieties. J Polym Res 8:143–150
22. Tasic S, Bozic B, Dunjic B (2004) Synthesis of new hyperbranched urethane-acrylates and their evaluation in UV-curable coatings. Prog Org Coat 51:321–328
23. Rajabhuvaneswari A, Pandurangan A, Subramanian K (2009) Radical copolymerization of photocrosslinkable cinnamoylphenylmethacrylate and acrylamide. J Polym Res 16:125–132
24. Mishra RS, Mishra AK, Raju K (2009) Synthesis and property study of UV-curable hyperbranched polyurethane acrylate/ZnO hybrid coatings. Eur Polym J 45:960–966
25. Hoidy WH, Al-Mulla EAJ, Al-Janabi KW (2010) Mechanical and thermal properties of PLLA/PCL modified clay nanocomposites. J Polym Environ 18:608–616
26. Wang R, Liu W, Fang L, Xu C (2010) Synthesis, characterization, and properties of novel phenylenesilazane-acetylene polymers. Polymer 51:5970–5976
27. Miao H, Cheng LL, Shi WF (2009) Fluorinated hyperbranched polyester acrylate used as an additive for UV curing coatings. Prog Org Coat 65:71–76
28. Maruyama K, Kudo H, Ikehara T, Nishikubo T, Nishimura I, Shishido A, Ikeda T (2007) Synthesis and properties of photo-cross-linkable hyperbranched poly(urethane)s containing both terminal methacryloyl groups and carboxyl groups. Macromolecules 40:4895–4900