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ORIGINAL PAPER

Synthesis and properties of hyperbranched aqueous poly(urethane–urea) via A_2 + bB_2 approach

**Dan Liu · Shaomin Zeng · Chang Yao ·
Aifang Chen · Zhonghua Chen · Zushun Xu**

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Abstract Hyperbranched aqueous poly(urethane–urea) (HBAPU) was synthesized via $A_2 + bB_2$ approach using 2,4-tolylene diisocyanate, polycarbonatediol, dimethylol propionic acid and diethanol amine as materials. The structure of the products were characterized by FT-IR and ^{13}C NMR. The results showed that the degree of the branching increased with increasing the molar ratio of the nNCO/nOH. The particle size, thermal and mechanical properties were measured by photon correlation spectroscopy, thermal gravimetric analysis and tensile tests, respectively. The particle size of HBAPU was much smaller than that of linear aqueous polyurethane; thermal stability of HBAPU enhanced with decreasing the molar ratio of nNCO/nOH. The tensile tests revealed that HBAPU exhibited excellent tensile properties and the maximum tensile strength was up to 33 MPa.

Keywords Hyperbranched · Aqueous poly(urethane–urea) · Synthesis properties

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D. Liu · S. Zeng · C. Yao · A. Chen · Z. Xu
College of Materials Science and Engineering,
Hubei University, 430062 Wuhan, People's Republic of China

Z. Xu (✉)
Ministry-of-Education Key Laboratory for the Green Preparation
and Application of Functional Materials,
Hubei University, 430062 Wuhan, People's Republic of China
e-mail: zushunxu@hubu.edu.cn

Z. Chen
College of Materials Science and Engineering,
South China University of Technology,
510641 Guangzhou, People's Republic of China

Introduction

Highly branched polymers including dendritic, hyperbranched, or multibranched polymers have being paid more and more scientific and industrial attention in recent years due to their unique features and properties such as three-dimensional architecture, low melting viscosity, good solubility, and large amount of terminal functional groups [1]. Monodisperse, well-defined, and perfectly branched dendrimers are prepared by a stepwise growth procedure, 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. Although hyperbranched polymers, as the analogue of the dendrimer, have some deficit in structure, they were typically synthesized by the polymerization of ABx-type ($x \geq 2$) monomers, which made the large-scale synthesis possible at a reasonable cost [2]. A series of hyperbranched polymer have been prepared, such as hyperbranched polyphenylenes [3], hyperbranched polyester [4], hyperbranched polyamides [5], and so on. And they have been wildly used in coatings [6], drug and gene delivery [7], modifiers and additives [8].

In the field of polyurethane, the reaction between free isocyanate and hydroxyl group was too fast to coexist in nature. So early efforts toward the preparation of hyperbranched polyurethanes focused on the synthesis of an ABx-type monomer, following two major pathways: the phosgene or phosgene substitute based approach [9] and the phosgene free preparation [10, 11]. First report on the successful preparation of hyperbranched polyurethanes did not appear until 1993 by Spindler and Fréchet [12, 13] via AB_2 step-growth polymerization. The AB_2 monomer contained one hydroxy group (A) and two blocked isocyanate groups (B), further polymerization between A and B formed hyperbranched polyurethane. Kumar and Ramakrishnan [14] also reported the preparation of hyperbranched polyurethane using a AB_2 type monomer 3,5-dihydroxybenzoyl azide by a Curtius-type rearrangement reaction. Bruchmann et al. [15] started from readily available polyurethane raw materials using intramolecular reactivity differences in combination with protective group chemistry towards AB_2-starting materials. Since then a number of other synthetic strategies for preparing hyperbranched polyurethanes had been reported, including high selective reactivity [16], nonisocyanate ways [17], and so forth [18].

As mentioned above, most of the AB_2 monomers were unavailable and had to be synthesized by researchers. Thus, alternatives had been found to the classical synthesis of hyperbranched polymers using available monomers. Similar hyperbranched structures could be obtained by the A_2 plus B_3 approach. The A_2 and B_3 methodology offered a facile route for gaining polymers with improving properties. Because the segments length of the hyperbranched polymers were sufficient for entanglements leading to enhanced mechanical properties [19]. In addition, the $A_2 + B_3$ approach was the commercial availability [20]. However, gelation occurred when the critical conversion reached. Thus the conversion, the stoichiometry of the monomers and the reaction conditions must be controlled extremely well to achieve soluble and reproducible products [21]. Long [22, 23] utilized isocyanate end-capped polyether as oligomeric A_2 and triamine or trimethylol as B_3

monomers to get different products. The resulting polymers exhibited excellent mechanical properties, but the reaction should proceed in diluted solution to avoid gelation. Recently, a facile route for preparation of hyperbranched polymers was reported which was called couple-monomer methodology (CMM) or $A_2 + bB_2$ approach. This strategy was based on the principle of selective reactions between specific functional groups allowing the formation of an AB_2 type intermediate. Compared to $A_2 + B_3$ systems, a more defined construction of hyperbranched polymers was obtained. The rapid reaction between A and b led to the formation of AB_2-type monomer. Further polymerization of the compounds formed in situ gave a soluble hyperbranched polymer rather than a gel. Bruchamann [24] synthesized hyperbranched polyurethane by reacting diisocyanates with NCO-groups of different reactivity, for example 2,4-tolylene diisocyanate (TDI) or isophorone diisocyanate (IPDI) with amino alcohols like diethanol amine (DEOA) or diisopropanolamine. The structure and end-group effects on bulk and surface properties of hyperbranched poly (urea urethane)s were also investigated [25]. Gao and Yan [26, 27] also used this method reacting TDI, IPDI and 4,4′-diphenylmethane diisocyanate with tri-, tetra- and penta-functional aminoalcohols. The degree of branching (DB) varied from 0.425 to 0.742 in different react conditions.

Basically, conventional PU are hydrophobic in nature, therefore the direct use of water as a solvent is not feasible. However, the incorporation of ionic groups into polyurethane made it possible to obtain aqueous polyurethane, which decreased the organic solvent emissions and expanded their applications [28]. The solvent-based systems had steadily been discouraged [29, 30], but the development of aqueous polyurethane had emerged as important alternatives due to increasing environmental awareness and economical requests [31]. Although many kinds of dendritic and hyperbranched polymers had been prepared, there was only a few reports on the hyperbranched aqueous polyurethanes. So our work was attempted to prepare hyperbranched aqueous poly(urethane–urea) (HBAPU) via $A_2 + bB_2$ approach using an isocyanate end capped polycarbonatediols (PCDLs) as an A_2 oligomeric monomer and diethanolamine as a bB_2 monomer. The structure of the hyperbranched aqueous poly(urethane–urea) was characterized by FTIR and ^{13}C NMR, the particle size was measured by photon correlation spectroscopy (PCS). Furthermore, the thermal and mechanical properties were measured by thermal gravimetric analysis (TGA) and tensile tests.

Experiment

Materials

All the chemical reagents were analytical grade. Polycarbonatediols (PCDL, Mn = 1,000, Asahikasei Chemicals Co., Japan) was degassed and dried under high vacuum (20 Pa) at 100 °C for 2 h before used. 2,4-tolylene diisocyanate (TDI, Tianjing Yuanli Chemical Co., China), 2,2-dihydroxymethylpropionic acid

(DMPA, Heshibi Reagent Co. Ltd, China), diethanolamine (DEOA, Sinopharm Group Chemical Reagent Co. Ltd., China), and catalyst didutyltin dilaurate (DBTL, Tianjing Chemical Co., China) were used as received. Acetone (Bodi Chemical Co., China) was dried by 4 Å molecular sieves for 48 h before used. *N*-methyl-l-2-pyrrolidone (NMP, Sinopharm Group Chemical Reagent Co. Ltd., China) was dried by 4 Å molecular sieves for 48 h and purified by reduced-pressure distillation.

Synthesis of hyperbranched aqueous poly(urethane–urea)

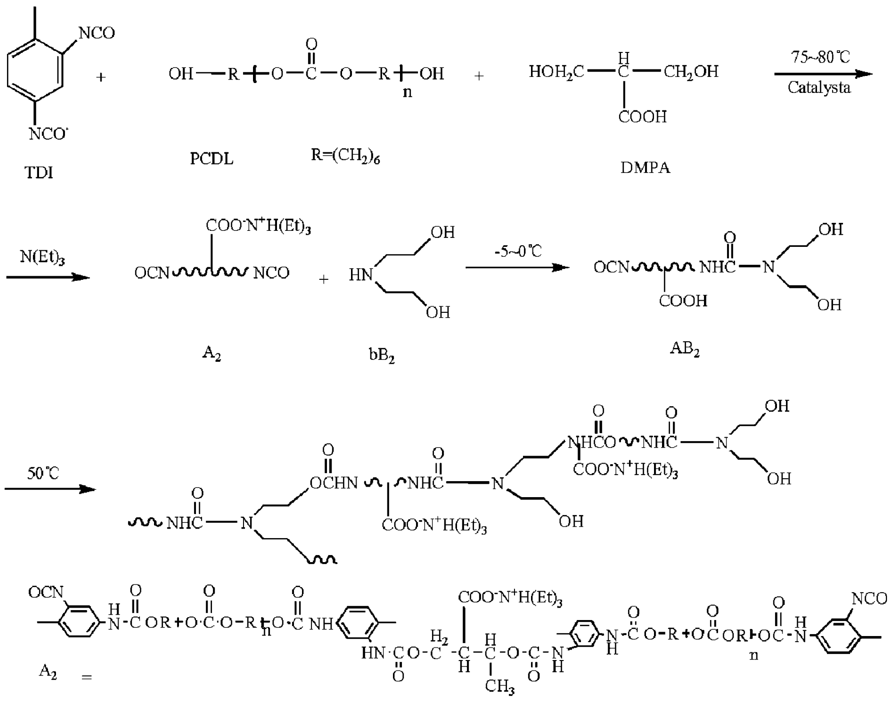
All the reactions were conducted in four-necked, round-bottom flasks equipped with a magnetic stirrer, thermometer, condenser and nitrogen inlet. The isocyanate end-capped A_2 oligomeric anionomer was formed through the reaction of PCDL, TDI and DMPA solution (in NMP) at 80 °C for 2–3 h with 50 ppm DBTL catalyst. The content of the NCO groups were measured by di-*n*-butylamine back-titration (DBBT) method. At the required NCO%, equivalent to a definite degree of prepolymerization, acetone was used to dissolve the prepolymer to form a 30 wt% solution, and the carboxylic groups were neutralized with triethylamine (NEt_3). Then the reaction temperature was cooled to 0 °C in ice bath, and the DEOA/NMP (bB_2) solution was added dropwise into the flask with an addition funnel. When all the DEOA solution was charged, the reaction temperature was raised to 50 °C and maintained for 12 h. Finally, the polymers were dispersed with deionized water at room temperature and the solvents were removed to obtain stable hyperbranched aqueous poly(urethane–urea) (solid content 30 wt%).

The HBAPU films were obtained by casting the dispersions on a polytetrafluoroethylene (PTFE) plates and allowing them to dry at room temperature for 5 days and then at 50 °C for 2 days. After molding, the films were submitted to vacuum drying for 24 h.

A schematic representation of the synthesis route for HBAPU was shown in Scheme 1. Different formulations of HBAPU were listed in Table 1.

Measurements

A Fourier transform infrared spectrometer (Spectrum One, Perkin-Elmer, USA) was used to identify the structure. Solid samples were dissolved in tetrahydrofuran and were coated on KBr disks. The ^{13}C NMR spectra were measured by a Varian INOVA-600 NMR spectrometer at 150 MHz, using DMSO-d6 as solvent and tetramethylsilane as internal reference. Quantitative ^{13}C NMR spectra were obtained using inverse-gated decoupling, 30° ^{13}C pulses, and a pulse delay of 6 s due to the nuclear Overhauser effect. Particle size was determined by photon correlation spectroscopy (PCS; Autosizer Loc-Fc-963 apparatus, Malvern Instruments Ltd.). The samples were diluted to an appropriate concentration and taken in a cuvette. The cuvette was placed in a sample holder and the temperature was maintained at 25 °C. The samples were measured with 670-nm-wave-length laser light at a 90° scattering angle. Gel permeation chromatography (GPC) measurements were conducted on an Agilent 1100 liquid chromatography–mass



Scheme 1 Synthesis route for the hyperbranched aqueous poly(urethane–urea)

Table 1 Synthesis parameters for HBAPU and DB of HBAPU

Sample name	nNCO/nOH/[a] nDEOA	Hard segment content (wt%)[b]	DMPA content (wt%)[c]	Mn	Mw	PDI	DB
HBAPU1	3/2/1	31	2.68	10,319	36,300	3.51	0.30
HBAPU2	2/1/1	39	2.68	5,555.4	46,278	8.33	0.32
HBAPU3	3/1/2	53	2.68	4,659.2	14,304	3.07	0.35

[a] nNCO/nOH = nTDI/(nPCDL + nDMPA)

[b] hard segment content = (mTDI + mDMPA + mDEOA)/(mTDI + mDMPA + mPCDL + mDEOA) × 100

[c] DMPA content = 100 × mDMPA/(mTDI + mDMPA + mPCDL + mDEOA)

spectrometry at 30 °C in THF with a flow rate of 1.0 ml/min using polystyrene standards. TGA analysis of the HBAPU 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. The tensile tests were performed on an electronic universal testing machine (Shenzhen Sans testing machine Co. Ltd., China) at 20 °C with a crosshead speed of 25 mm/min.

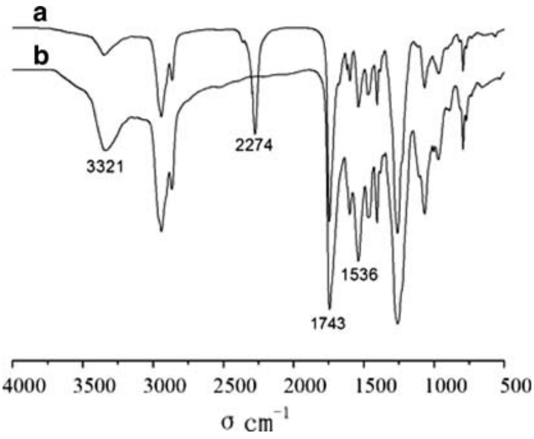


Fig. 1 FT-IR spectrum of the **a** prepolymer A_2 and **b** hyperbranched aqueous poly(urethane–urea)

Results and discussion

FT-TR spectra analysis

Figure 1 showed the FT-IR spectroscopic analyses of the synthesized prepolymer A_2 and hyperbranched aqueous poly(urethane–urea). The absorption peak of NCO at 2,274 cm^{-1} was very prominent in Fig. 1a, but the peak disappeared completely in the curve (b). The fact indicated that the reaction between A and B was thoroughly. Urethane groups were easily identified by their three main characteristic bands, the band at 3,321 cm^{-1} was fairly broad and corresponded to the stretching vibration of free and hydrogen-bonded N–H groups; the absorption bands at 1,743 cm^{-1} and 1,536 cm^{-1} were attributed to the functional groups of C=O stretching vibrations, N–H bending vibrations, respectively. These implied the presence of urethane linkages.

^{13}C-NMR spectra analysis

Figure 2 displayed the ^{13}C NMR spectrum of HBAPU. According to the literature [24], the signals were assigned as follows: 156.58–156.18 (C=O, urea), 154.75 (C=O, carboxylic ester), 154.38–153.63 (C=O, urethane), 138.66–136.37 (C_2, C_4, phenyl), 130.20–129.88 (C_6, phenyl), 125.6–122.63 (C_1, phenyl), 114.97–111.4 (C_3, C_5, phenyl), 62.71 [CH_2–OC(O)–NH, l and d], 60.59 (CH_2–OH, l), 60.26 (CH_2–OH, t), 50.91 (N–CH_2, l), 50.53 (N–CH_2, t), 46.65 (N–CH_2, l and d), 39.92–39.08 (CH_2, soft segment), 28.52–24.86 (CH_2, soft segment), 17.44–17.13 (CH_3), where l, d, and t represented linear units, dendritic units, and terminal units respectively, which gave the evidence of the formation of hyperbranched structure. Considering the reaction was stopped by the diethanolamine, degree of branching was calculated with Frey's equation [32]:

$$\mathrm{DB} = 2D/(2D + L) \quad (1)$$

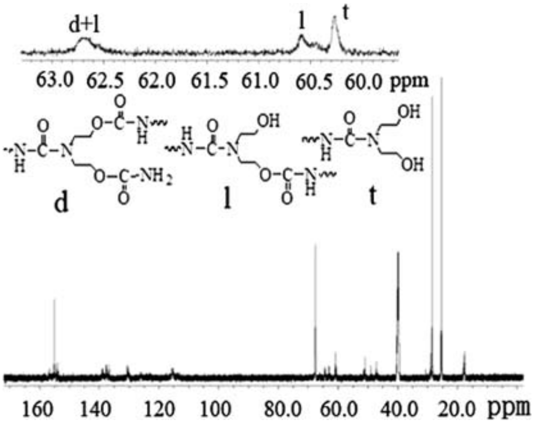


Fig. 2 ^{13}C NMR spectrum of hyperbranched aqueous poly(urethane–urea)

DB calculated from the integration of corresponding peaks was summarized in Table 1. When the molar ratio of *n*NCO/*n*OH increased form 1.5:1, 2:1 to 3:1, the DB of HBAPU increased from 0.30, 0.32 to 0.35, respectively. This could be easily understood based on steric hindrance. When the molar ratio of *n*NCO/*n*OH increased, both the molecular weight and the segment length of A_2 decreased. This resulted in poor steric hindrance between A and B groups. It was suggested that the weaker the steric hindrance was, the higher the branching unit was. The view from Ishida [33] also approved that a decrease in the degree of branching (DB) due to steric hindrance.

Particle size

Particle size played a major role in the mechanical properties and stability of the HBAPU dispersions. HBAPU with relatively large average particle sizes was usually unstable with respect to sedimentation. Generally, the particle size of aqueous polyurethane was significant affected by the content of hydrophilic groups in the polymer chains. Figure 3 showed the particle sizes of the HBAPU versus the content of the DMPA. It could be observed that the particle sizes of the HBAPU decreased with increasing the content of the DMPA. The main reason was that hydrophobic ionic groups were in the interior of the particles, whereas hydrophilic chain segments formed the surface of the particles. In our experiment, we found that the particle sizes of HBAPU varied from 65 to 15 nm with increasing the DMPA content from 0.15 mmol/g (2 wt%) to 0.5 mmol/g (6.7 wt%). Due to the three-dimensional structure and little chain entanglement of the hyperbranched structure, the particle size of HBAPU (20.6 nm) was smaller than that of line aqueous polyurethane (130.9 nm) with the same content of DMPA(0.4 mmol/g, 5.36 wt %). Moreover, HBAPU was dispersed more easily and sufficiently.

Thermogravimetric analysis

The decomposition temperature of polyurethane was mostly influenced by the chemical structure of the component having the lowest bond energy. As shown in

Fig. 3 Particle size of hyperbranched aqueous poly(urethane–urea)

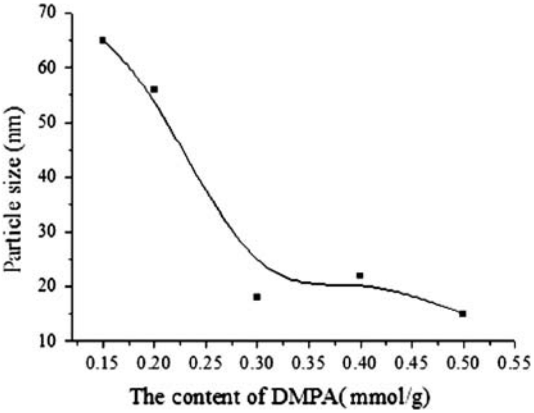


Fig. 4 TGA curves of HBAPU with variation in *n*NCO/*n*OH. (**a** *n*NCO/*n*OH = 1.2; **b** *n*NCO/*n*OH = 1.5; **c** *n*NCO/*n*OH = 2.0)

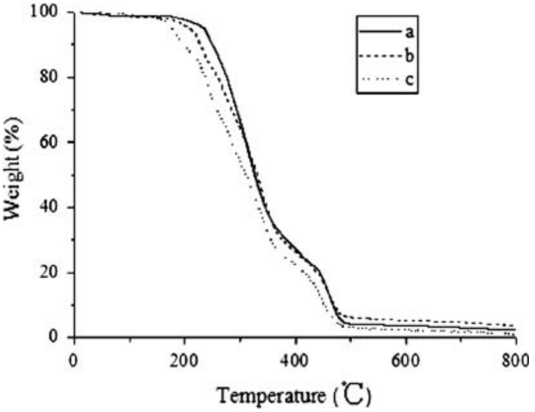


Table 2 Temperature at 10 and 50% weight loss of HBWPU samples

Samples	*n*NCO/*n*OH	Temperature at 10% weight loss (°C)	Temperature at 50% weight loss (°C)
a	1.2	249	330
b	1.5	227	326
c	2.0	195	329

Fig. 4, the degradation was comparatively slow in polyurethanes with less hard segment content. This indicated that the degradation temperature decreased with increasing hard segment content. All the HBAPU samples showed two-step process for degradation in nitrogen atmosphere. The first observable weight loss started from 100 to 450 °C attributed to the degradation of the urea and urethane groups, and the second step was the degradation of C–C bonds above 450 °C. Table 2 showed the temperature at 10 and 50% weight loss of HBAPU samples.

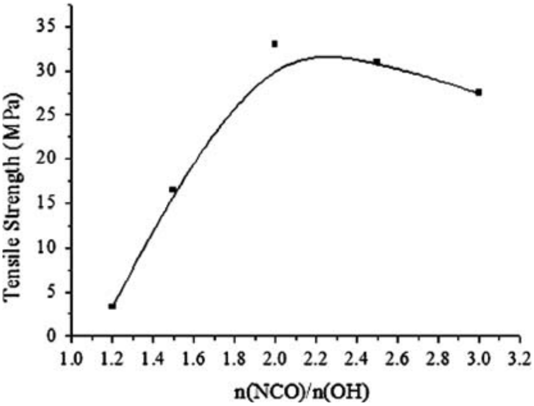


Fig. 5 The effect of the *n*(NCO)/*n*(OH) on the tensile strength of the HBAPU

Tensile properties

The tensile strength was governed mainly by the hard segments and flexibility of the soft segment. Generally, tensile strength increases and elongation decreases with an increase in hard segment content of the polymer. In addition, it had been suggested that the degree of branching also had great influence on the tensile strength in our experiments. The effect of the molar ratio of *n*NCO/*n*OH on the tensile strength was showed in Fig. 5. The tensile strength increased initially, and then decreased rapidly. It could be explained as follows, intermolecular interactions including the intermolecular force and hydrogen bonding enhanced with increasing the molar ratio of *n*NCO/*n*OH. So the tensile strength increased and the maximum value was up to 33 Mpa. However, beyond a critical value, the effect of the density of branching points on the tensile strength was more effective comparing with that of the molar ratio of *n*NCO/*n*OH. The increases of the density of branching points led to the tensile strength decreased, which was attributed to the large amount of interspaces among the molecular chains, which induced a negative effect on the chain–chain arrangement.

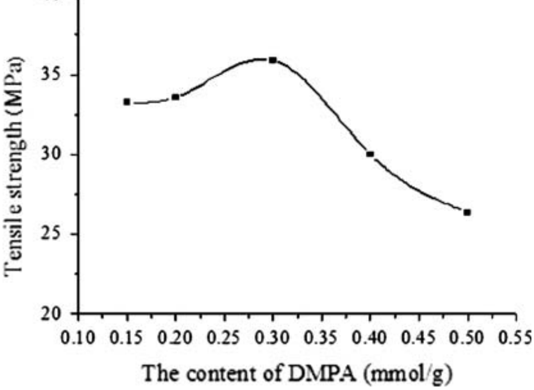


Fig. 6 The effect of the DMPA content on the tensile strength of the HBAPU

The effect of the DMPA content on the tensile strength of the films was showed in Fig. 6. It could be seen that tensile strength increased with a slow initial and then a rapid decreased as the DMPA content increased. The maximum value was up to 33 MPa when the DMPA content was 0.3 mmol/g (4 wt%). When the content of DMPA was less than 0.3 mmol/g, more DMPA segments were incorporated in the HBAPU backbone, thereby increasing the hard segment content of the polymer chain and hence the tensile strength increased. But when the content of DMPA was above 0.3 mmol/g (4 wt%), the results were opposite. The molecular weight of the A_2 decreased when more DMPA was introduced with the same molar ratio of nNCO/nOH. And the degree of branching increased because of the smaller steric hindrance, thereby increasing the interspaces among the molecular chains, which caused the tensile strength decrease.

Conclusions

A series of hyperbranched aqueous poly (urethane–urea) (HBAPU) was prepared via $A_2 + bB_2$ approach. The DB of HBAPU increased with increasing the molar ratio of nNCO/nOH because of the smaller steric hindrance. The DB value was 0.35 when the molar ratio of nNCO/nOH was 3:1. The particle sizes of HBAPU varied from 15 nm to 65 nm. And the particle size of the HBAPU was 20.6 nm comparing with that of line aqueous polyurethane with 130.9 nm when the content of DMPA was 0.4 mmol/g. The degradation temperature of the products was up to 200 °C. The HBAPU exhibited excellent tensile prosperities. Both the molar ratio of nNCO/nOH and the content of DMPA had great influence on the tensile strength. The tensile strength increased initially with increasing the molar ratio of nNCO/nOH and the content of DMPA, but it decreased when it got to 33 MPa.

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