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Preparation and Properties of Hyperbranched Polyurethanes via Oligomeric A_2 + bB_2 Approach

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Summary

Hyperbranched polyurethanes (HPUs) were synthesized from isocyanate end-capped poly(1,4-butylene adipate glycol) and diethanolamine via oligomeric A_2 + bB_2 approach. The structures of the resulting polymers were characterized by FT-IR, ^{13}C NMR. The degree of branching (DB) was calculated according to the ^{13}C NMR spectra. The properties of HPUs were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), X-ray diffraction (XRD), adhesion strength tests. It was found that the thermal stability of the HPU decreased with the increase of hard segment content. The HPU could be used as hot melt adhesive, and the maximum lap shear strength was up to 6.84 MPa.

Introduction

Dendritic macromolecules including dendrimers and hyperbranched polymers have attracted a great deal of attention due to their unique features such as three-dimensional structure, low intrinsic viscosity, good solubility, and large number of terminal functional groups [1-2]. Monodisperse, well-defined, and perfectly branched dendrimers are prepared by a stepwise growth procedure [3-4], but the stepwise nature of their synthesis makes large-scale production difficult since the growth of a single generation requires several reactions and purification steps. However, irregularly branched and polydisperse hyperbranched polymers are synthesized by a one-pot polymerization of AB_x-type ($x \geq 2$) monomers [5-6], which makes the large-scale synthesis possible at a reasonable cost. Therefore, hyperbranched polymers have being paid more and more scientific and industrial attention in recent years [7-9]. This kind of material may be potentially used as coatings [10], rheology modifiers [11], drug and gene deliveries [12], electroactive and photochemical molecular devices [13], conductive materials [14], and so on.

Hyperbranched polymers were first introduced by Flory in 1952 [15]. Flory presented hyperbranched polymers from a theoretical point of view, describing the intermolecular condensation of AB_x-type monomers. At that time, hyperbranched polymers seemed to be of low interest regarding bulk material because of their noncrystallinity, lacking entanglement which results in inferior mechanical strength [5].

The interest in hyperbranched polymers was not reawakened until the early 1990s when Kim and Webster [16] reported hyperbranched polyphenylenes. Later, a wide variety of hyperbranched polymers such as hyperbranched polyesters [17], hyperbranched polyamides [18], hyperbranched polyethers [19], and so forth have been synthesized and reported.

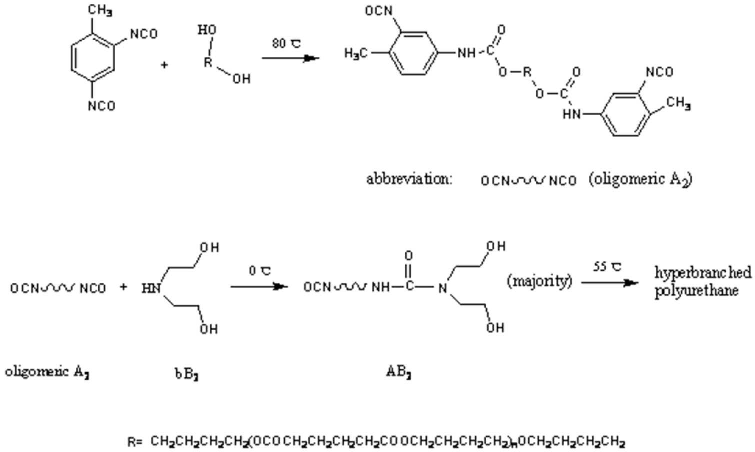
First reports on the successful preparation of hyperbranched polyurethanes appeared in 1993. Spindler and Fréchet [20] synthesized hyperbranched polyurethanes from the AB_2-type monomers which contained one hydroxyl group (A) and two blocked isocyanate groups (B). In the same year, Kumer and Ramakrishnan [21] reported the preparation of hyperbranched polyurethanes using an AB_2-type monomer 3,5-dihydroxybenzoyl azide in a Curtius type rearrangement. Azide chemistry has also been utilized by others [22] to prepare hyperbranched polyurethanes which were derived from AB_2-type monomers that contained very short ethylene oxide units. Recently, Gao and Yan [23] presented a novel approach for preparation hyperbranched poly(urea-urethane)s from commercially available A_2- and CB_n-type ($n \geq 2$) monomers. A_2-type monomers were diisocyanates and CB_n-type monomers were compounds containing one amino group and multihydroxyl groups. Bruchmann et al. [24] also proposed an $AA^* + B^*B_2$ route for hyperbranched poly(urea-urethane)s. Hyperbranched polymers based on the low molar mass A_2 and B_3 (or B^*B_2) have short distances between branch points, which do not enable entanglements, so they exhibit inferior mechanical properties. With regard to this problem, Unal et al. [25] reported the preparation of hyperbranched poly(ether ester)s via copolymerization of poly(ethylene glycol) oligomers (A_2) and 1,3,5-benzenetricarbonyl trichloride (B_3). This oligomeric A_2 and B_3 methodology based on poly(ethylene glycol) offered a facile approach for obtaining products with improved properties and performance. They [26] also prepared hyperbranched poly(urea-urethane) elastomers using oligomeric $A_2 + B_3$ approach. The resulting polymers displayed mechanical properties comparable to their linear analogues. However, this approach has an inherent difficulty in controlling the polymerization reaction with respect to the premature gelation as predicated in Carother's and statistical mechanics equations [27]. Although they [28] utilized the slow addition of oligomeric A_2 solution into the diluted B_3 solution to circumvent this problem, this route needed lots of solvent.

Traditional hyperbranched polymers showed a little mechanical property because they were lack of chain entanglement. In this work, hyperbranched polyurethanes with long segments between the branching points were synthesized via oligomeric $A_2 + bB_2$ approach, which could be used as hot melt adhesive. The oligomeric A_2 monomer was isocyanate end-capped poly(1,4-butylene adipate glycol), and the bB_2 monomer was diethanolamine. The rapid reaction between isocyanate group (A) and amino group (b) led to the in situ formation of the AB_2-type monomer [23-24]. Further polymerization of the AB_2-type monomer formed hyperbranched polyurethanes. No gelation was observed during the polymerization. The structures of the resulting polymers and their properties were investigated.

Experimental

Materials

All the chemical reagents were analytical grade. Poly(1,4-butylene adipate glycol) (PBA, Mn=1000, Aldrich) was degassed and dried in a round flask under high vacuum (20 Pa) at 80~90 °C for 1~2 h. 2,4-tolylene diisocyanate (TDI, Tianjing Yuanli Chemical Co.,China), diethanolamine (DEOA, Sinopharm Group Chemical Reagent Co. Ltd, China), and catalyst didutyltin dilaurate (DBTL, Tianjing Chemical Co., China) were used as received. N-methy-l-2-pyrrolidone (NMP, Sinopharm Group Chemical Reagent Co. Ltd, China) was dried by 4 Å molecular sieves for 24 h followed by reduced-pressure distillation before used.



Scheme 1. Synthesis route for the HPU

Table 1. Synthesis parameters for HPU and DB of HPU

Samples	PBA/TDI/DEOA [a]	Hard segment content [b] (wt.%)	*Mw*	PDI	DB
HPU1	3/4/1	14.91%	-	-	0.25
HPU2	2/3/1	23.88%	13346	2.24	0.29
HPU3	1/2/1	31.20%	12989	2.44	0.33
HPU4	1/2.5/1.5	37.23%	9894	2.09	0.38

[a] Feed molar ratio of PBA to TDA and to DEOA.

[b] Hard segment content = $(m_{TDI} + m_{DEOA}) / (m_{TDA} + m_{DEOA} + m_{PBA}) \times 100\%$.

Synthesis of hyperbranched polyurethane (HPU)

All the reactions were conducted in four-necked, round-bottom flasks equipped with a magnetic stirrer, thermometer, condenser, addition funnel and nitrogen inlet. The prepolymer was formed by the reaction of PBA and TDI in bulk at 80°C for 1~3h. The change of NCO value during the reaction was determined using a standard dibutylamine back-titration method [29]. Figure 1 shows that the content of NCO changed with time in prepolymerization during the preparation of HPU3. As can be seen, the content of NCO nearly didn’t change after 1.5h. After complete reaction, NMP was added to dissolve the prepolymer, the resulting solution was cooled to 0°C. The bB_2 monomer (DEOA), which was dissolved in NMP, was added dropwise at this low temperature until the solution of DEOA/NMP was charged into the flask. The temperature was raised with continued stirring and maintained at 55°C for 20 h, then the reaction was stopped by the addition of DEOA. The polymer was precipitated in water, filtered, and dried under vacuum. A schematic representation of the synthesis route for HPU is shown in Scheme 1. The feed ratios for the resulting HPUs are summarized in Table 1.

Measurements

FT-IR spectra were obtained on a Perkin-Elmer Spectrum One Fourier-transform infrared spectrometer. Solid samples were dissolved in tetrahydrofuran, and were coated on KBr disks. The ^{13}C NMR spectra were obtained at 150MHz on a Varian INOVA-600 NMR spectrometer using DMSO-d_6 as solvent and tetramethylsilane as internal reference. Gel permeation chromatography (GPC) measurements were conducted on an Agilent 1100 Liquid Chromatography-mass Spectrometry. GPC measurements were performed at 30 °C in THF with a flow rate of 1.0 ml/min using polystyrene standards. DSC thermograms were obtained on a Perkin-Elmer DSC-7 differential scanning calorimeter. Samples were placed in aluminum pans and measurements were performed under nitrogen atmosphere by raising the temperature from -60 to 150 °C at a rate of 20 °C/min. TGA was performed under nitrogen atmosphere from 30 to 600 °C at a heating rate of 10 °C/min using a Perkin-Elmer TGA-7 thermogravimetric analyzer. XRD patterns were obtained with a X-ray diffractometer (D/MAX-IIIC, Japan), using Cu Kα radiation at wavelength λ=1.5405 Å. Diffraction patterns were measured in 35 kV and 25 mA, with Bragg's angle 2θ from 2 to 45° at the rate of 5°/min. Lap shear strength was measured with a universal testing machine (Shzmadzu AG-10NA) according to ASTM D-1002-72. These tests were performed at 20 °C using aluminum alloy as the adherent, with a crosshead speed of 10 mm/min.

Results and Discussion

Structural analysis

The FT-IR spectrum of HPU is shown in Figure 2. The absorption band at 3500~ 3300 cm^{-1} is attributed to hydroxyl stretching vibrations and N-H stretching vibrations. The absorption bands at 1731 cm^{-1} and 1535 cm^{-1} are attributed to carbonyl stretching vibrations, N-H bending vibrations, respectively. These imply the presence of urethane linkages.

The ^{13}C NMR spectrum of HPU3 is shown in Figure 3. According to the literature [30], the signals are assigned as follows: 172.72 (C=O, ester), 156.58~156.18 (C=O, urea), 154.34~153.38 (C=O, urethane), 138.65~136.10 (C_2, C_4, phenyl), 130.20~129.88 (C_6, phenyl), 125.6~122.58 (C_1, phenyl), 115.4~112.56 (C_3, C_5, phenyl), 63.78~63.37 (CH_2, soft segment), 62.738 [CH_2-OC(O)-NH, l and d], 60.609 (CH_2-OH, l), 60.293 (CH_2-OH, t), 50.92 (N-CH_2, l), 50.54 (N-CH_2, t), 46.66 (N-CH_2, l and d), 39.94~39.08 (CH_2, soft segment), 33.16 (CH_2, soft segment), 25.39~23.96 (CH_2, soft segment), 17.16 (CH_3), where l, d, and t represent linear units, dendritic units, and terminal units, respectively. These signals suggest the formation of hyperbranched polyurethane.

Degree of branching (DB) is an important parameter for the structure of hyperbranched polymers. Fréchet [17], Muller [31], and Frey [32] independently proposed an equation to calculate the DB of hyperbranched polymers. Considering the reaction was stopped by diethanolamine, this work calculated DB with Frey's equation:

$$DB = 2D / (2D + L) \qquad (\mathbf{1})$$

Where D is the number of dendritic units, and L is the number of linear units. DB calculated from the integration of corresponding peaks is summarized in Table 1. As can be seen in Table 1, DB decreases in the order: HPU4>HPU3>HPU2>HPU1. This can be easily understood based on steric hindrance. When the molar ratio of PBA to TDA is increased, the molecular weight of oligomeric A_2 is increased, the steric hindrance is enhanced. The stronger the steric hindrance is, the less the branching unit is. Other study [33] also showed a decrease in the DB due to steric hindrance.

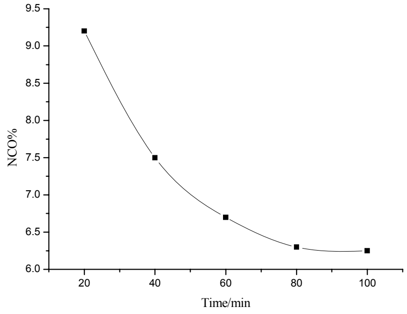


Figure 1. The content of NCO changed with time in prepolymerization during the preparation of HPU3

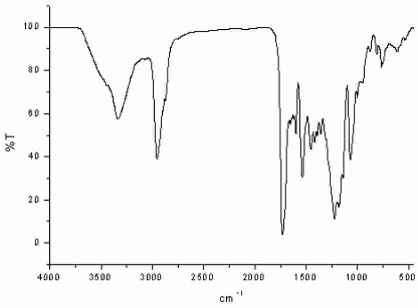


Figure 2. FT-IR spectrum of HPU

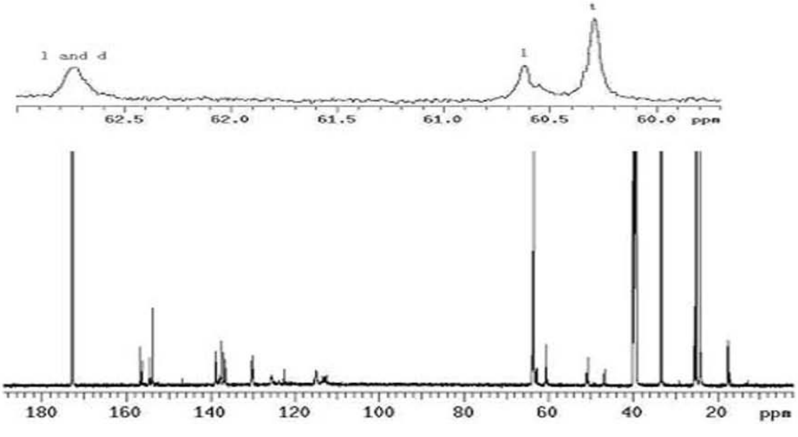


Figure 3. ^{13}C NMR spectrum of HPU3

Thermal properties

DSC thermograms of HPU2 and HPU3 are shown in Figure 4. All the DSC thermograms of HPUs exhibit a step inflection and a melting endotherm. The step inflection is corresponding to the glass transition temperature (T_g) of soft segment and the melting endotherm is corresponding to the crystalline melting temperature (T_m) of soft segment. The mid-point of the step inflection is taken as T_g and the peak temperature of the melting endotherm is taken as T_m. The results are summarized in Table 2. The T_g of soft segment in the HPU is in the range from -0.5 °C to 2 °C, which is extremely higher than the T_g of pure PBA (about -50 °C). Meanwhile, the T_m of soft segment in the HPU is in the range from 37.5 °C to 41 °C, which is lower than the T_m of pure PBA (about 50 °C). These results indicate that the polymers have a certain degree of soft and hard segment phase mixing. It is found that the T_m of soft segment decreases in the order: HPU1>HPU2>HPU3>HPU4. This result suggests that HPU with high hard segment content exhibits a low degree of crystallinity. One possible explanation may be that the degree of soft and hard segment phase mixing increases with the increase of hard segment content, and the hard segment in HPU can destroy the perfection of the crystallization, so the defects of crystal lattices increase with the increase of the hard segment content, which cause the crystals can be damaged at low temperature.

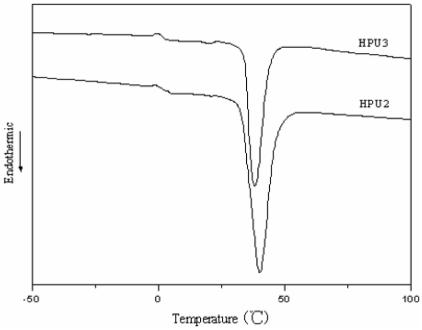


Figure 4. DSC thermograms of HPU2 and HPU3

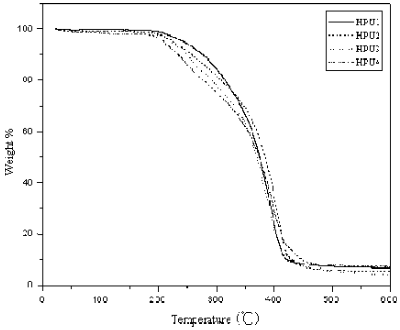


Figure 5. TGA thermographs of HPUs

Table 2. Thermal property of HPU samples measured by DSC analysis

Samples	T_g	T_m
HPU1	-0.5°C	41°C
HPU2	2°C	39.8°C
HPU3	0°C	38°C
HPU4	1°C	37.5°C

Table 3. Temperature at 10% and 40% weight loss of HPU samples

Samples	Temperature at 10% weight loss	Temperature at 40% weight loss
HPU1	276°C	385°C
HPU2	257°C	370°C
HPU3	248°C	356°C
HPU4	234°C	354°C

As is known, the T_g of soft segment depends on the degree of phase mixing of soft and hard segment. The better the miscibility of these two phases is, the higher the T_g of soft segment is. However, it can be seen that the T_g of soft segment of HPU2 is higher than that of HPU3, as shown in Table 2. The reason is discussed as follows. The DB of HPU can affect rotation of chain links, mobility, and chain-chain interaction. When the DB of HPU is decreased, intermolecular free volume is reduced, the chain-chain interaction is enhanced, the required energy of the segment motion is enhanced, and the T_g of soft segment of HPU is increased.

The thermal stability of the HPU was analyzed by TGA. In a nitrogen atmosphere all TGA curves display a slower initial and then a more rapid degradation process (Figure 5), suggesting a two-step mechanism for degradation. It is found that the degradation temperature decreases with increasing hard segment content. This indicates that the thermal stability of HPU decreases due to the increase of hard segment content. This is attributed to low degradation temperature of urethane and urea groups. The two-step process for degradation in nitrogen atmosphere was also reported by others [34]. Table 3 shows the temperatures at 10% and 40% weight loss of HPU samples.

XRD analysis

X-ray diffraction patterns of pure PBA and HPUs are shown in Figure 6. It is obviously observed that pure PBA and HPUs show similar diffraction. It implies that they have the same crystal structure and unit cell type. The HPUs show a lower diffraction peak height and broader half-width than pure PBA, which indicates that their crystal particles become small and their crystallinity decreases.

The crystallization of soft segment is disturbed pronouncedly in the polyurethane, due to the hindrance of hard segments [35]. As shown in Fig. 5, all HPUs appear very similar diffraction curve, but the intensity decreases with increasing the hard segment content. These suggest that the crystallization of soft segment in the HPUs is restricted due to the hindrance of hard segments. The disturbance enhances with the increase of hard segment content. These results are quite consistent with the results obtained by DSC.

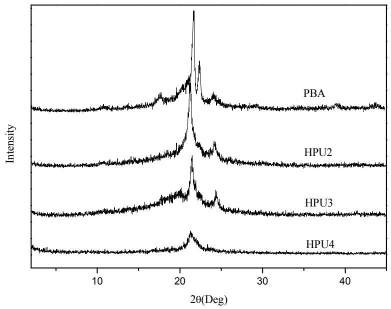


Figure 6. X-ray diffraction profiles of pure PBA and HPUs

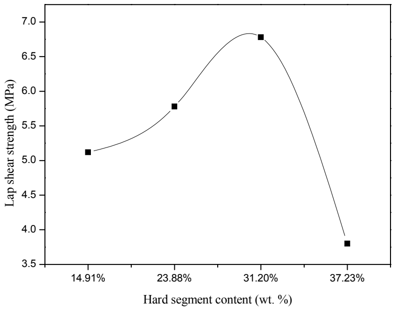


Figure 7. The effect of the hard segment content on the lap shear strength

Adhesion property

The HPUs are thermoplastic polymers, and can be used as hot melt adhesives. Figure 7 shows the effect of the hard segment content on the lap shear strength. It is seen that the lap shear strength increases initially, and then decreases dramatically with increasing the hard segment content. This can be explained as follows. When the hard segment content is increased, intermolecular interactions including the intermolecular force and hydrogen bonding are enhanced, which result in the increase of the adhesion strength. However, beyond a critical value, the stiffness of the polymer increases dramatically with the increase of hard segment content, which causes the adhesion strength decrease [36].

The maximum lap shear strength is up to 6.84 MPa, which indicates the resulting polymers have good adhesion property. Although conventional isocyanate reactive hot melt adhesives (RHMA) showed network and crystalline structure after cured, the maximum shear strength was about 8.57MPa even the RHMA cured for 28days [37].

Conclusions

Hyperbranched polyurethanes were successfully synthesized via oligomeric A_2 + bB_2 approach. The DB of HPU decreased with increasing the molar ratio of PBA to TDI. The DSC and XRD results suggested that the crystallinity of soft segment in the HPU decreased with the increase of hard segment content of the HPU. The TGA results showed that the thermal stability of HPU decreased with increasing hard segment content of the HPU. The maximum lap shear strength was up to 6.84 MPa, indicating the resulting polymers had good adhesion property. The HPU has a potential application in the field of hot melt adhesives.

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