Synthesis of UV-curable Hyperbranched Polyurethane (Meth)acrylate Oligomers via Thiol-ene "Click" Chemistry

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ABSTRACT: First, the second-generation hyperbranched poly(amine-ester) (G2-OH) was successfully prepared by thiol-ene "click" chemistry. Subsequently, a series of photosensitive hyperbranched oligomers (G2-ORs) were synthesized by facile modifications of the G2-OH with acryloyl chloride, methacryloyl chloride, IPDI-HEA, and IPDI-HEMA, respectively. The structures of hyperbranched oligomers were characterized by element analysis, FT-IR, ^{1}H NMR, GPC and viscosity measurement. It was shown that these synthesized oligomers have narrow molecular weight distribution and low intrinsic viscosity at 30°C. UV–vis spectra results showed that the G2-ORs had sharp absorption bands at around 202 nm. The results of photosensitivities measurement indicated that the G2-Macr shows the highest photosensitive than other hyperbranched oligomers in the absence of photoinitiator. In addition, these UV-cured photosensitive G2-ORs had good thermal properties. The solubilities of the synthesized hyperbranched oligomers were also examined. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 128: 4261–4270, 2013

INTRODUCTION

Hyperbranched polymers, especially hyperbranched polyesters (HBPEs), have become one of the research focuses in polymer research field and attracted a great deal of attention in recent decades. They own highly branched molecular structures, a large number of terminal functional groups and inner cavities, showing low viscosity, good solubility, and high chemical reactivity.[1–4] These polymers have been widely used in several applications, such as coatings, catalysis, additives, blends, etc.[5–8] A large number of HBPEs have been reported in the literature, and some are commercially available.[9–11] Investigation on the modification of HBPEs has become an important research direction.

UV-curing technology has many great interest features from the viewpoints of high efficiency, low energy consumption, and environmental friendliness and has been widely used in many fields such as coating, adhesives, printing inks and photoresist and so on.[12–14] UV-curable resin is the most important component of UV-curable system. In general, (meth)acrylate oligomers are one of the most important UV-curable resins. However, traditional (meth)acrylate oligomers are commonly linear molecules, which have some disadvantages, such as high viscosity, requiring more reactive diluents and low reactivity.[15,16] Introduction of hyperbranched polymer into UV-curing system has

drawn polymer scientists' considerable attention. For example, Wei et al.[17] synthesized a hyperbranched (meth)acrylated poly (amine ester) by the modification of the hydroxyl end groups of the second generation of a hyperbranched poly(amine ester) with acryloyl chloride and methacrylic anhydride. They also studied the UV curing behavior of methacrylated hyperbranched poly(amine-ester)s.[18] Tang et al.[19] prepared a series of hyperbranched poly(ester-amine)s with terminal acrylate groups through Michael addition between piperazine (A$_2$) and trimethylolpropanetriacrylate (TMPTA) (B$_3$) under molar ratios ranged from 1/2 to 1/1.08 and investigated their properties. Recently, novel high performance UV-curable coatings based on epoxy acrylate (EA) oligomer and hyperbranched polysiloxane (HPSi) were prepared by Liu et al.[20] Although all kinds of hyperbranched UV-curable oligomers have been synthesized, to the best of our knowledge, the hyperbranched UV-curable oligomers which was synthesized by thiol-ene "click" chemistry have few reported.[21,22]

In this article, the first and second-generation hyperbranched poly(amine-ester) (G1-OH, G2-OH) were prepared by 1,4-addition and thiol-ene "click" chemistry at first. Then a series of UV-curing hyperbranched oligomers were synthesized by modifying the hydroxyl groups of G2-OH with acryloyl chloride,
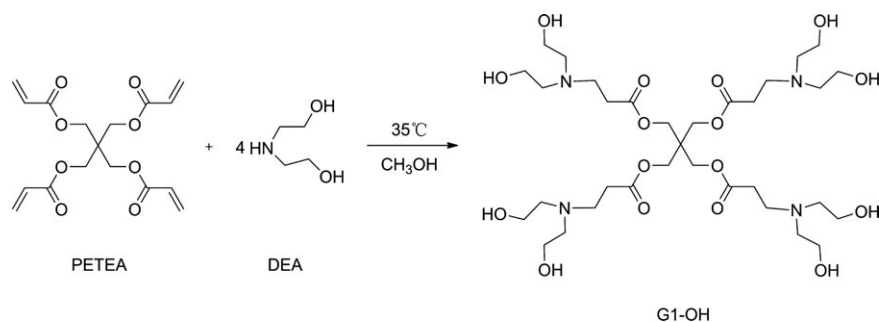
Scheme 1. Preparation of first-generation hyperbranched poly(amine-ester).

methacryloyl chloride and the half adduct of isophorone diisocyanate and 2-hydroxyethyl (meth)acrylate (IPDI-HEA, IPDI-HEMA). These reaction steps we chose are highly efficient, high yielding, and reproducible. The molecular structures of original and modified hyperbranched oligomers were characterized by element analysis, FT-IR, ^{1}H NMR, GPC, and viscosity measurement. The thermal properties of UV-cured hyperbranched oligomers were characterized by TGA. In addition, the UV–vis absorption spectrum, photosensitivity, and solubilities of the hyperbranched oligomers were also examined.

EXPERIMENTAL

Materials

Pentaerythritol tetraacrylate (PETEA) and trimethylolpropane diallyl ether were purchased from Aldrich, USA. The 2-hydroxyethyl acrylate (HEA), 2-hydroxyethyl methacrylate (HEMA), and isophorone diisocyanate (IPDI) were obtained from Aladdin Reagent (Shanghai, China). The 2-hydroxy-2-methylpropiophenone (HMPP) and 3-mercapto-1,2-propanediol were provided by TCI-EP (Tokyo Kasei, Japan). Methyl acrylate (MA), diethanolamine (EDA), 1,4-dioxane, dibutylamine, maleic anhydride (MAH) and dibutyltin dilaurate (DBTDL) were purchased from Lingfeng Chemical Reagent (Shanghai, China). Methanol, tetrahydrofuran (THF), dimethylformamide (DMF), dimethylacetamide (DMAC), ethyl ether, acetone, and methylbenzene were obtained from Sinopharm Chemical Reagent, China. All other common chemical reagents were all analytical grade and used as received.

Measurements

The FT-IR spectra were recorded on a Nicolet Magna IR650 Fourier transform infrared spectrometer (Madison, WI). The ^{1}H NMR spectra were recorded on a Bruker 300 MHz nuclear magnetic resonance instrument (Karlsruhe, Germany). The gel permeation chromatographic (GPC) analysis was performed on a GPC apparatus (Water, USA) at 25°C. THF was used as an eluent with an elution rate of 1.0 mLmin^{-1}. The standard PSt was used for the calibration of samples. Intrinsic viscosity measurements were carried out with an Ubbelohde viscometer in DMF at 30°C ± 0.1°C. Ultraviolet–visible (UV–vis) spectra of the hyperbranched oligomers were measured with UV–vis spectrophotometer (Simadzu UV-2450, Japan). The photosensitivity of the hyperbranched oligomers were monitored by FT-IR. Thermogravimetric analysis (TGA) was performed using a TA Instruments Q20 model TGA. The samples (about 10 mg) were run from 50 to 600°C at a heating rate of 20°C min^{-1} in an air flow. The hydroxyl values

of hyperbranched poly(amine-ester)s were determined by the following method. Hyperbranched poly(amine-ester)s were dissolved in excess phthalic anhydride with imidazole as a catalyst (in pyridine) at ~100°C for 3 h to acetylate the hydroxyl groups in hyperbranched poly(amine-ester)s. By back-titrating the above mixture with NaOH solution (0.1 molL^{-1}, in water) at room temperature, the hydroxyl values of hyperbranched poly(amine-ester)s were calculated. The content of isocyano (—NCO%) was determined according to GB/T 12009.4-1989. The solubilities of the oligomers were determined by the observation of the soluble process in different solvents at room temperature.
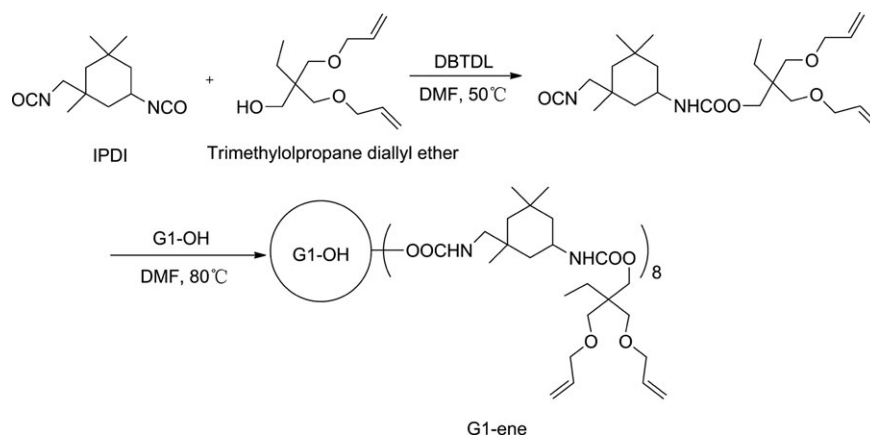
Preparation of First-Generation Hyperbranched Poly(amine-ester) (G1-OH)

G1-OH was synthesized according to Scheme 1. PETEA (3.52 g, 0.01 mol), DEA (4.21 g, 0.04 mol) and 30 mL methanol as solvent were added to a 150-mL three-necked flask, which was equipped with a cooler, nitrogen gas inlet, and a magnetic stirrer. The mixture was stirred for 36 h at 35°C under nitrogen atmosphere. After cooling to room temperature, the white precipitate was filtrated, washed with acetone, and dried under vacuum. The first-generation hyperbranched poly (amine-ester) was obtained, named G1-OH (Yield: 6.03 g, 78%).

IR (KBr, cm^{-1}): 3327.4 cm^{-1} (—OH), 2886.2–2955.7 cm^{-1} (—C—H stretching vibration), 1724.9 cm^{-1} (—C=O), 1452.1 cm^{-1} (—C—N—), 1126.9 cm^{-1} (—C—O), 871.6 cm^{-1} (—C—H deformation vibration). ^{1}H NMR (DMSO-d_6, ppm): 4.16–4.18 (—C—CH$_2$—O—), 3.31–3.35 (—CH$_2$—OH, —CH$_2$—N<), and 2.48–2.51 (—OOC—CH$_2$, —N—CH$_2$—).

Preparation of First-Generation Acrylate-Terminated Oligomer (G1-ene)

The G1-ene was synthesized via a two-step procedure. First, NCO bearing adduct was obtained by the reaction between the cycloaliphatic NCO group of IPDI and the OH groups of trimethylolpropane diallyl ether with DBTDL as catalyst. IPDI (4.45 g, 0.02 mol), hydroquinone (0.128 g), DBTDL (0.315 g), and 30 mL DMF were mixed in a four-necked flask equipped with a magnetic stirrer, nitrogen inlet, a thermometer, and a dropping funnel. The trimethylolpropane diallyl ether (4.29 g, 0.02 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 monoisocyanate by titration. Second, the resultant NCO bearing adduct was reacted with G1-OH (1.93 g, 0.0025 mol) dissolved in 10 mL DMF at 70°C. The reaction continued

Scheme 2. Preparation of first-generation acrylate-terminated oligomer.

until the NCO group was disappeared, and then the reaction mixture was poured into ethyl ether. The precipitate was collected and dried *in vacuo* to give a yellow viscous fluid (Yield: 9.07 g, 85%). The synthesis process is described in Scheme 2.

IR (KBr, cm^{-1}): 3379.6 cm^{-1}, 1544.9 cm^{-1} (—N—H), 2926.8–2955.7 cm^{-1} (—CH$_3$, —CH$_2$—), 1701.9 cm^{-1} (C=O), 1035.8 cm^{-1} (—C—O), 1649.6, 1405.6, and 778.7 cm^{-1} (C=C). ^{1}H NMR (DMSO-d_6, ppm): 8.00 (—N—H), 5.10–5.88 (O—C$\underline{H}_2$—CH=C$\underline{H}_2$), 4.19–4.26 (O—C$\underline{H}_2$—CH=CH$_2$), 3.81–3.90 (C—C$\underline{H}_2$—O), 2.49–2.77 (>N—C$\underline{H}_2$—, OO—CH$_2$—C$\underline{H}_2$—N<), 0.80–1.42 (—CH$_2$ and —CH$_3$ of IPDI).

Preparation of Second-Generation Hyperbranched Poly(amine-ester) by Thiol-Ene "Click" Chemistry (G2-OH)
G1-ene (8.53 g, 2 mmol) dissolved in 50 mL THF, 1.5 equiv of 3-mercapto-1, 2-propanediol (5.19 g, 48 mmol), trace amounts of the photoinitiator (2,2-dimethoxy-2-phenylacetophenone) were mixed in 100-mL round-bottomed single-necked flask equipped with a magnetic stirrer. The mixture was irradiated by a hand-held UV-lamp (λ_{ex} = 365 nm) for 30 min at room temperature, and then it was added into ethyl ether. The precipitate was collected and dried in a vacuum oven to give 9.6 g of pure G2-OH (yield: 10.97 g, 80%). The photoinitiator and excess thioglycolic can be easily removed by the precipitation. The synthesis process is described in Scheme 3.

IR (KBr, cm^{-1}): 3379.7 cm^{-1} (—CH$_2$—OH), 2874.5–2926.8 cm^{-1} (—C—H stretching vibration), 1696.1 cm^{-1} (—C=O), 1544.9 cm^{-1} (—N—H), 1034.4 cm^{-1} (—C—O), 1457.9 cm^{-1} (—C—N), 772.8 cm^{-1} (—C—H deformation vibration). ^{1}H NMR (DMSO-d_6, ppm): 8.0 (—N—H), 3.63–3.81 (—CH$_2$—OH), 3.21–3.36 (—CH$_2$—N<), 2.72–2.88 (>N—CH$_2$—, OO—CH$_2$—CH$_2$—N<), 2.49–2.58 (—CH$_2$—S), 0.79–1.45 (—CH$_2$ and —CH$_3$ of IPDI).

Preparation of IPDI-HEA and IPDI-HEMA
The IPDI-HEA and IPDI-HEMA were synthesized by the reaction of IPDI with HEA and HEMA in the presence of DBTDL as catalyst.[23] The specific procedure for the synthesis of IPDI-HEA was described as follows: IPDI (7.1 g, 32 mmol), 0.23 g DBTDL and 30 mL of acetone were added into a 100-mL three-necked flask equipped with a magnetic stirrer, nitrogen inlet and a dropping funnel. The flask was put into ice water, HEA (3.7 g, 32

mmol) was slowly dropped into the mixture at 0°C and stirred for 4 h. Then the temperature was raise to 50°C, and stirred for another 12 h until the theoretical value of isocyanate was obtained by titration. The obtained half-adduct was denominated as IPDI-HEA. The synthesis process is described in Scheme 4.

Synthesis of G2-Acr (G2-Macr)
A 100-mL single-necked flask equipped with a magnetic stir bar was charged with G2-OH (6.0 g, 1.0 mmol) and potassium carbonate (4.4 g, 32 mmol) in 40 mL of acetone (Scheme 5). The flask was cooled in a water/ice-bath, an excess amount (4.3 g, 48 mmol) of acryloyl chloride compound (methacryloyl chloride: 5.0 g, 48 mmol) diluted in 10 mL acetone was added slowly by syringe. The mixture was stirred at room temperature for 24 h. After filtration, the solvent was evaporated to yield the crude product. The obtained crude product was dissolved in CH$_2$Cl$_2$ and washed twice with a 10% Na$_2$CO$_3$ solution. The organic layer was separated, dried over MgSO$_4$, filtered, and then concentrated at reduced pressure to yellow viscous fluids, named G2-Acr (G2-Macr).

G2-Acr: (Yield: 5.9 g, 76%). IR (KBr, cm^{-1}): 3420.3 cm^{-1}, 1527.8 cm^{-1} (—N—H), 2955.7 cm^{-1} (—CH$_3$, —CH$_2$—), 1724.9 cm^{-1} (—C=O), 1185.1 cm^{-1} (—C—O), 1637.8, 1405.8, and 810.0 cm^{-1} (—C=C). ^{1}H NMR (DMSO-d_6, ppm): 8.21 (—N—H), 5.74–6.36 (—OOCH$_2$—CH=CH$_2$), 4.11–4.28 (C—CH$_2$—O—), 3.17–3.29 (—CH$_2$—N<), 2.49–2.62 (—OOC—CH$_2$, >N—CH$_2$—, —CH$_2$—S—), 0.78–1.73 (—CH$_2$ and —CH$_3$ of IPDI).

G2-Macr: (Yield: 7.6 g, 78%). IR (KBr, cm^{-1}): 3396.8 cm^{-1}, 1534.6 cm^{-1} (—N—H), 2932.6 cm^{-1} (—CH$_3$, —CH$_2$—), 1719.1 cm^{-1} (—C=O), 1150.3 cm^{-1} (—C—O), 1632.4, 1405.6, and 772.8 cm^{-1} (—C=C). ^{1}H NMR (DMSO-d_6, ppm): 8.30 (—N—H), 6.42–6.76 (—OOC(CH$_3$)=CH$_2$), 3.27–3.39 (—CH$_2$—N<, —CH$_2$—O—CH$_2$—(CH$_2$)$_2$—S—), 4.16–4.26 (C—CH$_2$—O—), 2.50–2.89 (—OOC—CH$_2$, >N—CH$_2$—, —CH$_2$—S—), 0.76–1.74 (—CH$_2$ and —CH$_3$ of IPDI).

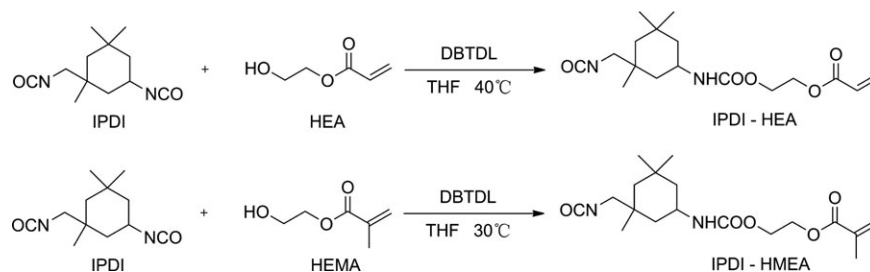**Synthesis of G2-HEA (G2-HEMA) (Scheme 5)**
G2-OH (6.0 g, 1.0 mmol) dissolved in 30 mL acetone was added into three-necked flask, which was equipped with a magnetic stirrer, a reflux condenser, and a thermometer. The IPDI-HEA (10.8 g, 32 mmol) diluted in acetone (IPDI-HEMA: 11.3 g, 32 mmol) was slowly dropped into the mixture and stirred
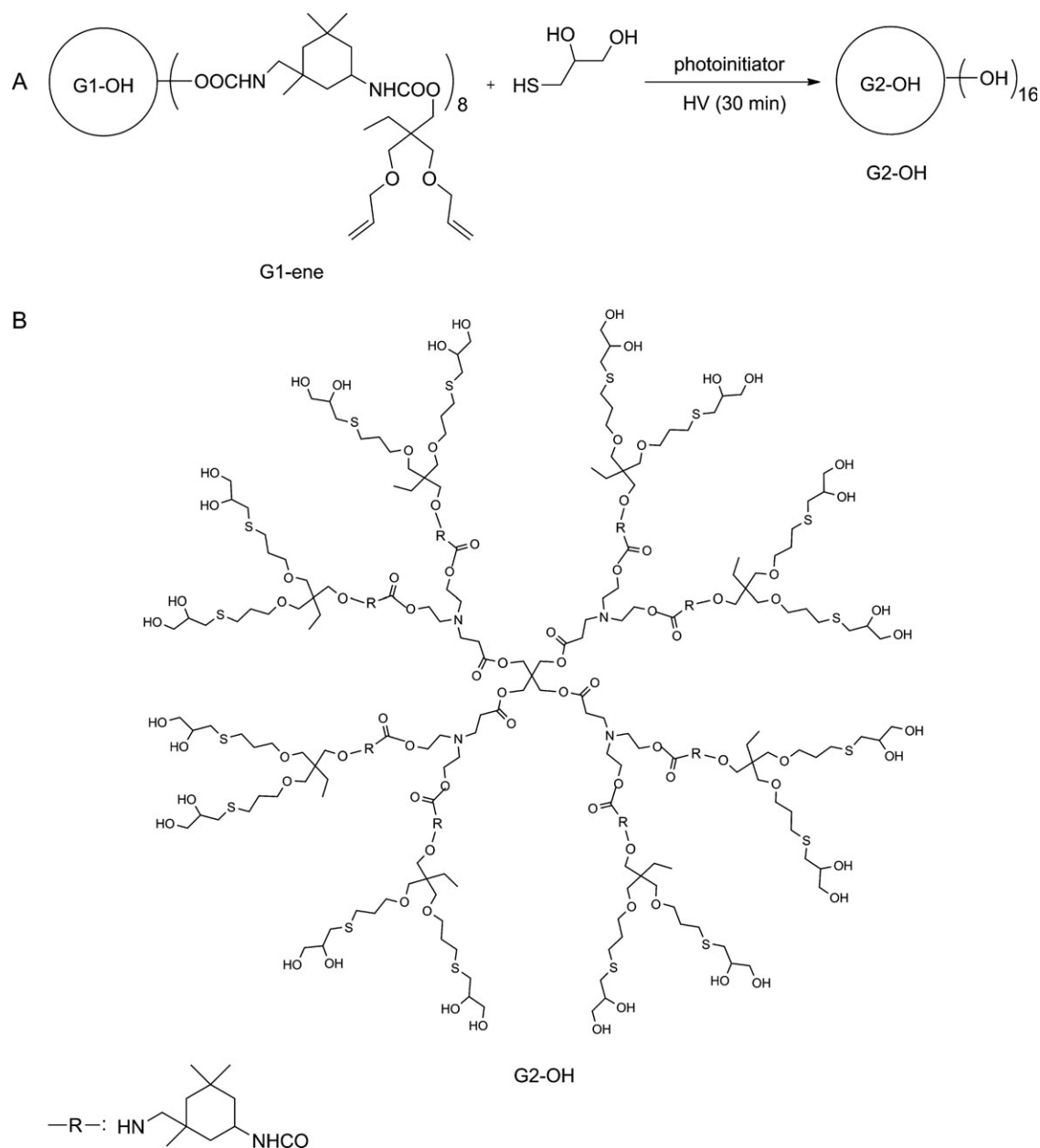
Scheme 3. (A) Preparation of second-generation hyperbranched poly(amine-ester) by thiolene click chemistry (G2-OH). (B) Idealized structures of G2-OH.

for about 4 h at 70°C until the content of isocyanate was <0.5 wt % by titration. After cooling down to the room temperature, the mixture was dropwise added into a large amount of ethyl ether. The precipitate was collected, washed with the mixture of acetone and ethyl ether (1:1) and dried in a vacuum oven. The refined G2-HEA (G2-HEMA) was obtained.

Scheme 4. Preparation of IPDI-HEA and IPDI-HEMA.
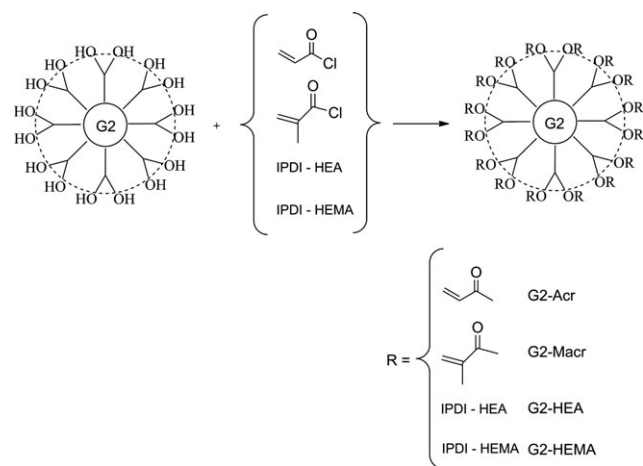
Scheme 5. Synthesis of UV-curable hyperbranched oligomers (G2-ORs).

G2-HEA: (Yield: 14.2 g, 85%). IR (KBr, cm^{-1}): 3391.4 cm^{-1}, 1533.6 cm^{-1} (—N—H), 2926.8–2955.7 cm^{-1} (—CH$_3$, —CH$_2$—), 1707.7 cm^{-1} (—C=O), 1185.1 cm^{-1} (—C—O), 1661.3, 1405.6, and 772.8 cm^{-1} (—C=C). ^{1}H NMR (DMSO-d_6, ppm): 8.24 (—N—H), 5.86–6.35 (—OOCH$_2$—CH=CH$_2$), 4.02–4.27 (C—CH$_2$—O—), 3.39–3.75 (—CH$_2$—N<), 1.84–2.52 (—OOC—CH$_2$, >N—CH$_2$—, —CH$_2$—S—), 0.78–1.72 (—CH$_2$ and —CH$_3$ of IPDI).

G2-HMEA: (Yield: 14.1 g, 82%). IR (KBr, cm^{-1}): 3339.1 cm^{-1}, 1533.6 cm^{-1} (—N—H), 2920.9–2961.6 cm^{-1} (—CH$_3$, —CH$_2$—), 1707.7 cm^{-1} (—C=O), 1185.1 cm^{-1} (—C—O), 1667.1, 1388.4, and 778.7 cm^{-1} (—C=C). ^{1}H NMR (DMSO-d_6, ppm): 8.26 (—N—H), 6.48–6.78 (—OOC(CH$_3$)=CH$_2$), 3.21–3.82 (—CH$_2$—N<, —CH$_2$—O—CH$_2$— (CH$_2$)$_2$—S—), 3.86–3.91 (C—CH$_2$—O—), 2.52–2.91 (—OOC—CH$_2$, >N—CH$_2$—, —CH$_2$—S—), 0.80–1.84 (—CH$_2$ and —CH$_3$ of IPDI).

RESULTS AND DISCUSSION

Preparation of G1-OH and G2-OH

The G1-OH was synthesized via 1,4-addition of pentaerythritol tetraacrylate and diethanolamine. The G2-OH was synthesized by thiolene addition with G1-ene as core and 3-mercapto-1, 2-propanediol as branched monomer. The reaction steps we chose are highly efficient, high yielding, and reproducible. The hydroxyl values (mg g^{-1}) KOH and element analyses of G1-OH and G2-OH are summarized in Table I. The hydroxyl value of G1-OH and G2-OH is 583.44 and 302.94, respectively. It is evident that the hydroxyl value of hyperbranched polyesters close to their theoretical ones.[24] The results of element analysis of N,
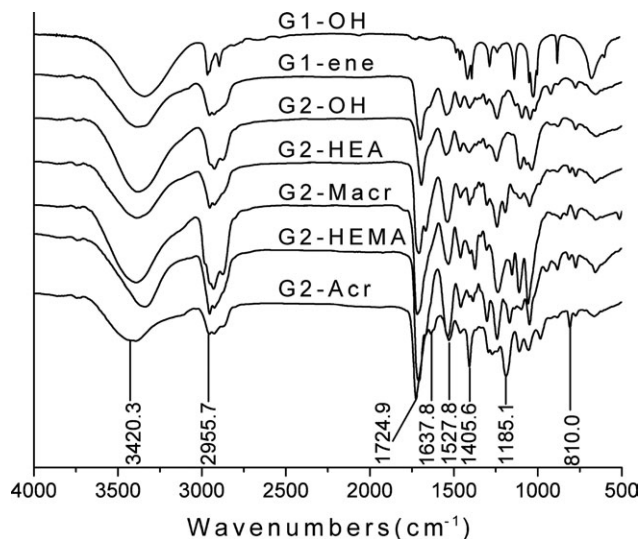

Figure 1. FT-IR spectra of hyperbranched oligomers.

C, and H in G1-OH and G2-OH were shown in Table I. The element contents of N, C and H in G1-OH are 7.12, 51.16, and 8.25%, and the corresponding values of G2-OH are 8.16, 52.04, and 8.20%, respectively. It shows that the measured results are closed to their theoretical ones.

FT-IR

Figure 1 shows the FT-IR spectra of G1-OH, G1-ene, G2-OH, and G2-ORs. As a representative sample, the characteristic peaks of G2-Acr were marked. It obviously seen that the peak for N—H stretching vibration at 3420.3 cm^{-1} appears, and the N—H bending vibration at 1527.8 cm^{-1} is also appeared, indicating that NCO bearing adduct was reacted with OH groups of G1-OH. The peaks at around 2955.7 cm^{-1} can be assigned to the stretching vibration for —CH$_2$ and —CH$_3$. The peaks at 1724.9 and 1185.1 cm^{-1} are assigned to C=O and —C—O, respectively. Three absorption peaks are observed at around 1637.8, 1405.8, and 810 cm^{-1} which indicates the double bonds of the acryl groups.[25] These FT-IR assignments demonstrate that acryloyl chloride had been reacted with OH groups of G2-OH.

^{1}H NMR

The ^{1}H NMR spectra of G1-OH, G1-ene, and G2-OH and part of these spectra assignments are shown in Figure 2(a–c). From the ^{1}H NMR spectrum of G1-OH in DMSO-d_6 [Figure 2(a)], the proton signals at 4.16–4.18 (—C—CH$_2$—O—), 3.31–3.35 (—CH$_2$—OH, —CH$_2$—N<), and 2.48–2.51 (—OOC—CH$_2$,

Table I. Characteristics of the G1-OH and G2-OH

Sample	Generation number	Theoretical functionality	Hydroxyl value (mg g^{-1}) KOH		Element analysis (%)					
			Theoretical	Measured	Theoretical			Measured		
					N	C	H	N	C	H
G1-OH	1	8	583.44	583.44	7.25	51.28	8.35	7.14	48.97	8.27
G2-OH	2	32	297.33	302.94	4.67	54.64	8.54	4.53	53.21	8.46

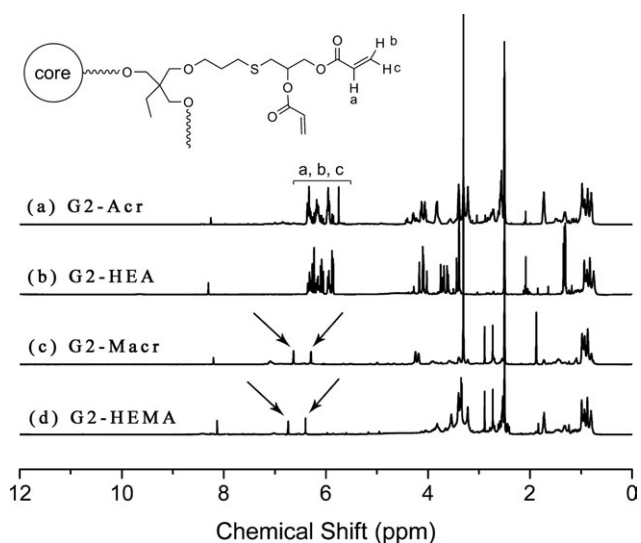**Figure 2.** ^{1}H NMR spectra of (a) G1-OH, (b) G1-ene, and (c) G2-OH.

Figure 3. ^{1}H NMR spectra of G2-ORs.

sis, it is confirmed that the NCO bearing adduct was reacted with G1-OH. Figure 2(c) shows the ^{1}H NMR spectrum of G2-OH. The new signal peaks attributed to thiol-ether proton ($-CH_2-S-$) are observed at 2.49–2.58 ppm and the signals belong to acrylate groups disappeared in Figure 2(c). It can be concluded that the thiolene "click" chemistry has taken place as expected.[27] Figure 3 shows the ^{1}H NMR spectra of G2-ORs. From the ^{1}H NMR spectrum of G2-Acr, three groups of peaks at 5.74–6.36 ppm can be observed. It is the characteristic peaks of the double bonds in acrylate groups, as shown in Figure 3(a). This indicated that the acrylyl chloride has been reacted with G2-OH. Figure 3(b) shows the ^{1}H NMR spectrum of G2-HEA. It can be seen that it is similar to that of G2-Acr. This is because that they have similar molecular structure. The two peaks at around 6.48 and 6.65 ppm should be assigned to the hydrogen atom of double bonds in methacrylate groups, as can be seen from Figure 3(c, d). Through the above analysis, it is confirmed that the hyperbranched oligomers are successfully synthesized.

Viscosity and Physical State

The intrinsic viscosity ($[\eta]$) of an oligomer is considered as one of the most important parameters as it affects its flow ability, photopolymerization rate and the properties of the UV-cured film. As we know, the $[\eta]$ of an oligomer is a measure of hydrodynamic volume and related to the molecular weight.[28,29] The $[\eta]$ of the synthesized oligomers were measured using an Ubbelohde viscometer in DMF at 30°C and the results are shown in Table II. The $[\eta]$ of G2-Acr, G2-Macr, G2-HEA, and G2-HEMA

Table II. Intrinsic Viscosity and Physical State of G2-ORs

Sample	$[\eta]_{DMF,30°C}$ (mL g^{-1})	Physical state (room temperature)
G2-HEMA	8.23	Yellow soft solid
G2-HEA	7.86	Yellow soft solid
G2-Macr	6.45	Yellow viscous fluids
G2-Acr	6.34	Yellow viscous fluids

$-N-CH_2-$) were observed. After completed the reaction of G1-OH and NCO bearing adduct, three groups of resonance signals at 5.10–5.88 ppm are obviously observed, which prove the existence of acrylate groups in the molecular structure of G1-ene, as shown in Figure 2(b).[26] The peak at around 8.00 ppm, which is assigned to the hydrogen atom of amide, can also be observed. Moreover, the signal peaks of NCO bearing adduct are observed, such as 4.19–4.26 ppm ($-O-CH_2-CH=CH_2$), 3.81–3.90 ppm ($-CH_2-O-$) and 0.80–1.42 ppm ($-CH_2$ and $-CH_3$ of IPDI). From above analy-
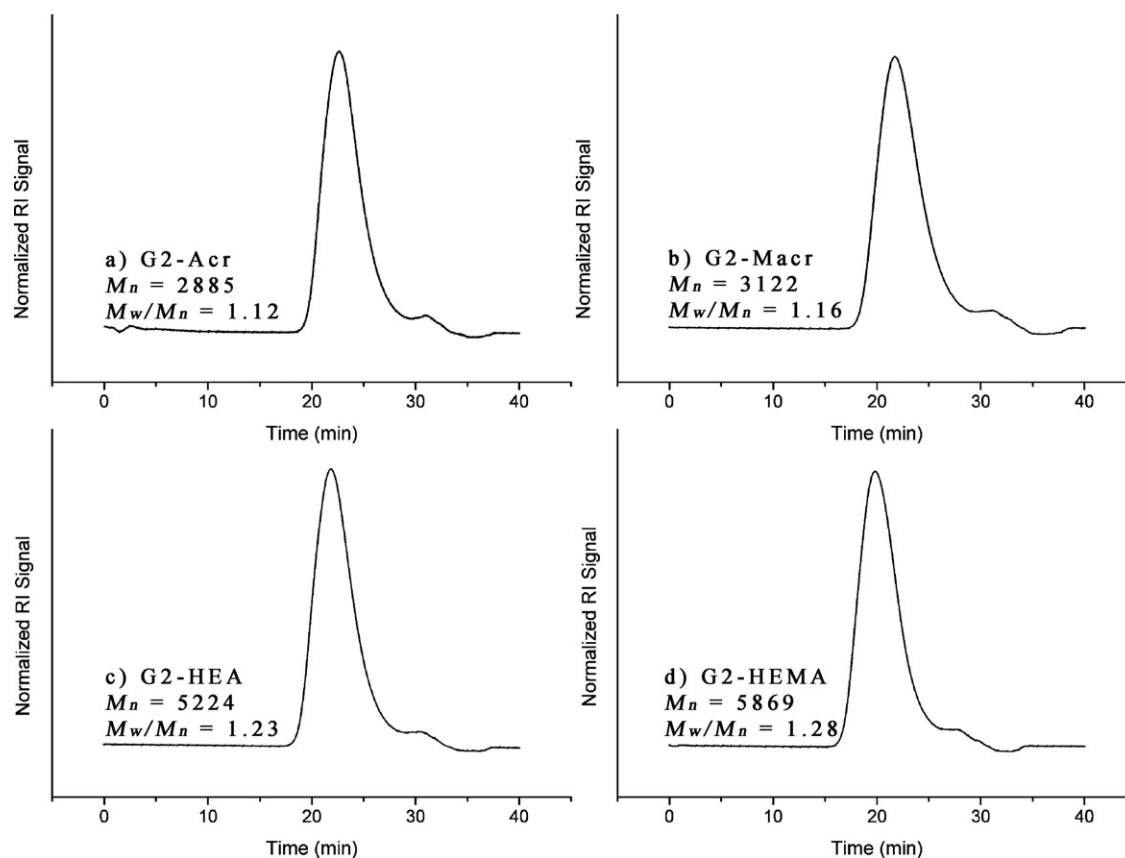
Figure 4. GPC curves of G2-Acr, G2-Macr, G2-HEA, and G2-HEMA.

were 6.34, 6.45, 7.86, and 8.23 mLg^{-1}, respectively. It is observed that the G2-HEMA shows the highest $[\eta]$ than other hyperbranched oligomers. This is because the G2-HEMA has more —OCONH— groups, which can form more inter/intramolecular hydrogen bonds, in its structure than the other hyperbranched oligomers. Moreover, the G2-HEMA has the highest molecular weight than the others. From Table II, we can also see that all the hyperbranched oligomers have low intrinsic viscosity. This is further confirmed that the hyperbranched polymers have small hydrodynamic dimension and compact molecular structure. The physical states of the hyperbranched oligomers are also list in Table II. It can be see that the G2-HEMA and G2-HEA are yellow soft solid, while the G2-Macr and G2-Acr are yellow viscous fluids at room temperature.

GPC

The number average molecular weight (M_n) and molecular weight distribution (M_w/M_n) of the hyperbranched oligomers were estimated by GPC with THF as eluent, as show in Figure 4. It can be seen that the elution curves shift towards shorter retention times with increasing molecular weight of hyperbranched oligomers. It can also be seen that the GPC curves of hyperbranched oligomers were symmetrical and relatively narrow, indicating a ideal structure. The GPC instrument was calibrated using linear polystyrene standard. The number average molecular weight of G2-Acr, G2-Macr, G2-HEA and G2-HEMA are 2885, 3122, 5224, and 5869, respectively. The results are much lower than their theoretical values because the hyper-

branched oligomers have smaller molecular sizes than the linear polystyrene with the same molecular weight. Thus, it is difficult to obtain exact molecular weight of hyperbranched polymer by GPC. Nevertheless, the GPC measurement is still useful in providing polydispersity of the hyperbranched polymers.[30,31] As can be seen in Figure 4, the polydispersity of G2-Acr, G2-Macr, G2-HEA, and G2-HEMA are 1.12, 1.16, 1.23, and 1.28, respectively. All the hyperbranched oligomers have narrow molecular weight distribution and the predicted and the observed values are in reasonable agreements. This was further proof that these synthesized hyperbranched oligomers have ideal structures.

UV–vis Spectra and Photosensitivity

The hyperbranched oligomers were dissolved in ethanol and diluted to 0.01 mmol L^{-1}. The solution put into quart glass cell and measured by UV–vis spectrum analyzer. The UV–vis absorbance spectra of G2-Acr, G2-Macr, G2-HEA, and G2-HEMA are shown in Figure 5. The cutoff wavelengths of the samples are in the range of 200–600 nm. The spectral shapes of the oligomers are very similar to each other and the absorption maxima are observed at around 202 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.[32,33] These results showed that the hyperbranched oligomers can be cured under UV irradiation. To investigate the photosensitivity of the hyperbranched oligomers, the samples were dissolved in ethanol at a solid content of 10 wt%. The films
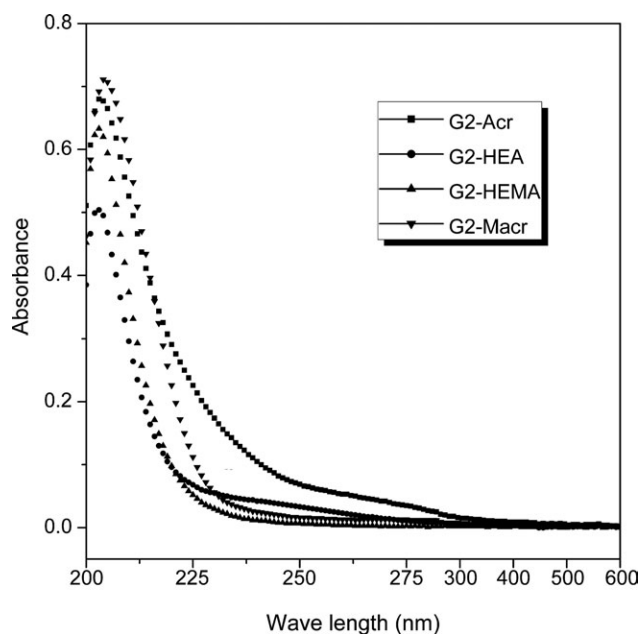
Figure 5. UV–vis absorbance spectra of G2-Acr, G2-Macr, G2-HEA, and G2-HEMA.

were prepared via spin-coating on a clean glass plate and pre-backed at 80°C for 30 min. The films were exposed to 23 mW cm^{-2} of 365 nm light at different exposure dose. The conversion rate of the (meth)acryloyl groups was calculated from the decrease of the absorbance at 810 cm^{-1} due to C=C bond in the G2-ORs by the FT-IR spectra. The sensitivity curves of G2-ORs were obtained by the plotting of the conversion (%) against the irradiated dose in the absence of photoinitiator, as shown in Figure 6. It can be seen that the reaction proceeded smoothly, and the conversion of G2-Macr, G2-HEMA, G2-Acr, and G2-HEMA
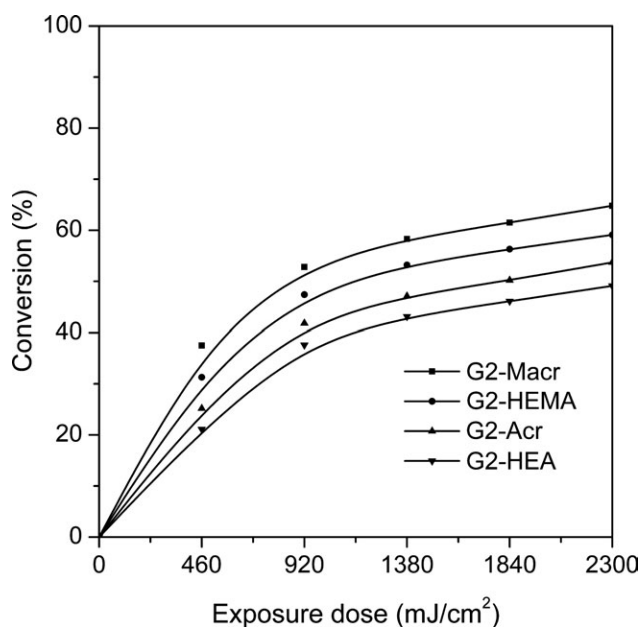
were 64.8, 58.1, 53.2, and 48.2% at 2300 mJ cm^{-2}. G2-Macr and G2-HEMA showed higher photochemical reactivity than G2-Acr and G2-HEA. This is because that both the G2-Macr and G2-HEMA have many methacryloyl groups at the end. The photochemical reactivity of methacryloyl groups is higher than that of acryloyl groups. From Figure 6, it can also be observed that G2-HEMA shows a lower photochemical reactivity than G2-Macr. This may be explained that G2-HEMA has less methacryloyl groups than that of G2-Macr at a certain weight.

TGA

To investigate the thermal properties of hyperbranched oligomers, the UV-cured films were prepared at first. A typical procedure for the preparation of G2-Macr was described as follows: G2-Macr and Irgacure 1173 were dissolved in ethanol. The solution was cast on a glass plate and dried to make film on the plate. The film, containing a photoinitiator on the plate, was irradiated with 23 mW cm^{-2} high pressure mercury lamp. The UV-cured films (∼10 mg) were investigated by TGA at a constant heating rate of 20°C min^{-1} in air atmosphere. The TG-DTA curves of UV-cured hyperbranched oligomers are shown in Figure 7. It can be seen that the four curves are similar. For G2-Macr, the onset temperature of decomposition was about 190°C. In the
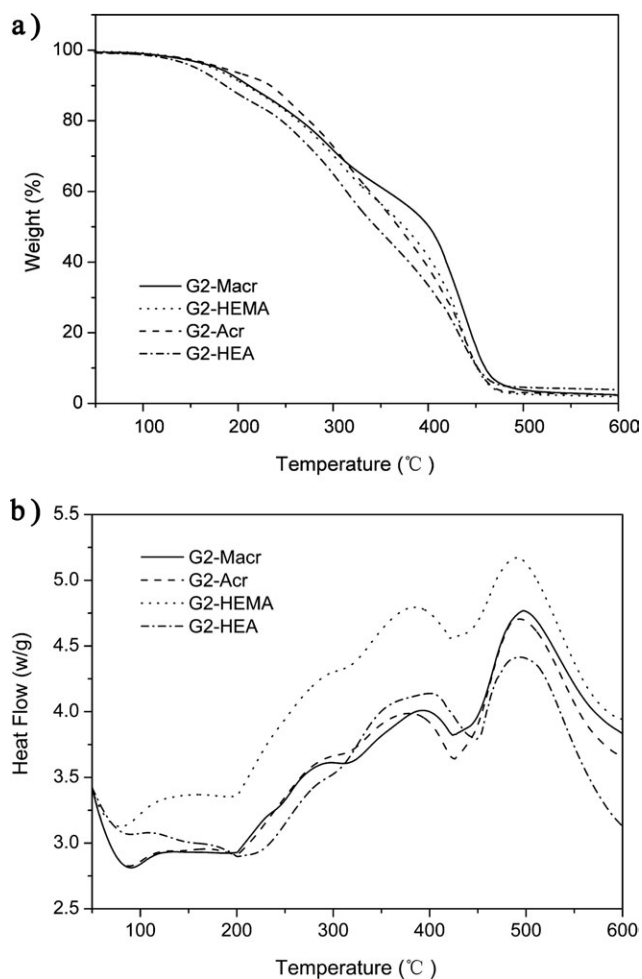

Figure 6. Photosensitivity of G2-Macr, G2-Acr, G2-HEA, and G2-HEMA.

Figure 7. (a) TGA and (b) DTA curves of G2-Macr, G2-Acr, G2-HEA, and G2-HEMA.

Table III. Solubility of the Hyperbranched Oligomers

Samples	Solvents						
	Water	Methanol	Acetone	DMF	DMAc	THF	DMSO
G1-OH	++	+	+	++	++	−	++
G1-ene	−	+	+	++	++	++	++
G2-OH	++	+	+	++	++	−	++
G2-Macr	−	+	+	++	++	++	++
G2-Acr	−	+	+	++	++	++	++
G2-HEMA	−	+	+	++	++	++	++
G2-HEA	−	+	+	++	++	++	++

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

temperature ranging from 190 to 450°C, about 90% weight loss was observed, accompanying several exothermic peaks. This was due to the decomposition of crosslinked terminal groups and lining structure. An obvious exothermic peak occurred between 450 and 600°C, accompanying about 10% weight loss. This exothermic peak was attributed to the decomposition of the core of G2-Macr. The onset decomposition temperature of G2-Macr is higher than that of G2-Acr, G2-HEMA and G2-HEA. It can be explained that the G2-Macr has higher photosensitivity than other hyperbranched oligomers. After UV exposure, it could be formed a more compact network structure than others. From above analysis, it can also be seen that the UV-cured hyperbranched oligomers have good thermal stability.[34,35]

Solubility

Table III contains the results of the solubility of the hyperbranched oligomers at room temperature. All the hyperbranched oligomers exhibited excellent solubility in common organic solvents, such as DMF, DMAc, and DMSO. The G1-OH is well soluble in water, and partially soluble in methanol and acetone. The G1-ene is insoluble in water, but well soluble in THF. This means that the solubility of G1-OH changed by modification of the hydroxyl end groups with NCO bearing adduct. The G2-OH and G1-OH have similar solubility. This is because that both the G2-OH and G1-OH have a large number of hydroxyl terminal groups. The solubility of G2-OH changed by functionalizing the hydroxyl end groups, as can be seen from G2-Macr, G2-Acr, G2-HEMA, and G2-HEA.[36,37]

CONCLUSION

The second-generation hyperbranched poly(amine-ester) was prepared by thiol-ene "click" chemistry at first. A series of photosensitive G2-ORs containing photosensitive groups were synthesized by modifying the hydroxyl groups of G2-OH. These synthesized hyperbranched oligomers showed sharp absorption bands at 202 nm and the G2-Macr shows the highest photosensitive than other hyperbranched oligomers. The UV-cured photosensitive G2-ORs had good thermal properties. Moreover, all the synthesized hyperbranched oligomers showed excellent solubility in common organic solvents, such as DMF, DMAc and DMSO. These photosensitive G2-ORs containing photosensitive groups can be used for UV-curing resin.

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