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Facile Synthesis and Characterization of Aromatic and Semiaromatic Hyperbranched Poly(ester−amide)s

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ABSTRACT: A fast and highly efficient approach to aromatic and semiaromatic hyperbranched poly(ester−amide)s via the polycondensation of AA′ and CB_x monomers has been described. 2,2-Diphenic anhydrides (AA′ monomers) with aromatic or aliphatic multihydroxyl primary amine (CB_x monomers) were thermally polycondensed to prepare aromatic and semiaromatic hyperbranched poly(ester−amide)s with multihydroxyl end groups without any catalyst. At the initial stage of the reaction, primary amino groups react rapidly with 2,2-diphenic anhydride, forming an intermediate, multihydroxyl amide acid, which conducts further self-polycondensation as a new AB_x monomer to yield hyperbranched poly(ester−amide)s. Analyses of FTIR, ^1H NMR, and ^{13}C NMR spectra revealed the structures of the resultant polymers. The DBs of the polymers were determined to be 0.53−0.63 by ^1H NMR or ^{13}C NMR inverse-gated decoupling and DEPT spectra. Each kind of hyperbranched poly(ester−amide)s contains two configurational isomers observed by ^{13}C NMR spectra. These polymers exhibit excellent solubility in a variety of solvents such as *N*,*N*-dimethylacetamide (DMAc), dimethyl sulfoxide (DMSO), tetrahydrofuran (THF), and chloroform and possess moderate molecular weights with broad distributions determined by size exclusion chromatography (SEC). The thermogravimetric analytic measurement revealed the decomposition temperature of the polymers at 10% weight-loss temperature (T_d^{10}) ranging from 333 to 397 °C in nitrogen.

1. Introduction

Highly branched macromolecules including dendritic, hyperbranched, or multibranched polymers have attracted considerable and increasing interest due to their fascinating unique structure, interesting and versatile performance, and promising applications.[1−4] In general, highly regular dendrimers were obtained in time-consuming and tedious synthetic procedures, which make them costly for wide range application. Resumptively, the broad research involved in highly branched polymers mainly focused on an effort to develop polymeric products with similar structures and performances to perfect dendrimers via more facile prepared approaches.[2] Many strategies have been developed to prepare the polymers with highly branched structures, especially the convenient and cheap one-step polycondensation of AB_x monomers has received significant attention.[1−5] However, most of the AB_x monomers are not always commercially available, but only accessible by monotonic multistep organic synthesis and limited in several types. All of these do not allow for convenient and low-cost scale-up. Therefore, new more facile synthetic routes, the polymerization of A_2 with B_3 or $B'B_2$ or CB_x monomers, which are all readily available, were developed in the synthesis of conventionally branched polymers.[6−20]

Many investigations of the synthesis of hyperbranched polymers via the synthetic methodology termed “$A_2 + B_3$” have been reported[8−14] since Jikei’s group[6] and Fréchet’s group[7] reported the synthesis of hyperbranched aromatic polyamides and polyether epoxies from A_2 and B_3 monomers, respectively, in 1999. The polycondensation reactions were stopped prior to the gel points, and the conditions need to be controlled carefully to avoid forming cross-linking polymers. Recently, the more facile synthetic approaches, namely “$A_2 + BB'_2$”,[15−17] “AA′ + CB_x”,[18,19]and “AB + CD_x”,[20] could avoid rising gelation more effectively have been developed one after the other. Although these facile approaches to hyperbranched polymers attracted significant attention, only limited families of hyperbranched polymers were reported. Our recent efforts have focused on the development of these facile approaches to synthesize more families of hyperbranched polymers.

We reported previously the synthesis of aliphatic hyperbranched poly(ester−amide)s from aliphatic cyclic carboxylic anhydrides (AA′) with aliphatic multihydroxyl primary amines (CB_x).[21] Before then, van Benthem and co-workers reported the facile and cheap synthesis of hyperbranched poly(ester−amide)s via the polycondensation of a cyclic carboxylic anhydride (AA′) with diisopropanolamine (CB_2).[18] However, to our best knowledge, there has not been any report about synthesis of aromatic hyperbranched poly(ester−amide)s from aromatic cyclic carboxylic anhydrides and primary amines because cyclic imide structure will be easily formed at high polymerization temperature.[21,22] It seems that poly(ester−amide)s can be hardly prepared from aromatic cyclic carboxylic anhydrides and primary amines. Well then, what will occur if the aromatic cyclic carboxylic anhydrides with large steric hindrance or contorted structure are used? It is expected that the formation of cyclic imide structure might be held back. In this paper, we report the successful synthesis and characterization of aromatic and semiaromatic hyperbranched poly(ester−amide)s via direct polycondensation of 2,2′-diphenic anhydride (AA′) with 1-(4- or

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3-aminophenyl)-1,1-bis(4-dihydroxyphenyl)ethane or multihydroxyl aliphatic amines (CB$_x$) without any catalyst.

2. Experimental Section

Materials. 2,2′-Diphenic anhydride (DPA) was purchased from ACROS and purified by sublimation before use. Tris(hydroxymethyl)aminomethane (THAM) and 2-amino-2-ethyl-1,3-propanediol (AEPO) were purchased from Aldrich and purified by vacuum distillation before use. 1-(4-Aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane and 1-(3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane were synthesized according to the procedure reported previously.[23] *N,N*-Dimethylacetamide (DMAc) and *N,N*-dimethylformamide (DMF) were purified by distilling from calcium hydride under reduced pressure. Other solvents and reagents were used as received.

Measurements. ^{1}H and ^{13}C NMR spectra (DMSO-d_6) were recorded using a Varian Unity 400 MHz or Bruker AV 300 MHz spectrometer with the residual ^{1}H solvent peak as reference and the solvent carbon signal as standard, respectively. FTIR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer Pyris 1 DSC with the heating/cooling rates of 10 °C/min, and the T_g was taken as the midpoint of the inflection tangent, upon the third or subsequent heating scan. TG measurements were performed with a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 20 °C/min in nitrogen. Size exclusion chromatography (SEC) was performed with a Waters 1525 fitted with two columns (Styragel HT3 and HT4 DMF 7.8 × 300 mm column) connected in series and 2414 refractive index detector with TEDIA dimethylformamide (DMF) containing 0.05 M LiBr as mobile phase. The inherent viscosities were measured with an automatic Ubbelohde viscometer thermostated at 25 °C.

Synthesis of Intermediates. *N*-{4-[1,1-Bis(4-hydroxyphenyl)]ethylphenyl}-2′-carboxyl-2-biphenic Amide, 1a. A solution of 1-(4-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane (10.30 g, 33.7 mmol) and 2,2′-diphenic anhydride (7.56 g, 33.7 mmol) in dry, deoxygenated DMAc (80 mL) was stirred for 24 h at room temperature under a slow stream of nitrogen, and then the reaction mixture was poured into water (500 mL). The precipitate was isolated by filtration and dried in a vacuum to give white powder **1a** (17.5 g, 99.5%); mp 158−160 °C. FTIR (KBr): 2500−3500 (O−H, N−H); 1701 (C=O, carboxyl); 1654 (C=O, amide); 1536 (N−H); 1594, 1510, 1438 (Ar−C); 1244, 1178 (C−O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 1.94 (s, 3H), 6.62 (d, J = 8.6, 4H), 6.76 (d, J = 8.8, 4H), 6.86 (d, J = 8.8, 2H), 7.21 (m, 2H), 7.28 (d, J = 8.6, 2H), 7.42 (m, 1H), 7.49 (m, 4H), 7.51 (m, 1H), 7.81 (s, 1H), 9.24 (s, 2H), 9.90 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 31.16, 51.09, 115.30, 119.82, 128.26, 129.19, 129.98, 130.12, 130.74, 131.38, 131.76, 132.19, 136.84, 137.26, 140.140, 140.84, 141.81, 145.93, 155.98, 167.62, 169.71.

***N*-{3-[1,1-Bis(4-hydroxyphenyl)]ethylphenyl}-2′-carboxyl-2-biphenic Amide, 1b.** Intermediate **1b** was synthesized by the reaction of 1-(3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane and 2,2′-diphenic anhydride. The synthesis procedure was similar to that for intermediate **1a**. Yield 98.5%; mp 148−151 °C. FTIR (KBr): 2500−3500 (O−H, N−H); 1707 (C=O, carboxyl); 1656 (C=O, amide); 1548 (N−H); 1610, 1511, 1486 (Ar−C); 1246, 1178 (C−O) cm^{-1}. ^{1}H NMR (DMSO-d_6): δ 1.96 (s, 3H), 6.63 (d, J = 8.2, 4H), 6.76 (d, J = 8.2, 4H), 6.83 (s, 1H), 7.10 (m, 1H), 7.16 (d, 2H), 7.39 (m, 2H), 7.42 (m, 2H), 7.46 (d, 2H), 7.60 (d, J = 6.5, 1H), 7.76 (d, J = 7.4, 1H), 7.96 (s, 1H), 9.26 (s, 2H), 9.78 (s, 1H). ^{13}C NMR (DMSO-d_6): δ 35.54, 55.78, 119.69, 122.21, 124.84, 128.89, 132.08, 132.32, 132.60, 132.72, 132.97, 134.36, 134.40, 134.96, 135.63, 136.07, 136.52, 141.18, 143.51, 145.03, 146.01, 160.39, 167.51, 171.93.

Synthesis of Hyperbranched Poly(ester−amide)s. The General Procedure of Synthesis of Hyperbranched Aromatic Poly(ester−amide)s. In a cylindrical glass reactor equipped with a mechanical stirrer, with gas inlet and outlet tubes, a 1:1 molar ratio of 1-(4- or 3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane and diphenic anhydride was introduced under a nitrogen atmosphere, and then a proper amount of dry DMF (45% solid content) was added. The DMF was distilled off after stirring for 24 h at room temperature. The reaction vessel containing intermediates was placed into an oil bath preheated to 120 °C. As soon as a homogeneous melt had formed, the reaction temperature was rapidly raised to the desired condensation temperature (160−200 °C). Vigorous stirring was necessary during the whole procedure until the mechanical stirring was very difficult; the evolving reaction water was removed by a slow stream of nitrogen and ultimately distilled off under reduced pressure for 1 h. The crude product was dissolved in DMAc and precipitated into cold ethanol. The precipitated product was isolated by filtration and dried in a vacuum.

Hyperbranched Polymer 2a. Prepared from 3.78 g of DPA (16.8 mmol) and 5.15 g of 1-(4-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane (16.8 mmol), yielding yellow powder polymer (34−61%). FTIR (cm^{-1}, KBr): 3530−3250 (OH, N−H); 1732 (phO*CO*); 1660 (NH*COO*); 1536 (N−H); 1597, 1511, 1490 (Ar−C); 1239, 1203, 1169, 1038 (C−O). ^{1}H NMR (DMSO-d_6): δ 10.60, 10.04, 9.93 (COOH), 9.54, 9.29, 9.23 (OH), 8.02, 7.81, 7.63 (N*H*COO), 6.62−7.51 (Ar−H), 1.86−2.12 (CH$_3$). ^{13}C NMR (DMSO-d_6): δ 169.70, 168.70, 167.72, 166.09, 156.00, 145.94, 141.88, 140.87, 140.40, 139.74, 137.29, 136.83, 132.07, 131.41, 131.06, 130.77, 130.23, 130.00, 129.93, 129.91, 129.21, 128.27, 128.22, 119.82, 115.48, 115.31, 80.24, 79.81, 79.37, 55.85, 51.51, 51.10, 31.15.

Hyperbranched Polymer 2b. Prepared from 3.06 g of DPA (13.6 mmol) and 4.16 g of 1-(3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane (13.6 mmol), yielding yellow powder polymer (58%). FTIR (cm^{-1}, KBr): 3500−3250 (OH, N−H); 1730 (phO*CO*); 1658(NH*COO*); 1535 (N−H); 1607, 1511, 1485, 1436 (Ar−C); 1239, 1205, 1170, 1039 (C−O). ^{1}H NMR (DMSO-d_6): δ 10.47, 10.07, 9.91 (COO*H*), 9.54, 9.29, 9.23 (O*H*), 7.60−8.12 (N*H*COO), 6.63−7.54 (Ar−*H*), 1.75−2.15 (C*H*$_3$). ^{13}C NMR (DMSO-d_6): δ 170.45, 169.12, 167.81, 167.69, 166.65, 165.11, 157.32, 155.36, 155.15, 150.49, 150.11, 149.64, 148.73, 148.30, 148.09, 146.53, 145.74, 143.13, 142.45, 142.15, 141.69, 141.04, 139.79, 139.20, 138.50, 136.87, 135.96, 13.42, 132.06, 131.31, 131.04, 130.53, 130.24, 129.73, 129.11, 128.95, 128.60, 128.05, 127.67, 127.30, 127.09, 123.54, 121.48, 121.27, 120.77, 120.56, 119.15−119.61, 117.17, 115.03, 114.60, 114.43, 66.99, 56.01, 51.34, 50.95, 50.54, 28.66.

The General Procedure of Synthesis of Hyperbranched Semiarmoatic Poly(ester−amide)s. In a cylindrical glass reactor equipped with a mechanical stirrer, with gas inlet and outlet tubes, a calculated amount of 2-amino-2-ethyl-1,3-propanediol or tris(hydroxymethyl)aminomethane was introduced under a nitrogen atmosphere, and then an equimolar amount of diphenic anhydride was added. The reaction vessel was placed into an oil bath preheated to a desired temperature, with vigorous stirring for several hours until the mechanical stirring was very difficult; the evolving reaction water was removed by a slow stream of nitrogen and ultimately distilled off in 1 h, under reduced pressure.

Hyperbranched Polymer 2c (prepared from DPA and THAM). FTIR (cm^{-1}, KBr): 3500−2500 (OH, N−H); 1716 (CH$_2$O*CO*); 1638 (NH*COO*); 1546 (N−H); 1598, 1575, 1440 (Ar−C); 1290, 1252, 1049 (C−O). ^{1}H NMR (DMSO-d_6): δ 12.25−12.50 (COO*H*), 7.70−7.90 (N*H*COO), 7.20−7.60, 7.00−7.20, 6.80−6.95 (Ar-*H*), 4.50−5.30 (O*H*), 3.50−4.25 (C*H*$_2$−O). ^{13}C NMR (DMSO-d_6): δ 172.15, 171.84 (*C*OOH), 170.02, 169.74, 169.25, 168.46 (NH*C*OO), 166.66, 166.15, 166.05, 165.76 (CH$_2$O*C*O), 143.09, 142.20, 142.07, 141.12, 141.03, 140.08, 139.92, 139.08, 138.85, 138.41, 138.31, 137.25, 136.50, 136.42, 131.70, 131.50, 130.37, 130.20, 129.64, 129.48, 129.26, 129.09, 128.98, 128.53, 128.44, 127.79, 127.67, 127.32, 127.22, 126.94 (*Ph*), 76.54, 74.32, 71.32, 62.87, 61.19, 60.56, 58.76 (*C*(CH$_2$OCO)$_n$(CH$_2$OH)$_{2-n}$), 64.07, 63.74, 60.85, 60.33, 60.20, 56.32 (C(*C*H$_2$OCO)$_n$(*C*H$_2$OH)$_{2-n}$).

Hyperbranched Polymer 2d (prepared from DPA and AEPO). FTIR (cm^{-1}, KBr): 3500−3250 (O−H, N−H); 1730 (phO*CO*); 1648 (NH*COO*); 1541 (N−H); 1597, 1573, 1440 (Ar−C); 1285, 1243, 1122, 1080, 1037(C−O). ^{1}H NMR (DMSO-d_6): δ 12.12−12.50 (COO*H*), 7.50−7.80 (N*H*COO), 7.25−7.48, 7.00−7.15 (Ar−H), 4.34−4.40 (OH), 3.40−4.02 (CH$_2$−O), 1.03,

Table 1. Reaction Conditions and the Results of Polymerization

entry	polymer	temp (°C)	time^a (h)	yield %	DB	η_{inh}^{b} (dL/g)	$\bar{M}_w$^{c} (kDa)	PDI ^{c}	T_g^{d} (°C)	T_d^{10} (°C)^e
1	**2a(1)**	160	48	25	0.63	0.05	6.30 (5.20)	2.15 (2.01)		332.9
2	**2a(2)**	180	30	30		0.08	14.39 (7.10)	2.26 (2.13)		395.5
3	**2a(3)**	200	25	54	0.62	0.11	17.47 (16.95)	2.22 (2.76)	149.6	386.8
4	**2a(4)**	220	20			cross-link				
5	**2a**	200	25	55	0.62	0.11	17.21 (16.30)	2.12 (2.73)	148.7	386.3
6	**2b**	200	25	58	0.53	0.11	22.50 (9.20)	2.57 (2.37)		381.3
7	**2c**	150	5		0.50	0.08	18.05 (11.90)	2.65 (2.56)		396.8
8	**2d**	150	30		0.58	0.18	76.55 (185.90)	2.78 (17.25)	101.6	361.5

[a] Including the time of the applied vacuum. [b] Measured at 25 °C with a concentration of 0.5 g/dL in DMAc. [c] The molecular weight was measured by SEC with DMF containing 0.05 M LiBr as eluent solvent. The data out of and within the parentheses are the results calibrated with PMMA and PS, respectively. [d] The glass transition temperature determined by DSC measurements with a heating and cooling rate of 10 °C/min in nitrogen. [e] The temperature of 10% mass loss determined by TGA measurements with a heating rate of 20 °C/min in nitrogen.

1.06, 1.08 (CCH_2CH_3), 0.20−0.62 (CCH_2CH_3).^{13}C NMR (DMSO-d_6): δ 169.33, 169.02, 168.73 (*C*OOH), 167.82, 166.57, 165.89 (NH*C*OO), 164.17, 162.98, 162.69 (CH_2OCO), 142.33, 141.75, 141.15, 137.60, 136.96, 136.87, 135.96, 132.54, 131.70, 131.30, 130.33, 129.75, 128.78, 127.19, 126.86, 126.22, 125.57 (*Ph*), 72.22, 72.37, 63.50 ($C(CH_2OCO)_n(CH_2OH)_{2-n}$), 72.57, 62.91, 54.01 ($C(CH_2OCO)_n(CH_2OH)_{2-n}$), 27.90 ($CCH_2CH_3$), 7.21 ($CCH_2CH_3$).

3. Results and Discussion

Synthesis and Structure of Aromatic Hyperbranched Polymers. It has been found that aromatic cyclic anhydrides such as phthalic anhydride react rapidly with aromatic or aliphatic primary amines to form imide mainly at high temperature in our previous research.[21] The major reason lies in the fact that the amide group formed and carboxyl groups are located on the same side of the phenyl, so stable five-numbered cyclic imide is easily formed. However, if 2,2′-diphenic anhydride with contorted structure takes the place of ophthalmic anhydride in the above-mentioned reaction, the amide group formed and carboxyl groups will be not located in the same plane; as a result, the unstable seven-numbered cyclic imides do not form in competition with polyesterification under the described polymerization reaction conditions.

Generally, the direct condensation of bisphenols and diacids cannot yield high molecular weight polyesters because of the strong leaving tendency of the phenylate moiety, so high molecular weight linear aromatic polyesters are prepared either by activated acid (acid chloride) or by acetylating or silylating the phenolic function. However, high molecular weight hyperbranched polyesters could be synthesized via self-polycondensation of the AB_2 monomer with two phenolic hydroxyls and one carboxyl group,[23] whereas the molecular weight of the polymers obtained by this method will be lower than that of the polymers prepared from the corresponding monomers activated as described above. This means that other families of hyperbranched polyesters with moderately high molecular weight can be obtained via the elaborate selection of monomers and the optimization of reaction conditions.

On the basis of the above-mentioned consideration, herein, we tried synthesizing aromatic and semiaromatic hyperbranched poly(ester−amide)s from 2,2′-diphenic anhydride and multihydroxyl primary amines. The syntheses of aromatic hyperbranhed poly(ester−amide)s via direct polycondensation of 1-(4- or 3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane with 2,2′-diphenic anhydride (DPA) were investigated.

To explore optimum polymerization condition, the aromatic hyperbranched poly(ester−amide) **2a** was first prepared by self-polycondensation of corresponding monomer **1a** (or intermediate). The polymerization conditions and results are summarized in Table 1 (entries 1−4). Various attempts were made for self-polycondensation of intermediate **1a** in the maximum temperature range of 160−220 °C. A completely soluble product was obtained at 160−200 °C; slight cross-linking was found at a reaction temperature of 220 °C. The molecular weight was relatively low when polymerization was conducted at 160 °C. The molecular weight of polymer increased with reaction temperature. The yielding and inherent viscosity of the poly(ester−amide)s obtained at 200 °C were relatively high. Thus, the direct polycondensation of 1-(4- or 3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane with DPA was conducted at this temperature.

On the assumption that there was only a minor tendency to form imides in competition with polyesters during the polycondensation, even moderately high molecular weight polymers could not have been gotten, as the sole carboxylic acid functionality in the intermediate molecule (AB_2 monomer) would have been consumed. Yet, we did get the hyperbranched poly(ester−amide)s with moderately high molecular weight under the described reaction conditions, which indicates that no cyclic imides formed, indeed, during the polycondensation.

To avoid the degradation of amines at high reaction temperature, since the melting temperature of the mixture is higher compared with the decomposition temperature of the amines, a proper amount of DMF (45% solid content) as solvent was added at the initial step. When the aromatic amines had reacted completely with DPA to form intermediates, the solvent was distilled off under reduced pressure, and then the reaction temperature was raised to 200 °C. The polymers obtained with two different procedures display almost the same properties. Therefore, the former one-pot procedure was also employed for the polycondensation of other aromatic amine and diphenic anhydride.

The characterization of the aromatic hyperbranched polymers was accomplished by combination of techniques including FTIR,^{1}H NMR, and ^{13}C NMR. FTIR spectra provided evidence for the chemical structure of the polymers, showing characteristic absorptions of the ester carbonyl at about 1732 cm^{-1} and amide carbonyl at 1660 cm^{-1} for polymer **2a** in Figure 1. No absorbance peaks were observed between 1750 and 1800 cm^{-1}, which provides the further evidence of the absence of imides in the polymers. There are several differences between the FTIR spectra of intermediate and those of the corresponding polymer. The strong and broad peak

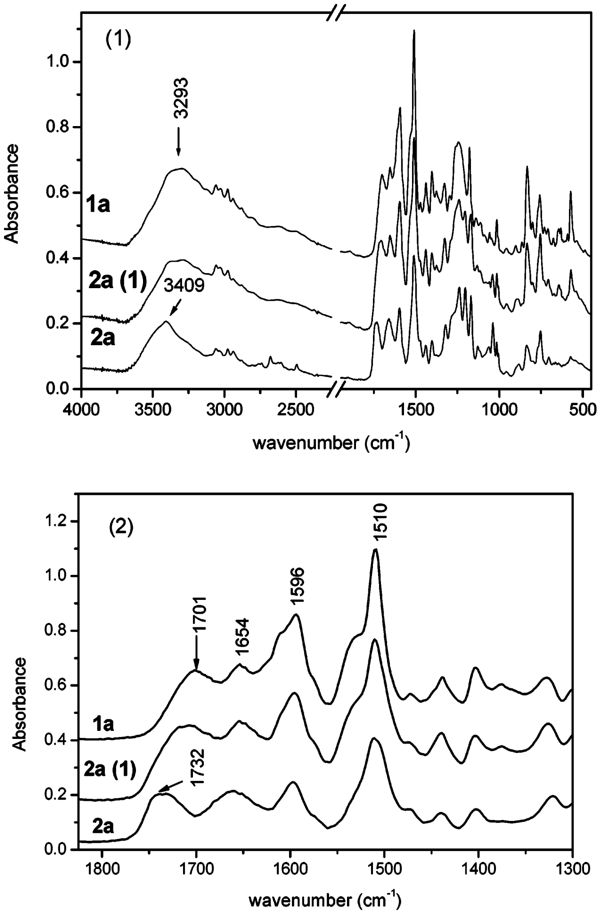
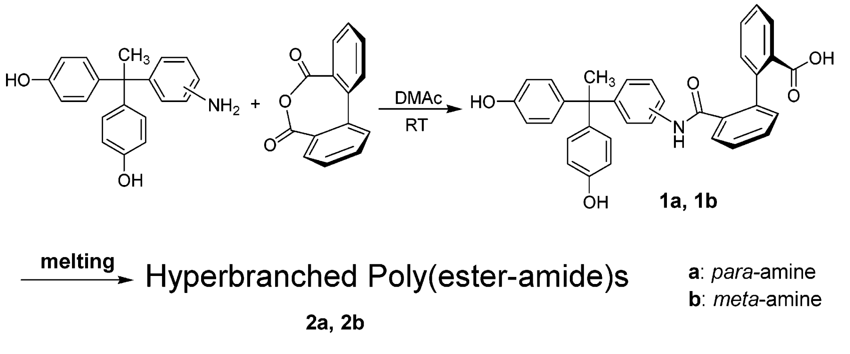


Figure 1. FTIR spectra of intermediate **1a** and polymers **2a-(1)** and **2a**.

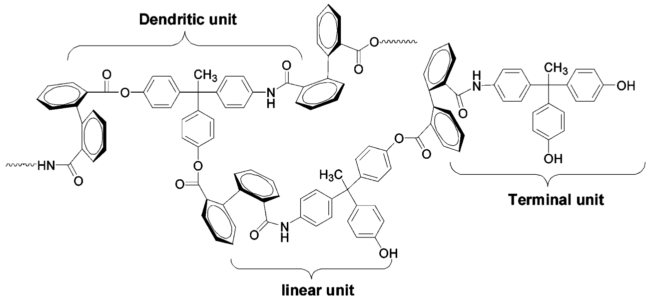
at 3300 cm^{-1}, chiefly attributed to O−H stretching of the H-bonded OH and COOH groups, which is the distinguishing feature of the phenol and carboxyl group, shifts to higher frequency band (3409 cm^{-1}) and becomes less broad for polymer **2a** because there is a greater separation of individual OH groups in larger polymer molecules. Moreover, with the increase of the molecular weight of the polymer, the amounts of COOH and OH groups reduce and the intermolecular H-bonds decrease. The higher frequency band (3409 cm^{-1}) is due to O−H stretching of "free" unassociated polymer molecules. In addition, a new absorption band appeared at 1732 cm^{-1} due to the carbonyl stretching of ester, overlapping the peak at 1701 cm^{-1} attributed to the carbonyl stretching of carboxylic acid. These data indicate that poly(ester−amide)s molecules were formed via thermal condensation occurring repetitiously between phenol hydroxyl and carboxyl groups of the monomer molecules.

The ^{1}H and ^{13}C NMR of polymers **2a(1)** and **2a** are shown in Figures 2 and 3, respectively. The peak assignments are based on the peak positions of corresponding intermediate **1a**. The hyperbranched polymers **2a(1)** and **2a** are composed of linear, dendritic, and terminal units, as shown in Scheme 2. Fréchet has described the degree of branching (DB) for hyperbranched polymers as the ratio of the sum of dendritic and terminal units vs the total units (linear, dendritic, and terminal units).[24] The DB of polymer **2a(1)** and **2a** can be determined by both ^{1}H NMR and ^{13}C NMR spectra of polymers **2a(1)** and **2a**. Compared with the ^{1}H NMR spectra of the intermediate, the peaks of ^{1}H NMR spectra of the corresponding polymers were broader, except the carboxyl acid proton, due to the repeat units and the branched architecture of the polymers. The peak of carboxyl proton became narrow and shifted to high field slightly (12.79, 12.70, 12.63 ppm) from intermediate **1a** to polymers **2a(1)** and **2a** because carboxyl groups were consumed more and more with the increase of molecular weight, and the hydrogen bond of them became weak gradually. This accords with the conclusion drawn from IR spectra. In addition, as shown in Figure 2, both amide proton **m** and hydroxyl proton **n** in intermediate **1a** displayed one group of single peaks (9.24 and 9.90 ppm, respectively), and one of phenyl protons, proton **l**, showed one group of double peaks (7.82 and 7.84 ppm), while the corresponding protons **l** and **m** in polymer showed three groups of signal peaks, 7.81−7.84, 7.86−7.92, 7.99−8.05 and 9.23, 9.29, 9.53 ppm, respectively; proton **n** displayed four groups of signal peaks (9.90, 10.04, 10.60, 10.74 ppm). The signal peak of 7.81−7.84 ppm in the polymer ^{1}H NMR spectra should be assigned to the proton **l** in terminal units, named T_l, because the structure of terminal units is similar to that of monomer. Similarly, the signal peaks of 9.23 and 9.90 ppm of the polymer ^{1}H NMR spectra should be assigned to protons **m** and **n** in the terminal units, named as T_m and T_{n1}, respectively. There is prominent H-bonding in OH of intermolecular because of the abundant OH in the terminal units of the polymer molecular. Since H-bonding diminishes shielding, the OH and the NH signals move downfield while intermolecular H-bonding is enhanced. The H-bonding is accompanied by exchange of H's from one molecule to anthother, resulting in signal broadening. Herein, there are two more broad signal peaks of hydroxyl group in ^{1}H NMR spectra of the polymer and the two peaks (10.60, 10.74 ppm) in lower density field should be contributed to the resonance of strong associated terminal (T_{n2}) and linear hydroxyl group (L_{n2}), respectively. In dendritic units of the polymer, there is no hydroxyl group. Therefore, the signal of 10.04 ppm

Scheme 1. Synthesis of Aromatic Hyperbranched Poly(ester−amide)s



Scheme 2. Structure of Polymer 2a



should be due to the resonance of less associated linear hydroxyl group of the polymer, named L_{n1}. Although H-bonding exists between the amide groups, it is much weaker than the hydroxyl group because the amide groups lie in the interior of the polymer molecule and the group's density is much smaller than the hydroxyl group; the amide protons of the polymer do not have so much signal peaks in ^{1}H NMR spectra like hydroxyl proton. In addition, the structure of linear units is closer to terminal units than that of dendritic units, which consequentially leads to the signals of NMR closer to that of terminal units. Furthermore, the integral of peaks 7.86−7.92 and 9.29 ppm are equal to that of L_{n1}. Hence, the signals at 7.86−7.92 and 9.29 ppm should be resonances of protons **l** and **m** in the linear units, respectively, L_l and L_m, and 7.99−8.05 and 9.53 ppm should be assigned to the resonance of **l** and **m** in the dendritic units of polymer **2a(1)**, namely, D_l and D_m, respectively. According to Fréchet's definition of DB and the integration ratio either of T_l, L_l, D_l or T_m, L_m, D_m, the DB of polymer **2a(1)** can be calculated to be 0.62 or 0.65; the average value is 0.63. Similarly, the DB of polymer **2a** was determined to be 0.62. The value is very close to the DB of **2a(1)**, which indicates that the DB of the polymer is independent of the molecular weight.

In the meantime, the DB of the polymer also can be determined by the ^{13}C NMR spectra. The signals of the quaternary carbon atoms of polymer **2a(1)** display two groups of three peaks, 51.08, 51.51, 55.85 ppm and 79.37, 79.81, 80.24 ppm, which should be assigned to the resonance of quaternary carbon atoms of the polymer with two configurations. This is similar to the case of the aliphatic hyperbranched poly(ester−amide)s reported previously;[21] there exist two conformational enantiomers (atropisomerism) in the polymers. It is very obvious that the peak of 51.08 ppm should be the resonance signal of the quaternary carbon atoms in terminal units (T_1) of polymer **2a(1)** because the resonance of quaternary carbon atom of intermediate **1a** (Figure 3) was at 51.09 ppm, and the terminal units possess a similar chemical environment to the intermediate. The signal at 51.51 ppm should be assigned to the resonance of quaternary carbons in linear units (L_1) of the polymer because it is closer to T_1, and the chemical environment of linear units is closer to that of the terminal units than that of the dendritic units. Well then, the peak at 55.85 ppm should be the resonance of quaternary carbons in the dendritic units. The other group signals containing three peaks, 79.37, 79.81, and 80.24 ppm, contributing to quaternary carbon atoms with the other kind of configuration, should be assigned to the terminal (T_2), linear (L_2), and dendritic units (D_2), respectively. The DB of **2a(1)** calculated from the integration ratio of T_1, L_1, D_1 and T_2, L_2, D_2 using Fréchet's definition was 0.62 and 0.66, respectively. The average value of DB was 0.64, which is in great

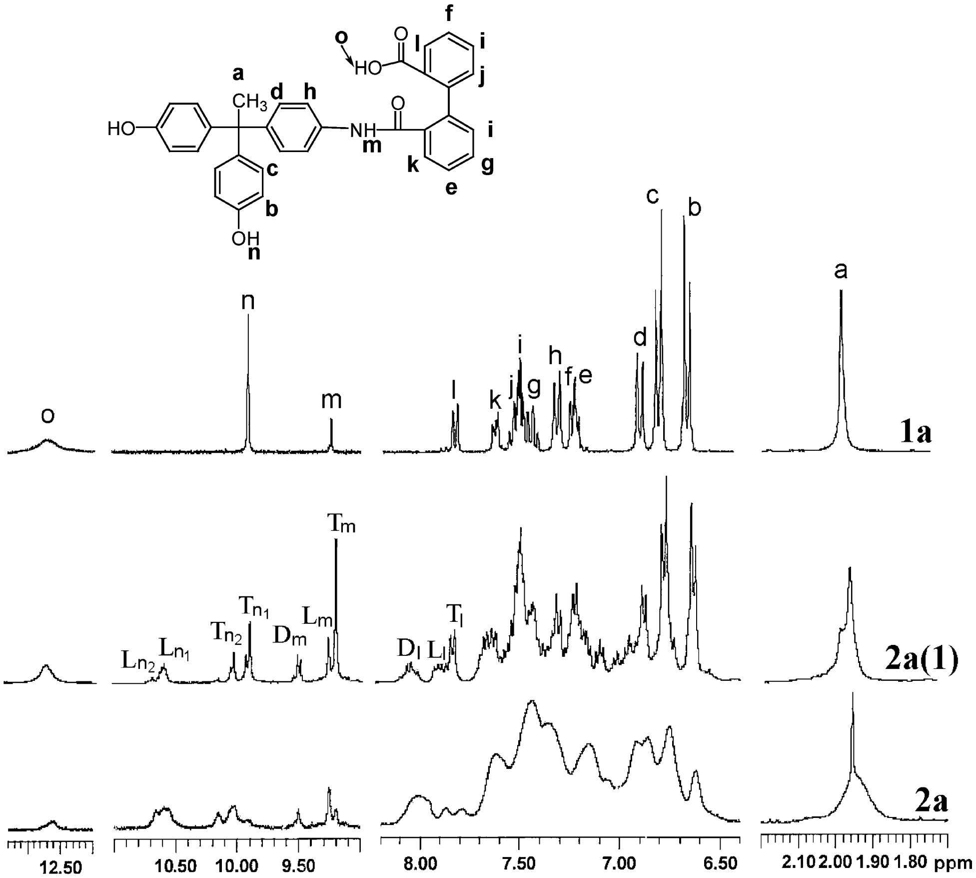


Figure 2. ^{1}H NMR spectra of intermediate **1a** and polymers **2a(1)** and **2a**.

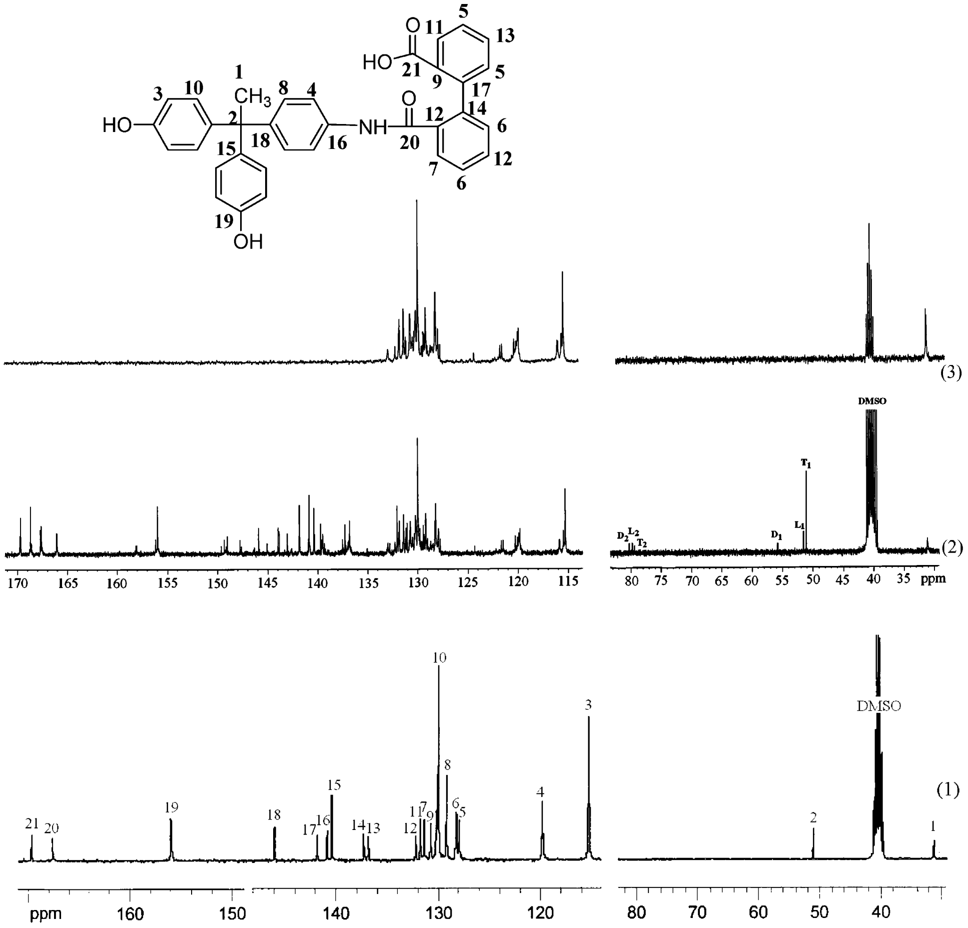
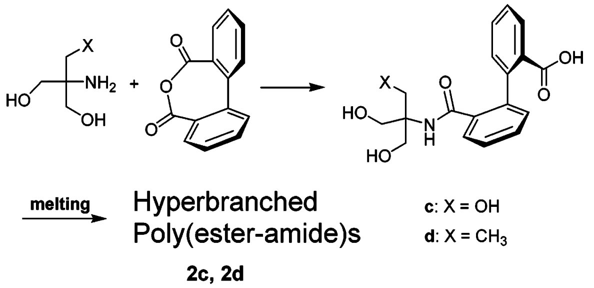


Figure 3. ^{13}C NMR spectra of intermediate **1a** and polymer **2a(1)**: (1) inverse-gated decoupling of intermediate **1a**; (2) inverse-gated decoupling of polymer **2a(1)**; (3) DEPT-135° (pulse angle) of polymer **2a(1)**.

Scheme 3. Synthesis of Semiaromatic Hyperbranched Poly(ester−amide)s



agreement with the result determined by ^{1}H NMR spectra of polymer **2a(1)**. Similarly, the DB of polymer **2b** can be determined to be 0.53. The DB value of polymer **2b** is lower than that of polymer **2a**, which may result from the fact that *meta*-oriented amides have more steric constraints in the proximity of the unreacted hydroxyl group than *para*-oriented amides, lowering its reactivity.

Synthesis and Structure of Semiaromatic Hyperbranched Polymers. The second part of this study was concerned with the facile synthesis of semiaromatic hyperbranched poly(ester−amide)s via the direct polycondensation of multihydroxylamines and 2,2′-diphenic anhydride without any solvent, as shown in Scheme 3. The melting points of multihydroxylamines were low enough to conduct directly melting condensation with DPA successfully, and the decomposition reaction of the amines and anhydride could not occur at this temperature. It is known that the nucleophilic reactivity of the amino group is much greater than that of the hydroxyl group.[25] Therefore, the intermediate with a carboxylic group and multihydroxyl groups may form at the initial stage of the reaction. Further polycondensations of the intermediates as AB$_x$ monomers would lead to hyperbranched poly(ester−amide)s without gelation, as shown in Scheme 3.

The conditions and the typical results of the polycondensation from DPA and tris(hydroxymethyl)aminomethane (THAM) or 2-amino-2-ethyl-1,3-propanediol (AEPO) are summarized in Table 1 (entries 7 and 8). The direct thermal polycondensations were carried out at 150 °C under nitrogen flush, yielding brown solid products. The water formed during the reaction was removed with nitrogen to promote the polymerization reaction.

The structures of polymers **2c** and **2d** were characterized by FTIR, ^{1}H NMR, and ^{13}C NMR spectroscopy. The FTIR of polymer **2c** is shown in Figure 4. The broad peak at 3363 cm^{-1} is typical for the stretching of H-bonded O−H and N−H groups. Peaks at 1716 and 1638 cm^{-1} are due to the characteristic C=O stretching of ester and amide, respectively. The bands at 1598 and 1575 cm^{-1} are due to aromatic ring C=C stretching. The bands at 1380 and 1500 cm^{-1} are due to C−H bending, and the bands at 1050 and 1290 cm^{-1} are due to the C−O stretching.

It is difficult to determine the DB by using ^{1}H NMR spectra for polymers **2c** and **2d** because the peaks

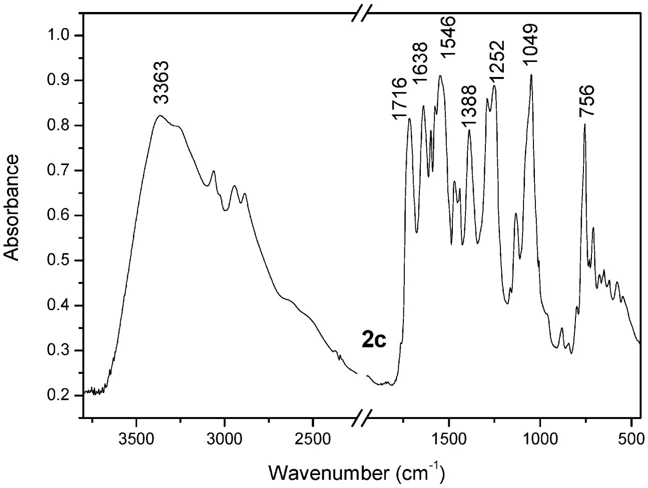
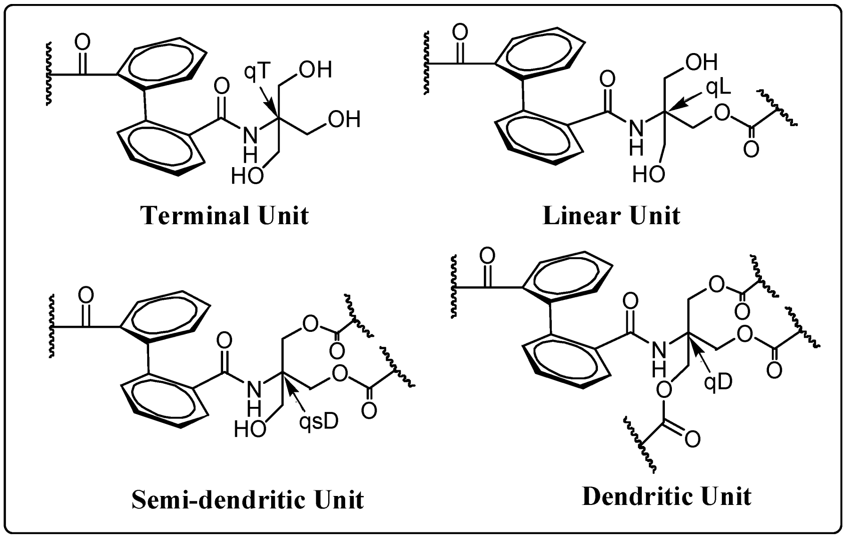


Figure 4. FTIR spectrum of polymer **2c**.

attributed to each unit were overlapped. However, the DB can be quantitatively measured by ^{13}C NMR and DEPT spectra of the polymer, as shown in Figure 5 for polymer **2c** as a typical example. Four different subunits are possible in polymer **2c**: terminal (T), linear (L), semidendritic (sD), and perfect dendritic (D) (Figure 5). Comparing ^{13}C NMR with DEPT spectrum of polymer **2c**, interestingly, it was found two groups of signals disappeared in the ^{13}C DEPT 135 NMR spectrum; one group is 58.76, 60.56, 61.19, 62.87 ppm with integrations of 0.855, 2.367, 4.993, 2.716, respectively. These signals should be assigned to the quaternary carbons of perfect dendritic, semidendritic, linear, and terminal fraction, respectively.[21,26] The DB of **2c** was 0.50 calculated from the integration of quaternary carbon attributed to each unit using the Frey's equation DB = 3(2D + sD)/2(3D + 2sD + L).[27] The other group, only including two peaks, 76.54 and 74.33 ppm with lower intensity, integrations of 0.503 and 0.402, respectively, should be assigned to the quaternary carbons in linear and terminal fraction of the other kind of configuration isomer, merely in the



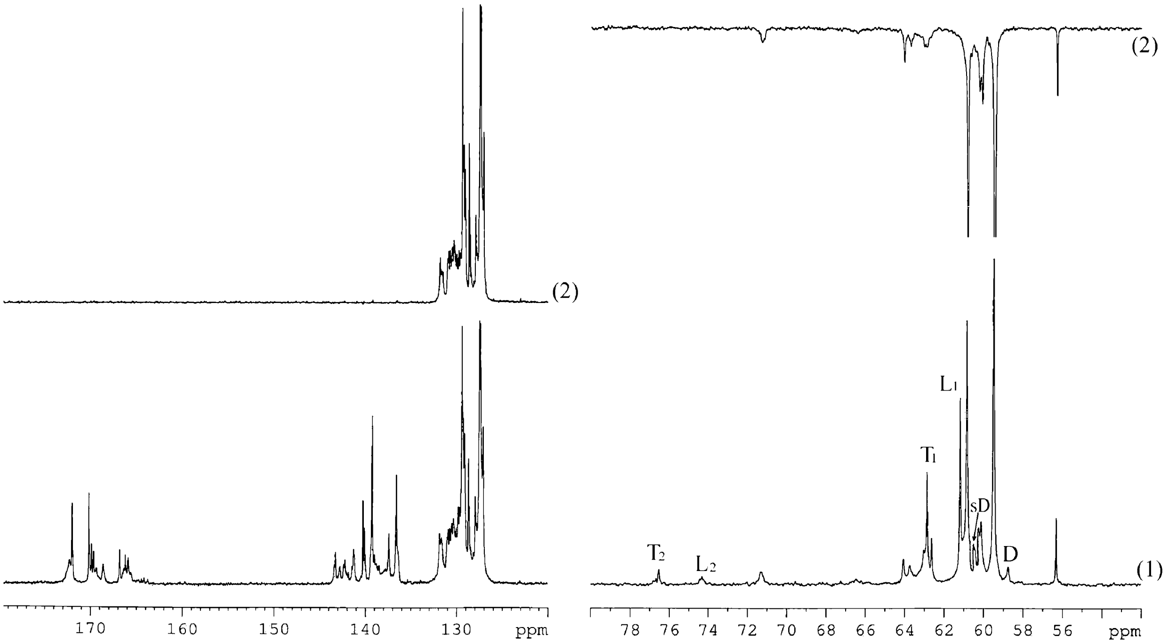


Figure 5. ^{13}C NMR spectra of polymer **2c**: (1) inverse-gated decoupling; (2) DEPT-135°.

minority of polymer **2c**.[21] The resonance peak due to the semidendritic unit might overlap with the peak due to CH_2 group (71.2 ppm), and that due to the perfect dendritic unit is so weak that it cannot be observed. Similarly to polymer **2c**, the DB of **2d** could be determined to be 0.58 by ^{13}C NMR and DEPT ^{13}C NMR using Fréchet's definition to DB.[24]

Properties of the Hyperbranched Polymers. Table 1 also illustrates the results of SEC measurements that were calibrated against narrow-dispersity polystyrene (PS) and broad-dispersity poly(methyl methacrylate) (PMMA) standards, respectively, with DMF as solvent and eluent to give the weight-average molecular weight ($\bar{M}_w$) and polydispersity indices (PDI) of the polymers. It is already known that this method has only limited suitability for hyperbranched polymers and usually underestimates the true molar mass of high molar mass branched polymers due to their smaller hydrodynamic radii compared to linear analogues.[2c,4d,5c,24,28] On the other hand, the marked difference in the polarity between polymer sample and standard can also lead to highly inaccurate values of molecular weight. The data calibrated against PMMA may be more reasonable than those calibrated against PS. In polar solvents, specific (i.e., enthalpic) interactions between the PS solute and the column packing (styrene−divinylbenzene) confound the calibration curve, causing substantial inaccuracies. The hyperbranched polymers exhibited moderate molecular weights with broad molecular weight distributions and relatively low inherent viscosity (0.05−0.18 dL/g) due to the highly branched structure. The PDIs were high, which was a typical result for AB_x polycondensation polymers predicted by Flory.[29]

The properties of **2a**, **2b**, **2c**, and **2d** are summarized in Table 1. The glass transition temperature (T_g) of polymers **2a** and **2d** was measured to be 149.6 and 101.6 °C, respectively, by DSC, while for **2b** and **2c**, there was no glass transition observed in their DSC curves. All the polymers display good thermal stability. The temperatures of 10% mass loss (T_d^{10}) of the hyperbranched polymers are higher than 332 °C. It can be found that the temperatures of 10% mass loss of **2a** was slightly higher than that of **2b**, which may be attributed to the fact *meta*-oriented amines have less dense polymer chain packing than *para*-oriented amines due to the smaller conformational entropy of *para*-oriented chain. As a result, the former has better thermal stability than the latter.[30] The thermal stability of polymer **2c** is better than that of polymer **2d** because of the stronger H-bonding resulted from more hydroxyl groups. All the hyperbranched poly(ester−amide)s are soluble in polar solvents such as DMAc, DMSO, and THF; polymer **2d** even has good solubility in $CHCl_3$.

4. Conclusion

A series of aromatic and semiaromatic hyperbranched poly(ester−amide)s with terminal hydroxyl group were successfully prepared by direct polycondensation of 2,2-diphenic anhydride with 1-(4- or 3-aminophenyl)-1,1-bis(4-hydroxyphenyl)ethane, tris(hydroxymethyl)aminomethane, or 2-amino-2-ethyl-1,3-propanediol. It was found that the optimum temperature of polycondensation is about 200 °C for the syntheses of the aromatic hyperbranched poly(ester−amide)s. The resulting hyperbranched poly(ester−amide)s having a degree of branching ranging from 0.53 to 0.63, moderate molecular weights with broad distributions, and low inherent viscosity exhibit good solubility in DMAc, DMSO, THF, and $CHCl_3$. The temperatures of 10 wt % mass loss (T_d^{10}) are above 333 °C, and T_gs are in the range of 102−150 °C, except for two of them not being observed. They depended on the structure of the monomers.

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