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Facile Syntheses and Characterization of Hyperbranched Poly(ester−amide)s from Commercially Available Aliphatic Carboxylic Anhydride and Multihydroxyl Primary Amine

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ABSTRACT: A new method for synthesis of novel hyperbranched poly(ester−amide)s from commercially available AA′ and CB_x type monomers has been developed on the basis of a series of model reactions. The hyperbranched poly(ester−amide)s with multihydroxyl end groups are prepared by thermal polycondensation of carboxyl anhydrides (AA′) and multihydroxyl primary amine (CB_x) without any catalyst and solvent. The reaction mechanism in the initial stage of polymerization was investigated with in situ ^{1}H NMR. In the initial stage of the reaction, primary amino groups of 2-amino-2-ethyl-1,3-propanediol (AEPO) or tris(hydroxymethyl)aminomethane (THAM) react rapidly with anhydride, forming an intermediate which can be considered as a new AB_x type monomer. Further self-polycondensation reactions of the AB_x molecules produce hyperbranched polymers. Analysis using ^{1} H and ^{13}C NMR spectroscopy revealed the degree of branching of the resulting polymers ranging from 0.36 to 0.55. These hyperbranched poly(ester−amide)s contain configurational isomers observed by ^{13}C and DEPT ^{13}C NMR spectroscopy, possess high molecular weights with broad distributions and display glass-transition temperatures (T_gs) between 7 and 96 °C. The thermogravimetric analytic measurements revealed the decomposition temperature at 10% weight-loss temperatures ($T_d^{10\%}$) ranging from 212 to 325 °C. Among the hyperbranched poly(ester−amide)s obtained, the polymers with cyclohexyl molecular skeleton structure exhibit the lowest branching degree, the highest glass-transition temperatures, and the best thermal stability.

Introduction

Highly branched three-dimensional macromolecules such as dendrimers[1] and hyperbranched[2] have recently attracted a great deal of attention due to the wide applicability to novel macromolecular architecture and functional polymers such as using as coating additives, drug and gene deliveries,[3,4] electroactive and photochemical molecular devices,[2c,h−k] conductive materials,[5] catalysts,[1k] nanomaterials,[6] and so forth. Hyperbranched polymers have been generally recognized as the economically more feasible counterparts of the monodisperse dendrimers since they can be manufactured more quickly and easily in a single step via a one-pot self-polycondensation of AB_x type monomers,[5] yet they maintain many of the architectural features and properties found in their well-defined dendrimer counterparts,[1a,2f,7] which are built up by tedious stepwise synthetic sequences.[1,8−11] Despite the numerous recent developments in the field of hyperbranched polymers, the main challenge, however, lies in the development of synthetic strategies that permit to prepare hyperbranched polymers on the basis of readily available commercial monomers. That is most AB_x monomers are not always commercially available and access to them sometimes involves in monotonic multistep organic synthesis and is limited to several types, which results in difficulties of preparation on a large scale for industrial applications. Consequently, it is very important to develop new routes to prepare hyperbranched polymers. Fréchet,[12] Kakimoto,[13−14] Long,[15] and Okamoto[16] groups independently developed an approach to prepare hyperbranched polymers from A_2 and B_3 type monomers. Recently, Yan,[17] Liu,[18] and Shu[19] et al. reported a new $A_2 + BB'_2$ approach for the synthesis of hyperbranched copoly(sulfone−amine)s, polyimides, poly(amide−imide), respectively, and van Benthem et al. reported the synthesis and the coating applications of hyperbranched poly(ester−amide)s via a $AA' + CB_2$. [20,3e] More recently, Yan and co-workers have developed another two novel routes $A_2 + CB_n$ (In fact, it should be called $AA' + CB_n$ because the isocyanates selected display large reactivity difference (k_1/k_2: 10−100) between two functional groups toward hydroxyl groups[21]) and $AB + CD_n$ for the synthesis of hyperbranched polymers with alternating ureido and urethano units[22] and water-soluble degradable hyperbranched polyesters,[23] respectively. The two approaches could avoid rising gelation.

The monomers involved in the approaches mentioned above are limited especially for synthesizing hyperbranched poly(ester−amide)s containing both ester groups and peptide links, which make them more potentially useful. There is little research on the synthesis of hyperbranched poly(ester−imide)s from commercial monomers except the synthesis of hyperbranched poly(ester−amide)s from carboxylic anhydrides and secondary amine with two hydroxyls by van Benthem and co-workers[3e,20] To our best knowledge, the prparation of hyperbranched poly(ester−amide)s from primary amines with hydroxyls and carboxylic anhydrides has not yet been reported. It may be due to the fact that this case will be prone to forming an imide structure with only B end groups. In this paper, we report the synthesis of new hyperbranched poly(ester−amide)s from a commercially available AA′ type difunc-

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tional monomer, carboxylic anhydride, with a CB$_x$ type tri- or tetrafunctional monomer, primary amine with two or three hydroxyls, based on a series of model reactions. The amino group (C) is more reactive than the hydroxyl (B) toward the carboxylic anhydride. At the initial stage of the polycondensation, the rapid reaction between C and A′ groups results in the formation of the dominant amide intermediate containing A group which is lower reactive to C than that of A′ group. The intermediate can be regarded as a new AB$_x$ type monomer, which contains one carboxyl and two or three hydroxyls. Without isolation, the AB$_x$ intermediate was subjected to further polycondesation without any catalyst.

Experimental Section

Materials. Glutaric anhydride (GA), *cis*-1,2-cyclohexanedicarboxylic anhydride (CHA), diglycolic anhydride (DGA), tris(hydroxymethyl)aminomethane (THAM), and 2-amino-2-ethyl-1,3-propanediol (AEPO) were purchased from ACROS and purified by vacuum distillation before use. Succinic anhydride (SA) was purchased from the domestic market and purified by vacuum sublimation before use. *tert*-Butylamine was bought from ACROS purified by distillation before use. Aniline and cyclohexylamine purchased from the domestic market were purified by vacuum distillation before use. *N,N*-Dimethylacetamide (DMAc), dimethylformamide (DMF), and triethylamine were distilled from calcium hydride under reduced pressure. The 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 the standard, respectively. FTIR spectra were obtained on a Bio-Rad FTS-135 spectrophotometer as thin films on KBr plates. Glass transition temperatures (T_g) were measured by differential scanning calorimetry (DSC) on a Perkin-Elmer Pyris 1 differential scanning calorimeter with the heating rates at 10 °C/min from −60 to +200 °C, and the T_g was taken as the midpoint of the inflection tangent, upon the third or subsequent heating scan. Thermogravimetric analyses were conducted on a Perkin-Elmer Pyris 1 thermogravimetric analyzer at a heating rate of 20 °C/min under nitrogen. HPLC were obtained on a Waters 1525 binary HPLC pump and 2487 dual λ absorbance detector with a Symmetry C$_{18}$ 5 μm 4.6 × 150 mm column as immobile phase and methanol as mobile phase. Gel permeation chromatography (GPC) was performed with a Waters 1525 fitted with two columns (Styragel HT3 and HT4 DMF or HT3 and HT4 THF 7.8 × 300 mm column) connected in series and 2414 refractive index detector with TEDIA dimethylformamide (DMF) containing 0.05 M LiBr or THF as mobile phase. The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 25 °C.

Model Reaction. To a cool solution of dicarboxylic anhydride in dry, deoxygenated *N,N*-dimethylacetamide was added an equimolar amount of amine by dropwise. The mixture was stirred for 24 h at room temperature under a slow stream of nitrogen, and then xylene was added (xylene/DMAc = 1:1), and afterward the reaction mixture was refluxed to dehydration for 48 h, with the water being collected in a Dean−Stark trap. After being cooled, the reaction mixture was poured into methanol. The precipitate was isolated by filtration, washed with methanol, and dried in a vacuum, to give imide characterized by FTIR and NMR spectra. The filtrate was poured into water, and the precipitate was isolated by filtration, washed with water, and dried to afford amide acid characterized by HPLC, IR and NMR spectra.

General Polymerization Procedure. 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 dicarboxylic anhydride was added. The reaction vessel was placed into an oil-bath preheated to 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 Poly(GA-AEPO). This was prepared from 6.190 g of GA (0.054 mol) and 6.460 g of AEPO (0.054 mol), yielding 10.69 g (85%) of pale-yellow translucent block solid polymer. FTIR (cm^{-1}, film coating): 3530−3250 (OH, N−H), 2968 (CH$_2$), 1732 (CH$_2$O*CO*), 1667, 1538, 1461 (NH*CO*O). ^{1}H NMR (DMSO-*d*6): δ 7.64, 7.43, 7.13, 6.99 (N*H*COO), 4.28−4.92 (OH), 3.81−4.23(CC*H*$_2$OCO), 3.27−3.60 (CC*H*$_2$OH), 2.29−2.35 (OOCC*H*$_2$CH$_2$CH$_2$CONH), 2.17−2.26 (OOCCH$_2$CH$_2$C*H*$_2$CONH), 1.73−1.77 (OOCCH$_2$C*H*$_2$CH$_2$CONH), 1.42−1.50 (CC*H*$_2$CH$_3$), 0.75−0.79 (CCH$_2$C*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 174.17 (COOH), 171.53, 172.02−172.35, 174.10−174.77 (NH*C*OO), 165.10−165.40, 165.70, 166.09−166.20, 166.44 (CH$_2$O*C*O), 74.60, 74.47, 72.53; 58.86, 57.21,56.44 (*C*(CH$_2$OCO)$_n$(CH$_2$OH)$_{2-n}$), 71.64,67.85, 5.24−66.16, 62.79−63.53, 61.98, 60.91 (C(*C*H$_2$OCO)$_n$(*C*H$_2$OH)$_{2-n}$), 34.80, 32.49 (OOCCH$_2$CH$_2$*C*H$_2$CONH), 28.15, 26.30 (OOC*C*H$_2$CH$_2$CH$_2$CONH), 22.25, 20.00 (OOCCH$_2$*C*H$_2$CH$_2$CONH), 23.28, 20.75 (C*C*H$_2$CH$_3$), 7.321 (CCH$_2$*C*H$_3$).

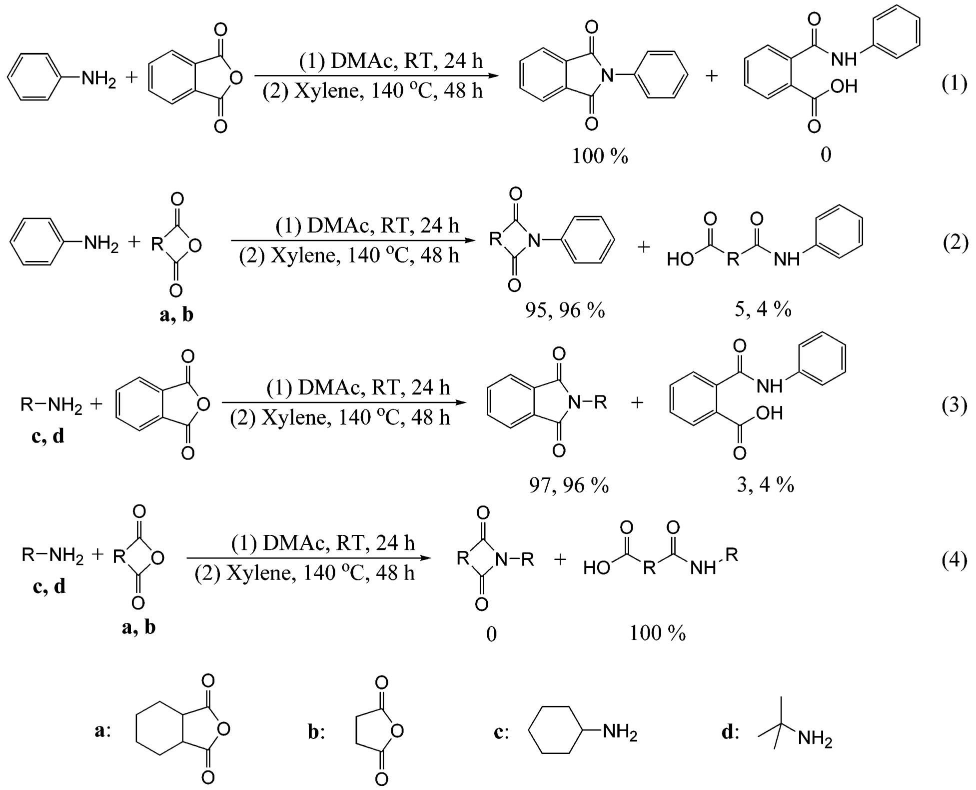
Hyperbranched Poly(SA-AEPO). This was prepared from 5.590 g of SA (0.056 mol) and 6.66 g of AEPO (0.056 mol), yielding 10.77 g (88%) of pale-yellow translucent block solid polymer. FTIR (cm^{-1}, KBr): 3505−3250 (OH, N−H), 2971 (CH$_2$), 1741 (CH$_2$O*CO*), 1668, 1548, 1463 (NH*COO*).^{1}H NMR (DMSO-*d*6): δ 7.52, 7.24, 7.09 (N*H*COO), 4.50−4.88(O*H*) 3.83−4.61 (CC*H*$_2$OCO), 3.05−3.39 (CC*H*$_2$OH), 2.37−2.60 (OOCC*H*$_2$C*H*$_2$CONH), 1.39−1.48 (CC*H*$_2$CH$_3$), 0.73−0.76 (CCH$_2$C*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 179.69, 179.27, 178.91, 177.98 (COOH), 173.57, 172.21, 171.56 (NH*CO*O), 166.49, 165.70, 164.76 (CH$_2$O*CO*), 74.55, 72.47, 72.06; 58.96, 58.62, 57.25 (*C*(CH$_2$OCO)$_n$(CH$_2$OH)$_{2-n}$), 67.81, 66.25, 63.38, 60.96 (C(*C*H$_2$OCO)$_n$(*C*H$_2$OH)$_{2-n}$), 31.79, 30.00, 28.58 (OOCCH$_2$*C*H$_2$CONH), 29.00, 28.12, 28.03 (OOC*C*H$_2$CH$_2$CONH), 23.86, 23.23, 22.50 (C*C*H$_2$CH$_3$), 7.13 (CCH$_2$*C*H$_3$).

Hyperbranched Poly(DGA-AEPO). This was prepared from 8.290 g of DGA (0.071 mol) and 8.510 g of AEPO (0.071 mol), yielding 15.18 g (90%) of orange-yellow translucent block solid polymer. FTIR (cm^{-1}, KBr): 3505−3250 (OH, N−H), 2972 (CH$_2$), 1759 (CH$_2$O*CO*), 1673, 1538, 1462 (NH*COO*).^{1}H NMR (DMSO-*d*$_6$): δ 7.74. 7.36, 7.03, 6.91 (N*H*COO), 4.79−4.95 (OH), 4.06−4.28 (OOCC*H*$_2$OCH$_2$CONH), 3.80−4.00 (OOCCH$_2$OC*H*$_2$CONH), 3.15−3.45 (C(C*H*$_2$OO)$_n$(C*H*$_2$OH)$_{2-n}$), 1.55−1.73 (CC*H*$_2$CH$_3$), 0.60−0.90(CCH$_2$C*H*$_3$).^{13}C NMR (DMSO-*d*$_6$): δ 171.69 (*C*OOH), 169.70, 169.12, 168.5 (CH$_2$O*C*O), 163.52, 163.12, 162.30 (NH*C*OO), 74.85, 72.67, 60.51, 58.75, 57.44 (*C*(CH$_2$OO)$_n$(CH$_2$OH)$_{2-n}$), 72.08, 70.48, 70.09 (OOCCH$_2$O*C*H$_2$CONH), 67.62, 67.25, 65.90 (C*C*H$_2$OCO), 64.66, 64.30, 63.60 (OOC*C*H$_2$OCH$_2$CONH), 61.50, 60.78 (*C*H$_2$OH), 27.97, 23.20 (C*C*H$_2$CH$_3$), 7.56, 7.30, 7.05 (CCH$_2$*C*H$_3$).

Hyperbranched Poly(CHA-AEPO). This was prepared from 9.620 g of CHA (0.062 mol) and 7.430 g of AEPO (0.05 mol), yielding 14.99 g (88%) of light reddish brown (cinnamon) translucent block solid polymer. FTIR (cm^{-1}, KBr): 3500−3250 (OH, N−H), 2937 (CH$_2$), 1737 (CH$_2$O*CO*), 1664, 1527, 1452 (NH*COO*).^{1}H NMR (DMSO-*d*$_6$): δ 7.00−7.50 (N*H*COO), 4.30−5.31 (OH), 3.78−3.96 (C(C*H*$_2$OO)$_n$(C*H*$_2$OH)$_{2-n}$), 2.30−3.33 (group, OOCC*H* and NHOCC*H* (hexamethylene)), 1.68−1.90 (OCCHC*H*$_2$CH$_2$ (hexamethylene) and CC*H*$_2$CH$_3$), 1.02−1.45 (OCCHCH$_2$C*H*$_2$ (hexamethylene)), 0.70−0.99 (CCH$_2$C*H*$_3$). ^{13}C NMR (DMSO-*d*$_6$): δ 181.34, 180.85, 180.05, 179.66 (*C*OOH), 175.78, 173.81, 172.62 (NH*CO*O), 169.33, 168.66, 166.86 (CH$_2$O*CO*), 74.31, 68.48, 57.00, 55.40 (*C*(CH$_2$O)$_n$(CH$_2$OH)$_{2-n}$), 67.81, 66.81, (C*C*H$_2$OCO), 63.19, 58.66 (C*C*H$_2$OH), 45.27, 44.10, 41.66 (*C*HCONH (hexamethylene)), 39.08, 38.88, 37.95 (*C*HCOO (hexamethylene)), 29.04, 28.29, 23.69, 21.637, 21.34, 21.05, 20.47 (group, *C*H$_2$ (hexamethylene)), 24.59 (group, *C*H$_2$CH$_3$), 7.59, 7.43, 7.10 (CH$_2$*C*H$_3$).

Hyperbranched Poly(GA-THAM). This was prepared from 11.410 g of GA (0.1 mol) and 12.114 g of THAM (0.1 mol), yielding 22.60 g (95%) of polymer as water white block solid.

Scheme 1. Model Reactions



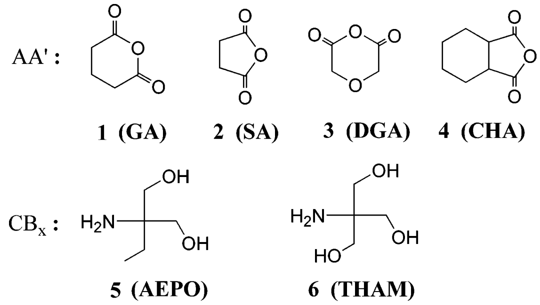
IR ($\mathrm{cm^{-1}}$, KBr): 3550−3250 (OH, N−H), 1739 ($\mathrm{CH_2O}\mathit{CO}$), 1658, 1557, 1462 ($\mathrm{NH}\mathit{COO}$). ^{1}H NMR (DMSO-$d_6$): δ 7.51, 7.26, 7.13 ($\mathrm{N}\mathit{H}\mathrm{COO}$), 4.70−5.20 (OH, broad), 4.00−4.25 ($\mathrm{C(C}\mathit{H}_2\mathrm{O)}_n$-$\mathrm{(CH_2OH)}_{3-n}$) 3.30−3.60 ($\mathrm{C(CH_2O)}_n\mathrm{(C}\mathit{H}_2\mathrm{OH)}_{3-n}$), 2.30−2.37 ($\mathrm{OOCC}\mathit{H}_2\mathrm{CH_2CH_2CONH}$), 2.18−2.28 ($\mathrm{OOCCH_2CH_2C}\mathit{H}_2\mathrm{CONH}$), 1.73−1.75 ($\mathrm{OOCCH_2C}\mathit{H}_2\mathrm{CH_2CONH}$). ^{13}C NMR (DMSO-$d_6$): δ 175.76 ($\mathit{CO}\mathrm{OH}$), 173.16−174.27, ($\mathrm{NH}\mathit{COO}$), 167.19−168.22 ($\mathrm{CH_2O}\mathit{CO}$), 76.98, 74.92, 72.91; 63.30, 60.43, 58.28 ($\mathit{C}\mathrm{(CH_2OO)}_n\mathrm{(CH_2OH)}_{3-n}$), 71.41, 66.75, 64.77, 62.89, 60.69, 59.33 ($\mathrm{C(}\mathit{C}\mathrm{H_2OO)}_n\mathrm{(}\mathit{C}\mathrm{H_2OH)}_{3-n}$), 35.94, 35.60, 34.34, 33.25 ($\mathrm{OOC}\mathit{C}\mathrm{H_2CH_2CH_2CONH}$), 26.70−27.33 (group, $\mathrm{OOCCH_2CH_2}\mathit{C}\mathrm{H_2CONH}$), 22.79, 22.63, 22.49, 21.45 ($\mathrm{OOCCH_2}\mathit{C}\mathrm{H_2CH_2CONH}$).

Hyperbranched Poly(SA-THAM). This was prepared from 10.007 g of SA (0.1 mol) and 12.114 g of TOAM (0.1 mol), yielding 20.89 g (94%) of polymer as water white block solid. FTIR ($\mathrm{cm^{-1}}$, KBr): 3550−3250 (OH, N−H), 1731 ($\mathrm{CH_2O}\mathit{CO}$), 1660, 1567, 1464 ($\mathrm{NH}\mathit{COO}$). ^{1}H NMR (DMSO-$d_6$): δ 7.22−7.77 ($\mathrm{N}\mathit{H}\mathrm{COO}$), 4.57−5.15(OH), 3.97−4.18 ($\mathrm{C(C}\mathit{H}_2\mathrm{O)}_n\mathrm{(CH_2OH)}_{3-n}$), 3.27−3.56 ($\mathrm{C(CH_2O)}_n\mathrm{(C}\mathit{H}_2\mathrm{OH)}_{3-n}$), 2.28−2.56 (group, $\mathrm{OOCC}\mathit{H}_2\mathrm{C}\mathit{H}_2\mathrm{CONH}$). ^{13}C NMR (DMSO-$d_6$): δ 176.13, 175.64, 175.61, 175.51 ($\mathrm{NH}\mathit{COO}$), 173.99, 173.64, 173.29, 173.08 ($\mathrm{CH_2O}\mathit{CO}$), 76.99, 63.12, 61.67, 59.45 ($\mathit{C}\mathrm{(CH_2OO)}_n\mathrm{(CH_2OH)}_{3-n}$), 71.41, 64.77, 61.33, 61.05, 60.24 ($\mathrm{C(}\mathit{C}\mathrm{H_2OO)}_n\mathrm{(}\mathit{C}\mathrm{H_2OH)}_{3-n}$), 32.57, 32.41, 32.10, 31.90 ($\mathrm{OOC}\mathit{C}\mathrm{H_2CH_2CONH}$), 31.30, 30.81, 30.22, 29.41 ($\mathrm{OOCCH_2}\mathit{C}\mathrm{H_2CONH}$).

Hyperbranched Poly(DGA-THAM). This was prepared from 11.607 g of DA (0.1 mol) and 12.114 g of THAM (0.1 mol), yielding 22.29 g (94%) of polymer as water white block solid. FTIR ($\mathrm{cm^{-1}}$, KBr): 3550−3250 (OH, N−H), 1757 ($\mathrm{CH_2O}\mathit{CO}$), 1664, 1542, 1459 ($\mathrm{NH}\mathit{COO}$). ^{1}H NMR (DMSO-$d_6$): δ 7.63. 7.13, 7.06 ($\mathrm{N}\mathit{H}\mathrm{COO}$), 4.57−4.98 (OH), 4.37, 4.35, 4.24, 4.22 ($\mathrm{OOCC}\mathit{H}_2\mathrm{OCH_2CONH}$), 4.00, 3.95, 3.91, 3.86 ($\mathrm{OOCCH_2OC}\mathit{H}_2\mathrm{CONH}$), 3.59, 3.56, 3.47, 3.98 ($\mathrm{C(C}\mathit{H}_2\mathrm{OO)}_n\mathrm{(C}\mathit{H}_2\mathrm{OH)}_{3-n}$). ^{13}C NMR (DMSO-$d_6$): δ 173.97(COOH), 173.05, 172.61, 172.16, 171.77 ($\mathrm{NH}\mathit{COO}$), 169.94−169.61, 169.50, 169.26, 169.03 ($\mathrm{CH_2O}\mathit{CO}$), 76.55, 74.25, 70.34, 61.78, 61.03, 58.48 ($\mathit{C}\mathrm{(CH_2O)}_n\mathrm{(CH_2OH)}_{3-n}$), 72.49, 70.65, 69.51, 69.03 ($\mathrm{OOC}\mathit{C}\mathrm{H_2O}\mathit{C}\mathrm{H_2CONH}$), 67.91, 67.63, 67.30, 67.14 ($\mathrm{OOCCH_2OCH_2}\mathit{C}\mathrm{ONH}$), 63.82, 62.17, 60.18, 59.35 ($\mathrm{C(}\mathit{C}\mathrm{H_2O)}_n\mathrm{(}\mathit{C}\mathrm{H_2OH)}_{3-n}$).

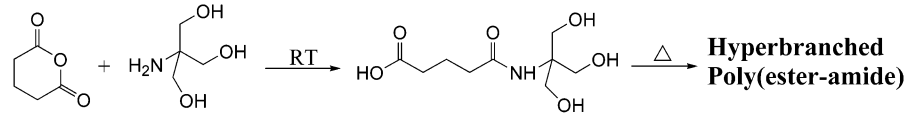
Hyperbranched Poly(CHA-THAM). This was prepared from 15.417 g of HHPA (0.1 mol) and 12.114 g of THAM (0.1 mol), yielding 25.33 g (92%) of polymer as water white block solid. FTIR ($\mathrm{cm^{-1}}$, KBr): 3550−3250 (OH, N−H), 1732 ($\mathrm{CH_2O}\mathit{CO}$), 1652, 1552, 1452 ($\mathrm{NH}\mathit{COO}$). ^{1}H NMR (DMSO-$d_6$): δ 7.32. 7.15, 7.06 ($\mathrm{N}\mathit{H}\mathrm{COO}$), 4.60−4.98 (OH), 4.02 (group, $\mathrm{OOCC}\mathit{H}$ (hexamethylene)), 3.84 (group, $\mathrm{NHOCC}\mathit{H}$ (hexamethylene)), 3.48, 3.40, 3.36, 3.33 ($\mathrm{C(C}\mathit{H}_2\mathrm{OO)}_n\mathrm{(C}\mathit{H}_2\mathrm{OH)}_{3-n}$), 1.93, 1.69, 1.23 (wide, $\mathrm{C}\mathit{H}_2$ (hexamethylene)). ^{13}C NMR (DMSO-d_6): δ 172.86−177.69 ($\mathrm{NH}\mathit{COO}$), 170.06, 169.58, 169.29, 168.75 ($\mathrm{CH_2O}\mathit{CO}$), 75.90, 74.02, 69.38, 62.16, 60.28, 58.49 ($\mathit{C}\mathrm{(CH_2O)}_n$-$\mathrm{(CH_2OH)}_{3-n}$), 70.53, 64.14, 62.10, 60.66, 59.71, 57.37 ($\mathrm{C(}\mathit{C}\mathrm{H_2O)}_n$-$\mathrm{(}\mathit{C}\mathrm{H_2OH)}_{3-n}$), 44.04−46.47 ($\mathit{C}$H (hexamethylene)), 29.67, 29.14, 28.75, 28.37; 24.37−25.34, 23.53, 21.52 ($\mathit{C}\mathrm{H_2}$ (hexamethylene)).

Scheme 2. AA′ and CB$_x$ Type Monomers Used



Synthesis of Model Compound M$_L$. GA (1.31 g, 11.5 mmol) and THAM (1.39 g, 11.5 mmol) were both dissolved in dry dimethylformamide and stirred for 24 h under nitrogen protecting, and then 1.31 of GA and 1.40 g of triethylamine (13.8 mmol) were added. After being stirred for 24 h, the mixture was poured into diethyl ether, forming two layers. The upper layer did not contain product and was removed. The solution lower layer was washed with diethyl ether several times, and dried at room temperature under vacuum and the remaining product was purifed by column chromatography (neutral alumina, hexane/EtOAc as an eluent). The final product was isolated as a clear oil liquid. Yield: 2.60 g (65%). ^{1}H NMR (DMSO-d_6): δ 7.25 ($\mathrm{N}\mathit{H}\mathrm{COO}$), 4.20 ($\mathrm{C(C}\mathit{H}_2\mathrm{OCO)(CH_2OH)_2}$), 3.55−3.90 (OH, broad), 3.40($\mathrm{C(CH_2OCO)(C}\mathit{H}_2\mathrm{OH)_2}$), 2.30($\mathrm{OOCC}\mathit{H}_2\mathrm{CH_2CH_2CONH}$), 2.23 ($\mathrm{HOOCC}\mathit{H}_2\mathrm{CH_2CH_2CONH}$,

Scheme 3. Reactions between GA and THAM



1 **6** **7**

4H), 2.12 ($\mathrm{HOOCCH_2CH_2C}H_2\mathrm{CONH}$), 1.70 ($\mathrm{HOOCCH_2C}H_2\mathrm{CH_2CONH}$, 4H). ^{13}C NMR (DMSO-$d_6$): δ 175.60 ($C\mathrm{OOH}$), 173.25, ($\mathrm{NH}CO\mathrm{O}$), 168.08 ($\mathrm{CH_2O}CO$), 74.97, 61.13, ($C\mathrm{(CH_2OCO)(CH_2OH)_2}$), 62.74 ($\mathrm{C(}C\mathrm{H_2OCO)(CH_2OH)_2}$), 61.13 ($\mathrm{CH_2OH}$), 34.90 ($\mathrm{CH_2OCOCH_2CH_2}C\mathrm{H_2COOH}$), 34.45 ($\mathrm{HOOC}C\mathrm{H_2CH_2CH_2CONH}$), 34.30 ($\mathrm{HOOCCH_2CH_2}C\mathrm{H_2CONH}$), 33.71 ($\mathrm{OCO}C\mathrm{H_2CH_2CH_2COOH}$), 21.79 ($\mathrm{HOOCCH_2}C\mathrm{H_2CH_2CONH}$), 21.01 ($\mathrm{CH_2OCOCH_2}C\mathrm{H_2CH_2COOH}$).

Synthesis of Model Compound $\mathbf{M_D}$. The process of synthesizing $\mathbf{M_D}$ was similar to that of $\mathbf{M_L}$ except that the molar weights of GA and triethylamine were three times those of synthesizing ML. ^{1}H NMR (DMSO-d_6): δ 7.80 ($\mathrm{N}H\mathrm{COO}$), 4.66 ($\mathrm{C}H_2\mathrm{OCO}$), 3.55−3.90 (OH, broad), 3.40 ($\mathrm{C(CH_2OCO)(C}H_2\mathrm{OH)_2}$), 2.30 ($\mathrm{OOCC}H_2\mathrm{CH_2CH_2CONH}$), 2.70 ($\mathrm{OCOC}H_2\mathrm{CH_2CH_2COOH}$, 6H), 2.32 ($\mathrm{HOOCC}H_2\mathrm{CH_2CH_2CONH}$, 8H), 2.19 ($\mathrm{HOOCCH_2CH_2C}H_2\mathrm{CONH}$, 2H), 1.70 ($\mathrm{OCOCH_2C}H_2\mathrm{CH_2COOH}$, 8H).

General Procedure for End-Capping Reactions. End-capping reagents (acetic anhydride or *tert*-butyldimethylsilyl chloride) and triethylamine were added to a solution of hyperbranched poly(ester−amide)s with hydroxyl end groups in dry DMAc. The reaction mixture was then kept at 60 °C for 24 h. After cooling, the reaction mixture was poured into water, and the precipitate was collected and washed several times with water to give the ester-terminated or *tert*-butyldimethylsilyl-terminated hyperbranched poly(ester−amide)s.

Results and Discussion

Monomers Selection. It is well-known that aromatic anhydrides and aromatic amines are prone to forming aromatic imides on the occasion of refluxing or in the presence of dehydrating agent such as acetic anhydride. In the case that one is aromatic, and the other is aliphatic, it is also easy to get imidizational compound.[24] However, few studies have been done for the case where both anhydride and amine are aliphatic. We found that the reactions of aliphatic amines and aliphatic anhydrides usually yield amide acids instead of imide compounds under similar conditions. As Scheme 1 shows, for reaction 1, the amide acid is cyclized completely to form imide. For reactions 2 and 3, the main products are also imides, and only a trace of amide acids can be detected by HPLC and NMR spectroscopy. For reaction 4, only amide acid could be formed. When the reaction mixture of aliphatic amine and aliphatic anhydride was poured into methanol or water and cooled, no precipitate can be found. After the solvent was removed by vacuum distillation, the crude product was analyzed by HPLC and NMR spectroscopy. The imidization compound can never be found, and the crude product was recrystallized with xylene to give the characterized amide acid. On the basis of the series model reaction, we found that it is not easy to cyclize the full aliphatic amide acid into a ring imide; thus, we chose a series of aliphatic carboxylic anhydrides and two primary aliphatic amines as AA′ and CB_x type monomers, respectively, for synthesizing hyperbranched poly(ester−amide)s.

Scheme 2 shows the selected monomers in the AA′ + CB_x approach presented. To access the hyperbranched polymers with ester and amide units, anhydride, hydroxyl, and amino groups are selected as A, B, and C groups, respectively. 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 multihydroxyls may form at the initial stage of the reaction. Further polycondensations of the intermediates as AB_x type monomers would lead to hyperbranched poly(ester−amide)s without gelation, as Scheme 3 showed.

In situ ^{1}H NMR spectra give the evidence of the intermediate formed at the initial stage of the reaction. Figure 1 displays the ^{1}H NMR of the reaction mixture of GA and THAM at 10−120 min at ambient temperature. The intermediate **7** was formed as soon as the mixing of GA and THAM. The proton of CONH could be observed clearly, but two kinds of proton signals (a and c) attributed to an intermediate amide acid, and transformed from the proton CH_2 (a-GA) signal of reacted anhydride shifting to higher field were partly overlaping at 10 min. Signals a and c departed from each other little by little with the reaction time and the splitting could be distinguished apparently until 2 h. Almost no changes could be observed between the spectrum recorded at 2 h and that at 24 h, which indicated that the reaction between GA and THAM finished in 2 h. Moreover, in this process, the B_6 core (Scheme 4) would not form due to the electrophilic reactivity of the carboxylic anhydride group to amino group being much greater than that of the carboxylic group.

Polymer Synthesis. The conditions and results of polymerization from four carboxylic anhydrides and two multihydroxylamines are summarized in Table 1. The direct thermal polycondensations were carried out at

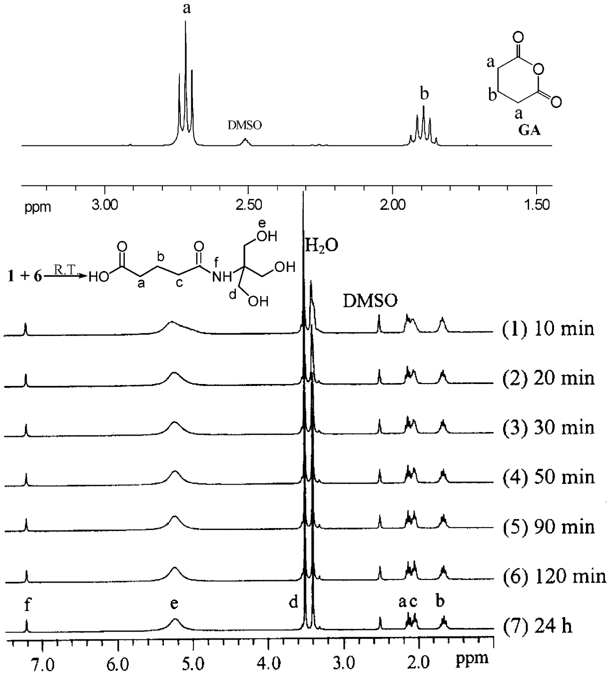


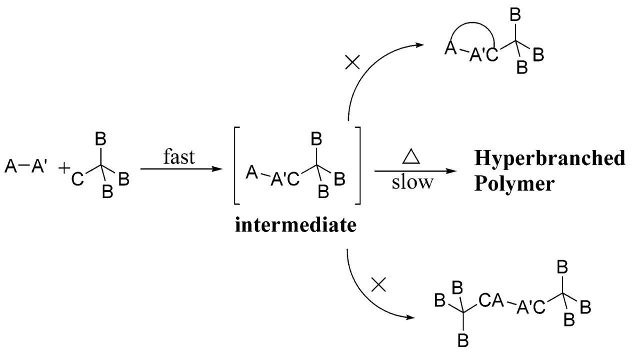
Figure 1. In situ ^{1}H NMR of the reaction system between GA and THAM in DMSO-d_6.

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

code	AA′ (mp, °C)	CB$_x$ (mp, °C)	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
P1	**GA** (52−55)	**AEPO** (35−37)	120	45	0.42	0.168	106.0 (9.24)	3.30 (3.72)	7.2	285.1
P2	**SA** (119−120)		130	45	0.55	0.102	70.3 (3.71)	2.36 (2.19)	34.1	288.8
P3	**DGA** (92−93)		110	18	0.47	0.055	39.4 (2.78)	2.60 (2.45)	38.4	290.3
P4	**CHA** (32−34)		125	29	0.36	0.051	28.9 (11.3)	2.32 (4.19)	61.9	325.2
P5	**GA**	**THAM** (168−172)	110	24	0.48	0.150	56.2	2.85	21.4	260.1
P6	**SA**		120	26	0.52	0.074	78.0	3.08	36.8	281.9
P7	**DGA**		110	6	0.49	0.060	42.5	2.11	34.4	211.7
P8	**CHA**		110	5	0.44	0.079	38.1	2.22	95.6	322.8

[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 0.05 M LiBr or THF as eluent solvent; the data within parentheses were obtained from GPC measurement with THF. [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.

Scheme 4. AA′ + CB$_3$ Approach to Hyperbranched Polymer



110−130 °C under nitrogen flush for 5−45 h, yielding transparent glasslike products. The product was brittle and could be broken into small pieces when cooled with liquid nitrogen. The water formed during the reaction was flushed away and removed with nitrogen to promote the polymerization. The melting polycondensations can be conducted because the decomposition temperatures of the monomers are much higher than their melting temperatures. The melting point of the carboxyl anhydrides and the multihydroxylamines is one of the most important factors considered for the selection of polycondensation condition. To explore the optimum conditions for the polycondensations, two methods for the reaction of GA and THAM were studied. (1) After a 1:1:1 mixture of GA, THAM, and DMF was stirred at 25 °C for 30 min, the reaction temperature was raised to 60 °C, and then DMF was removed under reduced pressure within 30 min. The mixture was kept stirring at 110 °C for 5 h with the nitrogen stream and then under reduced pressure for 30 min. (2) The 1:1 mixture of GA and THAM was melted homogeneously within 10 min when directly placed into an oil bath preheated to 110 °C and stirred for 6 h with the nitrogen stream and then under reduced pressure for 30 min. The reactions were found to proceed smoothly using the two different methods mentioned above, and no difference between the results of polymerizations was observed. Method 2 is simpler than method 1. Therefore, the same pathway as method 2, except that the reaction temperature and time were adjusted according to the polymerization degree, was then employed for the polymerization of other monomers.

The polycondensation reaction temperature was controlled above 110 °C to make the water formed during the reaction boil off completely and below 140 °C to avoid an etherification reaction. For polymers **P2** and **P6**, the reaction temperature was higher than that for other polymer because of the higher melting point of the monomer SA. The progression of molecular weight with reaction time for polymer **P1** was observed by determining the inherent viscosity of periodic samples. As shown in Figure 2, the inherent viscosity increases very slowly in the beginning but increases rapidly at high conversion, which indicates that the kinetics appears to be for a typical polycondensation reaction. Figure 2 also shows that the T_gs of the polymers from SA and THAM slightly increase in line with reaction time. In other words, the molecular weights of the hyperbranched poly(ester−amide)s, like other highly branched polymers,[26] play only a minor role in the glass transition, while the contribution of the end group becomes significant.[27]

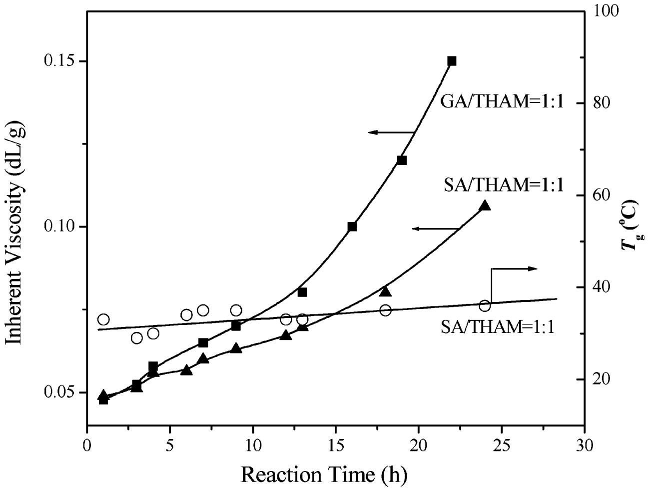


Figure 2. Plots of inherent viscosity and T_g vs polycondensation reaction time.

To further investigate the effect of end groups on the glass transition of the hyperbranched poly(ester−amide)s, some end-capping experiments were carried out. The IR and DSC of hyperbranched poly(SA-THAM) and poly(GA-THAM) with various end groups were shown in Figure 3 and Figure 4, respectively. The T_gs of hyperbranched poly(SA-THAM) and poly(GA-THAM) with hydroxyl end groups were 36.8 and 21.4 °C, respectively, and were reduced to 0.4 and 6.6 °C, respectively, after being modified by *tert*-butyldimethysilyl chloride (conversion was 74 and 87%, respectively, determined by ^{1}H NMR), while the T_g of poly(GA-THAM) changed more drastically, from +21.4 to −22.0 °C, after being modified by acetic anhydride (conversion was ca. 68%). The modified polymers exhibit much lower T_gs than the parent polymers due to both loss of H-bonding of the hydroxyl and the plasticization of the more flexible end groups.[27e,f] These results clearly indicate that the nature of end groups affect consider-

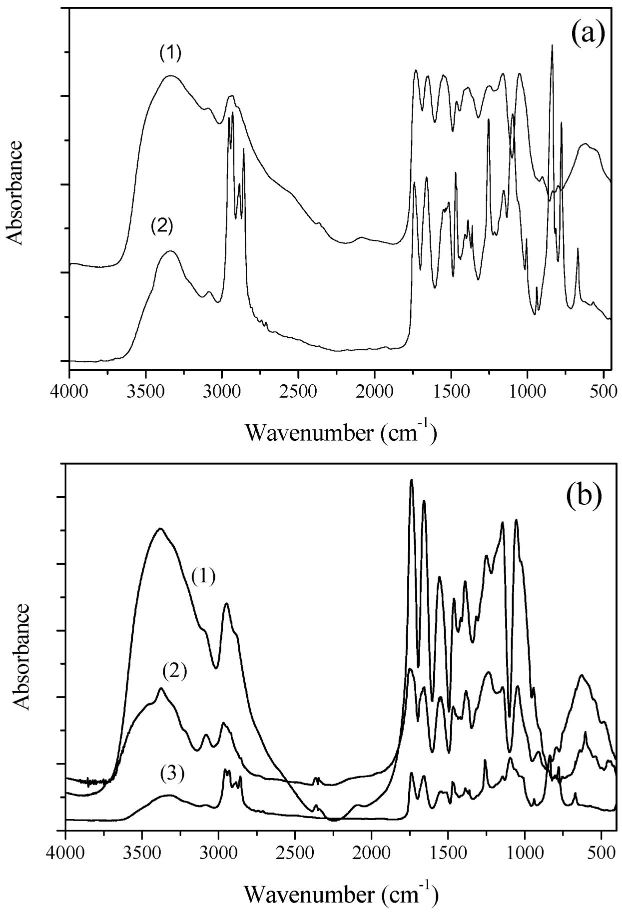


Figure 3. FTIR spectra of hyperbrached poly(ester−amide) with various terminals: (a) poly(SA-THAM)s with hydroxyls (1) and *tert*-butyldimethylsilyl end groups (2); (b) poly(GA-THAM) with hydroxyls (1), acetyl (2), and *tert*-butyldimethylsilyl end groups (3).

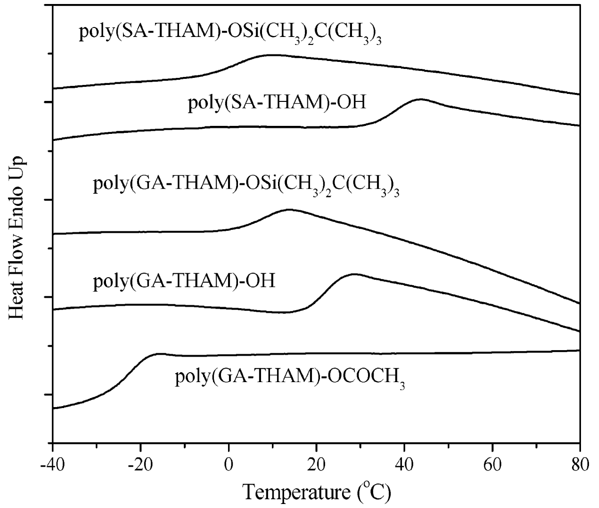


Figure 4. DSC of hyperbrached poly(ester−amide) with various terminals.

ably the glass transition of the hyperbranched poly(ester−amide)s, like other hyperbranched polymers.[26,27]

Polymer **P1** possesses the highest viscosity value, indicating that long reaction time is in principle favorable for a high conversion. The reaction was not stopped until the mechanical stirring was very difficult due to the high viscosity of the polymer. The reaction time of series AEPO (polymer **P1**−**P4**) was longer than series THAM (corresponding polymer **P5**−**P8**) because the melting viscosity of the mixture of anhydride and AEPO was lower than that of anhydride and TEMO. However, it does not mean that the reaction time can be limitless. When DA and AEPO were used to synthesize hyperbranched polymer, for example, if the reaction time was longer than 19 h, the product was a gel and could not dissolve in any solvent.

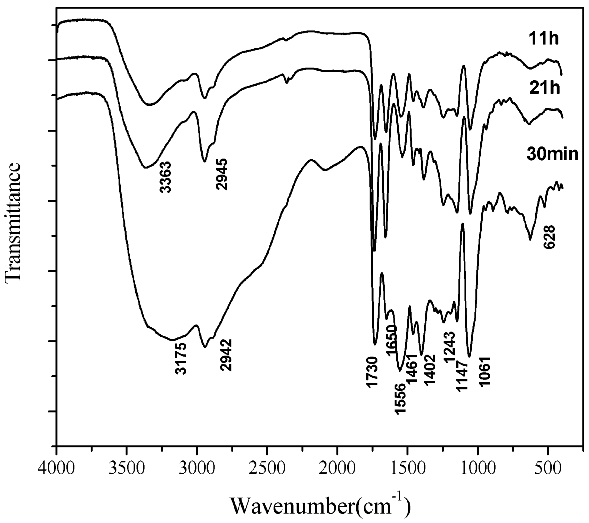


Figure 5. FTIR spectra of the reaction products from GA and THAM with a 1/1 feed ratio.

Structure and Properties of Polymers. The characterizations of the polymers were accomplished by a combination of techniques including FTIR, ^{1}H NMR, ^{13}C NMR, GPC, DSC, and TGA. FTIR spectroscopy provided evidence for the chemical structure of the polymers, showing characteristic amide carbonyl absorptions at 1658−1673 cm^{-1}, the bend vibration of N−H at 1527−1567 cm^{-1}, and ester carbonyl at 1730−1759 cm^{-1} for all the hyperbranched poly(ester−amide)s. A typical example, poly(GA-THAM), is illustrated in Figure 5. The absorption bands of the product obtained from reacting for 30 min have significant difference from those for the 11 h reaction. The absorption bands of hydroxyls and carboxylic groups (2500−3500 cm^{-1}) of the former are broader and stronger, and the absorption bands of the carbonyls of ester (around 1650 cm^{-1}) are weaker than those of the latter. This suggests that the product obtained in 30 min is an oligomer and has a large number of unreacted hydroxyls and carboxylic groups. The FTIR spectrum of the product obtained from reacting for 11 h is nearly similar to that for 21 h, which indicates that the condensation reaction has almost finished within 11 h.

The degree of branching (DB) is one of the most important molecular parameters of hyperbranched polymers since it characterize the difference in molecular structure in comparison with linear analogue. It could be determined by the ^{1}H, ^{13}C, and DEPT135 ^{13}C NMR of the polymer that were shown as Figure 6 and Figure 7 for polymer **P5** as a typical example. Four different subunits are possible in each of the polymers **P5**−**P8** prepared from THAM and different dicarboxylic anhydride: terminal (T), linear (L), semidendritic (sD), and perfect dendritic (D) (Figure 6). To distinguish these units, two kinds of model compounds were synthesized as shown in Scheme 5. During synthesis of $\mathbf{M_{D}}$, 15% $\mathbf{M_{sD}}$ was obtained simultaneously because the great steric hindrance of $\mathbf{M_{sD}}$ made it difficult to further

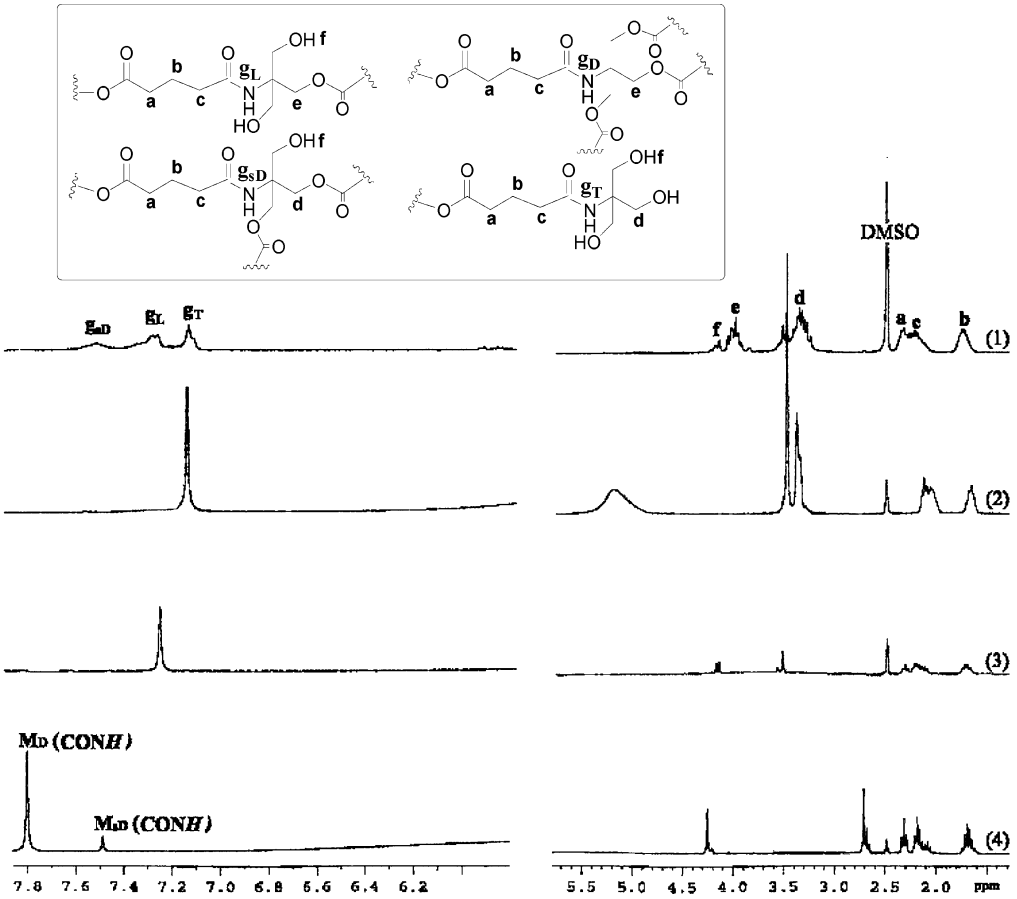


Figure 6. ^{1}H NMR spectrum of polymer and corresponding model compounds: (1) **P5**; (2) **7** or M_T; (3) M_L; (4) $M_D + M_{sD}$.

convert it to $\mathbf{M_D}$ completely. Their ^{1}H NMR spectra could be apparently assigned respectively even though they were not separated from each other. The signals of the methylene protons of **P5** overlap, whereas the signals of amino protons display three splitting peaks at 7.51, 7.26, and 7.13, with an integration ratio of 1:2.32:1.49, respectively, and the corresponding protons of the intermediate to T fraction, the model compound $\mathbf{M_L}$ to L fraction, $\mathbf{M_{sD}}$ to sD fraction, and $\mathbf{M_D}$ to D fraction were detected at 7.14, 7.25, 7.49, and 7.80 ppm, respectively. It obviously shows that the polymer **P5** only contains three units, semidendritic units (CON*H*, δ 7.51), linear units (CON*H*, δ 7.26), and terminal units (CON*H*, δ 7.13) without containing dendritic units. Therefore, the DB of **P5** was 0.48 calculated from the integration of proton attributed to each unit with Frey's DB definition for hyperbranched polymer made from AB_3 monomers.[28] Dendritic units were not observed, which may result from the hindrance of the molecular chain making it difficult for the third hydroxyl group to further react to form perfect dendritic units. Furthermore, the ^{13}C NMR of **P5** also confirmed the result from the ^{1}H NMR.

Comparing ^{13}C NMR with DEPT spectrum of **P5**, interestingly, it was found that two groups of symmetrical signals disappeared in the ^{13}C DEPT 135 NMR spectrum, one group is 76.98, 74.92, and 72.91 ppm, the other is 62.20, 60.96, and 58.28 ppm. These signals should be assigned to the quarternary carbons of the polymer.[29] The chemical shift of quarternary carbon showed that two kinds of symmetrical signals may be the result of two kinds of configuration isomers existing in the polymer, which could be further explained by the fact that only one group signal was observed when the ^{13}C NMR was conducted at high temperature (100 °C) due to the fast equilibration of molecular chain movement and molecular configuration at higher temperature,[30] as shown in Figure 7a. Moreover, the quarternary carbon signals of the model compound $\mathbf{M_L}$ corresponding to the linear fraction of the polymer and intermediate corresponding to the terminal fraction were observed at 74.97 and 76.65 ppm, respectively. Herein, the signals at 72.91, 74.92, and 76.98 ppm should be attributed to the quarter carbon of semidendritic, linear and terminal fraction, respectively. The DB of **P5** was 0.48 calculated from the integration of quarter carbon attributed to each unit with the Frey's equation mentioned above. The result is in agreement with that calculated from ^{1}H NMR. The DBs of **P6**–**P8** calculated with the similar method are listed in Table 1. Similarly, the DB of **P1**–**P4** could be determined by the ^{13}C NMR of corresponding polymer with the exception of using Fréchet's definition[31] for DB as the ratio of the sum of dendritic and terminal units vs total units (linear, dendritic, and terminal units) to calculate the values because the polymers were synthesized from potential AB_2 type monomers. A typical example, **P3**, is shown in Figure 8. The DB values of **P4** and **P8** prepared from CHA were the lowest among the polymers because they possess bulky cyclohexyl and could not be feasible to obtain more branching structure due to the huddle of the functional groups which are willing to form branched point.

Table 1 lists the results of GPC measurements that were calibrated against narrow-dispersity polystyrene standards with DMF or THF as solvent and eluent to

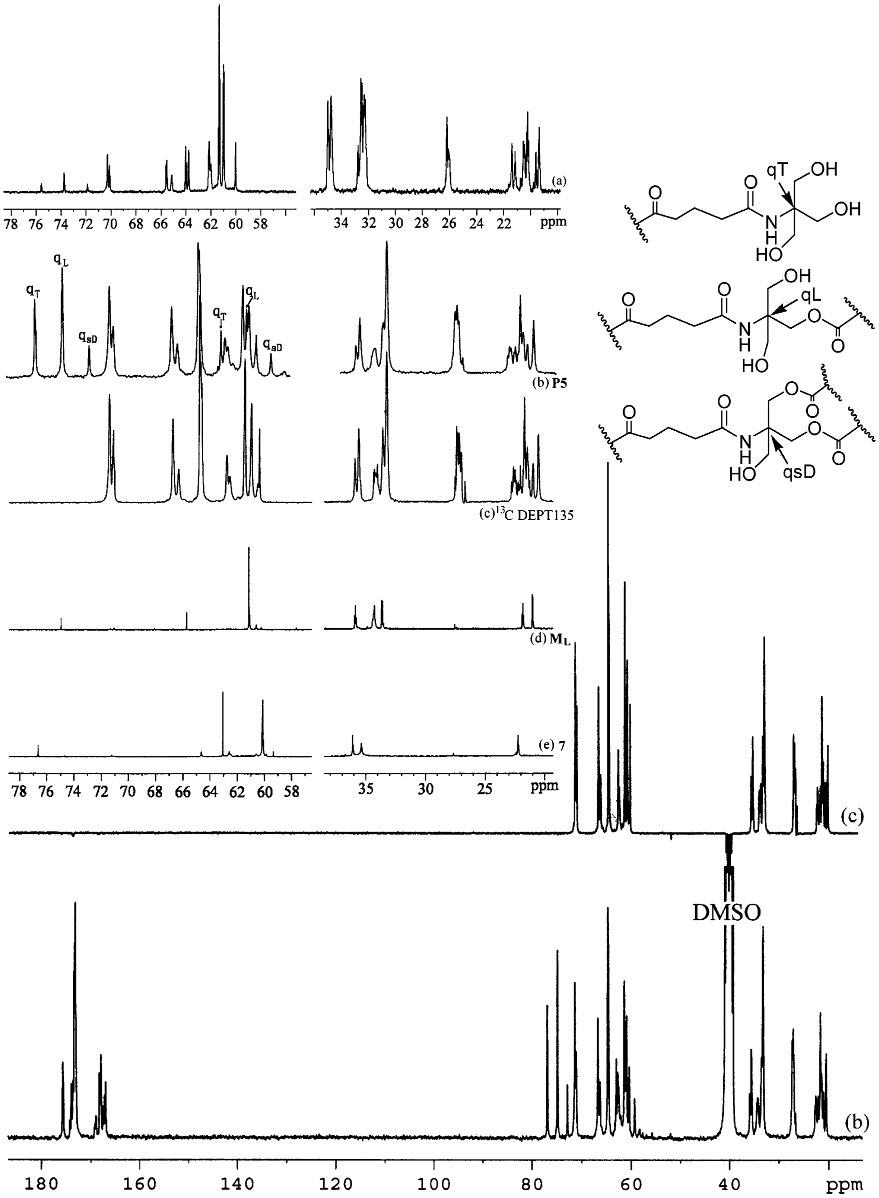


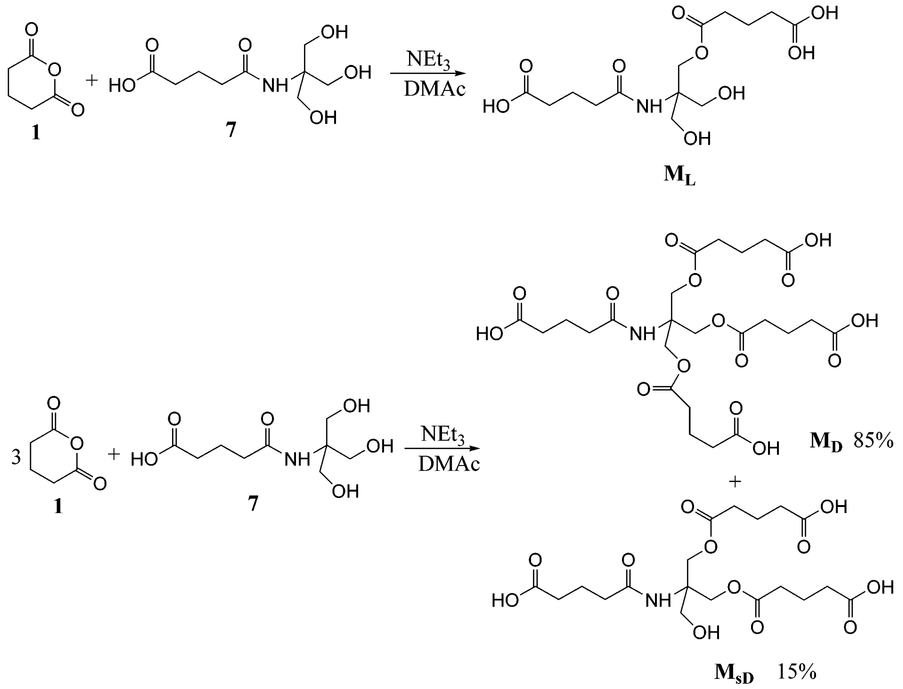
Figure 7. ^{13}C NMR spectrum of polymer and corresponding model compounds: (a) **P5** conducted at 100 °C; (b) **P5** conducted at 25 °C; (c) DEPT-135 at 25 °C (for convenience in comparing spectra, the CH_2 resonance directed below the baseline was adjusted to direct above the baseline); (d) $\mathbf{M_L}$; (e) **7** or $\mathbf{M_T}$.

give $\bar{M}_w$ and the polydispersity index (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[10,32−33] of high molar mass branched polymers due to their smaller hydrodynamic radii compared to linear analogues. On the other hand, interaction of the large number of polar end groups with solvent and GPC columns can lead to strong overestimation of molecular weight,[33b,c] which is also a reason for the marked difference between the results determined with different solvents. The molecular weight measured with DMF were much higher than those measured with THF, which is likely that stronger interactions of the polar end group with DMF than THF occurred. The interactions of the polar end group with solvent are stronger, the measurement results deviate the true value more seriously (stronger overestimation of molecular weight). Moreover, the end effect play a major role in the case of a molar mass of below 5000.[33b] In other words, the effect of the smaller hydrodynamic radius cannot overcome the end group effect. Therefore, the results ($\bar{M}_w$ = 2780−11300) determined with THF are more accurate. However, they are not absolute values still due to the reason mentioned above. Moreover, it cannot be performed the GPC measurement of **P5**−**P8** with THF because they were partially soluble in THF. Thereby a more detailed study and a more absolute method such as MALDI−TOF measurements will be necessary to be able to determine the true molecular weight.

All the polymers exhibited relatively low inherent viscosity (0.08−0.20 dL/g) and enhanced solubility in organic solvents due to the highly branched structure. They are highly soluble in typical polar solvents such as DMF, ethanol, acetone, chloroform, and tetrahydrofuran (THF).

The thermal properties of the hyperbranched polymers obtained are also listed in Table 1. The higher T_g of the polymer **P4** and **P8** in comparison with other polymers can be attributed to hindered segmental rotation and greater rigidity as a result of the existence of cyclohexyl, while **P1** and **P5** contain more flexible

Scheme 5. Synthesis of the Model Compound M_L, M_D, and M_{sD}



alkyl backbone, so their T_g values were lower. The building blocks of **P5** and **P6** with exactly the same chain ends (hydroxyl) are almost similar, but their T_gs have a discrepancy of above 15 °C. The T_g of **P6** is higher than that of **P5**. This can be ascribe to the difference of their end group densities as a result of the difference of their DBs. The DB of **P6** is higher than that of **P5**, which produce the greater terminal-group density and result in the stronger intermolecular interaction of the H-bond. The case of **P1** and **P2** is similar to that of **P5** and **P6**. As a result, T_g values increase with the increase of DB for the hyperbranched poly(ester−amide)s with hydroxyl end groups. After end-capping with *tert*-butyldimethysilyl, **P5** and **P6**'s T_g values are almost equal (shown in Figure 4). The discrepancy of T_g between the two polymers with *tert*-butyldimethysilyl end groups is not notable, which is due to the interaction of *tert*-butyldimethysilyl much lower than that of hydroxyl. In a word, the T_gs are hardly influenced by the DBs of hyperbranched poly(ester−amide)s bearing *tert*-butyldimethysilyl end groups, which is in agreement with the report[27b] that T_g values are not influenced by the DB of fluoro-terminated hyperbranched poly(ether ketone). The temperatures of 10% mass loss (T_d^{10}) of all the hyperbranced polymers are higher than 210 °C. Among all the polymers, **P4** and **P8** display the highest thermal stability due to special structures; their T_d^{10}s are above 320 °C.

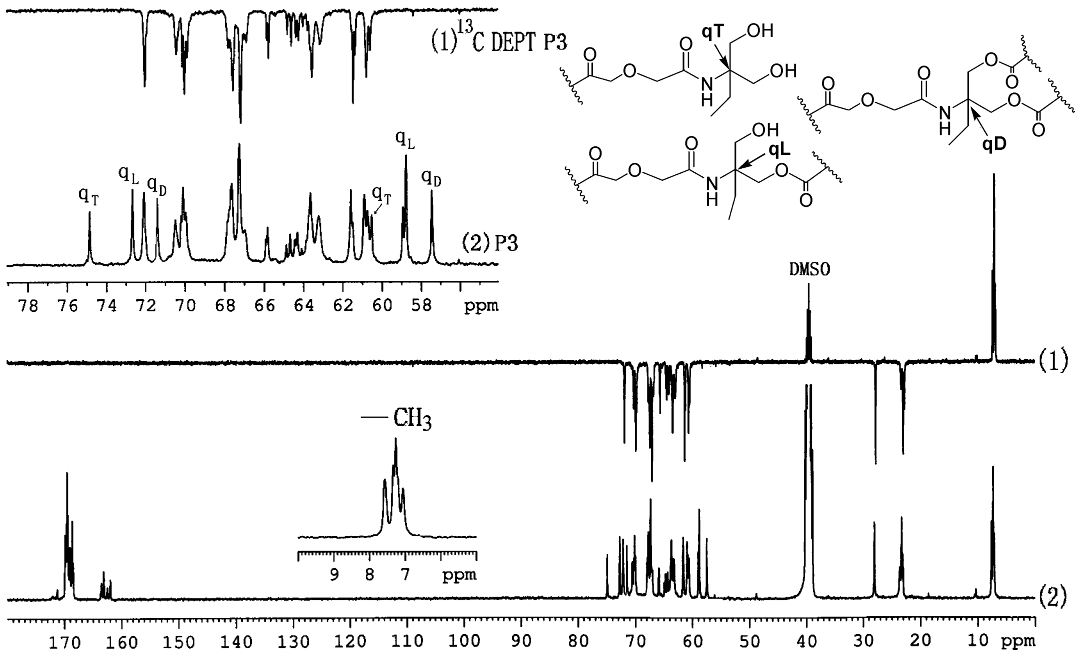


Figure 8. (1) DEPT-135 spectrum of polymer **P3**, where the CH_2 and CH_3 resonances are directed below the baseline and above the baseline, respectively, and (2) ^{13}C NMR spectrum of polymer **P3**.

Conclusions

The melting polycondensation of commercially available aliphatic carboxylic anhydrides (AA′) and multihydroxyl primary amine (CB_x) without any catalysts has been investigated as a novel approach to prepare hyperbranched poly(ester−amide)s bearing terminal hydroxyls. At the initial stage of polycondensation, primary amino groups of 2-amino-2-ethyl-1,3-propanediol or tris(hydroxymethyl)aminomethane react fast with anhydrides forming dominant dimers, which can be regarded as a new AB_x type monomers. Further self-polycondensations of the intermediates result in novel aliphatic hyperbranched poly(ester−amide)s. It was found that the optimum temperature of polycondensation is 110−120 °C. Among the hyperbranched poly(ester−amide)s obtained, those bearing cyclohexyl molecular skeleton structure display the lowest degree of branching, the highest glass transition temperature and the best thermal stability. All the polymers display high molecular weights with broad distributions and low inherent viscosity and good solubility in solvents such as ethanol, acetone, THF, DMF, and chloroform. The glass transition temperature of the hyperbranched poly(ester−amide)s was dramatically affected by changes in the chain end functional groups and also slightly depend on the DB for those bearing hydroxyl end groups. The temperatures of 10 wt % mass loss (T_d^{10}) are above 210 °C, and T_gs are in the range of 7−96 °C, depending on the structure of the monomers used.

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