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Synthesis and characterization of hyperbranched aromatic poly(ester–imide)s

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Abstract

The synthesis and characterization of hyperbranched aromatic poly(ester–imide)s are described. A variety of AB_2 monomers, *N*-[3- or 4-bis(4-acetoxyphenyl)toluoyl]-4-carboxyl-phthalimide and *N*-{3- or 4-[1,1-bis(4-acetooxyphenyl)]ethylphenyl}-4-carboxy phthalimides were prepared starting from condensation of nitrobenzaldehydes or nitroacetophenones with phenol and used for synthesis of hyperbranched poly(ester–imide)s containing terminal acetyl groups by transesterification reaction. These hyperbranched poly(ester–imide)s were produced with weight-average molecular weight of up to 6.87 g/mol. Analysis of ^{1}H NMR and ^{13}C NMR spectroscopy revealed the structure of the four hyperbranched poly(ester–imide)s. These hyperbranched poly(ester–imide)s exhibited excellent solubility in a variety of solvents such as *N*,*N*-dimethylacetamide, dimethyl sulfoxide, and tetrahydrofuran and showed glass-transition temperatures between 217 and 255 °C. The thermogravimetric analytic measurement revealed the decomposition temperature at 10% weight-loss temperature (T_d^{10}) ranging from 365 to 416 °C in nitrogen.

Keywords: Hyperbranched; Poly(ester–imide)s; AB_2 monomer

1. Introduction

In the past decade, two different topologies in the highly branched architecture, namely, dendrimer [1] and hyperbranched polymer [2] have attracted increased attention because their unique structures can be predicted to exhibit some unusual chemical and physical properties [3,4]. Though related, there are a number of similarities and differences between these two families of three-dimensional macromolecules. The essentially 'perfectly' branched and monodisperse dendrimers are built up by either a step-wise divergent or convergent approach [1a], while hyperbranched polymers are prepared in a one-step polymerization process (the direct polymerization of AB_x-type monomers) that gives irregular and polydisperse structures [5] and retains many of the important features of perfectly defined dendrimer counterparts (i.e. multiple end groups, high solubility, and reduced viscosities relative to their linear counterparts). As a result, hyperbranched macromolecules are much more readily available at lower costs than dendritic macromolecules, which is highly desirable for many applications. This significant feature has led to the development of novel synthetic routes for the preparation of such polymers [3,4].

Aromatic polyimides represent a class of polymers that have gained technical interest because of their excellent electrical, thermal stability, chemical resistance, and mechanical properties [6], and have a large number of applications in modern industries. Hyperbranched polyimides, poly(ether–imide)s, and poly(ester–imide)s prepared by a one-step approach have been reported [7–9]. Hyperbranched aromatic polyimide exhibiting good solubility was successfully prepared via polyamic acid methyl ester precursors [7]. Moore et al. [8a] synthesized a hyperbranched poly(ether–imide) by self-condensation of 3,5-[di(-*tert*-butyldimethylsiyloxy)phenyl]-4-fluorphthalimide, and revealed that hyperbranched aromatic poly(ether–imide)s have better solubility than their linear analogs, and can be used as special additives for other high performance polymer materials. Kricheldorf et al. [9] prepared the hyperbranched poly(ester–imide)s starting from 4,5-dichlorophthalic acid. In this paper, we report the

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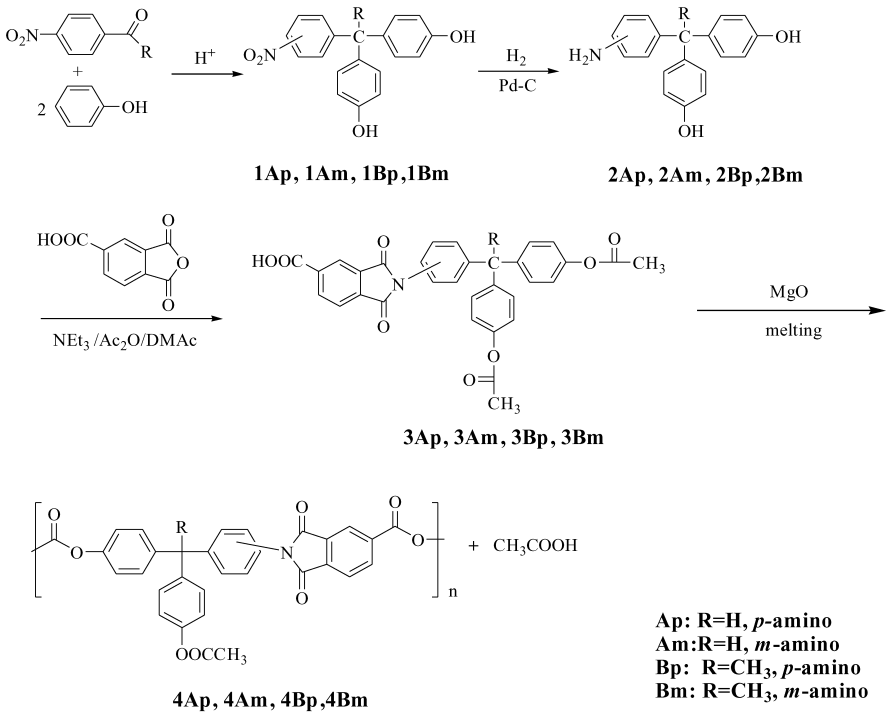


Scheme 1. The general procedure for the hyperbranched poly(ester–imide)s.

synthesis and characterization of a variety of aromatic hyperbranched poly(ester–imide)s from novel AB_2 monomers.

2. Experimental section

2.1. Chemicals

N,*N*-Dimethylacetamide (DMAc), *N*-methyl-2-pryolidinone (NMP), pyridine triethylamine were purified by distilling over calcium hydride under reduced pressure. Chloroform and tetrahydrofuran (THF) were used after distillation over P_2O_5 and sodium, respectively. Aniline was used after distillation under reduced pressure. Acetic anhydride was used after distillation over magnesium. 1,2,4-Benzenetricarboxylic anhydride was purified by recrystallization from a mixture of acetic anhydride and toluene before use. Other solvents and reagents were used as received.

2.2. Measurements

The NMR spectra were recorded on a Varian Unity or Bruker AV 400 MHz spectrometer. IR Spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Glass transition temperatures (T_g) were recorded on a Perkin–Elmer Pyris 1 DSC using a heating/cooling rate of 20 °C/min in nitrogen. TG measurements were performed with a Perkin–Elmer Pyris 1 Thermogravimetric Analyzer using a heating rate of 20 °C/min in nitrogen. Gel permeation chromatography (GPC) was performed with a Water 410 fitted with polystyrene-divinylbenzene columns (Styragel® HT3 THF) and a Waters 2414 refractive index detector in THF. The inherent viscosities were measured with an automatic Ubbelohde viscometer thermostated at 25 °C.

2.3. Synthesis of raw material of monomers and monomers

2.3.1. 4,4′-Dihydroxy-4″-nitrotriphenylmethane, *1Ap*

A solution of *p*-nitrobenzaldehyde (30.40 g, 0.20 mol) and phenol (37.6 g, 0.40 mol) in acetic acid (100 ml) was stirred and cooled slowly to 11–12 °C. A cool mixture of sulfuric acid (40 ml) and acetic acid (60 ml) was added dropwise. The reaction mixture was kept at 11–12 °C for 18 h, and then was precipitated with water, filtrated and was washed with water. The crude product was purified by recrystallization from benzene. The product separated from benzene partly as resin and partly as large, pale yellow prisms of the benzene adduct (29.5 g, 30%), which melted at 52–57 °C, solidified with a continued slow rise in temperature, and melted again at 212–214 °C. IR (KBr): 3373 (O–H); 3089 (Ar_3C–H); 3034 (Ar-H); 1611, 1510, 1477, 1438 (C=C); 1595, 1344 (NO_2) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 5.67 (s, 1H), 6.81 (d, $J = 8.8$ Hz, 4H), 6.99 (d, $J = 8.8$ Hz, 4H), 7.48 (d, $J = 8.8$ Hz, 2H), 8.26 (d, $J = 8.8$ Hz, 2H), 9.49 (s, 2H); ^{13}C NMR (DMSO-d_6, δ): 155.9, 153.2, 145.8, 133.3, 130.0, 128.3, 123.4, 115.3, 54.1.

*2.3.2. 1,1-Bis(4-hydroxyphenyl)-1-(4-nitrophenyl)ethane, **1Bp***

Zinc chloride (13.6 g, 0.10 mol) was added to a mixture of *p*-nitroacetophenone (82.6 g, 0.50 mol) and phenol (188.0 g, 2.0 mol), and the apparatus was purged with dry hydrogen chloride to remove the air, and then stirred at 81–82 °C under hydrogen chloride for 20 h. The reaction mixture was poured into 1 l hot water, and the precipitated product was recovered by filtration and washed with hot water several times. The yellow crude product was dissolved in a solution of sodium hydrogen carbonate (5%, 2.1 l), and then filtered. The filtrate was acidified with hydrochloric acid and the precipitate was recovered by filtration and washed with water to give light-yellow product **1Bp** (148 g, 88%). IR (KBr): 3400 (O–H); 3068, 3036 (Ar-H); 1594, 1510, 1479 (C=C); 1595, 1344 (NO_2) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.17 (s, 3H), 6.79 (d, J = 8.8 Hz, 4H), 6.93 (d, J = 8.8 Hz, 4H), 7.40 (d, J = 8.8 Hz, 2H), 8.24 (d, J = 8.8 Hz, 2H), 9.47 (s, 2H); ^{13}C NMR (DMSO-d_6, δ): 157.9, 155.6, 145.5, 138.21, 129.5, 129.2, 122.9, 114.8, 51.13, 30.1.

*2.3.3. 4,4′-Dihydroxy-3″-nitrotriphenylmethane, **1Am***

A solution of *m*-nitrobenzaldehyde (15.2 g, 0.10 mol) and phenol (18.8 g, 0.20 mol) in acetic acid (70 ml) was stirred and cooled to 3–4 °C. A cool mixture of sulfuric acid (6 ml) and acetic acid (30 ml) was added dropwise. The mixture, which turned orange, was kept at 3–4 °C for 48 h, and then poured into crushed ice and stirred. The resin separated was washed until free from acid, and freed from adhering water. A solution of the resin in hot benzene deposited some red resin on cooling, followed by yellow crystals of the benzene adduct (17.9 g, 37%) which melted at 72 °C, solidified on slowly raising the temperature, and melted again at 156–157 °C. IR (KBr): 3371 (O–H); 3089 (Ar_3C–H); 3034 (Ar-H); 1611, 1509, 1477 (C=C); 1595, 1529, 1344 (NO_2) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 5.70 (s, 1H), 6.82 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.0 Hz, 4H), 7.65 (m, 2H), 7.99 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 9.48 (s, 2H); ^{13}C NMR (DMSO-d_6, δ): 155.9, 147.5, 135.6, 133.4, 129.7, 128.3, 123.1, 121.1, 115.3, 53.6.

*2.3.4. 1,1-Bis(4-hydroxyphenyl)-1-(3-nitrophenyl)ethane, **1Bm***

Compound **1Bm** was synthesized by condensation of *m*-nitroacetophenone and phenol. The synthesis procedure was similar to that for **1Bp**, as shown in Scheme 1. Yield: 90%. IR (KBr): 3373 (O–H); 1611, 1510, 1477 (C=C); 1594, 1525, 1352 (NO_2) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.22 (s, 3H), 6.80 (d, J = 8.8 Hz, 4H), 6.94 (d, J = 8.4 Hz, 4H), 7.67 (m, 2H), 7.89 (s, 1H), 8.18 (d, J = 8.0 Hz, 1H), 9.48 (s, 2H); ^{13}C NMR (DMSO-d_6, δ): 155.6, 152.4, 147.4, 138.2, 135.1, 129.2, 122.4, 120.9, 114.8, 50.9, 30.1.

*2.3.5. 4-Amino-4′,4″-dihydroxytriphenyl methane, **2Ap***

5% Pd/C (1.60 g) was added to a solution of **1Ap** (13.76 g) in 80 ml ethanol, and then was purged with nitrogen then with hydrogen three times to remove oxygen and stirred vigorously at 35 °C under hydrogen for one week. The reaction mixture was then filtered, and the filtrate was evaporated to give 4-amino-4′,4″-dihydroxytriphenyl methane (8.18 g, 93%). IR (KBr): 3388, 3321 (N–H, O–H); 1596 (N–H), 1612, 1512, 1364 (C=C); 1252 (C–N); 1172 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 5.00 (s, 2H), 5.24 (s, 1H), 6.58 (d, J = 8.4 Hz, 2H), 6.76 (d, J = 8.8 Hz, 4H), 6.82 (d, J = 8.4 Hz, 2H), 6.96 (d, J = 8.8 Hz, 4H), 9.29 (s, 2H); ^{13}C NMR (DMSO-d_6, δ): 155.3, 146.5, 135.7, 132.3, 129.8, 114.9, 113.8, 53.8; calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.83; H, 5.79; N, 4.76.

*2.3.6. 1-(4-Aminophenyl)-1,1-bis(4-dihydroxyphenyl) ethane, **2Bp***

Compound **2Bp** was synthesized by reduction of **1Bp**. The procedure was similar to that for **2Ap**, as shown in Scheme 1. Yield: 88%. IR (KBr): 3387, 3317 (N–H, O–H); 1587 (N–H), 1608, 1505, 1365 (C=C); 1237 (C–N); 1182 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.05 (s, 3H), 5.00 (s, 2H), 6.56 (d, J = 8.4 Hz, 2H), 6.75 (m, 6H), 6.91 (d, J = 8.4 Hz, 4H), 9.29 (s, 2H). ^{13}C NMR (DMSO-d_6, δ): 154.9, 146.1, 140.5, 137.1, 129.2, 128.7, 114.3, 113.4, 49.8, 30.5; calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.05; H, 6.17; N, 4.55.

*2.3.7. 3-Amino-4′,4″-dihydroxytriphenyl methane, **2Am***

Compound **2Am** was synthesized by reduction of **1Am**. The synthesis procedure was similar to that for **2Am**, as shown in Scheme 1. Yield: 93%. IR (KBr): 3373, 3313 (N–H, O–H), 3018 (Ar_3C–H); 1596 (N–H), 1610, 1510, 1456 (C=C); 1235 (C–N); 1171 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 5.05 (s, 2H), 5.23 (s, 1H), 6.31 (d, J = 7.6 Hz, 1H), 6.40 (s, 1H), 6.47 (d, J = 7.6 Hz, 1H), 6.77 (d, J = 8.8 Hz, 4H), 6.98 (d, J = 8.8 Hz, 4H), 7.01 (d, J = 8.8 Hz, 1H), 9.32 (s, 2H); ^{13}C NMR (DMSO-d_6, δ): 155.4, 148.4, 145.7, 135.0, 129.9, 128.6, 116.9, 114.9, 114.8, 111.8, 54.7; calcd for $C_{19}H_{17}NO_2$: C, 78.33; H, 5.88; N, 4.81. Found: C, 78.83; H, 5.79; N: 4.76.

*2.3.8. 1-(3-Aminophenyl)-1,1-bis(4-dihydroxyphenyl) ethane, **2Bm***

Compound **2Bm** was synthesized by reduction of **1Bm**. The synthesis procedure was similar to that for **2Ap**, as shown in Scheme 1. Yield: 93%. IR (KBr): 3372, 3311 (N–H, O–H), 1593 (N–H), 1609, 1510, 1446 (C=C); 1243 (C–N); 1177 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.05 (s, 3H), 5.00 (s, 2H), 6.24 (d, J = 8.0 Hz, 1H), 6.39 (s, 1H), 6.47 (d, J = 8.0 Hz, 1H), 6.74 (d, J = 8.8 Hz, 4H), 6.94 (d, J = 8.8 Hz, 4H), 6.98 (m, 1H), 9.37 (s 2H); ^{13}C NMR (DMSO-d_6, δ): 155.0, 150.5, 147.9, 139.8, 129.2, 128.0, 116.2, 114.3, 111.4, 50.5, 30.4; calcd for $C_{20}H_{19}NO_2$: C, 78.66; H, 6.27; N, 4.59. Found: C, 78.12; H, 6.49; N, 4.59.

*2.3.9. N-[4-Bis(4-acetoxyphenyl)toluoyl]-4-carboxyl-phthalimide, monomer **3Ap***

A solution of **2Ap** (2.01 g, 6.90 mmol) and trimelletic anhydride (1.35 g, 7.03 mmol) dissolved in dry, deoxygenated DMAc (20 ml), and was stirred for 24 h at room temperature under a slow stream of nitrogen, then was added acetic anhydride (2.82 g, 28 mmol) and triethylamine (0.75 g, 7.0 mmol) and the mixture was kept at 40 °C for 48 h. After cooling the reaction mixture was poured into water (500 ml). The precipitate was isolated by filtration, recrystallized from a mixture of water and ethanol (10/1), dried in vacuum, to give white powder **3Ap** (3.61 g, 95%), mp 140–145 °C. IR (KBr): 3483 (O–H), 1757, 1725 (C=O); 1604, 1504 (Ar-H); 1371 (C–N); 1203 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.26 (s, 6H), 5.77 (s, 1H), 7.11 (d, $J = 8.8$ Hz, 4H), 7.21 (d, $J = 8.4$ Hz, 4H), 7.30 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 7.6$ Hz, 1H), 8.30 (s, 1H), 8.41 (d, $J = 7.6$ Hz, 1H); ^{13}C NMR (DMSO-d_6, δ); calcd for $C_{32}H_{23}NO_8$: C, 69.94; H, 4.22; N, 2.55. Found: C, 70.25; H, 4.04; N, 2.60.

*2.3.10. N-{4-[1,1-Bis(4-acetoxyphenyl)]ethylphenyl}-4-carboxyl-phthalimide, monomer **3Bp***

Monomer **3Bp** was synthesized by condensation of **2Bp** and trimelletic anhydride and acylation of acetic anhydride simultaneously. The synthesis procedure was similar to that for monomer **3Ap**, as shown in Scheme 1. Yield 94%, mp 146–150 °C (microscopy). IR (KBr): 3484 (O–H), 1724 (C=O); 1604, 1505 (Ar-H); 1372 (C–N); 1204 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.20 (s, 3H), 2.26 (s, 6H), 7.12 (d, $J = 8.8$ Hz, 4H), 7.22 (d, $J = 8.4$ Hz, 4H), 7.37 (d, $J = 8.4$ Hz, 2H), 7.43 (d, $J = 8.4$ Hz, 2H), 8.07 (d, $J = 7.6$ Hz, 1H), 8.31 (s, 1H), 8.40 (s, $J = 7.6$ Hz, 1H); ^{13}C NMR (DMSO-d_6, δ): 169.1, 166.2, 165.8, 148.7, 148.4, 145.6, 136.8, 135.4, 134.7, 131.9, 129.7, 129.2, 128.6, 126.6, 123.7, 123.4, 121.3, 114.7, 51.5, 30.2, 20.8; calcd for $C_{33}H_{25}NO_8$: C, 70.33; H, 4.47; N, 2.49. Found: C, 70.59; H, 4.30; N, 2.58.

*2.3.11. N-[3-Bis(4-acetoxyphenyl)toluoyl]-4-carboxyl-phthalimide, monomer **3Am***

Monomer **3Am** was synthesized by condensation of **2Am** and 1,2,4-benzenetricarboxylic anhydride and acylation of acetic anhydride simultaneously. The synthesis procedure was similar to that for monomer **3Ap**, as shown in Scheme 1. Yield 96%, mp 146–150 °C (microscopy). IR (KBr): 3456 (O–H), 1723 (C=O); 1604, 1504 (Ar-H); 1373 (C–N); 1203 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.25 (s, 6H), 5.76 (s, 1H), 7.10 (d, $J = 8.4$ Hz, 4H), 7.21 (d, $J = 8.4$ Hz, 4H), 7.30 (s, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.51 (m, $J = 8.0$ Hz, 1H), 8.04 (d, $J = 8.0$ Hz, 1H), 8.27 (s, 1H), 8.39 (d, $J = 8.0$ Hz, 1H), 13.78 (s, 1H); ^{13}C NMR (DMSO-d_6, δ): 169.1, 166.2, 165.9, 148.9, 144.3, 140.7, 136.9, 135.3, 134.7, 132.0, 131.9, 129.9, 128.9, 128.7, 127.6, 125.3, 123.6, 123.3, 121.8, 54.3, 20.8; calcd for $C_{32}H_{23}NO_8$: C, 69.94; H, 4.22; N, 2.55. Found: C, 70.02; H, 3.95; N, 2.65.

*2.3.12. N-{3-[1,1-Bis(4-acetoxyphenyl)]ethylphenyl}-4-carboxyl-phthalimide, monomer **3Bm***

Monomer **3Bm** was synthesized by condensation of **2Bm** and 1,2,4-benzenetricarboxylic anhydride and acylation of acetic anhydride simultaneously. The synthesis procedure was similar to that for monomer **3Ap**, as shown in Scheme 1. Yield 95%, mp 162–166 °C (microscopy). IR (KBr): 3447 (O–H), 1779, 1725 (C=O); 1603, 1504 (Ar-H); 1373 (C–N); 1204 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.16 (s, 1H), 2.25 (s, 6H), 7.07 (d, $J = 8.8$ Hz, 4H), 7.12 (d, $J = 8.4$ Hz, 4H), 7.30 (s, 1H), 7.35 (d, $J = 8.0$ Hz, 2H), 7.47 (m, $J = 8.0$ Hz, 1H), 8.03 (d, $J = 8.0$ Hz, 1H), 8.26 (s, 1H), 8.39 (d, $J = 8.0$ Hz, 1H); ^{13}C NMR (DMSO-d_6, δ): 169.09, 166.20, 165.80, 149.25, 148.68, 145.54, 136.40, 135.38, 134.85, 132.00, 131.56, 129.26, 128.44, 127.98, 127.07, 125.04, 123.67, 123.34, 121.28, 51.61, 30.22, 20.80; calcd for $C_{33}H_{25}NO_8$: C, 70.33; H, 4.47; N, 2.49. Found: C, 70.21; H, 4.50; N, 2.67.

2.4. General procedure for the synthesis of hyperbranched poly(ester–imide)s

The monomer was weighed into a cylindrical glass-reactor equipped with a mechanical stirrer, with gas-inlet and outlet tubes. The reaction vessel was placed into an oil-bath preheated to 150 °C. As soon as a homogeneous melt had formed, the temperature was rapidly raised to the desired condensation temperature (240–300 °C) over a period of 2 h, and the evolved acetic acid was removed with a slow stream of nitrogen. Finally vacuum was applied for 1 h. A catalytic amount of MgO was added at 150 °C before raising the temperature. The ratio of MgO to monomer was 0.05/1. The product was dissolved in refluxing DMAc and precipitated into cold ethanol. The precipitated product was isolated by filtration and dried at 120 °C in vacuum. Yield 85–91%.

2.5. The synthesis of the model compounds

*2.5.1. N-[4-Bis(4-hydroxyphenyl)toluoyl]-4-carboxyphthalimide, **6Ap***

4-Amino-4′,4″-dihydroxytriphenyl methane (**2Ap**) (2.00 g, 6.86 mmol) and 1,2,4-benzenetricarboxylic anhydride (1.32 g, 6.87 mmol) were dissolved in dry, deoxygenated dimethyl acetamide (20 ml). After stirring for 24 h at room temperature under a slow stream of nitrogen, xylene (20 ml) was added, and then the mixture was refluxed to dehydrate for 10 h. After distilling off the xylene, the reaction mixture was poured into water (200 ml). The precipitate was isolated by filtration, recrystallized from *n*-hexane/ethanol (5/1), dried in vacuum for 24 h, to give white powdery product **6Ap** (2.98 g, 88%). IR (KBr): 3402 (O–H), 1779, 1717 (C=O); 1611, 1509 (Ar-H); 1379 (C–N) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 5.45 (s, 1H, –CH–), 6.71–6.73 (d, 4H, Ar-H), 6.94–6.92 (d, 4H, Ar-H), 7.20–7.22 (d, 2H, Ar-H), 7.36–7.38 (d, 2H, Ar-H), 8.07–8.09 (d, 1H, Ar-H), 8.31 (s, 1H, Ar-H), 8.41–8.43 (d, 1H, Ar-H),

9.30 (s, 2H, –OH), 13.77 (s, 1H, –COOH); calcd for $C_{28}H_{19}NO_6$: C, 72.25; H, 4.11; N, 3.01. Found: C, 71.97; H, 4.08; N, 3.04.

2.5.2. N-[3-Bis(4-hydroxyphenyl)toluoyl]-4-carboxyl-phthalimide, *6Am*

6Am was synthesized by condensation of **2Am** and 1,2,4-benzenetricarboxylic anhydride. The synthesis procedure was similar to that for **6Ap**. Yield 90%. IR (KBr): 3415 (O–H), 1780, 1717 (C=O); 1611, 1511 (Ar-H); 1376 (C–N); 1218 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 5.45 (s, 1H, –CH–), 6.69–6.71 (d, 4H, Ar-H), 6.94–6.96 (d, 4H, Ar-H), 7.17–7.21 (m, 2H, Ar-H), 7.26–7.28 (d, 1H, Ar-H), 7.43–7.47 (m, 1H, Ar-H), 8.05–8.07 (d, 1H, Ar-H), 8.28 (s, 1H, Ar-H), 8.39–8.41 (d, 1H, Ar-H), 9.29 (s, 2H, –OH), 13.76 (s, 1H, –COOH); calcd for $C_{28}H_{19}NO_6$: C, 72.25; H, 4.11; N, 3.01. Found: C, 72.33; H, 4.15; N, 2.98.

2.5.3. N-{4-[1,1-Bis(4-hydroxyphenyl)]ethylphenyl}-4-carboxyl-phthalimide, *6Bp*

6Bp was synthesized by condensation of **2Bp** and trimelletic anhydride. The synthesis procedure was similar to that for monomer **6Ap**. Yield 94%. IR (KBr): 3393 (O–H), 1779, 1720 (C=O); 1610, 1509 (Ar-H); 1379 (C–N); 1217 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.07 (s, 3H), 6.68–6.70 (d, 4H, Ar-H), 6.87–6.85 (d, 4H, Ar-H), 7.16–7.18 (d, 2H, Ar-H), 7.34–7.36 (d, 2H, Ar-H), 8.07–8.09 (d, 1H, Ar-H), 8.31 (s, 1H, Ar-H), 8.41–8.43 (d, 1H, Ar-H), 9.31 (s, 2H, –OH), 13.77 (s, 1H, –COOH); calcd for $C_{29}H_{21}NO_6$: C, 72.64; H, 4.41; N, 2.92. Found: C, 72.50; H, 4.38; N, 2.95.

2.5.4. N-{3-[1,1-Bis(4-hydroxyphenyl)]ethylphenyl}-4-carboxyl-phthalimide, *6Bm*

6Bm was synthesized by condensation of **2Bm** and 1,2,4-benzenetricarboxylic anhydride and acylation of acetic anhydride simultaneously. The synthesis procedure was similar to that for **6Ap**. Yield 92%. IR (KBr): 3447 (O–H), 1779, 1725 (C=O); 1603, 1504 (Ar-H); 1373 (C–N); 1204 (C–O) cm^{-1}. ^1H NMR (DMSO-d_6, δ): 2.05 (s, 1H), 6.66–6.68 (d, 4H, Ar-H), 6.85–6.87 (d, 4H, Ar-H), 7.06–7.08 (d, 1H, Ar-H), 7.21 (s, 1H, Ar-H), 7.28–7.30 (d, 1H, Ar-H), 7.44–7.40 (m, 1H, Ar-H), 8.03–8.05 (d, 1H, Ar-H), 8.27 (s, 1H, Ar-H), 8.39–8.41 (d, 1H, Ar-H), 9.29 (s, 2H, –OH), 13.72 (s, 1H, –COOH); calcd for $C_{29}H_{21}NO_6$: C, 72.64; H, 4.41; N, 2.92. Found: C, 72.68; H, 4.37; N, 2.95.

2.5.5. Model compounds *6Ap-M, 6Am-M, 6Bp-M, 6Bm-M*

A 5 mmol amount of the compound **6Ap**, **6Am**, **6Bp**, **6Bm** and equimolar amount of acid chloride **5**[1] were dissolved in 50 ml of dry THF (Scheme 3). A 6 mmol amount of triethylamine in 10 ml of dry THF was added dropwise with stirring. The reaction mixture was stirred overnight at room temperature, and then refluxed for 12 h. The reaction mixture was poured into water (400 ml). The precipitate was isolated by filtration, recrystallized from ethanol, dried in vacuum. The products were characterized by ^1H NMR and IR spectra.

2.5.6. Model compounds *6Ap-D, 6Am-D, 6Bp-D, 6Bm-D*

A 5 mmol amount of the phenol compound **5Ap**, **5Am**, **5Bp**, **5Bm** and twice amount of acid chloride **5**[1] were dissolved in 50 ml of dry THF. A 6 mmol amount of triethylamine in 10 ml of dry THF was added dropwise with stirring. The reaction mixture was stirred overnight at room temperature, and then refluxed for 12 h. The reaction mixture was poured into water (400 ml). The precipitate was isolated by filtration, washed with ethanol for several times and then recrystallized with a mixture of ethanol and THF, dried in vacuum. The product was characterized by ^1H NMR and IR spectra.

3. Results and discussion

3.1. Synthesis of monomers

A series of AB_2-type monomers, **3Ap**, **3Am**, **3Bp**, and **3Bm** were successfully prepared in three steps from nitrobenzaldehyde or nitroacetophenone as shown in Scheme 1. The synthesis of **2Ap** or **2Am** was performed by the condensation reaction of *p* or *m*-nitrobenzaldehyde with phenol in cold acetic acid to give compound **1Ap** or **1Am** [10], followed by the hydrogenation reaction catalyzed by Pd/C. **2Bp** or **2Bm** was synthesized starting from nitroacetophenones. Condensation of *p*- or *m*-nitroacetophenone and excess phenol in the presence of a mixture of zinc chloride and hydrogen chloride at 60–70 °C afforded **1Bp** or **1Bm** in good yields. Compounds, **2Bp**, **2Bm**, were easily prepared by hydrogenation of corresponding compounds, **1Bp**, **1Bm**, in the presence of Pd/C. Reactions of **2Ap**, **2Am**, **2Bp** and **2Bm** with tremellitic anhydride, followed by adding acetic anhydride and triethylamine yielded corresponding monomers, **3Ap**, **3Am**, **3Bp** and **3Bm**. The subsequent treatment with acetic acid had two positive consequences, namely the cyclization of the amic acid and the acetylation of the hydroxy groups catalyzed by triethylamine. The yields of these reactions were above 94%. The structures of **3Ap**, **3Am**, **3Bp** and **3Bm** were characterized by ^1H NMR, ^{13}C NMR, and IR spectrum, and confirmed by elemental analysis. These results were showed in Section 3. It turned out that the melting point of the imide monomers **3Ap**, **3Am**, **3Bp** and **3Bm** were significantly lower (below 170 °C, **3Bp** below 150 °C) and thus more promising for successful polycondensation in bulk.

[1] Compound **5** was obtained as a light yellow powdery product: 80% total yield starting from aniline and 1,2,4-benzenetricarboxylic anhydride; IR (KBr) 1750 (–COCl), 1723, 1784 cm^{-1} (imide group); ^1H NMR (DMSO-d_6) δ 8.41–8.43 (d, 1H, Ar-H), 8.30 (s, 1H, Ar-H), 8.07–8.09 (d, 1H, Ar-H), 7.53–7.58 (m, 2H, Ar-H), 7.49–7.44 (m, 3H, Ar-H) ppm.

Table 1
The reaction condition, yields and properties of the hyperbranched poly(ester–imide)s T_d^{10}

Polymer	T^a (°C)	Yield (%)	$\eta_{inh}{}^b$ (dl/g)	$\bar{M}_n$ (kg/mol)	$\bar{M}_w$ (kg/mol)	PDI	$T_g{}^c$ (°C)	T_d^{10d} (°C)	Solubility[e]			
									DMAc	DMSO	THF	$CHCl_3$
4Bp	280	97	0.16	7.54	52.19	6.92	237	416	++	++	++	+ −
4Bp	260	82	0.15	5.86	30.59	5.22	230	416	++	++	++	+ −
4Bp	300	75	0.13	4.44	9.67	2.18	253	380	+ −	+ −	+ −	+ −
4Bp	240	98	0.20	9.05	68.76	7.60	255	388	++	++	++	+ −
4Bm	280	40	0.09	4.07	8.05	1.98	227	384	+ −	+ −	+ −	+ −
4Bm	240	93	0.11	5.81	32.37	5.57	224	365	++	++	++	+ −
4Ap	240	93	0.30	9.55	50.35	5.27	242	416	++	++	++	+ −
4Am	240	98	0.15	7.66	42.81	5.59	217	396	++	++	++	+ −

[a] Maximum polymerization temperature.
[b] The inherent viscosity measured at a concentration of 5 g/l in DMAc at 25 °C.
[c] The glass transition temperature determined by DSC with a heating and cooling rate of 20 °C/min in nitrogen.
[d] The temperature of 5% mass loss determined by TGA with a heating rate of 20 °C/min in nitrogen.
[e] ++, Soluble; − −, insoluble; + −, partial soluble.

3.2. Synthesis and structure characterization of hyperbranched poly(ester–imide)s

The reaction conditions and results concerning the imide monomers are summarized in Table 1. Various attempts were made to polycondense **3Bp** and **3Bm** in the maximum temperature range of 240–300 °C using MgO as transesterification catalyst. Completely soluble product was obtained at 240–290 °C for **3Bp**, slightly crosslinking was found at a reaction temperature of 300 and 280 °C for **3Bp** and **3Bm**, respectively. The inherent viscosity and T_g of the poly(ester–imide)s obtained from corresponding monomer reacting at 240 °C were relatively high and thus further polycondensations of **3Ap** and **3Am** were conducted at this temperature with addition of MgO as transesterification catalyst.

The characterization of the polymers was accomplished by a combination of techniques including ^{1}H NMR, ^{13}C NMR, FTIR and GPC. FTIR spectroscopy provided evidence for the chemical structure of the polymers, showing characteristic the imide carbonyl absorptions about at 1760 and ester carbonyl at 1725 cm^{-1} for the polymers in Fig. 1. Compared with the FTIR spectra of monomers, the FTIR spectra of polymers were more

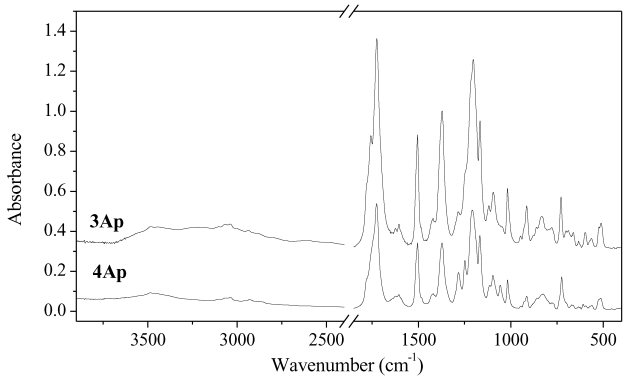


Fig. 1. FTIR spectra of monomer **3Ap** and polymer **4Ap**.

complicated because of the repeat units and the branched architecture of the polymers. The ^{1}H NMR and ^{13}C NMR of the polymer **4Ap** were showed as Figs. 2 and 3, respectively. The peak assignments were based on the peak positions of corresponding monomer **3Ap**. Neither the ^{1}H NMR (δ CH_3 2.26 ppm) nor the ^{13}C NMR (δ CH_3 20.8, CO 169.2 ppm) spectra of the polymer displayed any splitting of the signals of the acetate groups, which reflects a similarity in chemical environment for the protons of the linear units and terminal units in the polymer. The signal of the carbon atoms of the methine (δ 54.1 ppm) are single peak in both monomers and corresponding polymers, but the proton signal displays three splitting peak (δ 5.89, 5.82, 5.77 ppm), and the corresponding protons for the monomer were observed at 5.77 ppm. It shows that the polymer contain three different units, dendritic units, linear units and terminal units. Moreover, the resonance of C_6 of the monomer can be observed at 140.7 ppm whereas the signal of the corresponding carbons of the polymer is split at 141.4 and 140.7 ppm, which also indicates there are branched structures in the polymer. The chemical environment of the C_6 in the dendritic units is different from that in the linear units and terminal units, so they have different chemical shifts. Therefore, it is very clearly that the peak at 140.7 ppm should be assigned to the C_6 in the linear units and terminal units by comparison to the monomer, and the other peak (141.4 ppm) should be assigned to the C_6 in the dendritic units. Although the signals of the aromatic protons partly overlap, they can be assigned as those of the monomer (Fig. 1.). Distinct resonances for the carbon 2 of polymer appeared at 163.2 ppm compared with the monomer (165.8 ppm), it shifts to higher density field because of the disappearance of the intermolecular hydrogen bonding.

As shown in Scheme 2, the hyperbranched poly (ester–imide)s contain linear, dendritic, and terminal units. The degree of branching (DB) of hyperbranched polymer was defined as the ratio of the sum of dendritic and terminal units versus total units (linear, dendritic, and

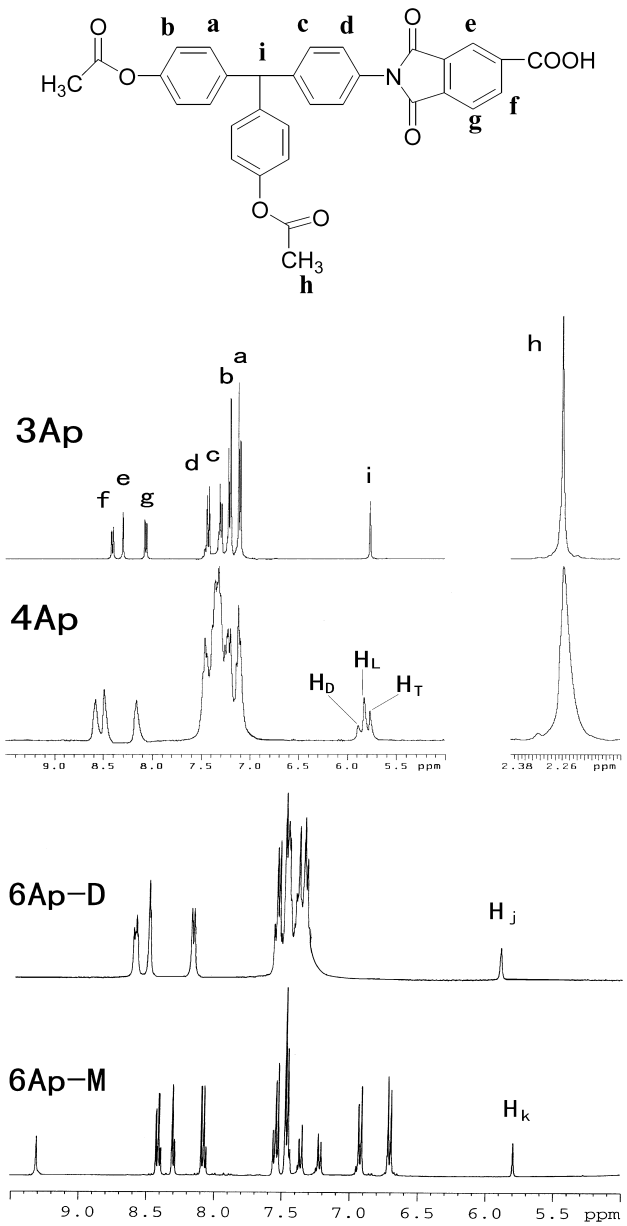


Fig. 2. ^{1}H NMR of monomer **3Ap**, polymer **4Ap** and model compounds **6Ap-D**, **6Ap-M**.

terminal units) [12]. DB of the resulting hyperbranched poly(ester–imide)s **4Ap**, **4Am**, **4Bp**, **4Bm** could be determined by ^{1}H NMR analysis as shown in Figs. 2 and 4. A series of model compounds were prepared as shown in Scheme 3. Characteristic methine peaks (H_i, H_j and H_k) attributed to methine of terminal model compound **3Ap**, dendritic model compound **6Ap-D** and linear model compound **6Ap-M** were detected at 5.77, 5.87 and 5.80 ppm (Fig. 2), respectively. In spectrum of corresponding polymer **4Ap**, three kinds of peaks, H_T, H_D and H_L, were observed at 5.77, 5.88 and 5.80 ppm with an integration ratio of 0.23, 0.17 and 0.37, respectively (Fig. 2). As compared with the spectrum of the model compounds, H_T, H_D and H_L can be assigned to the terminal units, dendritic

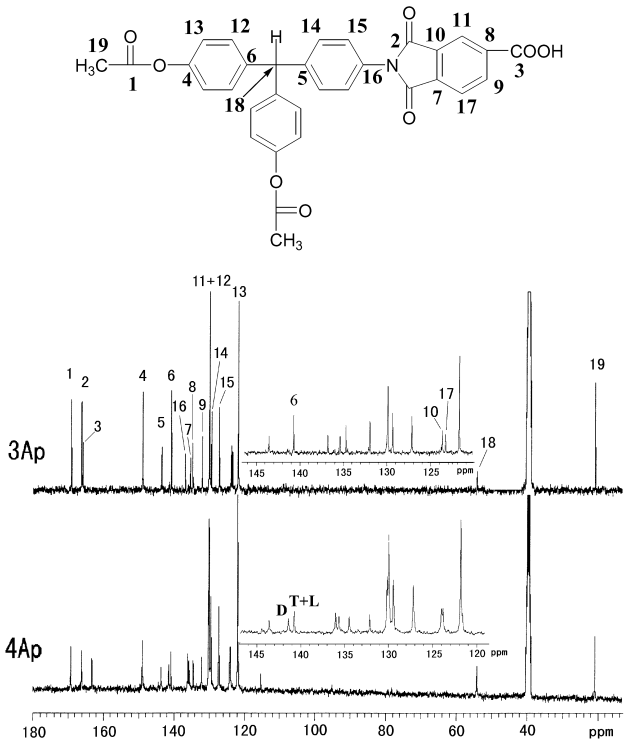


Fig. 3. ^{13}C NMR of monomer **3Ap** and polymer **4Ap**.

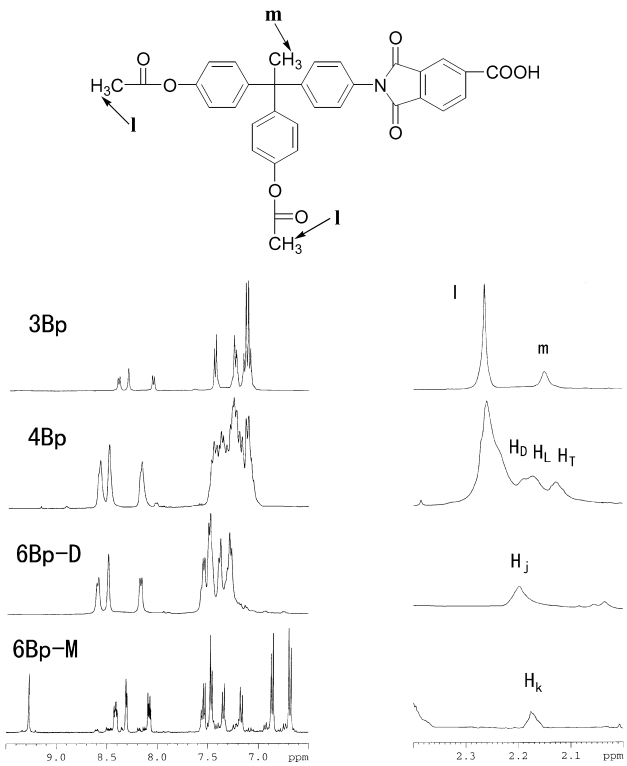
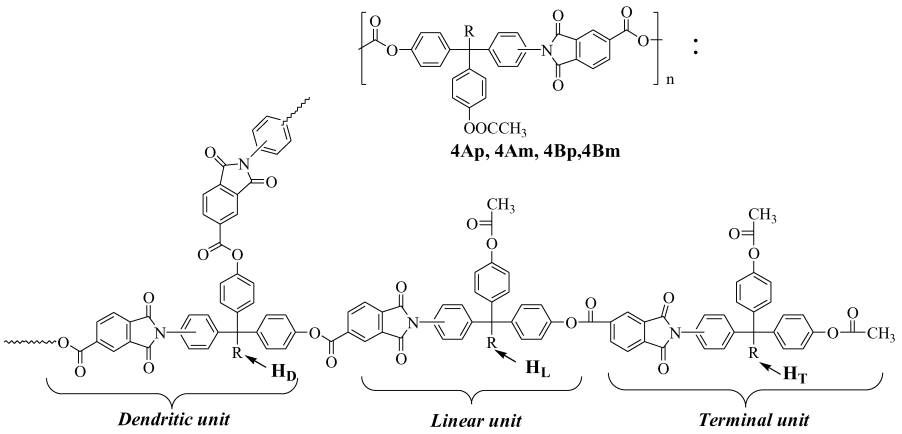


Fig. 4. ^{1}H NMR of monomer **3Bp**, polymer **4Bp** and model compounds **6Bp-D**, **6Bp-M**.

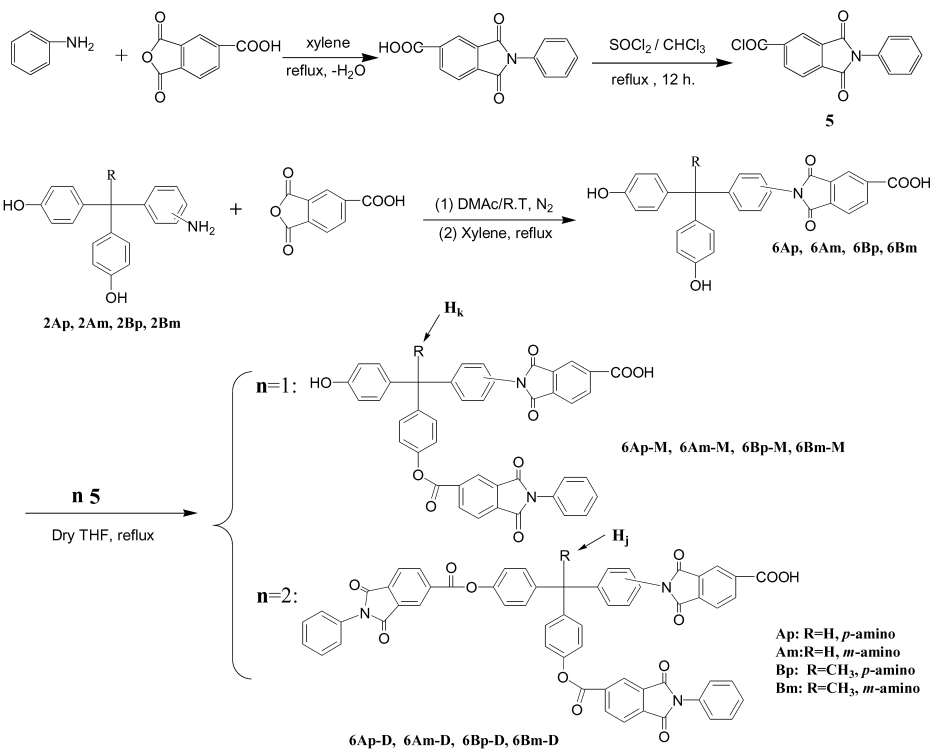


Scheme 2. The three kinds of repeat units of the polymers.

unit and linear unit of **4Ap**, respectively. Therefore, DB of **4Ap** was determined to be 0.52 by calculating the integration ratio of these three peaks. As same as **4Ap**, DB of **4Bp** (integration $H_T = 0.38$, $H_D = 0.21$, $H_L = 0.56$) was determined to be 0.51.

The DB of **4Bp** and **4Bm** also can be estimated from integrated intensities of the distinct proton resonance of the methyl of **4Bp** (triplet at H_D 2.17, H_L 2.15, H_T 2.13 ppm) and **4Bm** (triplet at H_D 2.16, H_L 2.15, H_T 2.10 ppm) as **4Ap** compared with three model compounds as shown in Fig. 4. H_D, H_L and H_T correspond to dendritic unit, linear unit and terminal unit, respectively. For **4Bp**, the integrations ratio of H_D, H_L and H_T were 0.37, 0.67 and 0.63, respectively. So the DB of **4Bp** was 0.60. Estimated similarly to **4Bp**, the DB of **4Bm** (integration $H_D = 0.50$, $H_L = 0.60$, $H_T = 0.72$) was 0.67.

Table 1 illustrates the results of GPC measurements that were calibrated against narrow-dispersity polystyrene standards to give $\bar{M}_n$, $\bar{M}_w$ and polydispersity data of the polymers. All the polymers exhibited moderate molecular weights with broad distributions and relatively low inherent viscosity (0.09–0.20 dl/g) due to the highly branched structure. The polymer obtained from corresponding monomer reacting at 240 °C had higher molecular weight



Scheme 3. The synthesis of the model compounds.

and inherent viscosity varied from 240 to 300 °C for similar polymer structure.

3.3. Characterization of physical properties

The properties of **4Bp**, **4Bm**, **4Ap** and **4Am** are listed in Table 1. The higher T_g of polymer **4Bp** (255 °C) in comparison with **4Ap** (242 °C) can be attributed to hindered segmental rotation as a result of the added methyl groups on the methine carbon atoms. Similarly, the polymer **4Bm** possesses higher T_g (224 °C) than the polymer **4Am** (217 °C). The polymer of **4Bm** and **4Am** from *meta*-oriented amines have denser polymer chain packing than **4Bp** and **4Ap** from the corresponding *para*-oriented amines due to the larger conformational entropy of the meta-oriented chain [11], consequently, the latter (*para*-oriented) has higher glass transition temperature (T_g) than former (*meta*-oriented). So is the thermal stability and in all cases, the thermal stability of polymers is still good. The temperatures of 10% mass loss (T_d^{10}) of the hyperbranched polymers are higher than 365 °C. All the hyperbranched poly(ester–imide)s are soluble in polar solvents such as DMAc, DMSO and THF.

4. Conclusion

A series of hyperbranched aromatic poly(ester–imide)s that contain terminal acetyl group were successfully prepared by the self-condensation of a several of novel AB_2 monomers synthesized starting from nitrobenzaldehydes or nitroacetophenones with phenol. It was found that the optimum temperature of polycondensation is about 240 °C. The resulting hyperbranched aromatic poly(ester–imide)s have high DB (51–67%) and moderate molecular weights with broad distributions and low inherent viscosity and exhibit good solubility in polar solvents such as DMAc, DMSO and THF. The temperatures of 10 wt% mass loss (T_d^{10}) are above 365 °C, and T_gs are in the range of 217–255 °C. They were dependent on the structure of the monomers.

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