

Synthesis, Characterization, and Properties of PCDL Aliphatic Hyperbranched Polyurethane Coatings

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ABSTRACT: The isocyanate-terminated polyurethane pre-polymer (PPU) was synthesized via the step-growth polymerization approach by using polycarbonate diol (PCDL, $M_n = 2000$) and isophorone diisocyanate (IPDI) as monomers, dibutyltin dilaurate (DBTDL) as the catalyst. Subsequently, the hyperbranched polyurethane (HBPU) was synthesized by graft copolymerization using PPU, hyperbranched poly(amide-ester) polyol (HPAE) and 1,4-butanediol (BDO). The molecular structure of HBPU was characterized by means of FTIR, $^1\text{H-NMR}$, and $^{13}\text{C-NMR}$. It was observed that HBPU was synthesized as anticipated. The thermal and mechanical properties, the microstructure, and morphologies of the filmed HBPU and LPU (linear polyurethane) were tested, respectively. The filmed HBPU, revealed better thermal stability, and higher T_g accompanied with lower viscosity than those of filmed LPU. Additionally, the mechanical experiment showed that the filmed HBPU exhibited enhanced mechanical properties because it contained certain amounts of HPAE. Compared with its linear analog (LPU) specimen, the tensile strength of the filmed HBPU containing 10 wt % HPAE increased by 1.9 times (up to 28.15 MPa), and its elongation at break increased by 1.5 times (up to 543.8%), resulting from the dual effects of the hydrogen bonding and the crosslinking density in the HBPU system. The morphologies of filmed HBPU were characterized by means of WAXD and SEM, which indicated that increasing the content of HPAE lowers the crystallinity of HBPU. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2013

KEYWORDS: hyperbranched polyurethane; coatings; synthesis; characterization; properties

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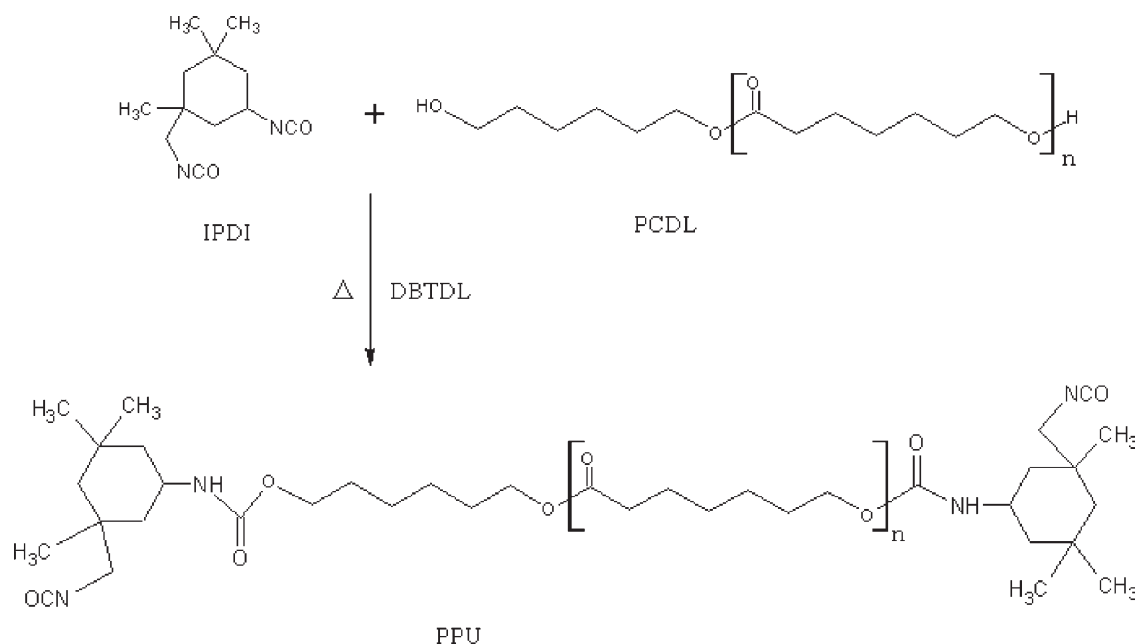
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INTRODUCTION

Dendrimers with novel spatial structure and unique performance have attracted considerable interests,^{1–7} but they are not widely used due to the complicated synthesis process and high cost. It is proved that Hyperbranched polymers, have similar structure and performance as the dendrimers but can be synthesized easily,^{8,9} so they have been regarded as new materials in the 21st century. Therefore, it has been drawn more attention and become a research focus in macromolecule field.^{10,11}

With non-yellowing performance, aliphatic diisocyanate has been widely used for synthesizing aliphatic polyurethane (PU) materials such as coatings, elastomers, foams, and adhesives. Compared with comparable aromatic PU, the aliphatic PU materials always exhibit poor mechanical properties, especially the one synthesized with isophorone diisocyanate (IPDI).^{12–14} The mechanical properties can be enhanced through the increase of the hard-segment content, but it would lead to a high cost for the increased amount of the expensive aliphatic diisocyanate which must be used to achieve this purpose.

Recently, a lot of studies on the application of hyperbranched polymers in PU field have been reported. A series of morphology hyperbranched polyurethane (HB-PU) and hyperbranched shape memory polyurethane (HB-SMPU) has been prepared by Cao and co-workers,^{15–18} they found that hard segment content has a significant influence on the properties of PU. Okrasa and co-workers^{19,20} studied the molecular dynamics in polyurethane network and molecular relaxations synthesized by hyperbranched polyesters (trade name Boltorn[®]). They found that the macrobiol length had a strong influence on the glass transition and the α -relaxation process correlated with it. Sheth and co-workers²¹ observed the structure-property behavior of highly branched pre-polymer (PPU) and its linear analog synthesized with bis (4-isocyanatocyclohexyl) methane and polyether polyol, etc. They drew the conclusion that the tensile strength of the highly branched PPU was lower than that of the linear analog synthesized. The tensile tests of hyperbranched aqueous poly(urethane-urea) (HBAPU) by Liu et al.^{22,23} revealed that HBAPU exhibited excellent tensile properties, maximum tensile strength, and higher T_g accompanied with lower viscosity.



Scheme 1. The synthesis of PPU.

In this article, the synthesis, characterization, and properties of polycarbonate diol (PCDL) aliphatic hyperbranched polyurethane (HBPU) coatings were studied through a series of experiments. The hydroxyl-terminated hyperbranched structure was introduced into polycarbonate-based aliphatic polyurethane pre-polymer to form a novel polymer with space network. It has changed the original linear polyurethane structure to some extent. At the same time, the modern instrumental analysis technique was applied to characterize the molecule structure and the thermal properties of LPU (linear polyurethane) and HBPU. Compared with its linear analog (LPU), the mechanical properties of the HBPU was enhanced dramatically, which could be correlated with the microstructure and the morphologies of these polyurethane materials.

EXPERIMENTAL

Materials

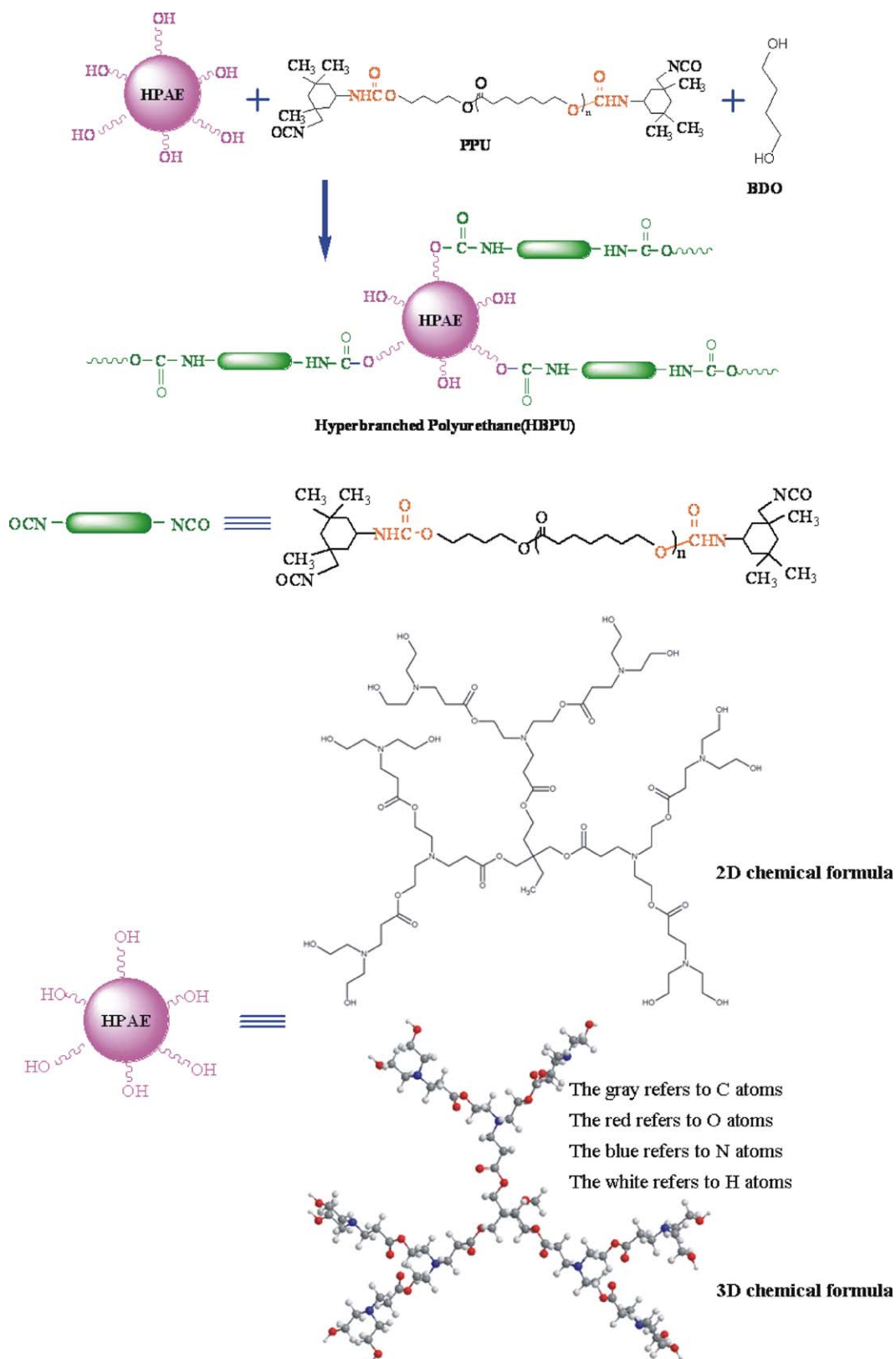
Polycarbonate diol (PCDL, $M_n = 2000 \text{ g mol}^{-1}$) was analytical pure grade and was produced by Tianjin Kemiou Chemical Reagent Co., China, was dried in vacuum at $100 \pm 5^\circ\text{C}$ for 2 h to remove the H_2O before use. 1,4-Butanediol (BDO), Isophorone diisocyanate (IPDI), were obtained from Shanghai No. 1 Chemical Reagent Factory. *N,N*-Dimethyl-formamide (DMF) and dibutyltin dilaurate (DBTDL) were purchased from Tianjin Fuchen Chemical Reagent Factory (Tianjin, China). The above chemicals were analytical grade and used as received without further purification. Hydroxyl-terminated hyperbranched poly(amine-ester) polyols (HPAE), was made and purified by ourselves.²⁴

Experimental Procedure

Polycarbonate-based aliphatic polyurethane pre-polymer (PPU) was synthesized by a step polymerization technique as shown in Scheme 1.

First, a stoichiometric amount of PCDL2000, DBTDL (0.007 wt % based on the total mass of raw materials, used as the catalyst) were charged into a 250 mL four-necked round-bottom flask equipped with a N_2 inlet, a thermometer and a mechanical stirrer, a constant voltage dropping funnel with a certain amount of IPDI. Then, the flask was fastened in an oil bath at about 50°C to melt the PCDL2000. When the temperature was raised to $70\text{--}80^\circ\text{C}$, IPDI was added dropwise into the flask and kept stirring at 400 rpm with a continuous nitrogen flow until the NCO content reached the theoretical value determined by the standard dibutylamine back-titration method. During the process, when the viscosity of the system increased, and even lead to the phenomenon of pole-climbing, DMF would be used as a solvent. PPU was finally obtained after the solvent had been recycled through a reflex condenser.

Scheme 2 shows the synthesis of HBPU. A stoichiometric amount of HPAE and BDO (used as a chain extender) were charged into a constant voltage dropping funnel. It was then added dropwise into a 250 mL four-necked round-bottom flask equipped with a N_2 inlet, a thermometer and a mechanical stirrer. HBPU-5, HBPU-10, and HBPU-15 were synthesized respectively in accordance with the formulation listed in Table I. By keeping the temperature at 80°C , the reactants were stirred at 400 rpm with a continuous nitrogen flow for about 4 h until the NCO content reached the theoretical value (approaching almost to 0, indicated that the end group NCO of PPU has been completely reacted) determined by the standard dibutylamine back-titration method. HBPU was finally obtained after the solvent had been recycled through a reflex condenser. During the process, All the hard segment contents of HBPU-5, HBPU-10, and HBPU-15 were fixed to about 40 wt % while solid contents were fixed to about 40 wt %. LPU, which has the same hard segment contents and solid contents with HBPU,



Scheme 2. The synthesis of HBPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Table I. Composition, Viscosity, and T_g of LPU and HBPU

Sample	Composition (g)				Viscosity (cps, 30 °C)	T_g (°C)
	IPDI	PCDL2000	BDO	HPAE		
HBPU-5	34.2	70	10.4	5.3	4217	1.25
HBPU-10	30.1	70	7.3	11.6	4947	3.92
HBPU-15	28.3	70	4.5	17.2	2118	1.70
LPU	35.6	70	11.3	0	9678	-15.88

The content of the hard segment = $(W_{IPDI} + W_{BDO} + W_{HPAE}) / (W_{IPDI} + W_{PCDL2000} + W_{BDO} + W_{HPAE})$.

was synthesized for later comparable test. The viscosity of LPU and HBPU were tested and the related data were listed in Table I.

Preparation of Specimens

The HBPU mixture (solid content: 40 wt %) was rapidly cast into a glass mold (20 cm × 15 cm × 2 mm). After the solvent evaporation, it was cured at 50°C for 7 h in a vacuum drying oven. Thus the specimen was obtained. Then it was taken out and put into the desiccator for mechanical test. LPU and PPU were obtained in the same way.

Measurements

Fourier-transform infrared (FTIR) spectrometer spectrum of the HBPU-10 specimen was recorded with a BRUKER (German) VETOR-2 Fourier-transform infrared spectrometer. The solid sample was dissolved in tetrahydrofuran first, and then was coated on KBr disks.

The nuclear magnetic resonance ($^1\text{H-NMR}$ and $^{13}\text{C-NMR}$) measurements were performed with a BRUKER (German) ADVANCE β 400 MHz spectrometer at 25°C. Acetone- d_6 and TMS were used as the solvent and internal standard substance, respectively.

Viscosity was measured by a QNX Model spinning viscometer (Tianjin Instrument Co., Tianjin, China) at 30°C.

Thermogravimetric (TG) analysis was performed under nitrogen atmosphere from 40°C to 600°C at a heating rate of 10°C min $^{-1}$ using a TGA-Q500 thermogravimetric analyzer (American).

Differential scanning calorimetry (DSC) was carried out using a TA DSC 2010 from -100°C to +100°C at a heating rate of 10°C min $^{-1}$ under nitrogen.

AGT-U55 testing machine were purchased from Taiwan High Speed Rail Corporation and used for the mechanical properties of LPU and HBPU specimens. The test was conducted under a 50 mm min $^{-1}$ cross-head rate at 25°C and the dumb-bell shaped specimens were prepared according to in accordance with GB1040-79. The average value was calculated after each specimen was tested for five times.

A D/max2200PC analyzer of Rigaku (Japan) was used to analyze the phase morphology by means of wide-angle X-ray diffraction (WAXD). The analysis was conducted at 40 kV and 40 mA with Bragg's angle 2θ from ca. 5° to 60° at the rate of 5° min $^{-1}$.

Coated with gold, the surface morphology was observed using a scanning electron microscope (SEM) (model SPI3800N/SPA400, NSK LTD).

RESULTS AND DISCUSSION

Characterization of HBPU

FTIR spectrum of HBPU-10 is shown in Figure 1. According to the characteristic bands of the HBPU-urea samples in literature,^{13,25,26} the signals were assigned as follows. There are three stretching vibration absorption peaks assigned to the characteristic functional groups of -NHCOO-, i.e., N-H at 3383 cm $^{-1}$, C=O at 1688 cm $^{-1}$, and C-N at 1463 cm $^{-1}$. The absorption peaks of inflection vibration assigned to N-H in -NHCOO- can be found at 790 and 661 cm $^{-1}$. The appearance of the peaks mentioned above indicated the formation of -NHCOO- through the reaction of -NCO and -OH. It indicated that the experiment was conducted as anticipated

Figure 2 shows the $^{13}\text{C-NMR}$ spectrum of HBPU-10. The solvent was Ace- d_6 . According to the literature,^{14,27} the signals were assigned as follows. The carbon chemical shifts in -NHCOO- characteristic group of HBPU can be seen at 155.72 and 157.05 ppm, respectively. This phenomenon proved that the characteristic group -NHCOO- of HBPU was formed through the reaction of -OH in HPAE and -NCO in PPU,

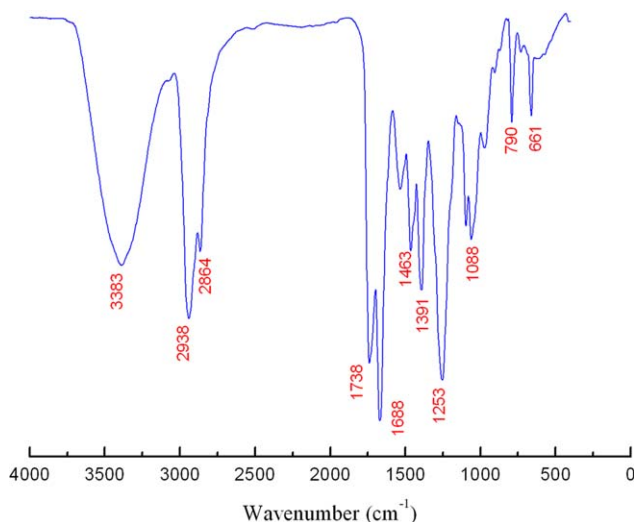


Figure 1. FTIR spectrum of HBPU-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

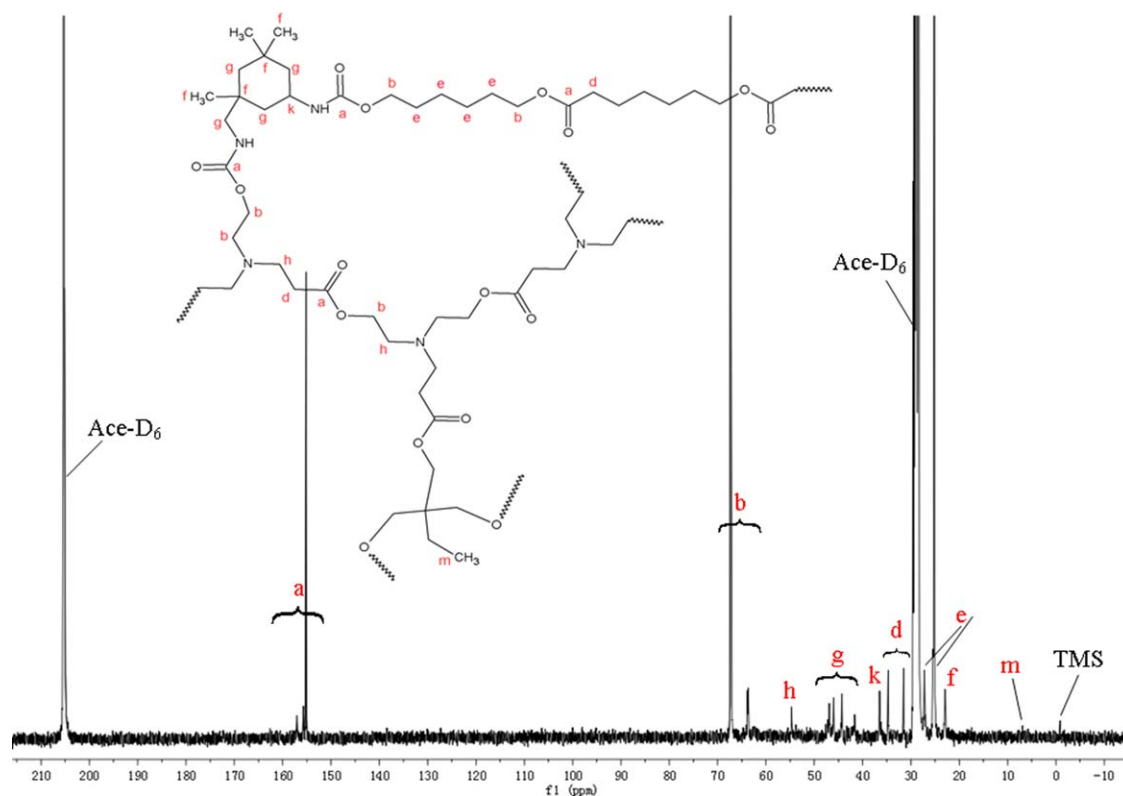


Figure 2. ^{13}C -NMR spectrum of HBPU-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

signifying that the HBPU has been synthesized. The result is consistent with that of FTIR analysis.

It is worth noting that two strong peaks at 67.27 and 27.22 ppm appeared as well in Figure 2. They are assigned to the carbon chemical shifts in PPU structure. But the former is assigned to the carbon chemical shift in $-\text{CH}_2-$ connected to $-\text{COO}-$. The latter is assigned to the carbon chemical shift in $-\text{CH}_2-$ neither connected to $-\text{COO}-$ nor to $-\text{NHCOO}-$. The presence of strong peaks is attributed to the existence of large number of carbon atoms in $-\text{CH}_2-$ due to the monomer PCDL2000 used in the synthesis.

Figure 3 shows the ^1H -NMR spectrum of HBPU-10. The solvent is $\text{Ace-}d_6$. In Figure 3, the peak at 6.17 ppm was caused by the proton chemical shift in $-\text{NHCOO}-$, indicating that the reaction was performed as anticipated. The result is consistent with the analysis of Figures 1 and 2. In addition, strong peaks can be obviously observed at 4.14, 1.69, and 1.44 ppm. The peak at 4.14 ppm is assigned to the proton chemical shift in $-\text{CH}_2-$ connected to oxygen atom in $-\text{COO}-$ in the PPU structure. The peaks at 1.69 ppm and 1.44 ppm were assigned neither to the proton chemical shifts of $-\text{CH}_2-$ connected with $-\text{COO}-$ nor to $-\text{NHCOO}-$.

Viscosity

As indicated in Table I, when HPAE was added in the system, the viscosity of the products was decreased for a large degree. When the content of HPAE was 5%, the viscosity of HBPU-5 is 4217 cps, was decreased by 56.4% as compared with which of

LPU. The results revealed that the viscosity of hyperbranched polymers was lower than its linear analog.

Thermal Properties

Thermogravimetric-derivative thermogravimetric (TG-DTG) is a simple but accurate method for studying the decomposition pattern and the thermal stability of polymers. The TG and DTG curves of polyurethane were illustrated in Figure 4. The decomposition of LPU and HBPU-10 can be divided into two stages, similar findings can be found in the literature.^{28–30} From Figure 4, it can be found that the TG and DTG curves of HBPU were evidently right shifted in comparison with curves of LPU. The data were listed in Table II.

It is observable in Table II that the first stage of decompositions of LPU and HBPU was located at 275–358°C and 263–364°C respectively, which was merely due to the decomposition of urethane bond in the system. The second stage located at 358–436°C and 364–450°C respectively was merely due to the decomposition of carbon-carbon bond in the system. Significantly, the maximum decomposition temperature of HBPU was about 10°C higher than that of LPU regardless of the stage.

Equivalently, with 20% weight loss, the temperature of HBPU-10 went up to 354°C, increasing by 16°C compared with that of LPU, i.e., 338°C, whereas with 50% weight loss, the temperature of HBPU-10 rose to 411°C, which was 15°C higher than that of LPU, i.e., 396°C. The phenomenon indicates that HBPU had a better thermal stability than LPU, resulting from the chemical crosslink performed by HPAE in HBPU. This is because the

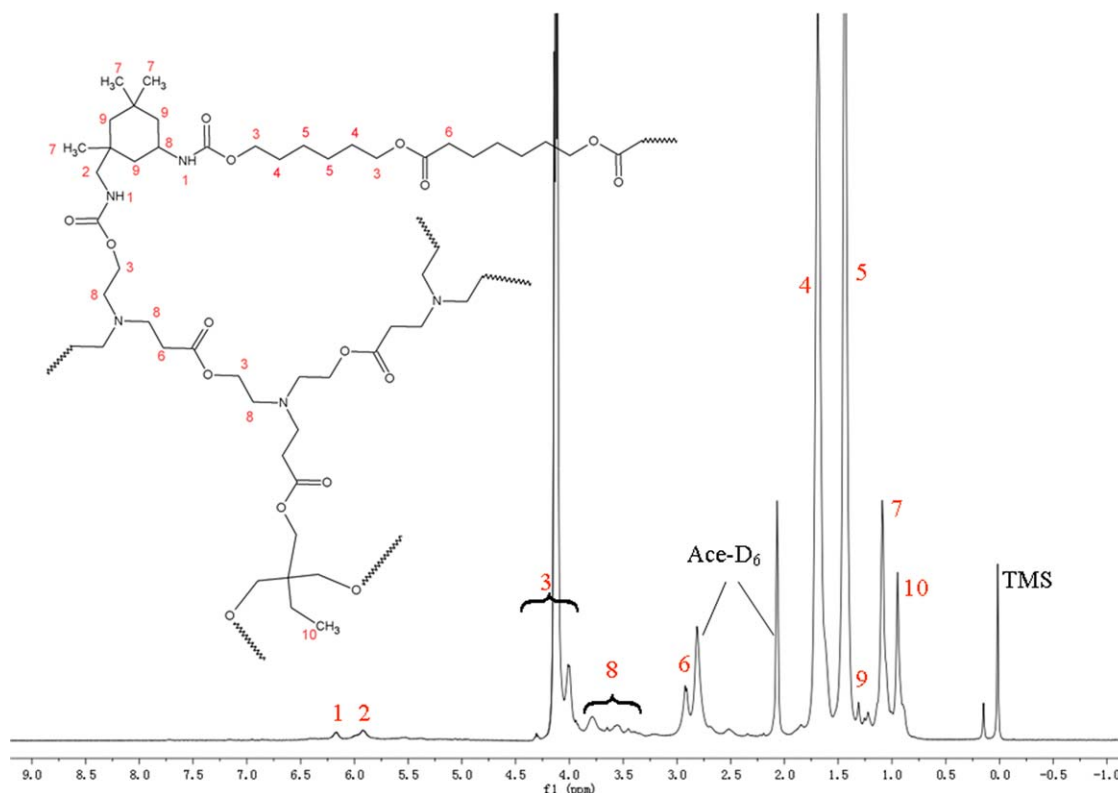


Figure 3. $^1\text{H-NMR}$ spectrum of HBPU-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

crosslink had the advantage of hindering the moving of polymer chains. In this way, the thermal stability of the coatings was enhanced and the wide application of HBPU to industrial fields was made possible.

As we can see from Table I, the T_g of the HBPU was high than its linear analog. The T_g of LPU is -15.88°C , when the content of HPAE is 5%, the T_g of HBPU-5 increased to 1.25°C , and when the content of HPAE is 10%, the T_g of HBPU-10 increased to 3.92°C .

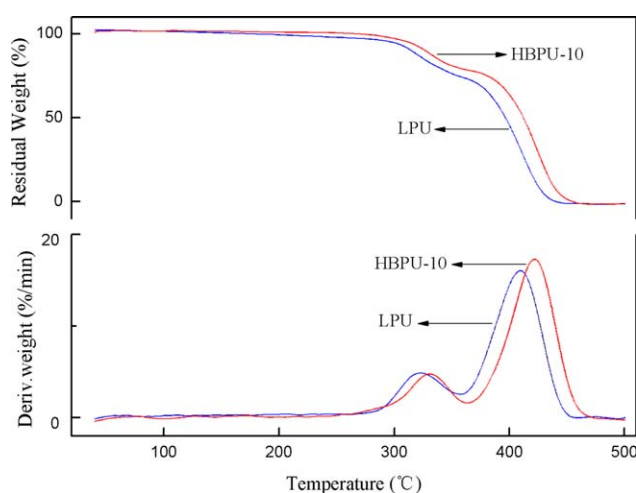


Figure 4. TGA and DTG curves of LPU and HBPU-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Mechanical Properties

The mechanical properties data of LPU and HBPU were listed in Table III. It shows significantly that the properties of LPU films including those of Young's modulus, tensile strength, and elongation at break are lower than those of HBPU. This behavior could be attributed to the easier intermolecular motion when polymer chains of LPU with a linear structure were imposed by a certain amount of external force.

When the content of HPAE was increased to 10%, the elongation at break reached the maximum value of 543.8% with a better tensile strength (28.15 MPa). Compared with the LPU without HPAE, the tensile strength of the filmed HBPU increased by 1.9 times, the elongation at break increased by 1.5 times, and its Young's modulus increased by 2.9 times (up to 2.52 MPa). The reason was listed as follows. When HPAE content was introduced, the crosslink in HBPU occurred, leading to the increase of cohesive energy density and the strong intermolecular hydrogen bond. Therefore, the intermolecular interactions could be increased and the mechanical properties were enhanced.

From Table III, we can also see that the mechanical properties (including Young's modulus, tensile strength, and elongation at break) increased and then decreased with the increase of HPAE content. When HPAE was increased to a certain value, the cohesive energy density of the branch points increased. Consequently, a large number of pores appeared among the molecular chain, affecting the closely packing of the molecule. As a result, the tensile strength of HBPU was lowered. When the HPAE was

Table II. Thermal Decomposition Data of LPU and HBPU-10

Sample name	Decomposition stage	Decomposition temperature range (°C)	Maximum decomposition temperature (°C)	20% loss, T _{20%} (°C)	50% loss, T _{50%} (°C)
LPU	Stage I	275-358	323	338	396
	Stage II	358-436	410		
HBPU-10	Stage I	263-364	331	354	411
	Stage II	422-450	422		

increased to 15%, the tensile strength of HBPU was lowered from 28.15 to 27.93 MPa, Meanwhile, its elongation at break reduced from 543.8% to 510.9%. Thus, we can draw the conclusion that increasing certain amount of hyperbranched polymer can significantly improve the mechanical properties of aliphatic polyurethane.

Morphological Study

The WAXD spectra of PCDL2000 and HBPU-10 are shown in Figure 5. A broad diffraction peak was found at around $2\theta = 21^\circ$ in HBPU-10, corresponding to the structure of crystalline state constituted by the soft segments of PCDL2000, indicating that the crystallization was attributed to the soft segments of HBPU. This was also found to be well-improved in the prepared HBPU. HBPU-10 exhibits a much lower crystallinity than that of PCDL2000 (HBPU-10: 4.42%, PCDL2000: 29.68%). The hyperbranched structure of HBPU gave rise to the increase of the microphase mixing of the hard and soft segments. Consequently, the relative motion of the soft segments was seriously restricted, resulting in the substantial decline in crystallinity.

Figure 6 shows the WAXD spectra of HBPU-5, HBPU-10, and HBPU-15. It can be seen that all diffraction peaks of HBPU with 5, 10, and 15% HPAE content were at around $2\theta = 21^\circ$. But with the increase of content of HPAE moiety, the crystallinity of HBPU decreased gradually. The WAXD analysis of HBPU-5, HBPU-10, and HBPU-15 were performed on A D/max2200PC analyzer of Rigaku (Japan) at 40 kV and 40 mA with Bragg's angle 2θ from *ca.* 5° to 60° at the rate of 5° min^{-1} . The degree of crystallinity was accordingly calculated with the aid of Jade 5.0 software (Materials Data), the data respectively were: 6.52, 4.46, and 3.30%, respectively.

The crystallinity of HBPU-5, HBPU-10, and HBPU-15 was 6.52, 4.46, and 3.30%, respectively. It can be explained as follows: the introduced hyperbranched structure increased the compatibility between the soft and hard segments but minimized the phase separation, therefore hindering the mutual

Table III. Mechanical Properties of LPU and HBPU

Sample	Young's modulus (MPa)	Tensile strength (MPa)	Elongation at break (%)
LPU	0.87	14.61	359.6
HBPU-5	1.63	19.53	457.6
HBPU-10	2.52	28.15	543.8
HBPU-15	1.86	27.93	510.9

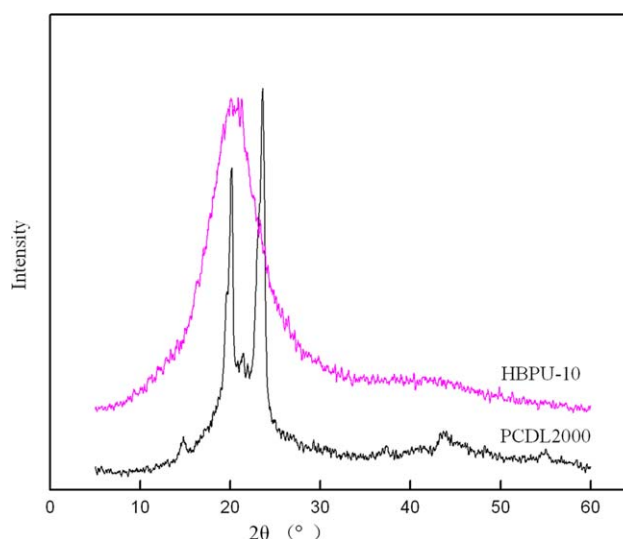


Figure 5. WAXD curves of PCDL2000 and HBPU-10. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

accumulation between soft segments. The ordered degree of the soft segments then dropped. As a result, the crystalline region reduced, displaying in the spectrum as increasingly wide diffraction peaks.

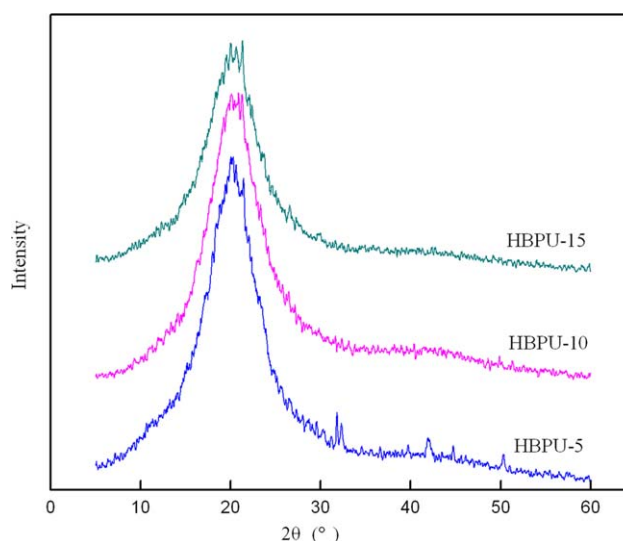


Figure 6. WAXD curves of HBPU. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

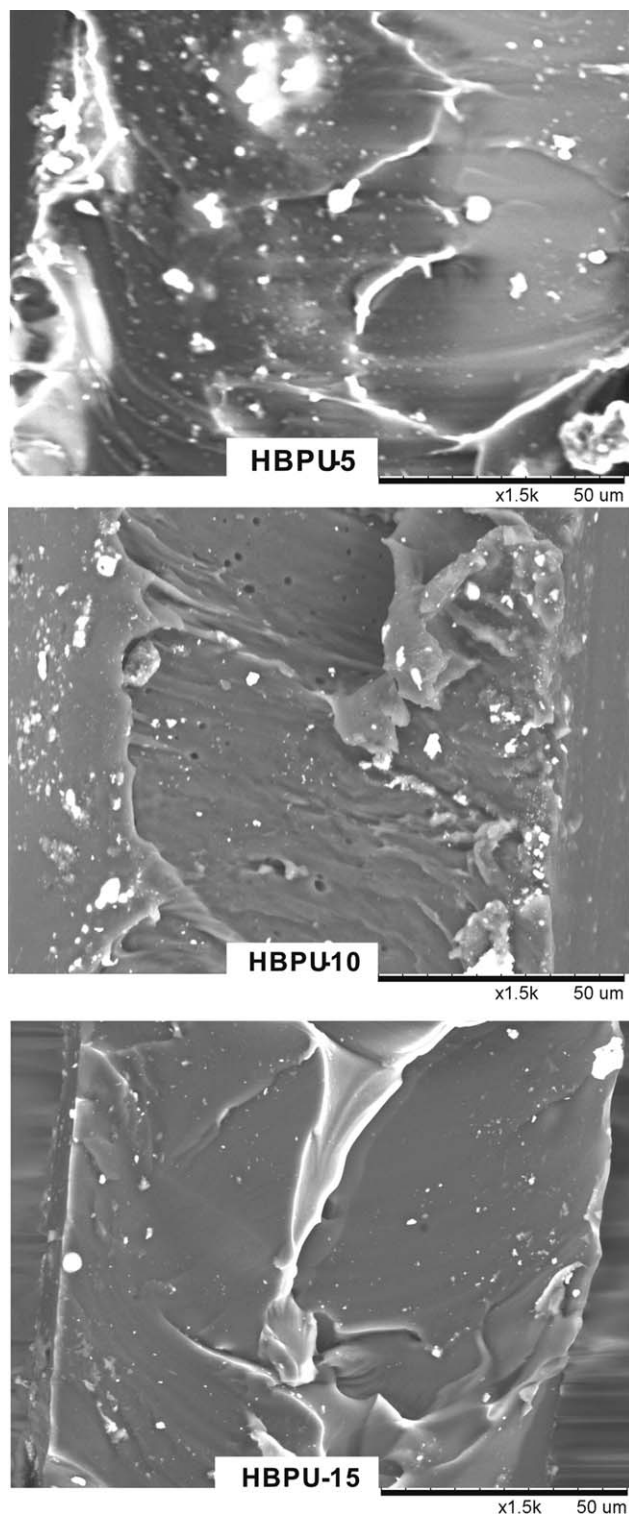


Figure 7. SEM pictures of LPU and HBPU.

Figure 7 shows the SEM micrographs of HBPU-5 HBPU-10, and HBPU-15 coatings. Both the bright area and dark area can be clearly seen. The white dots in the bright area constitute the crystalline region of HBPU while the dark area shows the non-crystalline region. The similar statements about crystalline

region were also found from the literature of Deka and Xu.^{7,11,31} Obviously, the crystalline region of HBPU-5 is the largest, while the crystalline region of HBPU-15 is the smallest. The result shows that the crystallization is influenced with the content of HPAA moiety. That is, the higher the content of the HPAA, the smaller the crystalline region, which is consistent with WAXD analysis.

CONCLUSIONS

The PCDL aliphatic hyperbranched polyurethane containing hyperbranched poly(amide-ester) polyol was synthesized and characterized. The experimental data showed that HBPU possesses better performance over its linear analog. Because of the chemical crosslink performed by HPAA, The decomposition temperature of HBPU was about 10°C higher than that of LPU regardless of the stage. The mechanical experiment results showed that the HBPU containing small amount of HPAA exhibited the enhanced hydrogen bonding. As compared with the linear analog LPU specimen, the tensile strength of the HBPU containing 10 wt % HPAA increased by 1.9 times, and the elongation at break increased by 1.5 times. The morphology tested by WAXD and SEM was also found to be well-improved in the prepared HBPU, and the results showed that increasing the content of HPAA lowers the crystallinity of HBPU.

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