

Preparation and Characterization of Hyperbranched Polyesteramides

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Summary

An A-a-B-B'₂ type monomeric unit DH was prepared based on A₂ type monomer cis-hexahydrophthalic anhydride and BB'₂ type monomer bis(2-hydroxypropyl)amine. Hyperbranched polyesteramides were synthesized by the polycondensation of DH and excess bis(2-hydroxypropyl)amine, and characterized by chemical titration, Fourier transform infrared spectroscopy (FTIR), ¹H NMR spectroscopy and gel permeation chromatography (GPC). The hyperbranched polyesteramides obtained had high molecular weights and polydispersities from 1.19 to 1.60, exhibiting narrow molecular weight distributions. The thermal behavior of hyperbranched polyesteramides was studied by thermogravimetric analysis (TG). The result showed that the hyperbranched polyesteramides synthesized had excellent thermal stability, and only 20% weight lose at 300°C. The degree of branching (DB) in the hyperbranched polyesteramides was measured by high performance liquid chromatography (HPLC), and the value of DB was 0.4914.

Introduction

Hyperbranched polymers have drawn much attention of various research groups for 20 years [1-4]. The interest in such macromolecules stems from the possibility that, owing to their novel, highly branched, globular, and unentangled structure, they may be expected to show new and interesting properties both in solution and in bulk [5-6]. Compared to linear analogues, hyperbranched polymers have high solubility and low viscosity. A variety of hyperbranched polymers have been prepared [7-10]. Recently, Jikei and Kakimoto [11], Gao and Yan [12] have encompassed the synthesis, application, and development of hyperbranched polymers. Articles on synthesis concepts and application aspects of hyperbranched polymers are continuing to be published [13-15].

Random polymerization of monomers leads to extremely broad molecular weight distributions, and the polydispersity would get a significant increase when the monomer conversion reaches about 90% [16-17]. With respect to applications, hyperbranched polymers might require narrow polydispersity, so it is essential to control over molecular weight or degree of polymerization (DP_n) and polydispersity

[18-20]. Hyperbranched polymers are generally prepared via core-dilution or slow addition method. Ralf Hanselmann et al [21] introduced the addition of AB_m monomers to B_f core molecules in solution (core-dilution method) to prepare hyperbranched polymers in a controlled manner, and the polydispersity was narrow. However, the addition of B_f core monomers easily produced outgrowth, so it was difficult to purify the product. Fréchet et al [22] reported a slow addition procedure for the synthesis of hyperbranched polyethers some years ago. The monomer, 5-(bromomethyl)-1,3-dihydroxybenzene, underwent self-condensation in the presence of potassium carbonate and 18-crown-6 to give polymers with weight-average molecular weights over 10^5 . However, the molecular weight distribution was broad, and the gelation occurred easily when the hyperbranched polymer had high molecular weight.

Contrary to the above mentioned methods, here we report a method for the preparation of hyperbranched polyesteramides with a narrow polydispersity and adequate molecular weight by controlling the amount of monomer added. A_2 monomer was slowly added to the BB'_2 monomer which was present in molar excess. The excess BB'_2 monomer limited the molecular weight to increase and narrow polydispersity was obtained, ranging from $M_w/M_n = 1.19$ to 1.60. In the progress of synthesis, the excess BB'_2 monomer played the role of core monomers, which made the molecular weight high. Due to the excess BB'_2 monomer, when the number-average molecular weight M_n reached $42400 \text{ g}\cdot\text{mol}^{-1}$ and the weight-average molecular weight M_w reached $66400 \text{ g}\cdot\text{mol}^{-1}$, the risk of gel formation would be avoided. Compared to the core-dilution method, the current synthetic approach was much simpler, and was not easier to produce outgrowth. Compared with the slow addition method, the current synthetic approach was more convenient, and was easier to achieve high molecular weight without the occurrence of gelation.

Experimental

Materials

Bis(2-hydroxypropyl)amine and cis-hexahydrophthalic anhydride were purchased from Fluka Chemika and purified by vacuum distillation before use. Dimethylbenzene (99% purity), which was used as a suitable water-taking agent for the synthesis, was purified by vacuum distillation before use.

Measurements

Infrared absorption spectra of the samples in nujol were measured with a Fourier transform infrared spectrometer (FTIR, Nicolet-5DX, USA). ^1H NMR spectrum was recorded with the spectrometer (NMR, Varian Unity-Inova 400 MHz, USA). Trichloromethane- d_1 (CDCl_3-d_1) was used as solvent, and tetramethylsilane (TMS) served as an internal standard. The weight-average molecular weight (M_w), number-average molecular weight (M_n) and molecular weight distribution [weight-average molecular weight/number-average molecular weight (M_w/M_n)] of the polymers were measured by gel permeation chromatography (GPC, Waters Breeze, USA) with polystyrene (PS) as a standard on the apparatus equipped with a Polymer Lab mixed 10- μ column, and the eluent was *N*-dimethylformamide (DMF) containing 0.01 mol/L lithium bromide at a flow rate of 1.0 ml/min at 40°C. Thermogravimetric analysis

(TG, Netzsch STA-449C, Germany) studies were done using the apparatus at a heating rate of 10°C/min under nitrogen from 25 to 600°C.

Polymerization

Bis(2-hydroxypropyl)amine (15.32 g, 0.115 mol) and dimethylbenzene (50 mL) were introduced into a three-necked flask equipped with stirrer, thermometer, and single water dispenser. The system was heated by an oil bath and the flask was filled with pure nitrogen. Then a solution of 15.42 g (0.10 mol) of cis-hexahydrophthalic anhydride in 50 mL of dry dimethylbenzene was added dropwise. The reaction mixture was gradually heated to approximately $65 \pm 2^\circ\text{C}$, and reacted under a dry nitrogen atmosphere for 3-4 hours. Then, with mechanical stirring the reaction mixture was gradually heated to 140°C. Until no more water could be removed through single water dispenser, the product was taken from the reactor, after evaporating of dimethylbenzene and cooling, a crude product was obtained as an almost colorless glassy mass. The crude product was purified by precipitation from tetrahydrofuran into ether, filtered and washed with distilled water and dried under vacuum at 50°C for 48 hours. The yield of resulting polymer was 26.71 g (87%).

Determination of the degree of branching

Methylation of Hyperbranched Polyesteramides

The synthesized hyperbranched polyesteramides were dissolved in dry acetone. Then methyl iodide and silver oxide were added slowly. The reaction, which was initially exothermic, was continued with stirring at 60°C under nitrogen for 24 hours. The reaction mixture was then filtered, and evaporated to dryness. The crude product was purified by precipitation from tetrahydrofuran into ether. The methyl ether-terminated hyperbranched polyesteramides were obtained as a white solid.

Hydrolysis of Methyl Ether-terminated Hyperbranched Polyesteramides

The methyl ether-terminated hyperbranched polyesteramides were dissolved in tetrahydrofuran, and then aqueous sodium hydroxide solution and sufficient ethanol were added into the system. The reaction mixture was heated to reflux and kept for 72 hours. After cooling, the solution was evaporated to dryness, and the product was dissolved in water and acidified with HCl. The hydrolysed product was extracted with ether, and evaporated to dryness.

Hydrolysis Products analyzed by HPLC

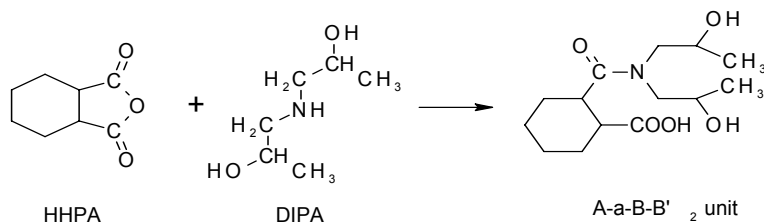
The hydrolysis products were dissolved in the mixture of water and Methanol, and treated with 1% Phosphoric acid as retarding agent, and the hydrolysis products were analyzed by high performance liquid chromatography (HPLC, Agilent 1100, USA). From the percentages of each degradation products, the degree of branching of hyperbranched polyesteramides would be calculated.

Results and Discussion

Synthesis

In our approach, hyperbranched polyesteramides were prepared based on BB'₂ type monomer bis(2-hydroxypropyl)amine and A₂ type monomer cis-hexahydrophthalic

anhydride as starting materials. However, one “A” group denoted “a” of the A_2 compound, and the “B” group of the BB'_2 compound, which was present in molar excess, was preferentially reactive toward each other. In this way, A-a-B-B'₂ units (i.e., functional AB_2 type units) were formed while the molar excess of BB'_2 units was retained in the system. This excess limited molecular weight buildup and eliminated the risk of gel formation at higher molecular weights, which is contrary to the classic A_2/BB'_2 approach. The first reaction was the formation of an amide bond producing an A-a-B-B'₂ unit (with “A” carboxylic acid and “B” alcohol groups), which was depicted in Scheme 1.



Scheme 1. An A-a-B-B'₂ Unit DH Produced from HHPA and DIPA

On the first reaction, aliquots of the reaction mixture were taken from the reactor, and acid value was measured. From the changes of acid value, the reaction time might be confirmed. The changes of acid value with reaction time were summarized in Table 1.

Table 1. The Changes of Acid Value with Reaction Time

Reaction time (h)	0	1	2	3	4	5
I_H^+ (mgKOH/g)	405.93	295.01	249.32	217.79	210.91	209.09

Table 1 showed that the acid value had changed sharply on the first phases of the reaction, then after the reaction time of 3 hours, the acid value of the reaction mixture did not change largely. It indicated that the first reaction, which was the formation of an amide bond, completely resulted in an A-a-B-B'₂ unit (with “A” carboxylic acid and “B” alcohol groups), so the time of the first reaction just needs approximately 3–4 hours with stirring.

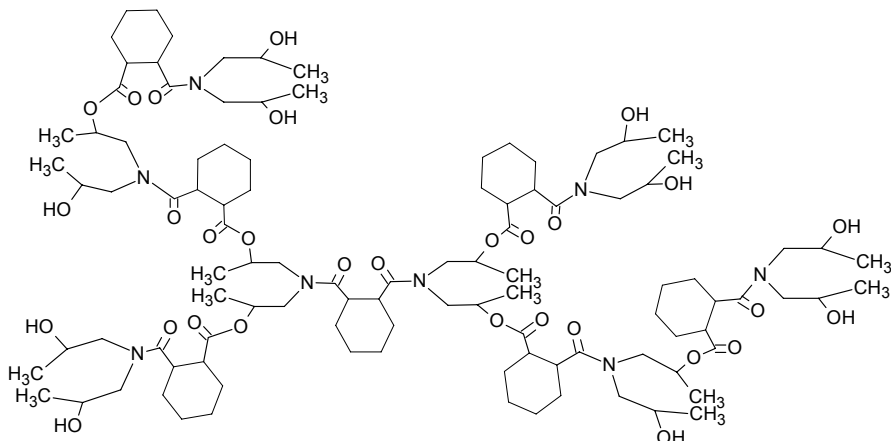
The following reaction was esterification giving rise to hyperbranched structures. The typical molecular structure of hyperbranched polyesteramides was shown in Scheme 2.

In order to confirm the reaction time acid values of the crude products were measured, which were shown in Table 2.

Table 2. The Acid Values of Crude Products with Different Reaction Time

Reaction time (h)	0	1	2	3	4	5	6
I_H^+ (mgKOH/g)	209.09	105.07	59.41	19.63	8.96	2.59	2.13

From Table 2, it can be seen that the acid value changed very little after 5 hours' reaction, which indicated that the carboxyl had mostly reacted with alcohol groups,



Scheme 2. Representation of Molecular Structure of Hyperbranched Polyesteramides

and the A-a-B-B'₂ units had esterified to give rise to hyperbranched structures. So the mixture should be gradually heated to 140°C and kept at this temperature for 5 hours to finish the esterification of A-a-B-B'₂ units.

FTIR Spectra

For the polymerization of DIPA and HHPA, the reaction process was investigated in situ with FTIR. As shown in Figure 1, in the FTIR spectrum of DH, a broad absorption band from 3400 to 3200 cm⁻¹ ($\nu_{\text{O-H}}$), which appeared in the FTIR spectrum of DIPA, was still observed, and it implied that there were a large number of hydroxy groups in DH. In the FTIR spectrum of HHPA, the characteristic absorption peaks of anhydride groups at 1860 cm⁻¹, 1791 cm⁻¹, 1679 cm⁻¹ disappeared, while two new absorption peaks at 1623 cm⁻¹ ($\nu_{\text{C=O}}$ in imide groups) and 1546 cm⁻¹ ($\nu_{\text{C=O}}$ in carboxyl groups) appeared, which indicated second amine in DIPA had reacted with anhydride groups present in HHPA producing imide groups and carboxyl groups. The outcomes obtained from FTIR spectra were in agreement with those found by chemical titration

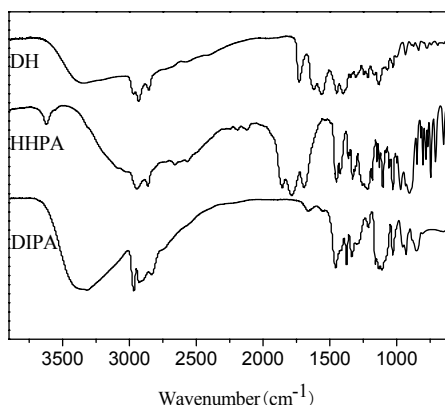


Figure 1. FTIR Spectra of DH, HHPA and DIPA

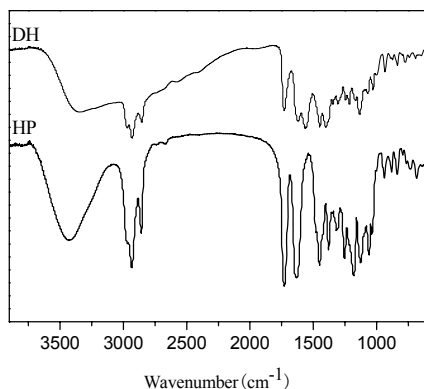


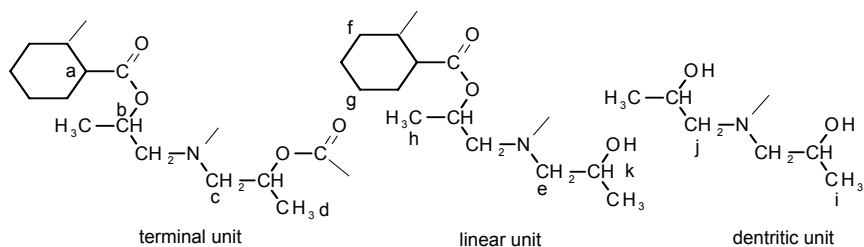
Figure 2. FTIR Spectra of DH and HP

of acid values. Therefore, the dimers that could be regarded as a new kind of A-a-B-B'₂ type monomers may be the dominant intermediate at the beginning of the reaction. The polycondensation of DH produced hyperbranched polyesteramides, which was investigated in situ with FTIR also. As shown in Figure 2, in the FTIR spectrum of DH, a broad absorption band from 3500 to 2500 cm⁻¹ (assigned to hydroxy groups) indicated that there were very strong Wasserstoffbruecken-Bindungen, which was the librating behavior of hydroxy groups in carboxyls. In the FTIR spectrum of HP, the broad absorption band from 3500 to 2500 cm⁻¹ became narrow, which implied that the Wasserstoffbruecken-Bindungen disappeared and the librating behavior of hydroxy groups did not exist, and there were no carboxyl groups in the polymer chains or just a little. This outcome was in agreement with the result obtained by chemical titration of acid values. The FTIR spectra of HP revealed that the peaks at 2933cm⁻¹ (C-H asymmetric stretching) and 1253cm⁻¹ (symmetric stretching) were the characteristic absorption of cyclohexane, and the peaks at 1781 cm⁻¹, 1722 cm⁻¹ and 731 cm⁻¹ could be attributed to the absorptions from amide carbonyl groups, and the bands at 1378–1383 cm⁻¹ originated from imide C-N groups of the polymers, and the peak at 1728cm⁻¹ ($\nu_{\text{C=O}}$ in ester bond), these being the characteristic absorption bands of hyperbranched polyesteramides. Based on the previous results, these data indicated that the polymer contained hydroxy groups, ester bonds, cyclohexanes and amide groups, which were in agreement with our objective polymers.

¹H NMR spectra

Hyperbranched polyesteramides have highly branched and globular structure, so it is complex about the chemical shifts of the protons in HP. The bitty structures of hyperbranched polyesteramides is shown in Scheme 4, and the protons of HP are signed by a, b, c, d, e, f, g, h, i, j, k and l.

The structure of the hyperbranched polyesteramides synthesized was confirmed by ¹H NMR spectroscopy. As shown in Figure 3, the ¹H NMR spectrum showed signals assignable to the protons of hyperbranched polyesteramides. The signals at chemical shifts of 5.2–3.8 ppm corresponded to the protons of the tertiary carbon atoms, and the areas of these peaks were expressed as a, b and k. Because the “a” and “b” protons of the tertiary carbon atoms linked with ester groups, the chemical shifts of “a” and “b”



Scheme 3. Representation of Bitty Structure of Hyperbranched Polyesteramides

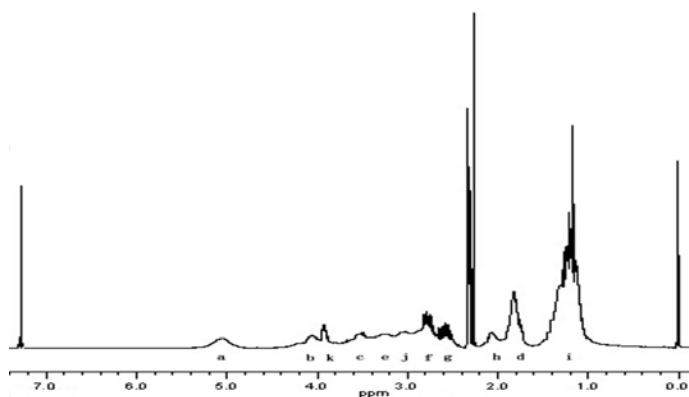


Figure 3. ^1H NMR Spectra of Hyperbranched Polyesteramides

were shifted to low field. The signals at chemical shifts of 3.6–2.4 ppm were assigned to methylene protons, and the signals at chemical shifts of 2.65 and 2.85 ppm were attributed to the protons of the cyclohexane. We synthesized hyperbranched polyesteramides through the polycondensation of DH and excess bis(2-hydroxypropyl)amine in dimethylbenzene, which was a suitable water-taking agent for the synthesis. Therefore, there was surplus dimethylbenzene in the products, so the sharp peaks at chemical shifts of 2.3 ppm showed signals assignable to the methyl protons on dimethylbenzene. The signals at chemical shift of 2.1–1.0 ppm were associated with the methyl protons, and the chemical shift of methyl protons at 1.4–1.0 ppm was shifted to upfield due to the influence of hydroxy groups.

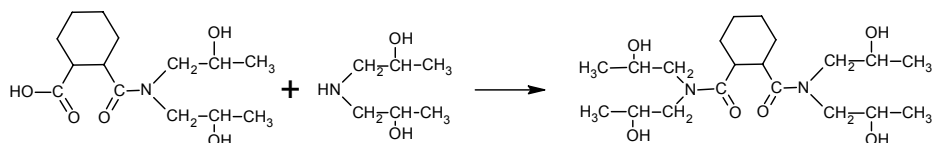
Molecular weights and polydispersity by GPC

Molecular weights and polydispersities of the synthesized polyesteramides were presented in Table 3. The data of Table 3 show that using the present synthetic strategy one can get hyperbranched polyesteramides with high molecular weights and low polydispersity. When the number-average molecular weight M_n reached $42400 \text{ g}\cdot\text{mol}^{-1}$, the reaction system had no risk of gel formation, and narrow molecular weight distributions were obtained, and the polydispersity M_w/M_n ranged from 1.60 to 1.19, which was excellent in agreement with recent theoretical predictions of Ralf Hanselmann [21].

Table 3. Molecular Parameters as Obtained Using GPC

T/h	$M_n/\text{g}\cdot\text{mol}^{-1}$	$M_w/\text{g}\cdot\text{mol}^{-1}$	M_w/M_n
1	9700	12400	1.28
2	16300	19400	1.19
3	28800	39700	1.38
4	41300	61800	1.50
5	42400	66400	1.60

Ralf Hanselmann predicted that slow addition of AB_m monomers to B_f core molecules in solution could be used to prepare hyperbranched polymers in a controlled manner, and the polydispersity for the core-dilution/slow addition process obeyed the expression $M_w/M_n = 1 + 1/f$ (f was the functionality of core molecule). In our synthetic strategy, the reaction of HP was initiated from DH with little DIPA, and DIPA was easier to react with DH than DH itself, so little core molecules existed in the reaction mixture, as shown in scheme 4. In the core molecule, $f = 4$, according to the express $M_w/M_n = 1 + 1/f$, $M_w/M_n = 1.25$.

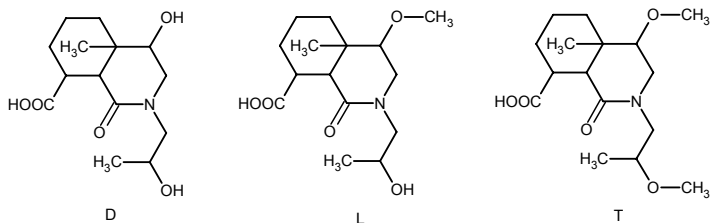


Scheme 4. The Core Molecules Produced from DH with DIPA

As shown in Table 3, molecular weights and the polydispersity indices (M_w/M_n) increased with increasing the reaction time (T). While the molecular weights increased, the polymer volume became larger and larger, which resulted in more random reaction of DH monomers with the macromolecules and made the molecular weight distributions become broad accordingly.

The degree of branching in HP

After hyperbranched polyesteramides were modified with methyl iodide, the methyl ether-terminated hyperbranched polyesteramides were hydrolyzed by an aqueous sodium hydroxide solution. The molecular structures of the hydrolysis products were shown in Scheme 5.

Scheme 5. The degradation products of Hyperbranched Polyesteramides^a

^aD-The degradation product of dentritic unit; L-The degradation product of linear unit;

T-The degradation product of terminal unit.

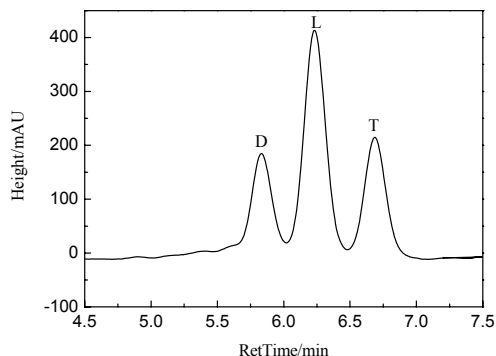


Figure 4. HPLC Representation of the Hydrolysis Products

The three type hydrolysis products have different molecular structures. The degradation product of dentritic unit has two hydroxyl groups, and the product of linear unit one hydroxyl group and one methyl ether-terminated group, and the product of terminal unit two methyl ether-terminated groups. Hydroxyl group is polar and hydrophilic, and methyl ether-terminated group is non-polar and hydrophobic. The polarity of hydroxyl group and methyl ether-terminated group can affect the retention time of the degradation products in HPLC. Therefore three different degradation products were analyzed by high performance reversed phase chromatography, and octadecylsilane was used as fixed phase, which was also non-polar. So the retention time of the degradation product of terminal unit was the longest, and the retention time of the product of dentritic unit was the shortest. The retention times of the degradation products were shown in Figure 4.

The relative percentages of different peak areas for D, T and L were shown in Table 4. According to the theory introduced by Frechet [22], $DB = (\sum D + \sum T) / (\sum D + \sum T + \sum L) = 0.4914$.

Table 4. The Results Obtained by HPLC

Peak	Ret Time/min	Height/mAU	Area/%
D	5.832	187.95	22.48
L	6.232	419.03	50.86
T	6.687	222.64	26.66

Thermal behavior of HP measured by TG

The thermal behavior of hyperbranched polyesteramides is useful for their application. Therefore, we measured the TG curves of the hyperbranched polyesteramides. The measurement of TG curves was conducted under the flow of nitrogen, and the result was presented in Figure 5.

As shown in Figure 5, the hyperbranched polyesteramides exhibited excellent thermal stability. The weight losses of HP_a and HP_b were just 5% at 161°C and 206 °C respectively. The weight losses reached 10% when the temperatures were raised to 186°C and 265°C respectively for HP_a and HP_b . There were two different traces of weight loss for HP_a and HP_b . The weight losses of HP_b was much higher than that of HP_a when they were heated to the same temperature in the range of 100–300°C. The

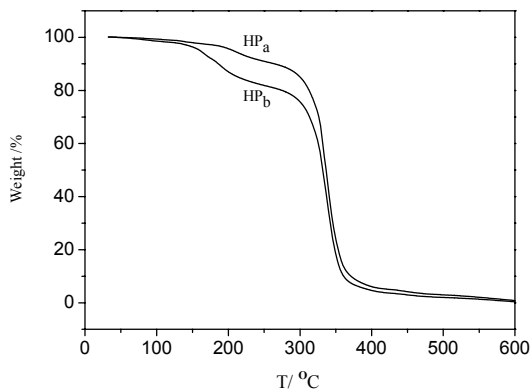


Figure 5. Different TG curves of Hyperbranched Polyesteramides:

HP_a, which was the product obtained after the reaction time of 5 hours, $M_n = 42400 \text{ g}\cdot\text{mol}^{-1}$

HP_b, which was the product obtained after the reaction time of 2 hours, $M_n = 16300 \text{ g}\cdot\text{mol}^{-1}$

reason might be that there were more carboxyl groups (see Table 2) in HP_b than in HP_a. These carboxyls easily reacted with alcohol groups to produce water, which evaporated at high temperature. Therefore, HP_b lost more weight during heating. When the temperature reached the range of 300–360°C, TG curves of the hyperbranched polyesteramides descended sharply. The reason might be that the amide carbonyl groups and ester bonds in the hyperbranched polyesteramides decomposed at 300–360°C.

Conclusion

An A-a-B-B'₂ type monomeric unit DH was prepared based on BB'₂ type monomer bis(2-hydroxypropyl)amine and A₂ type monomer cis-hexahydrophthalic anhydride as starting materials. Hyperbranched polyesteramides were obtained through the polycondensation of DH and excess bis(2-hydroxypropyl)amine in dimethylbenzene, which was a suitable water-taking agent for the synthesis. Hyperbranched polyesteramides were characterized by chemical titration, FTIR, ¹H NMR spectroscopy and GPC. The hyperbranched polyesteramides had high molecular weights and narrow polydispersities from 1.19 to 1.60 exhibiting narrow molecular weight distributions. The thermal behavior of the hyperbranched polyesteramides was studied by TGA. The results show that the hyperbranched polyesteramides exhibited excellent thermal stability, and when the decomposition temperature reached 300°C the weight loss was 20%. The degree of branching of the hyperbranched polyesteramides was determined by HPLC and the DB of the synthesized polymer was 0.4914.

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