Application of Thiol-ene “click” Chemistry to Preparation of Hyperbranched Polyurethane Acrylate Oligomers Containing Carboxyl Groups

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A new type of hyperbranched polyurethane terminated by carboxyl groups (HBP-COOH) has been synthesized by thiol-ene “click” reaction. The carboxyl groups of HBP-COOH were further modified by glycidyl methacrylate at different feed ratio to produce a series of hyperbranched polyurethane acrylate oligomers containing carboxyl groups (HBPUA-COOHs). The structures of products were characterized by FT-IR, $^1$H-NMR spectroscopy and gel permeation chromatography (GPC). The photosensitive groups of these synthesized HBPUA-COOHs were measured with UV-Vis spectrophotometer. It was shown that the HBPUA-COOHs had sharp absorption bands at about 205 nm. The photosensitivities were characterized by FT-IR with different curing time. The thermal properties of samples were characterized by DSC and TGA. In addition, the solubilities and viscosity of the HBPUA-COOHs were also examined. These synthesized hyperbranched polyurethane acrylate oligomers containing carboxyl groups, which have well-defined structures with very narrow polydispersities, can be used in many fields such as coatings, adhesives and photoresists, etc.

Keywords: Hyperbranched polyurethane acrylate, Synthesis, Click chemistry, UV-curing

1. Introduction

In recent decades, UV-curable coatings are becoming increasingly attractive for their fast curing, low pollution, low energy consumption and high production efficiency, etc [1-4]. They have played important roles in coatings, adhesives, electronic materials, and printing plates. In the conventional UV-curing coatings system, the structures of photosensitive resins are mostly linear, and these linear photosensitive resins have high viscosity and low reactivity [5-7]. To overcome the disadvantage, all kinds of hyperbranched photosensitive resins have been developed in recent years.

Hyperbranched polymer as a kind of new functional material has densely branched structures and large number of endgroups, which possess lower viscosity, higher reactivity, and better solubility than their linear counterparts [8-10]. Hyperbranched polymers are usually prepared by the polymerization of AB$_2$ or A$_2$ + B$_3$ type monomer [11]. Recently, several new methods have been developed to synthesize hyperbranched polymers, such as the ring-opening polymerization [12], self-condensation vinyl polymerization [13], and proton transfer polymerization etc [14]. Very recently, thiol-ene “click” reaction has been used for preparing dendrimers. The thiol-ene reaction is highly efficient, high yielding, and environmentally benign [15-17].

Introduction of hyperbranched structure into photosensitive resins could obtain oligomers with low viscosity and high functionality. Although some hyperbranched photosensitive resin has been developed, the hyperbranched polyurethane methacrylate oligomers containing carboxyl groups which have good compatibility with fillers and dyes has been little reported to our knowledge.

In this paper, a novel hyperbranched polyurethane terminated by carboxyl groups was prepared via thiol-ene “click” reaction at first, then a series of hyperbranched polyurethane methacrylate oligomers containing carboxyl groups (HBPUA-COOHs) were synthesized by modification the carboxyl groups with glycidyl methacrylate (GMA) at different feed ratio. The structures of samples were characterized by FT-IR, $^1$H-NMR and GPC. UV-Vis spectra of the HBPUA-COOHs were measured with UV-Vis spectrophotometer. The photosensitivities were characterized by FT-IR with different curing time. Furthermore, the viscosity, thermal properties, and solubilities of samples were also studied.
2. Experimental

2.1 Materials

Trimethylolpropane diallyl ether was purchased from Aldrich, USA. Glycidyl methacrylate (GMA), thioglycolic and isophorone diisocyanate (IPDI) were obtained from Aladdin Reagent Co. (Shanghai, China). Diethanolamine, methylacrylate, pentaerythritol (PE), 1, 4-dioxane, hydroquinone and dibutyltin dilaurate (DBTDL) were purchased from Lingfeng Chemical Reagent Co. Ltd. (Shanghai, China). Ethyl ether, acetone, methanol, p-toluene sulphonic acid and 2, 2-dimethoxy-2-phenylacetophenone were obtained from Sinopharm Chemical Reagent Co. Ltd, China. All the other chemical reagents were used as received without further purification.

2.2 Preparation of hyperbranched poly (amine-ester) (HBPE)

The hyperbranched poly (amine-ester) (HBPE) was synthesized according to the following procedure (Scheme 1). First, the N, N - diethylol - 3 - amine methylpropionate was synthesized via Michael addition of diethanolamine and methyl acrylate according to the previously reported literature. Subsequently, 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 - necked flask, which was equipped with a mechanical stirrer, a thermometer, a nitrogen gas inlet and a water segregator. After the mixture was stirred for 4 h at 120 °C in the presence of p - toluene sulphonic acid (p - TSA) as catalyst, it was distilled to remove DMF under vacuum. Then, the HBPE was obtained. Finally, the obtained HBPE was redissolved into dried 1, 4 - dioxane and 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 yield of HBPE was 7.48 g (83%).

IR (KBr, cm\(^{-1}\)): 3327.4 cm\(^{-1}\) (-OH), 2886.2 cm\(^{-1}\) (-C-H stretching vibration), 1724.9 cm\(^{-1}\) (-C=O), 1452.1 cm\(^{-1}\) (-C-N-), 1040.8 cm\(^{-1}\) (-C-O), 871.6 cm\(^{-1}\) (-C-H deformation vibration). ^1H-NMR (DMSO-\(d_6\), ppm): 4.16-4.18 (-C-CH\(_2\)-O-), 3.30-3.35 (-CH\(_2\)-OH, -CH\(_2\)-N<), and 2.48-2.50 (-OOC-CH\(_2\), -N-CH\(_2\)-).

Scheme 1. Preparation of hyperbranched poly (amine-ester) (HBPE)

2.3 Preparation of hyperbranched polyurethane methacrylate (HPBUA)

HPBUA was synthesized according to a two-step procedure: NCO bearing adduct was obtained by the reaction of equimolar amounts of IPDI and trimethylolpropane diallyl ether in the first, and then reacted with appropriate amount of HBPE.

IPDI (4.45 g, 0.02 mol), hydroquinone (0.128 g), DBTDL (0.315 g) and 50 ml DMF were mixed in a four-neck flask equipped with a magnetic stirrer, nitrogen inlet, a thermometer, and a dropping funnel. 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 mono - isocyanate by titration. After the replenishing of catalytic amount of DBTDL, the HBPE (1.93 g, 2.5 mmol) dissolved in DMF was added into the reaction mixture. The temperature was increased to 80 °C, and the reaction mixture was stirred for another 5 h. After the solvent (DMF) was evaporated, the yellowish viscous liquid was obtained (yield: 8.75 g, 82%). The synthesis process is described in Scheme 2.

IR (KBr, cm\(^{-1}\)): 3373.6 cm\(^{-1}\), 1539.2 cm\(^{-1}\) (-N-H), 2920.4 – 2955.7 cm\(^{-1}\) (-CH\(_3\), -CH\(_2\)_), 1701.9 cm\(^{-1}\) (C=O), 1649.5, 1405.6 and 780.0 cm\(^{-1}\) (C=C), 1039.8 cm\(^{-1}\) (-C-O). ^1H-NMR (DMSO-\(d_6\), ppm): 8.00 (-N-H), 5.10-5.88 (O-CH\(_2\)=CH\(_2\)), 4.10-4.23 (O-CH\(_2\)=CH\(_2\)), 3.82-3.89 (C-CH\(_2\)-OH), 2.49-2.77 ( > N-CH\(_2\)_), 0.74-1.42 (-CH\(_2\) and –CH\(_3\) of IPDI).
2.4 Synthesis of hyperbranched polyurethane acrylate oligomers containing carboxyl groups by thiol-ene “click” chemistry (HBPUA-COOH)

The hyperbranched polyurethane terminated by carboxyl groups (HBP - COOH) must be well prepared through thiol-ene “click” chemistry at the first step. The procedure was as follows: HBPUA (8.52 g, 2 mmol) dissolved in methanol, 1.5 equiv of thioglycolic (4.42 g, 48 mmol), trace amounts of the photoinitiator (2, 2-dimethoxy-2-phenylacetophenone) were mixed in 50 ml round-bottomed flask. 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, washed with cold methanol and dried in a vacuum oven. The photoinitiator and excess thioglycolic can be easily removed by the precipitation. The yield of HBP-COOH was 9.16 g (80%).

At the second step, the stoichiometry for the modification of carboxylic groups of HBP-COOH into methacrylate groups was adjusted in three different ratios, 16:0, 12:4 and 8:8. The obtained hyperbranched oligomers were named HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8), respectively. One typical process for synthesizing HBPUA-COOH (12:4) was described as follows: HBP-COOH (5.74 g, 1 mmol), hydroquinone (0.01 g) and 50 ml DMF were mixed into a 250 ml three-neck flask, which was equipped with a magnetic stirrer, a thermometer and a separatory funnel. GMA (1.71 g, 12 mmol) was slowly dropped into the stirring mixture and stirred at 70 °C for 12 h until the content of carboxyl groups reached the theoretical value. Finally, the HBPUA-COOH (12:4) was obtained after the DMF was evaporated (yield: 5.81 g, 78%). The synthesis process is described in Scheme 3.

HBPUA-COOH: IR (KBr, cm^{-1}): 3391.2 (OH), 2921.3 (CH), 1713.5 (C=O), 1661.9 (COOH), 1539.3 (N-H), 1403.8, 780.0 (C=C), 1039.8 (C=O), 1138.7, 1243.4 (C-O). 1H-NMR (DMSO-d_6, ppm): 7.95 (NH), 6.70-7.07 (C-CH_2-O-), 5.68-6.12 (-C(CH_3)=CH_2), 4.01 (C-CH_2-COO), 3.80-3.87 (-CH_2-OOC), 3.53 (-OH), 3.36-3.39 (-CH_3-OH), 2.49 (-CH_2-S), 0.78-1.45 (-CH_3, -CH_2) of IPDI.
hyperbranched oligomers were measured with UV-vis spectrophotometer (Shimazu UV-2450 Japan). The photosensitivity of the samples was monitored by FT-IR. Differential scanning calorimetry (DSC) measurements were deduced from a TA Instruments Q10 instrument (New Castle, DE) under a nitrogen purge at a heating rate of 10 °C/min from -70 °C to 200 °C. The thermal stabilities of the UV-cured hyperbranched oligomers were characterized by thermogravimetric analysis (TGA). TGA spectra were recorded on a TA Instruments Q20 instrument (New Castle, DE) under nitrogen 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.

3. Results and discussion

3.1 FT-IR

FT-IR was used to ascertain the structures of hyperbranched oligomers. The FT-IR spectra of HBPE, HBPUA, HBP-COOH and HBPUA-COOH (12:4) are shown in Fig. 1. In Fig. 1, the characteristic peaks of HBPUA-COOH (12:4) were marked. The peak at 3391 cm⁻¹ is assigned to –OH stretching vibration. This indicates that the carboxyl groups of HBP-COOH have reacted with epoxy group of GMA. The peak at 2921 cm⁻¹ is assigned to stretching vibration of –CH₂. The strong peak at 1713 cm⁻¹ is assigned to the carbonyl bonds of methacrylate groups. The peak at 1661 cm⁻¹ indicates the existence of carboxyl groups. The peak at 1539 cm⁻¹ is assigned to the N-H deformation vibration. It is confirmed that the -NCO of IPDI has been reacted with the –OH of trimethylolpropane diallyl ether. The peaks at 1400 and 780 cm⁻¹ assigned to the double bonds of methacrylate groups.¹⁹ These peaks further confirmed that the HBP-COOH had been reacted with GMA. It can also be seen that the peak at 2558 cm⁻¹, which assigned to the stretching vibration of –S-H, has not appeared. This indicates that the thiol-ene “click” chemistry has been reacted as expected.

3.2 ¹H-NMR

The ¹H-NMR spectra of HBPE, HBPUA, HBP-COOH and HBPUA-COOH (12:4) and part of these spectra assignments are shown in Fig. 2 (A-D). Fig. 2 (A) shows the ¹H-NMR spectrum of HBPE. The proton signals at δH (300MHz, DMSO-d₆) 4.16-4.18 (–C-CH₂-O–), 3.30-3.35 (–CH₂-OH, –CH₂-N<), and 2.48-2.50 (–OOC-CH₂, –N-CH₂-) were observed. After completed the reaction of HBPE and NCO bearing adduct, which was obtained by the reaction of equimolar amounts of IPDI and trimethylolpropane diallyl ether, three groups of characteristic peaks at 5.10-5.88 ppm are obviously observed, which prove the existence of methacrylate groups in the molecular structure of HBPUA, as shown in Fig. 2(B)²⁰. The peak at 8.00 ppm, which is assigned to the hydrogen atom of amide, can also be observed. From above analysis, it is confirmed that the HBPUA was successfully synthesized. Fig. 2 (C) shows the ¹H-NMR spectrum of HBP-COOH. The peak at 2.52 ppm, which belongs to the –CH₂-S–, is observed. It can be concluded that the thiol-ene “click” chemistry has taken place as expected. The peak at 11.0 ppm is assigned to the hydrogen atom of carboxyl groups. After the modification of HBPE by GMA, two groups of peaks at 5.68-6.12 ppm can be observed. It is the characteristic peaks of the double bonds in methacrylate groups, as shown in Fig. 2 (D).

Through above analysis of FT-IR and ¹H-NMR, it can be concluded that all the hyperbranched oligomers were successfully synthesized.
3.3 Molecular weight and molecular weight distribution

The molecular weights and molecular weight distributions of the HBPUA-COOHs were estimated by GPC with THF as eluent, as show in Table 1. The weight molecular weight and the number molecular weight of HBPUA-COOH (16:0) are 2850 and 2523, and the corresponding values of HBPUA-COOH (12:4) are 2358 and 1872, respectively. The GPC instrument was calibrated using linear polystyrene standard. The molecular weights of hyperbranched oligomers, which are obtained by GPC measurements, are generally much lower than their theoretical values because the hyperbranched oligomers have a much smaller hydrodynamic volume than the corresponding linear polymers with the same molecular weight.21-23 Nevertheless, the GPC measurement is still useful in providing polydispersity of the hyperbranched oligomers. As can be seen in Table 1, all the HBPUA-COOHs have narrow molecular weight distribution. The molecular weight distributions of HBPUA-COOH (12:4) and HBPUA-COOH (8:8) are slightly higher than HBPUA-COOH (16:0). It can be interpreted that the HBPUA-COOH (12:4) and HBPUA-COOH (8:8) retained some carboxyl groups can't well dissolved in THF.

Table 1. GPC results of HBPUA-COOHs

<table>
<thead>
<tr>
<th>Samples</th>
<th>$M_w$</th>
<th>$M_n$</th>
<th>$M_w/M_n$</th>
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<tr>
<td>HBPUA-COOH (16:0)</td>
<td>2850</td>
<td>2523</td>
<td>1.13</td>
</tr>
<tr>
<td>HBPUA-COOH (12:4)</td>
<td>2358</td>
<td>1872</td>
<td>1.26</td>
</tr>
<tr>
<td>HBPUA-COOH (8:8)</td>
<td>2168</td>
<td>1792</td>
<td>1.21</td>
</tr>
</tbody>
</table>

3.4 Viscosity and physical state

The intrinsic viscosity ($[\eta]$) is one of the most important parameters of an oligomer. As general knowledge, the $[\eta]$ of an oligomer is related to the molecular weight when polymer, temperature and solvent are determined.24 The $[\eta]$ of the synthesized oligomers were measured using an Ubbelohde viscometer in DMF at 30 °C. The viscosity and physical state of the oligomers are shown in Table 2. The $[\eta]$ of HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8) are 7.23, 6.12 and 5.34, respectively. HBPUA-COOH (16:0) presents at solid state at room temperature and has higher intrinsic viscosity than that of HBPUA-COOH (12:4) and HBPUA-COOH (8:8). This is because the HBPUA-COOH (16:0) has the highest viscosity than other HBPUA-COOHs. When reserving some carboxyl groups in HBPUA-COOH, the molecular weight decreased, so the intrinsic viscosity went down. The HBPUA-COOH (12:4) and HBPUA-COOH (8:8) are all yellow viscous fluids at room temperature. It can also be seen that the HBPUA-COOHs have low intrinsic viscosity and changed little. It can be explained that all the HBPUA-COOHs have similar structures and there are little entanglement among molecular chain.

Table 2. Intrinsic viscosity and physical state of synthesized oligomers

<table>
<thead>
<tr>
<th>Sample</th>
<th>$[\eta]$ DMF, 30 °C (ml/g)</th>
<th>Physical state</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBPUA-COOH</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(16:0)</td>
<td>7.23</td>
<td>Soft solid</td>
</tr>
<tr>
<td>HBPUA-COOH</td>
<td>6.12</td>
<td>Yellow viscous</td>
</tr>
<tr>
<td>(12:4)</td>
<td></td>
<td>fluids</td>
</tr>
<tr>
<td>HBPUA-COOH</td>
<td>5.34</td>
<td>Yellow viscous</td>
</tr>
<tr>
<td>(8:8)</td>
<td></td>
<td>fluids</td>
</tr>
</tbody>
</table>

3.5 UV-Vis absorption spectrum

UV-Vis spectrum analyzer was used to characterize the photosensitive groups of the hyperbranched oligomers. The HBPUA-COOHs were dissolved in ethanol with 10 mg of oligomers.
in 1 mL of solvent before analysis. The UV-Vis absorbance spectra of HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8) are shown in Fig. 3 and 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 205 nm. The molecular structures of oligomers contain methacrylate groups which have conjugate carbon-carbon double bond (C = C) and carbon-oxygen double bond (C = O). They can produce π-π* electronic transitions. The HBPUA-COOH (16:0) has the highest absorption maximum than other HBPUA-COOHs. It could be because the HBPUA-COOH (16:0) has more methacrylate groups than HBPUA-COOH (12:4) and HBPUA-COOH (8:8). More containing methacrylate groups had higher absorption maximum. The absorption maximum are varied in the increasing order: HBPUA-COOH (16:0) > HBPUA-COOH (12:4) > HBPUA-COOH (8:8). These results showed that the HBPUA-COOHs can photopolymerize under UV illumination.

![Fig. 3. UV-Vis absorbance spectra of HBPUA-COOHs.](image)

3.6 Photosensitivity

For UV-curable materials, the HBPUA-COOHs have conjugated carbon-carbon double bonds (C=C) as the photosensitive group. They can be cured under UV irradiation. In order to investigate the photosensitivity of the hyperbranched polyurethane acrylate oligomers, the samples were prepared by the following two steps. First, the oligomers were dissolved in ethanol at a solid content of 10 wt%, and then the mixture was spin-coated on a clean glass plate using a spin coater. Second, the polymer film thus obtained was prebacked at 80°C for 30 min, and exposed to 23 mW/cm² of 365 nm light for increasing amounts of time. The UV-curing process was monitored by FT-IR. Fig. 4 shows the FT-IR spectra of HBPUA-COOH (12:4) with different time (30, 60, 90, 120, and 150 s) in the absence of photoinitiator. The change in the C-H out of plane deformation vibration of the acrylate double bond near 778 cm⁻¹ was monitored. The variation in film thickness (due to shrinkage) was compensated by normalizing the methacrylate band to a band at 2951 cm⁻¹ which is related to the C-H stretching band. The conversion of double bond is calculated using the following equation:

\[
\text{Double bond conversion (\%)} = \left( \frac{A_{778}/A_{2951}}{A_{778}/A_{2951}} \right) \times 100
\]

Where \(A_{778}/A_{2951}\) is the peak area at 778 cm⁻¹ after irradiation for \(t\) seconds, \(A_{778}/A_{2951}\) is the peak area at 778 cm⁻¹ before irradiation.

![Fig. 4. FT-IR spectra of the course of UV-curing (HBPUA-COOH (12:4)).](image)

The sensitivity curves of HBPUA-COOHs were obtained by the plotting of the double bond conversion against the irradiated time, as shown in Fig. 5. It can be seen that all the HBPUA-COOHs have lower conversions, and the conversions of HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8) were 69.4, 62.0, and 58.2% at 150 s. The HBPUA-COOH (16:0) shows the higher photosensitive than HBPUA-COOH (12:4) and HBPUA-COOH (8:8). This may be explained that the HBPUA-COOH (16:0) has more carbon-carbon double bonds (C=C) than HBPUA-COOH (12:4) and HBPUA-COOH (8:8). Furthermore, the hyperbranched polyurethane methacrylate oligomers containing carboxyl groups (HBPUA-COOH (12:4) and HBPUA-COOH (8:8)) have lower viscosities than HBPUA-COOH (16:0), so that oxygen can easily penetrate into the surface layers which can inhibit the polymerization. So the photosensitivity of the oligomers are varied in the increasing order: HBPUA-COOH (16:0) >
HBPUA-COOH (12:4) > HBPUA-COOH (8:8).

3.7 DSC

DSC was used to determine the thermal transitions of the hyperbranched oligomers. The DSC curves of HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8) are presented in Fig. 6. The glass transition temperatures ($T_g$) were determined from the middle point of the heat capacity change and the $T_g$ of HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8) are -13, -28 and -32 $^\circ$C, respectively. With more carboxyl groups were modified by GMA, the $T_g$ value of the hyperbranched oligomers increased. The increase of $T_g$ was caused by multiple factors: polymer structure, molecular weight, free volume, side groups, and so on. With more carboxyl groups were modified by GMA, the $T_g$ value of the hyperbranched oligomers increased. The increase of $T_g$ was caused by multiple factors: polymer structure, molecular weight, free volume, side groups, and so on. With more carboxyl groups were modified by GMA, the $T_g$ value of the hyperbranched oligomers increased. The increase of $T_g$ was caused by multiple factors: polymer structure, molecular weight, free volume, side groups, and so on. With more carboxyl groups were modified by GMA, the $T_g$ value of the hyperbranched oligomers increased. The increase of $T_g$ was caused by multiple factors: polymer structure, molecular weight, free volume, side groups, and so on. With more carboxyl groups were modified by GMA, the $T_g$ value of the hyperbranched oligomers increased. The increase of $T_g$ was caused by multiple factors: polymer structure, molecular weight, free volume, side groups, and so on. With more carboxyl groups were modified by GMA, the $T_g$ value of the hyperbranched oligomers increased. The increase of $T_g$ was caused by multiple factors: polymer structure, molecular weight, free volume, side groups, and so on.

3.8 TGA

In order to investigate the thermal properties of the UV-cured HBPUA-COOHs, the films were prepared as the following steps: The HBPUA-COOHs were firstly dissolved in ethanol and 2% Dorocure 1173 was added in the solution. Then the mixture was painted on a glass plate and prebaked at 80 $^\circ$C for 30 min to remove the solvent. Finally, the mixture was fully cured by irradiation with 23 mW/cm$^2$ of 365 nm UV lamp. The UV-cured films (~10 mg) were investigated by TGA at a constant heating rate of 20 $^\circ$C min$^{-1}$ in nitrogen atmosphere. The TG curves of UV-cured HBPUA-COOH (16:0), HBPUA-COOH (12:4) and HBPUA-COOH (8:8) films are shown in Fig. 7. It is obvious that the TG curves of HBPUA-COOH (16:0) are analogous to that of HBPUA-COOH (12:4) and HBPUA-COOH (8:8). The onset temperature of decomposition was 225 $^\circ$C. In the temperature ranging from 225 to 550 $^\circ$C, about 90% weight loss was observed. These were due to the decomposition of crosslinked urethane-methacrylate terminal groups. From 550 to 700 $^\circ$C, about 10% weight loss observed. This may be attributed to the decomposition of the core of HBPUA-COOH (16:0). The onset decomposition temperature of HBPUA-COOH (16:0) is higher than that of HBPUA-COOH (12:4) and HBPUA-COOH (8:8). This may be explained that the HBPUA-COOH (16:0) has more methacrylate groups than HBPUA-COOH (12:4)
and HBPUA-COOH (8:8). When exposed under UV irradiation, the crosslinking network of HBPUA-COOH (16:0) is more compact than that of HBPUA-COOH (12:4) and HBPUA-COOH (8:8). The TGA results clearly showed that the UV-cured HBPUA-COOHs have good thermal stability.32

Fig. 7. TGA curves of UV-cured HBPUA-COOHs in nitrogen atmosphere.

3.9 Solubility

Table 3 presents the results of the solubility tests of the hyperbranched oligomers at room temperature. All of the hyperbranched oligomers are easily dissolved in strong polar organic solvents, such as DMF, DMAc and DMSO. HBPE have a large number of hydroxyl terminal groups, it can be well dissolved in water. HBPUA-COOH is not soluble in water, but soluble in THF. This means that the solubility of HBPE changes by the introduction of NCO bearing adduct, which was obtained by the reaction of equimolar amounts of IPDI and trimethylolpropane diallyl ether, into the end of hyperbranched polyester. The solubility of HBPUA and HBPUA-COOH (16:0) are similar because they have the same structure. The HBPUA-COOH, HBPUA-COOH (12:4) and HBPUA-COOH (8:8), which have some carboxyl groups at the end of hyperbranched oligomers, can be well dissolved in methanol and acetone. It can be explained that the carboxyl groups are polar groups and they can be well dissolved in polar solvent.

Table 3. Solubility of the hyperbranched oligomers

<table>
<thead>
<tr>
<th>samples</th>
<th>Water</th>
<th>Methanol</th>
<th>Acetone</th>
<th>DMF</th>
<th>DMAc</th>
<th>THF</th>
<th>DMSO</th>
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<tbody>
<tr>
<td>HBPE</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>-</td>
<td>++</td>
</tr>
<tr>
<td>HBPUA</td>
<td>-</td>
<td>++</td>
<td>+</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>++</td>
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<td>HBP-COOH</td>
<td>+</td>
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<td>++</td>
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<tr>
<td>HBPUA-COOH (12:4)</td>
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<tr>
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4. Conclusions

Using thiol-ene “click” reaction, the HBP-COOH was prepared with HBPUA and thioglycolic. A series of new HBPUA-COOHs were successfully synthesized by further reacting with GMA at different feed ratio. The chemical structures of the hyperbranched oligomers were characterized by FT-IR, ¹H-NMR and GPC. The HBPUA-COOHs showed sharp absorption bands 205 nm and had lower photosensitivity in the absence of photoinitiator. The glass transition temperatures (Tg) of all HBPUA-COOHs are in the range of -13 ~ -32°C, and there is a strong melting peak for each of the oligomers. The UV-cured HBPUA-COOHs have good thermal stability as measured by TGA. Moreover, all of the HBPUA-COOHs have low intrinsic viscosity and excellent solubilities in strong polar organic solvents (e.g., DMF, DMAc, DMSO). These results show that the synthesized HBPUA-COOHs may be good materials for applications in the field of coatings, adhesives and photoresists, etc.
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