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Synthesis and Characterization of Hyperbranched Poly(ester-amide)s from Commercially Available Dicarboxylic Acids and Multihydroxyl Primary Amines

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ABSTRACT: A new method for syntheses of hyperbranched poly(ester-amide)s from commercially available A_2 and CB_x type monomers has been developed on the basis of a series of model reactions. The aliphatic and semiaromatic hyperbranched poly(ester-amide)s with multihydroxyl end groups are prepared by in situ thermal polycondensation of intermediates obtained from dicarboxylic acids (A_2) and multihydroxyl primary amines (CB_x) in *N*,*N*-dimethylformamide. Analyses of FTIR, ^{1}H NMR, and ^{13}C NMR spectra revealed the structures of the polymers obtained. The MALDI-TOF MS of the polymers indicated that cyclization side reactions occurred during polymerization. The hyperbranched poly(ester-amide)s contain configurational isomers observed by ^{13}C and DEPT ^{13}C NMR spectroscopy. The DBs of the polymers were determined to be 0.38−0.62 by ^{1}H NMR or quantitive ^{13}C NMR and DEPT 135 spectra. These polymers exhibit moderate molecular weights, with broad distributions determined by size exclusion chromatography (SEC), and possess excellent solubility in a variety of solvents such as *N*,*N*-dimethylacetamide, dimethyl sulfoxide, tetrahydrofuran, and ethanol, and display glass-transition temperatures (T_gs) between −2.3 and 53.2 °C, determined by DSC measurements. The thermogravimetric analytic measurement revealed that the decomposition temperature of the polymers at 10% weight-loss temperature (T_d^{10}) ranged from 333 to 397 °C in nitrogen.

Introduction

Dendrimers and hyperbranched polymers, together classified as dendritic polymers, have attracted considerable and increasing attention in recent years due to their unusual structure and unique properties.[1−5] In contrast to linear macromolecules, dendritic polymers have a tree-like structure and a number of branching points and terminal groups. Hyperbranched polymers have imperfectly branched structures. However, they can be synthesized cost-efficiently and possess desirable properties similar to dendrimers such as low viscosity, high solubility, and lack of significant entanglement in the solid state. These attractive features have led to the development of novel synthetic routes to such polymers.[1,2] Various hyperbranched polymers have been prepared conveniently in a one-pot procedure via self-polycondensation or an addition polymerization reaction of AB_x-type monomer,[6,7] ring-opening polymerization,[8] self-condensation vinyl polymerization,[9] atom transfer radical polymerization (ATRP),[10] or reversible addition fragmentation chain transfer (RAFT) polymerization.[11] Thereinto, the most general approach, one-pot self-polycondensation of AB_x monomers, has been used to synthesize a wide variety of hyperbranched polymers. However, most of AB_x monomers are prepared by several steps, which make it against the rapid production of hyperbranched polymers on a large scale for industrial applications. Therefore, the syntheses of hyperbranched polymers with much more straightforward, more cost-effective, and novel procedures are still desirable. Many researchers have devoted themselves to developing facile, versatile, and cost-effective routes toward hyperbranched polymers. Fréchet,[12] Kakimoto,[13] Okamoto,[14] Long,[15] Fossum,[16] Xu,[17] Scheel,[18] Smet,[19] and Nishikubo[20] groups independently reported the preparation of hyperbranched polymers from A_2 and B_3 type monomers through strictly controlled polymerization conditions, and Schmaljohann and Voit[21] reported the kinetic evaluation of hyperbranched A_2 + B_3 polycondensation reactions. Yan,[22] Liu,[23] and Shu[24] groups reported the synthesis of hyperbranched copoly(sulfone-amine)s, polyimides, and poly(amide-imide), respectively, by the A_2 + BB'_2 approach. van Benthem and co-workers reported the synthesis and coating applications of hyperbranched poly(ester-amide)s via direct polymerization of cyclic carboxylic anhydrides (AA′-type monomers) with di-2-propanolamine (CB_2-type monomer).[3e,25] Recently, Yan and co-workers reported the synthesis of hyperbranched polymers with alternating ureido and urethano units by direct polycondensation of diisocyanates (AA′-type monomers) with multihydroxylamines (CB_n-type monomers),[26] and water-soluble degradable hyperbranched polyesters from methyl acrylate (AB) and diethanolamine (CD_2) or *N*-methyl-D-glucamine (CD_5).[27] More recently, Liu has developed an approach, $2A_2$ + BB′B″, to hyperbranched poly(amino ester)s by the Michael addition polymerization of 1-(2-aminoethyl)piperazine (BB′B″) with double molar 1,4-butanediol diacrylate (A_2).[28]

To date, only limited families of hyperbranched polymers have been prepared through the methods aforementioned. Our recent efforts have focused on the facile synthesis of more types of novel hyperbranched polymers with various architectures and structures.[29,30] We found that it was a good method to synthesize aliphatic hyperbrached poly(ester-amide)s with a short-chain or ring alkane backbone from cyclic carboxylic anhydrides (AA′-type monomers) and multihydroxyl primary amines (CB_n-type

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monomer). However, this route is incapable of preparing hyperbranched poly(ester-amide)s containing a long-chain alkane backbone because it is difficult to obtain cyclic carboxylic anhydrides with above six members. Therefore, we apply ourselves to search a more flexible route in generating diverse hyperbranched poly(ester-amide)s. In this paper, we report the synthesis of new hyperbranched poly(ester-amide)s from a commercially available A_2 type monomer, carboxylic acids with a CB_x type monomer, and a primary amine with two or three hydroxyl groups based on a series of model reactions to optimize polymerization conditions.

Experimental Section

Materials. Homophthalic acid (HPA) and *p*-benzene dicarboxylic acid (BDA) were purchased from Aldrich and Merck, respectively, and purified by sublimation before use. Succinic acid (SUA), adipic acid (ADA), sebacic acid (SEA), benzoic acid, and phenylacetic acid were purchased from the domestic market and purified by sublimation before use. Propionic acid, *n*-butyric acid, and *n*-caproic acid were purchased from the domestic market and purified by reduced-pressure distillation 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. *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. Thermogravimetric analytic (TGA) measurements were performed with a Perkin-Elmer Pyris 1 thermogravimetric analyzer with a heating rate of 20 °C/min in nitrogen. MALDI-TOF MS (matrix-assisted laser desorption/ionization time-of-flight mass spectrometry) was carried out using an Applied Biosystems Voyager-DE-STR MALDI-TOF mass spectrometer (Applied Biosystems, Inc., Framingham, MA) equipped with delayed extraction. A 337 nm UV nitrogen laser producing 3 ns pulses was used, and the mass spectra were obtained in the linear and reflector mode using 2,5-dihydroxybenzoic acid (DHB) as the matrix and water as the solvent for matrix and sample. 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 a 2414 refractive index detector with TEDIA dimethylformamide (DMF) containing 0.05 M LiBr as the mobile phase. The inherent viscosities were measured with an automatic Ubbelohde viscometer thermostated at 25 °C.

Model Reaction. A solution of carboxylic acid and tris(hydroxymethyl)aminomethane or 2-amino-2-ethyl-1,3-propanediol in dry, deoxygenated DMF was stirred for 1 or 26 h at the desirable temperature under a slow stream of nitrogen and then removed DMF under reduced pressure to give amide acid or ester characterized by FTIR spectra.

General Polymerization Procedure. In a cylindrical glass reactor equipped with a mechanical stirrer and 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 dicarboxylic acid and a proper amount of DMF (50−60%) was added. The reaction vessel was placed into an oil bath preheated to the desired temperature (60−80 °C) with vigorous stirring for a period of time, and then the DMF was removed under reduced pressure. Then, the temperature of the mixture was raised to 110−120 °C with vigorous stirring and kept for several hours until the mechanical stirring was very difficult, then the evolving reaction water was removed by a slow stream of nitrogen and ultimately distilled off under reduced pressure in 1 h.

Hyperbranched Poly(SUA-THAM), $\mathbf{P_{1a}}$. Prepared from 5.82 g of SUA (0.049 mol) and 5.97 g of THAM (0.047 mol), yielding 10.02 g (85%) of polymer as water-white transparent block solid. FTIR (cm^{-1}, KBr): 3550−3250 (OH, NH), 1741 ($\mathrm{CH_2O\mathit{CO}}$), 1661, 1560, 1466 (NH*CO*). ^{1}H NMR (DMSO-*d*6 δ): 7.33, 7.21, 7.18 (NHCO), 4.19−4.50 (OH), 3.91−4.12 ($\mathrm{C(C\mathit{H}_2O)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$), 3.28−3.61 ($\mathrm{C(CH_2O)_{\mathit{n}}(C\mathit{H}_2OH)_{3-\mathit{n}}}$), 2.28−2.56 (group, $\mathrm{OOCC\mathit{H}_2C\mathit{H}_2}$-CONH). ^{13}C NMR (DMSO-*d*6 δ): 175.61 (*CO*OH), 173.92, 173.55, 173.27 (NH*CO*O), 173.16, 173.02, 172.64 ($\mathrm{CH_2O\mathit{CO}}$), 77.02, 74.95, 70.96, 63.18, 63.03, 62.86, 61.61 ($\mathrm{\mathit{C}(CH_2OCO)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$), 71.45, 64.76, 62.74−63.04 61.25, 60.89, 60.25, 57.76 ($\mathrm{C(\mathit{C}H_2OCO)_{\mathit{n}}}$-$\mathrm{(\mathit{C}H_2OH)_{3-\mathit{n}}}$), 32.41−33.02, 30.70−31.14 ($\mathrm{OCO\mathit{C}H_2CH_2CONH}$), 29.93−30.32, 29.40−29.45 ($\mathrm{OCOCH_2\mathit{C}H_2CONH}$).

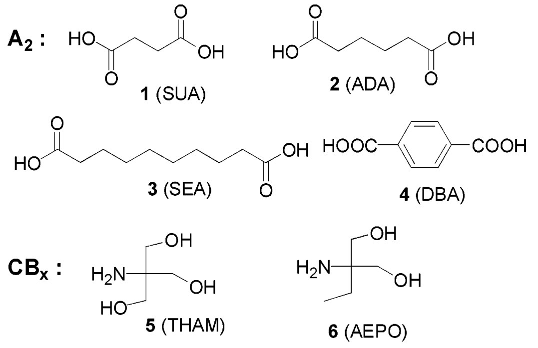
Hyperbranched Poly(ADA-THAM), $\mathbf{P_{2a}}$. Prepared from 5.03 g of ADA (0.034 mol) and 4.17 g of THAM (0.034 mol), yielding 7.64 g (83%) of polymer as jade-green transparent block solid. IR (cm^{-1}, KBr): 3510−3250 (OH, NH), 1736 ($\mathrm{CH_2O\mathit{CO}}$), 1655, 1560, 1459 (NH*CO*). ^{1}H NMR (DMSO-*d*6 δ): 7.44, 7.24, 7.11 (N*H*COO), 4.70−5.08 (OH, broad), 4.00−4.30 ($\mathrm{C(C\mathit{H}_2O)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$) 3.30−3.52 ($\mathrm{C(CH_2O)_{\mathit{n}}(C\mathit{H}_2OH)_{3-\mathit{n}}}$), 2.25−2.32 ($\mathrm{OCOC\mathit{H}_2(CH_2)_3}$-CONH), 2.02−2.25 ($\mathrm{OCO(CH_2)_3C\mathit{H}_2CONH}$), 1.30−1.50 ($\mathrm{OCOCH_2}$-$\mathrm{(C\mathit{H}_2)_2CH_2CONH}$). ^{13}C NMR (DMSO-*d*6 δ): 174.56 (*CO*OH), 173.54, 173.11, 172.57 (NH*CO*), 168.23, 167.37, 166.37 ($\mathrm{CH_2O\mathit{CO}}$), 76.16, 74.10, 72.10, 58.46 ($\mathrm{\mathit{C}(CH_2OCO)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$), 65.91, 65.47, 64.05, 61.14−62.64, 60.77, 60.06, 59.84, 56.30 ($\mathrm{C(\mathit{C}H_2OCO)_{\mathit{n}}}$-$\mathrm{(\mathit{C}H_2OH)_{3-\mathit{n}}}$), 35.56, 35.38 ($\mathrm{OCO\mathit{C}H_2(CH_2)_3CONH}$), 33.66, 33.05 (broad, OCO $\mathrm{(CH_2)_3\mathit{C}H_2CONH}$), 27.05, 26.94, 24.89, 24.64, 23.73 ($\mathrm{OCOCH_2(\mathit{C}H_2)_2CH_2CONH}$).

Hyperbranched Poly(SEA-THAM), $\mathbf{P_{3a}}$. Prepared from 6.12 g of SEA (0.030 mol) and 3.66 g of THAM (0.030 mol), yielding 8.38 g (86%) of polymer as stretchable pale-yellow transparent slightly soft body. IR (cm^{-1}, KBr): 3510−3250 (OH, NH), 1738 ($\mathrm{CH_2O\mathit{CO}}$), 1659, 1536, 1463 (NH*CO*). ^{1}H NMR (DMSO-*d*6 δ): 7.40, 7.20, 7.08 (N*H*CO), 4.60−5.03 (OH, broad), 4.18, 4.02, 3.85 (group, $\mathrm{C(C\mathit{H}_2O)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$), 3.50 ($\mathrm{C(CH_2O)_{\mathit{n}}(C\mathit{H}_2OH)_{3-\mathit{n}}}$), 2.24 ($\mathrm{OCOC\mathit{H}_2(CH_2)_7CONH}$), 2.00−2.20 ($\mathrm{OCO(CH_2)_7C\mathit{H}_2CONH}$), 1.46 ($\mathrm{OCOCH_2C\mathit{H}_2(CH_2)_4C\mathit{H}_2CH_2CONH}$), 1.22 ($\mathrm{OCO(CH_2)_2(C\mathit{H}_2)_4}$-$\mathrm{(CH_2)_2CONH}$). ^{13}C NMR (DMSO-*d*6 δ): 174.71 (*CO*OH), 173.87, 173.40, 173.04 (NH*CO*O), 172.68, 172.52, 168.36, 167.37, 166.47 ($\mathrm{CH_2O\mathit{CO}}$), 76.14, 74.16, 72.16, 62.21, 60.28, 58.46 ($\mathrm{\mathit{C}(CH_2OCO)}$-$\mathrm{(CH_2OH)_{3-\mathit{n}}}$), 70.47, 70.20, 65.87, 65.40, 64.08, 61.91, 61.69, 60.83, 60.41, 59.85 ($\mathrm{C(\mathit{C}H_2OCO)_{\mathit{n}}(\mathit{C}H_2OH)_{3-\mathit{n}}}$), 35.86, 34.02, 33.89 ($\mathrm{OCO\mathit{C}H_2(CH_2)_7CONH}$), 33.55, 33.51 (broad, $\mathrm{OCO(CH_2)_7\mathit{C}H_2}$-CONH), 28.62, 28.48, 27.43, 27.30 (broad, $\mathrm{OCO(CH_2)_2(\mathit{C}H_2)_4}$-$\mathrm{(CH_2)_2CONH}$), 25.56, 25.34 ($\mathrm{OCO(CH_2)_6\mathit{C}H_2CH_2CONH}$), 24.64, 24.41 ($\mathrm{OCOCH_2\mathit{C}H_2(CH_2)_6CONH}$).

Hyperbranched Poly(BDA-THAM), $\mathbf{P_{4a}}$. Prepared from 5.11 g of BDA (0.031 mol) and 3.73 g of THAM (0.031 mol), yielding 8.16 g (92%) of polymer as white solid. FTIR (cm^{-1}, KBr): 3510−3000 (OH, NH), 1725 ($\mathrm{CH_2O\mathit{CO}}$), 1644, 1573, 1462 (NH*CO*), 1612, 1535, 1508 (Ph-C). ^{1}H NMR (DMSO-*d*6 δ): 7.75, 7.56, 7.21, 7.04 (N*H*CO), 8.26, 7.94 (broad, ph) 5.00−5.29 (OH), 4.82, 4.60, 4.43, 4.31, 4.14 (group, $\mathrm{C(C\mathit{H}_2O)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$), 3.84, 3.62, 3.48 (group, $\mathrm{C(CH_2O)_{\mathit{n}}(C\mathit{H}_2OH)_{3-\mathit{n}}}$). ^{13}C NMR (DMSO-*d*6 δ): 166.74 (*CO*OH), 164.67, 164.54, 163.93, 163.75, 163.63, 163.56 (NH*CO*), 162.81, 162.61, 162.43, 162.30, 162.11, 161.11, 161.90, 161.76, 161.66, 161.45 ($\mathrm{CH_2O\mathit{CO}}$), 135.35, 133.48, 133.24, 132.86, 132.65, 132.29, 131.99, 131.75, 131.42, 130.88, 130.42, 130.17, 129.86, 129.46, 129.37, 128.23, 127.86 (Ph), 77.30, 75.19, 73.14, 60.32, 59.83, 59.04, 58.77 ($\mathrm{\mathit{C}(CH_2O)_{\mathit{n}}(CH_2OH)_{3-\mathit{n}}}$), 71.97, 71.59, 71.20, 70.92, 67.17, 66.74, 65.53, 64.98, 63.98, 63.78, 63.50, 63.34, 61.52, 61.26, 60.45, 60.04, 59.71 ($\mathrm{C(\mathit{C}H_2O)_{\mathit{n}}(\mathit{C}H_2OH)_{3-\mathit{n}}}$).

Hyperbranched Poly(SUA-AEPO), $\mathbf{P_{1b}}$. Prepared from 4.89 g of SUA (0.041 mol) and 4.93 g of AEPO (0.056 mol), yielding 7.51 g (76%) of polymer as a golden transparent block solid. FTIR (cm^{-1}, KBr): 3505−3250 (OH, NH), 3079 (CH_3), 2972 (CH_2), 1741 ($\mathrm{CH_2O\mathit{CO}}$), 1706 (COOH), 1669, 1549, 1463 (NH*CO*). ^{1}H

Scheme 1. A_2 and CB_x Monomers Used in This Work



NMR (DMSO-*d*6 δ): 7.51, 7.23, 7.08 (N*H*CO), 4.50−4.86 (O*H*) 3.80−4.20 (CCH_2OCO), 3.28−3.49 (CCH_2OH), 2.37−2.60 ($OCOCH_2CH_2CONH$), 1.59, 1.46 (CCH_2CH_3), 0.74 (CCH_2CH_3). ^{13}C NMR (DMSO-*d*6 δ): 178.85 (COOH), 172.20, 172.00, 171.60, 171.49, 171.28, 171.09 (NH*CO*), 166.41, 166.28, 165.71, 165.57, 165.12, 164.66, 164.56, 164.38 (CH_2OCO), 74.50, 72.42, 64.28, 58.88, 57.18, 53.15 ($C(CH_2OCO)_n(CH_2OH)_{2-n}$), 72.06, 67.87, 67.18, 66.92, 66.76, 66.20, 66.07, 64.28, 63.36, 63.08, 61.74, 60.89 ($C(CH_2OCO)_n(CH_2OH)_{2-n}$), 31.77, 31.29, 30.24, 30.12, 29.96, 29.80 ($OCOCH_2CH_2CONH$), 29.12, 28.96, 28.80, 28.53, 28.10, 27.71, 26.84 ($OCOCH_2CH_2CONH$), 23.80, 23.20, 23.00, 22.82, 22.63, 22.45 (CCH_2CH_3), 7.20, 7.08, 6.92 (CCH_2CH_3).

Hyperbranched Poly(ADA-AEPO), P_{2b}. Prepared from 5.38 g of ADA (0.037 mol) and 4.38 g of AEPO (0.037 mol), yielding 8.08 g (83%) of polymer as stretchable water-white transparent slightly soft body. IR (cm^{-1}, KBr): 3500−3200 (OH, NH), 2966, 2939, 2881 (CH_2), 1732 (CH_2OCO), 1666, 1537, 1461 (NH*CO*). ^1H NMR (DMSO-*d*6 δ): 7.42, 7.13, 7.03 (N*H*CO), 4.60−4.94 (OH), 3.88−4.20 ($C(CH_2O)_n(CH_2OH)_{3-n}$) 3.30−3.52 ($C(CH_2O)_n(CH_2OH)_{3-n}$), 2.43−2.72, 2.42, 2.28, 2.12 ($OCOCH_2(CH_2)_2CH_2CONH$), 1.30−2.20 ($OCOCH_2(CH_2)_2CH_2CONH$ and CCH_2CH_3), 0.78, 0.76, 0.74 (CCH_2CH_3). ^{13}C NMR (DMSO-*d*6 δ): 174.33 (*CO*OH), 172.87, 172.48 (NH*CO*), 166.41, 165.46 (CH_2OCO), 74.51, 72.45, 60.87, 58.44, 56.36 ($C(CH_2OCO)_n(CH_2OH)_{3-n}$), 71.63, 67.76, 66.17, 63.46, 63.14, 62.70, 62.09, 60.97 ($C(CH_2OCO)_n(CH_2OH)_{3-n}$), 35.56, 35.38, 33.35, 33.07 ($OCOCH_2(CH_2)_2CH_2CONH$), 28.20, 28.08, 27.06, 26.93, 26.82, 25.13, 24.98, 24.79, 23.94, 23.79, 23.21, 22.82 ($OCOCH_2(CH_2)_2CH_2CONH$ and CCH_2CH_3), 7.53, 7.32, 7.10, 6.95 (CCH_2CH_3).

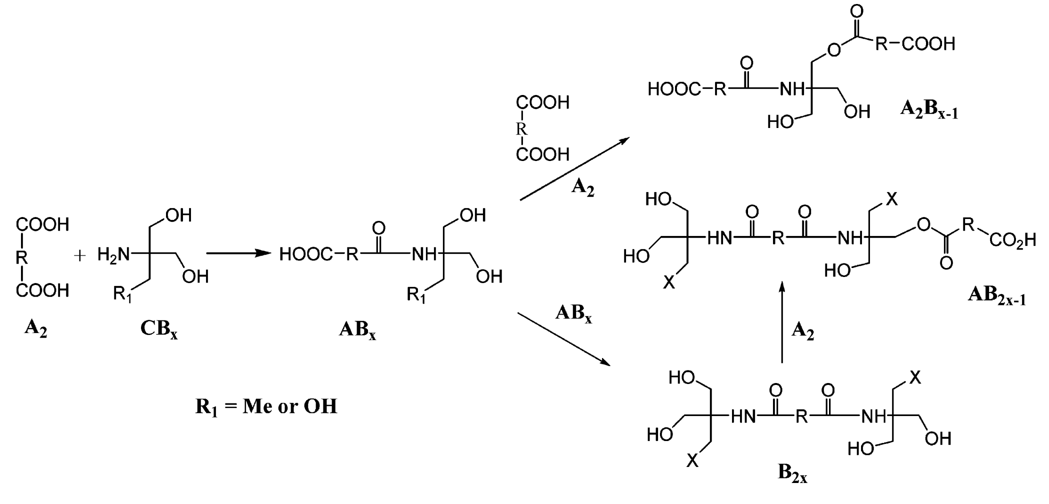
Hyperbranched Poly(SEA-AEPO), P_{3b}. Prepared from 6.77 g of SEA (0.033 mol) and 3.99 g of AEPO (0.033 mol), yielding 9.06 g (84%) of polymer as a golden transparent dope. IR (cm^{-1}, KBr): 3510−3050 (OH, NH), 2929, 2855 (CH_2), 1733 (CH_2OCO), 1667, 1537, 1463 (NH*CO*). ^1H NMR (DMSO-*d*6 δ): 7.38, 7.09, 7.00 (N*H*CO), 4.60−4.80 (OH), 3.80−4.48 (group, $C(CH_2O)_n(CH_2OH)_{3-n}$), 3.43 ($C(CH_2O)_n(CH_2OH)_{3-n}$), 2.26 ($OCOCH_2(CH_2)_7CONH$), 2.24, 2.16, 2.03 ($OCO(CH_2)_7CH_2CONH$), 1.50, 1.47 ($OCOCH_2CH_2(CH_2)_4CH_2CH_2CONH$ and CCH_2CH_3), 1.22, 1.04 ($OCO(CH_2)_2(CH_2)_4$ $(CH_2)_2CONH$), 0.78, 0.76 (CCH_2CH_3). ^{13}C NMR (DMSO-*d*6 δ): 174.49 (*CO*OH), 173.22, 172.60 (NH*CO*), 166.57, 166.33, 165.71 (CH_2OCO), 74.50, 72.50, 60.87, 58.77, 57.13 ($C(CH_2OCO)_n(CH_2OH)_{3-n}$), 71.71, 71.53, 67.71, 66.22, 63.15, 62.70, 62.22, 60.99 ($C(CH_2OCO)_n(CH_2OH)_{3-n}$), 35.90, 35.83, 33.72, 33.55 25.63, 25.46 ($OCOCH_2(CH_2)_6CH_2CONH$), 28.59, 28.44, 28.23, 28.10, 27.31, 27.18 ($OCOCH_2(CH_2)_6CH_2CONH$), 24.51, 24.45, 23.24, 22.86 (CCH_2CH_3), 7.52, 7.32, 7.11, 6.94 (CCH_2CH_3).

Hyperbranched Poly(BDA-AEPO), P_{4b}. Prepared from 6.52 g of BDA (0.039mol) and 4.75 g of AEPO (0.031mol), yielding 10.08 g (89%) of polymer as a pale-yellow transparent block solid. FTIR (cm^{-1}, KBr): 3650−3050 (OH, NH), 3064 (CH_3), 2969, 2937 (CH_2), 1724 (CH_2OCO), 1648, 1573, 1461 (NH*CO*), 1612, 1536, 1508 (Ph-C). ^1H NMR (DMSO-*d*6 δ): 7.71, 7.45, 7.08 (N*H*CO), 8.25, 7.94 (broad, ph) 5.00−5.10 (OH), 3.80−4.80 (group, $C(CH_2O)_n(CH_2OH)_{3-n}$), 3.22−3.70 (group, $C(CH_2O)_n(CH_2OH)_{3-n}$), 1.95, 1.74, 1.22 (CCH_2CH_3), 0.88, 0.86, 0.83 (CCH_2CH_3). ^{13}C NMR (DMSO-*d*6 δ): 166.52 (*CO*OH), 164.74, 164.53, 163.76, 163.57 (NH*CO*), 162.26, 162.09, 161.88, 161.67, 161.32, 161.17, 160.95, 160.73 (CH_2OCO), 139.33, 135.26, 134.59, 133.77, 133.55, 133.39, 133.21, 132.83, 131.91, 131.59, 131.31, 130.77, 130.32, 130.04, 129.78, 129.47, 129.26, 128.57, 128.09, 127.78, 127.09 (Ph), 75.54, 73.50, 59.01, 58.56, 57.53 ($C(CH_2O)_n(CH_2OH)_{3-n}$), 72.67, 72.34, 72.25, 68.58, 67.23, 65.94, 64.66, 64.48, 64.41, 60.87 ($C(CH_2O)_n(CH_2OH)_{3-n}$), 28.22, 24.12, 23.59, 23.28 (CCH_2CH_3), 7.50, 7.29, 7.16, 6.90 (CCH_2CH_3).

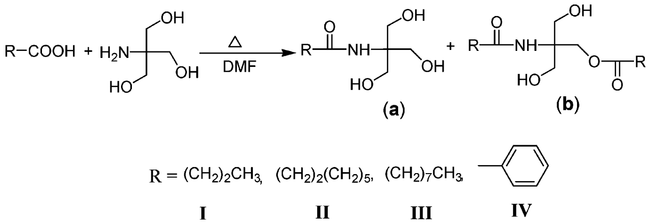
Results and Discussion

Monomer Selection and Polymer Synthesis. Previous research indicated that aliphatic hyperbranched poly(ester-amide)s could be prepared successfully via polycondensation of aliphatic cyclic carboxylic anhydrides (AA′ type monomers) with aliphatic multihydroxyl primary amines (CB_x type monomers).[29] This method benefits from the fact that the amino group (C) is more reactive than the hydroxyl (B) toward the carboxylic anhydride, and the reaction of aliphatic primary amine and aliphatic anhydride yields an amide acid instead of an imide compound. However, these routes are helpless for preparing hyperbranched poly(ester-amide)s with a long aliphatic chain because cyclic carboxylic anhydrides bearing more than six-membered rings are very unstable or even nonexistent. Hence, we try to synthesize hyperbranched aliphatic and semiaromatic poly(ester-amide)s via the controlled polycondensation reaction of aliphatic multihydroxyl primary amines with aliphatic or

Scheme 2. Reactions between Diacid and Multihydroxyl Primary Amine



Scheme 3. Model Reactions



aromatic carboxylic acids (except for ortho isomers). The A_2 and CB_x type monomers used in this work are shown in Scheme 1.

It is noteworthy that the reaction of a diacid (A_2) with a multihydroxyl primary amine is more complicated than that of an anhydride (AA′) with a multihydroxyl primary amine, as shown in Scheme 2. Usually, the reaction of an aliphatic cyclic anhydride (AA′) with an aliphatic multihydroxyl primary amine (CB_x) produces only an AB_x monomer, but no B_{2x} type intermediate, because of the much lower activity of the carboxyl than toward the amino group than anhydride. On the other hand, the reaction of a dicarboxylic acids with an aliphatic multihydroxyl primary amine (CB_x) will yield AB_x monomer and some B_{2x} type intermediate because the difference of the reactivities between carboxyl of the AB_x monomer formed and free diacid is not great enough. Note that forming the B_{2x} intermediate means existence of unreacted diacids (A_2) in the reaction system, and the free diacids will react with both the AB_x monomers obtained and the B_{2x} intermediate to yield more complicated products such as A_2B_{x-1} and AB_{2x-1}, respectively (see Scheme 2), which makes it complicated for subsequent polycondensation reactions to synthesize hyperbranched polymers. The A_2B_{x-1} intermediate may increase the possibility of cross-linking during the formation of hyperbranched molecules.[25,31]

Therefore, the key to get hyperbranched polymers successfully is to control the reaction condition to avoid producing the B_{2x} intermediate at the initial stage of the reaction. A series of model reactions were conducted as shown in Scheme 3. Four carboxylic acids, **I**−**IV**, corresponding to four dicarboxylic acids **1**−**4** shown in Scheme 1 reacted with THAM at various temperatures in DMF, and the resulting products were characterized by FTIR spectra. The result shows that, for the reactions of aliphatic acids **I**−**III** with THAM above 100 °C, the products contain ester (absorbance peak around 1733 cm^{-1} in FTIR spectra shown in Figure 1 as an example), even for 1 h, while under 80 °C, only amide can be produced, even for a longer reaction time (over 26 h), and for the reaction of aromatic acid **IV** with THAM above 70 °C, the products contain ester. Thus, at the initial stage of the polycondensation, the reaction temperature was kept at 80 and 50 °C for dicarboxylic acids **1**−**3** and for dicarboxylic acids **4**, respectively, to inhibit cross-linking when hyperbranched polymers formed.

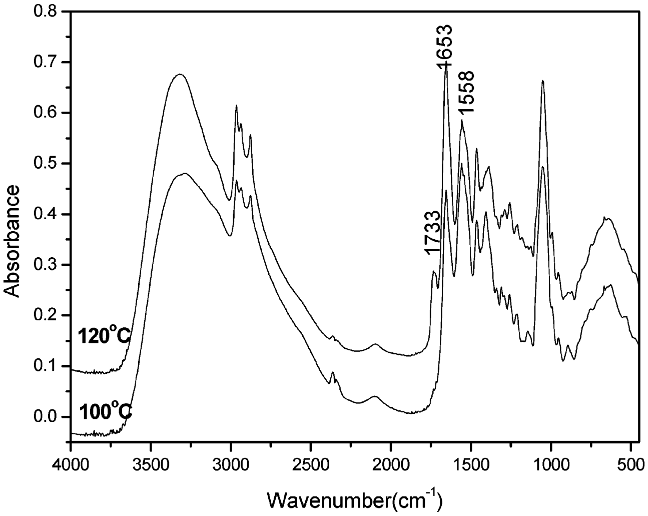


Figure 1. FTIR spectra of the products of reaction of butyric acid with THAM at 110 and 100 °C, respectively, for 26 h.

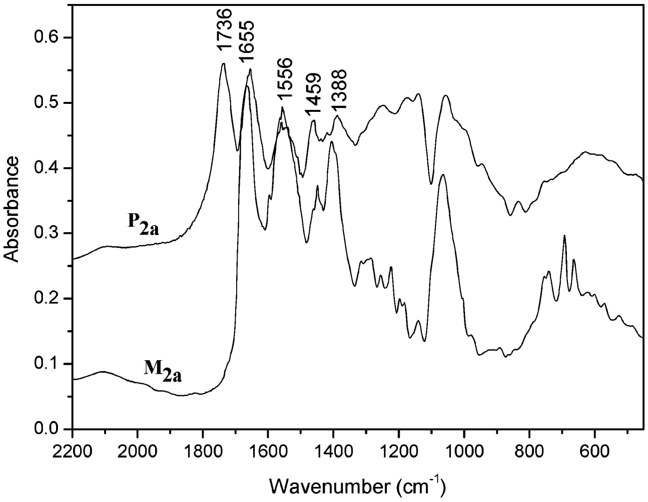


Figure 2. FTIR spectra of polymer $\mathbf{P_{2a}}$ and intermediate $\mathbf{M_{2a}}$.

Under the feasible condition, dicarboxylic acids **1**−**4** were reacted with multihydroxyl primary amines **5** or **6** to form a dominant amide intermediate regarded as the new AB_x type monomers, which contains one carboxyl and two or three hydroxyls. Without isolation, the AB_x monomers was subjected to further polycondensation after DMF was distilled off. As a typical example, the intermediate $\mathbf{M_{2a}}$ was produced at the first step of the polymerization of dicarboxylic acid **2** and THAM in the presence of DMF at 60 °C. Then, DMF was distilled off and the self-polycondensation of the $\mathbf{M_{2a}}$ occurred when the temperature was risen to 110 °C. The water formed during the reaction was flushed and removed with streaming nitrogen to promote the polycondensation. The intermediate $\mathbf{M_{2a}}$ was characterized by FTIR and NMR spectra shown in Figure 2 and Figure 3, respectively.

The conditions and results of the polycondenstations of other carboxylic acids and two multihydroxylamines are summarized in Table 1. The direct thermal polycondensations of their intermediates were carried out at 110−120 °C under flushed nitrogen for 9−48 h, yielding transparent glasslike solid products except $\mathbf{P_{2b}}$ and $\mathbf{P_{3a}}$ (transparent slightly soft) and $\mathbf{P_{3b}}$ (transparent dope). The reaction temperature was controlled above 100 °C to boil the water formed away and below 130 °C to avoid a possible etherifying reaction. For polymer $\mathbf{P_{4a}}$ and $\mathbf{P_{4b}}$, the reaction temperature was higher than that of the other polymer because of the higher melting point and the lower reactivity of their intermediates.

Long reaction time is in principle favorable for high molecular weight so the reaction was not stopped until the mechanical stirring became very difficult due to the high viscosity of the polymers. The reaction time of series AEPO (polymer $\mathbf{P_{1-4b}}$) was longer than series THAM (corresponding polymer $\mathbf{P_{1-4a}}$) as the literature reported.[29] In addition, we found that the diacids and multihydroxylamines reaction system more readily to forms cross-linking than the anhydride and multihydroxylamine system because the $\mathbf{A_2B_{x-1}}$ (Scheme 2) intermediate may lead to the cyclization and increases the possibility of cross-linking as mentioned above. Therefore, the controlling of reaction conditions is of major importance in the present work.

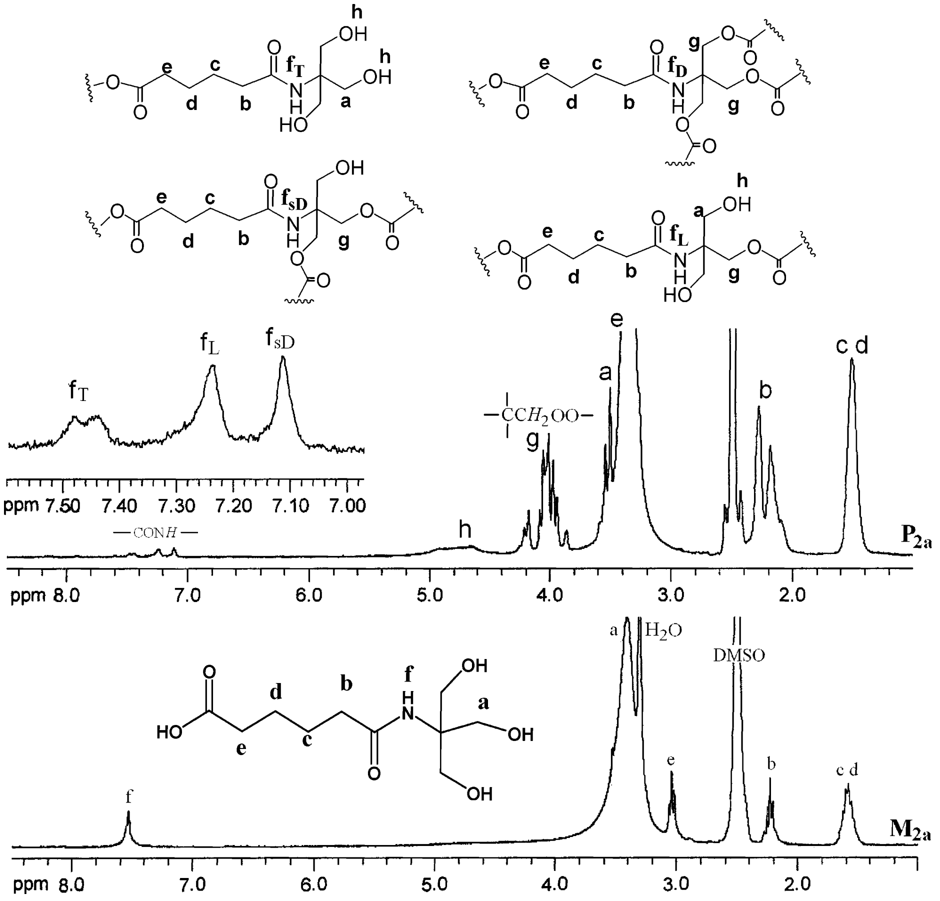


Figure 3. ^{1}H NMR spectra of polymer $\mathbf{P_{2a}}$ and intermediate $\mathbf{M_{2a}}$.

Table 1. Reaction Conditions and Results of AA′ and CB$_x$ Monomers

									solubility		
polymer	temp (°C)	time[a] (h)	DB	η_{inh} [b] (dL/g)	$\bar{M}_w$ [c] (kDa)	PDI[c]	T_g[d] (°C)	$T_d^{10\%}$ (°C)[e]	DMAc	THF	EtOH
$\mathbf{P_{1a}}$	80	48	0.52	0.17	9.28	2.18	37.5	233.8	++	−	−
	110	26									
$\mathbf{P_{2a}}$	60	14	0.38	0.26	11.63	2.36	19.7	301.0	++	−	+−
	110	9									
$\mathbf{P_{3a}}$	60	20	0.42	0.20	10.02	2.28	7.5	333.2	++	+−	+−
	110	16									
$\mathbf{P_{4a}}$	60	24	0.38	0.14	12.02	2.08	51.1	311.0	++	+−	−
	120	48									
$\mathbf{P_{1b}}$	80	10	0.55	0.20	34.84	3.37	23.0	272.6	++	++	++
	110	29									
$\mathbf{P_{2b}}$	70	12	0.53	0.23	6.50	1.96	1.5	278.2	++	++	++
	110	39									
$\mathbf{P_{3b}}$	60	11	0.62	0.24	8.24	2.11	−2.3	366.1	++	−	−
	110	46									
$\mathbf{P_{4b}}$	60	18	0.62	0.07	4.11	1.45	53.2	281.3	++	++	−
	120	46									

[a] Including the time of the applied vacuum. [b] Measured at 25 °C with $c = 0.5$ g/dL in DMAc. [c] The molecular weight was measured by GPC with DMF containing 0.05M LiBr. [d] DSC measurements with a heating rate of 10 °C/min in nitrogen. [e] TGA measurements with a heating rate of 20 °C/min in nitrogen.

Polymer Characterization. The characterizations of hyperbranched poly(ester-aminde)s were accomplished by a combination of techniques including FTIR, ^{1}H NMR, ^{13}C NMR, MALDI-TOF MS, SEC, DSC, and TGA. FTIR spectroscopy provided evidence for the chemical structure of the polymers, showing characteristic amide carbonyl absorptions at 1644−1669 cm^{-1}, the bend vibration of N−H at 1537−1573 cm^{-1}, and ester carbonyl at 1724−1741 cm^{-1} for all the hyperbranched poly(ester-amide)s. For polymer $\mathbf{P_{4a}}$ and $\mathbf{P_{4b}}$, the characteristic absorptions of aromatic ring are at 1612, 1507, and 1461 cm^{-1}. As a typical example, the FTIR spectrum of polymer $\mathbf{P_{2a}}$ is illustrated in Figure 2.

The degree of branching (DB) of these hyperbranched polymers could be determined by the ^{1}H, ^{13}C, and DEPT135 NMR spectra shown in Figures 3 and 4 for polymer $\mathbf{P_{2a}}$ as a typical example. In the ^{1}H NMR spectra of polymer $\mathbf{P_{2a}}$, it is clear that there are three groups of peaks (7.44, 7.24, 7.11 ppm) attributed to the proton of amide, suggesting several kinds of structural units in the polymer chain. In fact, four different subunits are possible in each of the polymers $\mathbf{P_{1a-4a}}$: terminal (T), linear (L), semidendritic (sD), and perfect dendritic (D) (shown in Figure 3 for $\mathbf{P_{2a}}$). Similar to the case of the paper reported,[29] the signal peaks at 7.44, 7.24, and 7.11 ppm should be assigned to the amide proton of the terminal, linear, and

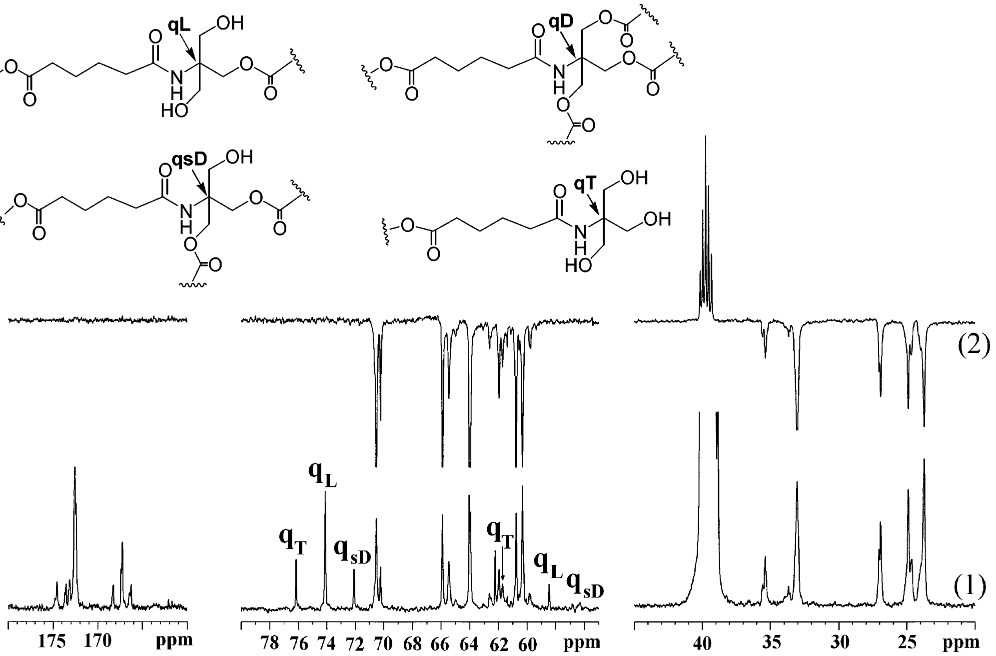


Figure 4. ^{13}C NMR spectra of polymer $\mathbf{P_{2a}}$: (1) inverse-gated decoupling spectrum; (2) DEPT-135 spectrum, the CH_2 resonances are directed below the baseline.

semidendritic units, respectively. Therefore, the DB of $\mathbf{P_{2a}}$ was 0.40, calculated from the integration of the proton attributed to each unit with Frey's DB definition for hyperbranched polymer made from AB_3 monomers.[32] Dendritic units were not observed, which may be due to the fact that the hindrance of the molecular chain restrains the third hydroxyl group from reacting with semidendritic units to form dendritic units.

To obtain further confidence in the result from ^1H NMR spectra, the ^{13}C NMR experiments of $\mathbf{P_{2a}}$ were also conducted. Comparing ^{13}C NMR with the DEPT spectrum of $\mathbf{P_{2a}}$, it was found that two groups of symmetrical signals disappeared in the DEPT 135 NMR spectrum, one is 76.16, 74.10, and 72.10 ppm, the other is 62.14, 58.46, and 56.30 ppm. These signals should be assigned to the quarter carbons of the polymer.[33] The chemical shift of the quarter carbon showed two kinds of symmetrical signals, possibly corresponding to two kinds of configuration isomeric units in the polymer. The signals at 76.16, 74.10, and 72.10 ppm should be attributed to the quarter carbon of semidendritic, linear, and terminal fraction, respectively. The DB of $\mathbf{P_{2a}}$ was 0.37 calculated from the integration of the quarter carbon attributed to each unit with the Frey's equation mentioned above. The result is in agreement with that calculated from ^1H NMR. The DB of polymer $\mathbf{P_{2a}}$ listed in Table 1 was the average value of the two values obtained from ^1H NMR and ^{13}C NMR.

The ^{13}C NMR and DEPT spectra of polymers $\mathbf{P_{3a}}$ and $\mathbf{P_{4a}}$ shown as Figure 5 and **6** display homologous results. The DBs of $\mathbf{P_{1a}}$, $\mathbf{P_{3a}}$, and $\mathbf{P_{4a}}$ calculated with the similar method were also listed in Table 1. Likewise, the DB of $\mathbf{P_{1b-4b}}$ could be determined by the ^{13}C NMR of corresponding polymer using Fréchet's definition[34] of DB for the hyperbranched polymers from potential AB_2 type monomers (DB = (D + T)/(D + T + L)). As a typical example, the ^{13}C NMR and DEPT spectra of polymer $\mathbf{P_{2b}}$ are shown as Figure 7.

Intramolecular cyclization reactions have been well recognized in polycondensation for synthesizing linear and hyperbranched aliphatic polyester.[35,36] It was also found that the occurrence of cyclization reactions depend strongly on the monomer structure,[37−39] and the extent of cyclization may depend on the synthetic techniques and would affect the property of endproduct. Some researches indicated that the existence of cyclization reactions was very important for the successful syntheses of hyperbranched polymers from A_2- and B_3-type monomers. The internal cyclizations during polymerizations greatly reduce the danger of gelation (gel point is shifted), still allowing a rather high molar mass in the $A_2 + B_3$ approach.[37−39] Therefore, it is necessary to investigate the cyclization reactions during polymerization within these approaches. However, it is noteworthy that intramolecular cyclization reactions and cyclic products are hardly confirmed by spectroscopic techniques such as FTIR and NMR because the ester bond in the cycle is similar to those formed upon intermolecular polymerization.

Fortunately, MALDI-TOF MS can be used for direct analysis of the extent of cyclization at each degree of polymerization in addition to polymer molecular weights, molecular weight distributions, and chemical composition, including end group identity and functionality type distribution.[27,40−41] It has been found that molecular weights provided by MALDI-TOF MS agree with the ones by conventional techniques only in the case of samples with narrow molecular weight distributions, whereas with polydisperse polymers MALDI-TOF MS fails to yield reliable molecular weight values and can only detect a low-molecular-weight fraction.[42,43] However, because cycles present mainly in this fraction, MALDI-TOF MS is a useful tool to determine whether cycles have been formed during the polymerization.[36,44]

To gain insight into the polycondensation of diacids (A_2) and multihydroxylamines and compare the method "$A_2 + CB_x$" with "$AA' + CB_x$",[29] MALDI-TOF MS has been recorded. The polymerization of the intermediate leads to the formation of D_nA_m reaction products, where D corresponds to anhydride or diacid and A is THAM. The molecular mass is calculated by

$$M(D_nA_m) = n(M_D - 18) + m(M_A - 18) + M_{end} \qquad (1)$$

where M_D = 118 Da is the molecular mass of succinic acid, M_A = 121 Da is the molecular mass of THAM, and M_{end} = 18 Da is the mass of a water end group.[44c] Several series of structurally related homologous oligomers can be discerned from

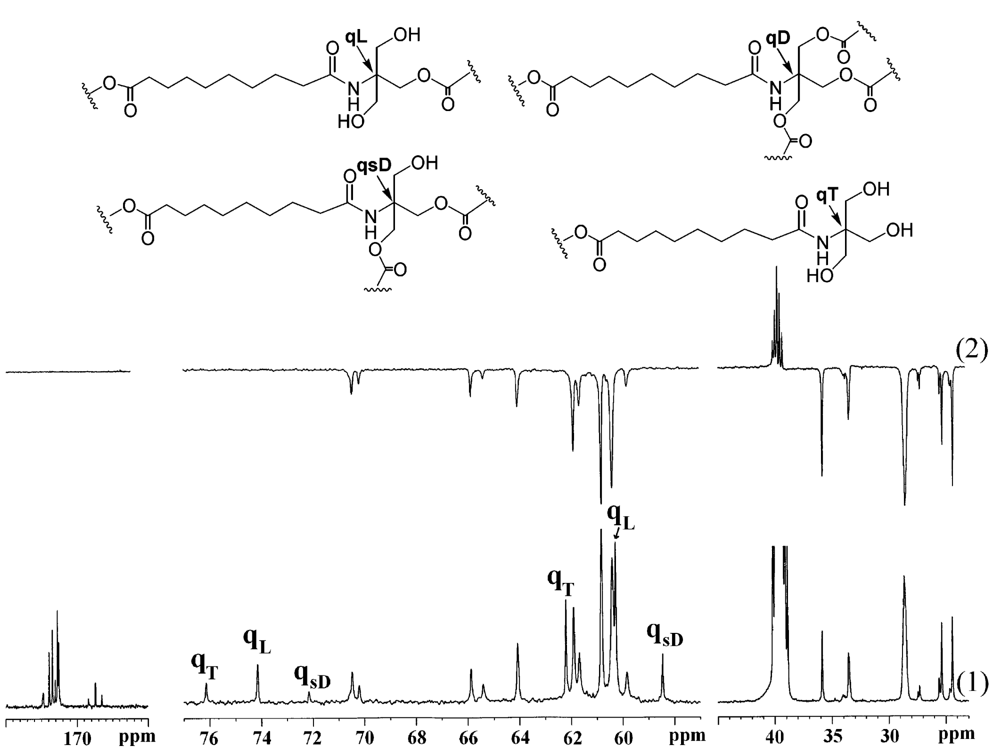


Figure 5. ^{13}C NMR spectra of polymer $\mathbf{P_{3a}}$: (1) inverse-gated decoupling spectrum; (2) DEPT-135 spectrum, the CH_2 resonances are directed below the baseline.

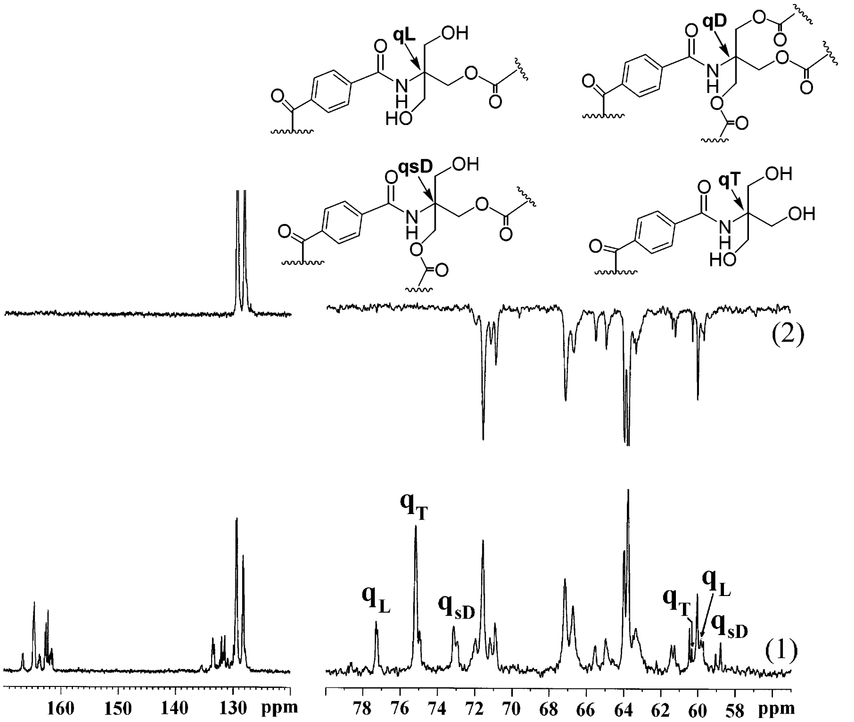


Figure 6. ^{13}C NMR spectra of polymer $\mathbf{P_{4a}}$: (1) inverse-gated decoupling spectrum; (2) DEPT-135 spectrum, the CH_2 resonances are directed below the baseline.

the MALDI-TOF MS (Figure 8). The labeled peaks at *m/z* 628, 731, 831, 931, and so forth are associated with the cationized products D_nA_m $[M + H]^+$. The second series of peaks at *m/z* 610, 713, 813, 913, and so forth is assigned to $[M + H]^+$ $D_nA_m-H_2O$ oligomers. Other peaks are assigned as shown in Figure 8. The cyclization products are evident to be ions that are 18 *m/z* units smaller than the mass of each main ion, owing to the loss of one H_2O (from one A plus B chain ends or from one B plus B) (Scheme 4). Similarly, a series of very weak peaks which are 36 *m/z* units smaller correspond to $[M + H]^+$ $D_nA_m-2H_2O$. As the method reported,[36] the rate of water loss can be calculated. As to $\mathbf{P'_{1a-4h}}$, the peak ratios of $D_nA_m-H_2O$ and $D_nA_m-2H_2O$ to D_nA_m were 39−42% and 5% (the percent values named as $\mathbf{A_1}$% and $\mathbf{A_2}$%), respectively.

Thus, does the loss of H_2O take place during the synthesis or the mass spectral ionization? It has been[37c] reported that, for hyperbranched poly(ester-amide)s, some end-groups prepared from hexahydrophthalic anhydride and diisopropanolamine are lost in syntheses and others are lost by in-source decay (ISD) upon MALDI-TOF MS. However, we can give evidence that

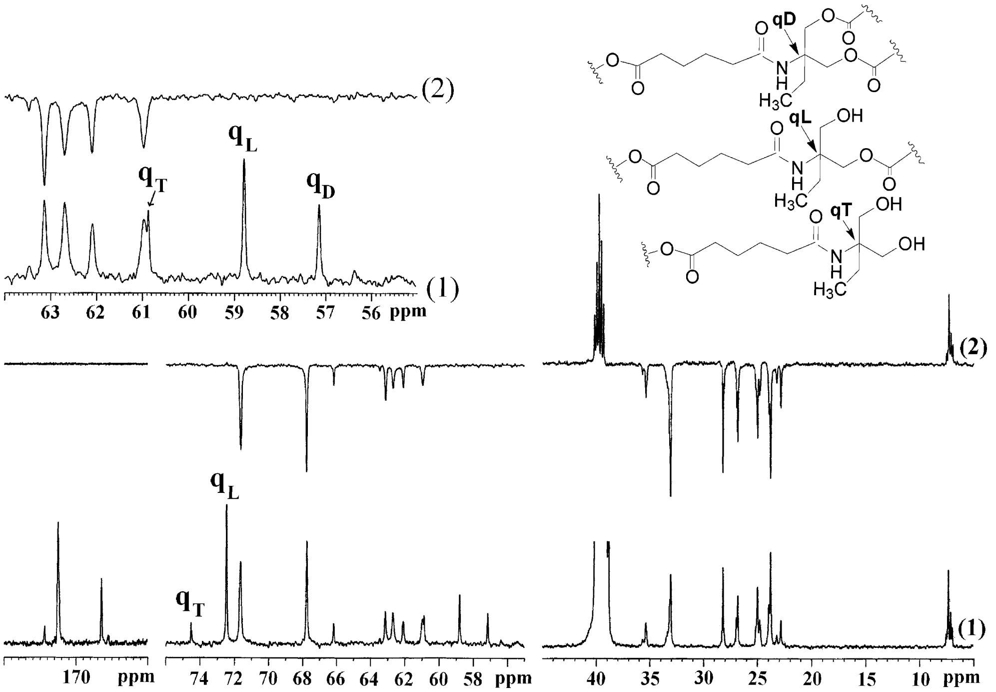


Figure 7. ^{13}C NMR spectra of polymer $\mathbf{P_{2b}}$: (1) inverse-gated decoupling spectrum; (2) DEPT-135 spectrum, the CH_2 and CH_3 resonances are directed below the baseline and above the baseline, respectively.

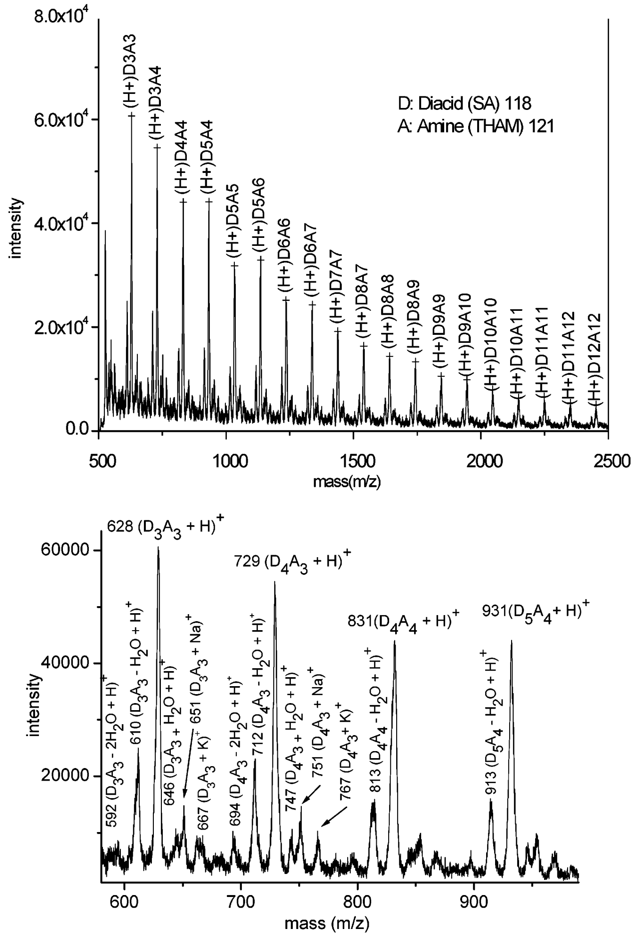
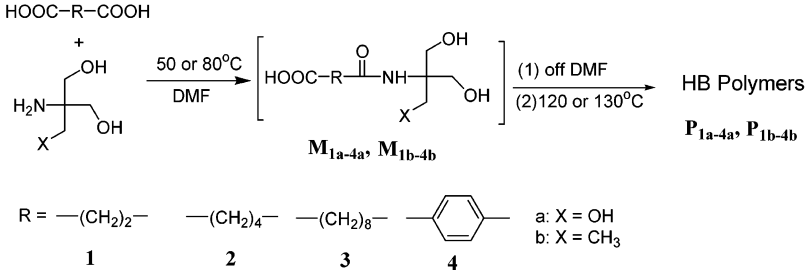


Figure 8. MALDI-TOF MS spectra of the polymer $\mathbf{P'_{1a-4h}}$ obtained from the polycondensation of succinic anhydride and THAM at 120 °C for 4 h.

the loss of H_2O leading to the cyclization of the hyperbranched poly(ester-amide)s occurs during polymerization rather than caused by mass spectral ionization. As shown in Figure 8, a series of peaks at m/z 646, 749, 849, and 949 etc is assigned to the ions, $[M + H]^+$ $D_nA_m + H_2O$ in which H_2O may combine with the oligomers D_nA_m by interaction of H-bonding. This demonstrates that, during the ionization of mass spectra, H-bonding cannot be destroyed, which is more for the carbon—oxygen covalent bond with higher energy, which suggests that the loss of H_2O is not caused by mass spectral ionization but occurs during the cyclization of the hyperbranched poly(ester-amide)s. Moreover, the extent of cyclization depends on the reaction conditions. The MALDI-TOF MS (Figure 9) of hyperbranched polymer ($\mathbf{P'_{1a-6h}}$) obtained from the polycondensation of succinic anhydride and THAM at 120 °C for 6 h shows that the oligomers with mass below 1000 disappear and the ion peaks of $[M + H]^+$ $D_nA_m-2H_2O$ are present. The $\mathbf{A_1}$% and $\mathbf{A_2}$% increased to 53% and 15%, respectively. The MALDI-TOF MS (Figure 10) of polymer $\mathbf{P_{1a-10h}}$ prepared from succinic acid and THAM at 110 °C for 10 h also includes the peaks corresponding to H^+, Na^+, and K^+-cationized oligomers, while the extent of the cyclization ($\mathbf{A_1}\% = 44\%$, $\mathbf{A_2}\% = 8\%$) is less than polymer $\mathbf{P'_{1a-6h}}$, even comparable to polymer $\mathbf{P'_{1a-4h}}$, although with longer reaction time. This suggests again that cyclization occurs in the synthesis because the extent of the cyclization is influenced by the reaction conditions and synthesis methods. It increases with the reaction time and molecular weight, which is due to the increase of the density of the end groups. The degree of cyclization during the polymerization of A_2- and CB_x-type monomers is relatively smaller than that of $AA' + CB_x$ because, in the former case, the probability of formation of B_{2x} (Scheme 2) core is larger. This is in good agreement with the result reported before.[44a]

There have been reported that, for the polymerizations of some AB_x monomers, the cyclic species might be formed through the intermolecular reactions of hyperbranched molecules besides the intramolecular cyclization.[32] However, for the polycondensation of flexible multihydroxyl acids (AB_x monomer), only intramolecular cyclizations could be observed. At high temperature, etherification as a side reaction will also take place beside the esterification reaction. Therefore, cyclization

Scheme 4. Synthesis of Hyperbranched Poly(ester-amide)s from Diacids and Multihydroxyl Amines



species could be formed via intramolecular esterification or etherification reaction. If intramolecular esterification and etherification reactions both occur in single hyperbranched molecules, multi-ringed species will be yielded. On the other hand, intermolecular etherifications will produce some greater mass molecules containing more than one A group (acids) and multi-B group (hydroxys). More than one intramolecular esterification reaction will take place for the high-molecular-weight species formed, also yielding some multi-ringed species. For some polymerizations of A_2 or AA′ and CB_x type monomers, similar things will also take place. Therefore, in our present system, the ion peaks of $[M + H]^+$ $D_nA_m-H_2O$ could be assigned to the cyclic species from intramolecular cyclization of D_nA_m (ester bond formed by condensation reaction of an A and a B group), and $[M + H]^+$ $D_nA_m-2H_2O$ could be assigned to those from intermolecular cyclization of $D_{n-x}A_{m-y}$ and D_xA_y or intramolecular cyclization $D_nA_m-H_2O$ by reaction between B groups, further losing one water molecule and forming an ether bond, nevertheless, the possibility of the latter case was rarer.

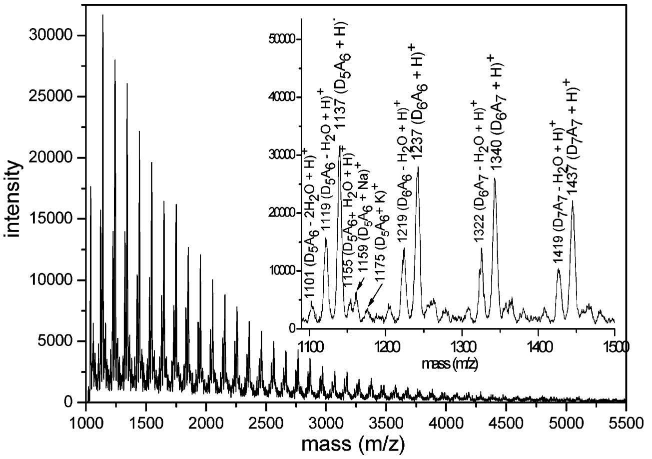


Figure 9. MALDI-TOF MS spectra of the polymer P'_{1a-6h} obtained from the polycondensation of succinic anhydride and THAM at 120 °C for 6 h.

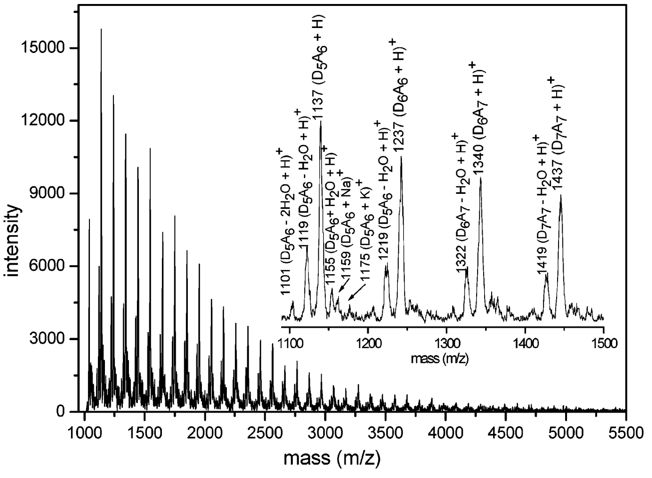


Figure 10. MALDI-TOF MS spectra of the polymer P_{1a-10h} obtained from the polycondensation of succinic acid and THAM at 110 °C for 10 h.

Table 1 lists the $\bar{M}_w$ and polydispersity index (PDI) of the resulted polymers by SEC analysis. 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.[34,45−46] On the other hand, the interactions of the polar end group with solvent are stronger, which overestimates the true value of molecular weight. But for a hyperbranched polymer containing a long linear aliphatic chain, these two effects maybe weaken and the determined result may be close to true value. Moreover, the hyperbranched polymers exhibited moderate molecular weights with broad molecular weight distributions and relatively low inherent viscosities (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.[7a]

The thermal and soluble properties of the hyperbranched polymers obtained are also listed in Table 1. The higher T_g of the polymer $\mathbf{P_{4a}}$ and $\mathbf{P_{4b}}$ in comparison with other polymers can be attributed to hindered segmental rotation and greater rigidity resulted from the existence of benzene ring. While the T_g of $\mathbf{P_{2a-3a}}$ and $\mathbf{P_{2b-3b}}$ were lower because they contain a more flexible alkyl backbone. The T_g of the polymer also depends on the density of the chain end groups. The T_gs of polymer (series a) prepared from THAM are higher than those of corresponding polymers (series b) from AEPO because the stronger H-bonding resulted from more hydroxyl groups. The temperatures of 10% mass loss (T_d^{10}) of all the hyperbranched polymers are higher than 233 °C. All of the hyperbranched poly(ester-amide)s are soluble in polar solvents such as DMAc and DMSO, and some have good solubility in THF and ethanol.

Conclusions

A series of novel long-chain aliphatic or semiaromatic hyperbranched poly(ester-amide)s with a terminal hydroxyl group was successfully prepared by in situ polycondensation of the intermediates, which were obtained from the reaction of dicarboxylic acids with multihydroxyl primary amines in DMF. By carefully controlling reaction conditions at the initial stage of polycondensation, primary amino groups react with one carboxylic group, forming dominant dimers, which can be regarded as new AB_x type monomers. Further self-polycondensations of the intermediates result in novel hyperbranched poly(ester-amide)s. Cyclization side reactions occur in the polymerization, and the extent of the cyclization is influenced by the reaction conditions and synthesis methods. The DBs of the hyperbranched poly(ester-amide)s range from 0.38 to 0.62. All of the polymers display moderate molecular weights with broad distributions and low inherent viscosity and good solubility in polar solvent. The inherent viscosity of the polymers increases with the length of the alkyl chain. The temperatures of 10 wt % mass loss (T_d^{10}) are above 233 °C, and T_gs are in the range of −2.3 to 53.2 °C, depending on the structure of the monomers used.

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