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Polymerization of A_2 with B_3 Monomers: A Facile Approach to Hyperbranched Poly(aryl ester)s

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ABSTRACT: Hyperbranched polymers have received significant attention due to their unique combination of low viscosity, excellent solubility, and facile synthesis. This paper describes an efficient approach to hyperbranched poly(aryl ester)s via the polycondensation of A_2 and B_3 monomers. A dilute bisphenol A (A_2) solution was added slowly to a dilute 1,3,5-benzenetricarbonyl trichloride (B_3) solution at 25 °C to prepare hyperbranched poly(aryl ester)s in the absence of gelation. The molar ratio of A_2:B_3 was maintained at 1:1, and the maximum final monomer concentration was ~0.08 M. ^{1}H NMR spectroscopy and derivitization of terminal groups indicated that the phenol functionalities were quantitatively consumed during the polycondensation. Two model compounds were synthesized to identify ^{1}H NMR resonances for linear, dendritic, and terminal units, and the final degree of branching was determined to be ~50%. Moreover, the hyperbranched polymers exhibited lower glass transition temperatures relative to their linear analogues.

Introduction

Flory initially described an approach for the preparation of hyperbranched polymers from AB_2 monomers in 1952.[1] Extensive research resumed approximately 10 years ago in an effort to develop polymeric products with similar structures and performance as perfect dendrimers via more facile approachs.[2] Many strategies were developed to prepare polymers with highly branched structures, and the one-step polycondensation of AB_n monomers has received significant attention.[3−10] Although some families of hyperbranched polymers with narrow molecular weight distributions were reported, hyperbranched polymers prepared via the one-step polycondensation of AB_2 monomers typically exhibited highly irregular structures and large molecular weight distributions.[11] Thus, it was suggested that hyperbranched polymers resembled conventional networks immediately prior to the gel point.[12−14] The similarity of intermediates in an A_2 and B_3 process to intermediates in the formation of polymeric networks led chemists to consider the polycondensation of A_2 with B_3 monomers as an alternative synthetic route. This complementary method is attractive since many A_2 and B_3 monomers are readily available and have received significant attention in the synthesis of conventionally branched polymers.[15−24]

Jikei and co-workers reported the synthesis of hyperbranched aromatic polyamides, which were derived from aromatic diamines (A_2) and trimesic acid (B_3), and Jikei, Voit and co-workers investigated this family of hyperbranched polymers in more detail.[15,20,21] Kinetic calculations predicted that the first condensation reaction of A_2 with B_3 was faster than subsequent propagation, thus leading to an accumulation of A-ab-$(B)_2$ intermediates. Thus, the remainder of the process resembled the more common AB_2 polycondensation, and the final products exhibited comparable structures to the products derived from the polymerization of AB_2 monomers. On the basis of this concept, a novel synthetic methodology termed $A_2 + B'B_2$ was developed.[24] Fréchet and co-workers reported the synthesis of hyperbranched polyether epoxies via proton-transfer polymerization from 1,2,7,8-diepoxyoctane (A_2) and 1,1,1-tri(hydroxymethyl)ethane (B_3) using a 1:1 molar ratio of monomers (2 equiv of A groups and 3 equiv of B groups).[16,17] These reactions were stopped immediately prior to the gel points to form highly branched molecules. After these two pioneering reports, this more facile approach to hyperbranched polymers attracted a significant attention, and several novel families of hyperbranched polymers were reported using this methodology.[18−24] For example, Okamoto and co-workers synthesized hyperbranched polyimides via a slow addition of a dilute solution of A_2 to a dilute solution of B_3.[22] Moreover, Kricheldorf and co-workers demonstrated that a cyclization reaction prevented intermolecular cross-linking and resulted in products bearing several cyclic structures.[23] Only limited families of hyperbranched polymers prepared via polymerization of A_2 and B_3 monomers have received attention, and the polymerization mechanism and structures of the final products remain unclear.

Our recent efforts have focused on the synthesis of hyperbranched analogues of engineering polymers to obtain the combined properties of hyperbranched polymers (low melt viscosity, multifunctionality, and the possibility of acting as molecular encapsulants) and good thermal stability.[8] These novel hyperbranched polymers are useful as modifiers in blends with linear polymers, thin coatings, gas separation membranes, and microelectronic materials.[25,26] Poly(aryl ester)s are a class of engineering thermoplastics that exhibit high glass transition temperatures, good thermal stability, and selective gas permeation.[27,28] Turner and co-workers reported the synthesis of hyperbranched poly(aryl ester)s using commercially available AB_2 monomers, such as 5-acetoxyisophthalic acid and 5-(2-hydroxyethoxy)isophthalic acid.[29,30] In addition, several bisphenols containing different linking groups, such as biphenol, 4,4′-(hexafluoroisopropylidene)diphenol, 4,4′-sulfonyl-

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diphenol, or 4,4′-bis(hydroxyphenyl)phenylphosphine oxide, were investigated to improve the performance of linear poly(aryl ester)s.[27,31] These monomers lead to hyperbranched polymers with unique properties such as liquid crystalline morphologies, high thermal stabilities, and low dielectric constants. The preparation of hyperbranched poly(aryl ester)s derived from A_2 and B_3 monomers represents a facile route to novel hyperbranched poly(aryl ester)s. In contrast to previous reports of hyperbranched polyamides using less reactive diacid monomers,[15] a much more reactive functional monomer, tri-acid chloride, was used, and a synthetic methodology, i.e., slow addition of a reactive monomer, was developed to avoid gelation. The synthesis of hyperbranched poly(aryl ester)s that are derived from bisphenol A and 1,3,5-benzenetricarbonyl trichloride are reported herein.

Experimental Section

Materials. Bisphenol A (Bis A) (monomer grade) was graciously donated by the Dow Chemical Co. and was dried in a vacuum oven (0.50 mmHg) at 80 °C for 18 h. 1,3,5-Benzenetricarbonyl trichloride (BTC) (99%), anhydrous triethylamine (TEA) (99%), phenol (99%), and acetyl chloride (99%) were purchased from Aldrich and used as received. Chloroform (Burdick & Jackson, high purity) was stirred over calcium hydride and distilled under nitrogen. Methanol was purchased from EM Science and used as received.

Synthesis of Hyperbranched Poly(aryl ester)s and Corresponding Model Compounds. Synthesis of a Hyperbranched Poly(aryl ester)s with Ammonium Carboxylate Terminal Groups (P-1). BTC (1.99 g, 0.0075 mol) was dissolved in 50 mL of freshly distilled chloroform in a 250 mL, thoroughly dried, three-necked flask equipped with a magnetic stir bar, reflux condenser, and addition funnel. Bis-A (1.71 g, 0.0075 mol) and 1.52 g (0.015 mol) TEA were added to 100 mL of freshly distilled chloroform in an addition funnel, and slight heating was required to completely dissolve the Bis-A. After a homogeneous solution was obtained, the solution was slowly added to the reaction flask over 1 h. The homogeneous reaction was maintained at 23 °C for 24 h. Water (10 mL) was subsequently added to quench the residual acid chloride, and the heterogeneous solution was stirred for 30 min. The solution was washed twice with basic water, acidic water, and deionized water then precipitated into methanol. The white product was filtered and dried at 40 °C in a vacuum oven for 24 h. ^{1}H NMR (chloroform-*d*, ppm): δ 1.42 (br, $-\mathrm{NCH_2C}\mathit{H}_3$), 1.75 (br, 6H, $-\mathrm{Ar{-}C(CH_3)_2{-}Ar}-$), 4.44 (br, $-\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.34 (br, 4H, aromatic protons from Bis-A), 7.50 (br, 4H, aromatic protons from Bis-A), 8.93−9.22 (br, 3H, aromatic protons from BTC).

Synthesis of a Hyperbranched Poly(aryl ester)s with Methyl Ester Terminal Groups (P-2). The synthetic method was similar to P-1 preparation except that the reaction solution was directly poured into methanol without the addition of water. The white product was filtered, redissolved in chloroform, and then washed with basic water, acidic water, and deionized water twice. The purified product was precipitated into methanol and collected in a filter funnel. The product was dried at 40 °C in a vacuum oven for 24 h. ^{1}H NMR (chloroform-*d*, ppm): 1.42 (br, $-\mathrm{NCH_2C}\mathit{H}_3$), 4.00 (br, 2.9 H, $-\mathrm{OCH_3}$), 4.44 (br, $-\mathrm{NC}\mathit{H}_2\mathrm{CH_3}$), 7.18 (br, 4H, aromatic protons from Bis-A), 7.34 (br, 4H, aromatic protons from Bis-A), 8.99−9.93 (br, aromatic protons from BTC). ^{13}C NMR: (chloroform-*d*, ppm): 14.8 ($-\mathrm{N}\mathit{C}\mathrm{H_2CH_3}$), 31.6 ($-\mathrm{Ar{-}C(}\mathit{C}\mathrm{H_3)_2{-}Ar}-$), 42.3 ($-\mathrm{Ar}-\mathit{C}\mathrm{(CH_3)_2{-}Ar}-$), 53.4 ($-\mathrm{OCH_3}$), 62.4 ($-\mathrm{NCH_2}\mathit{C}\mathrm{H_3}$), 121.6 (Bis A), 128.7 (Bis A), 148.6 (Bis A), 154.2 (Bis A), 132.1−136.3-(BTC), 164.9−165.6 (C=O).

Synthesis of Hyperbranched Poly(aryl ester)s with Methyl Ester Terminal Groups (P-3, P-4, P-5). The synthetic method was similar to P-2 preparation except that different monomer concentrations and polymerization times were used as summarized in Table 1.

Table 1. Molecular Weights and Glass Transition Temperatures of Hyperbranched Poly(aryl ester)s

sample	[M][a] (mol/L)	M_n (g/mol)	M_w (g/mol)	M_w/M_n	T_g (°C)
P-1[b]	0.05	3300	10 000	3.03	178
P-2[b]	0.05	3540	12 300	3.48	136
P-3[b]	0.06	5600	15 700	2.81	150
P-4[b]	0.08	7950	22 200	2.79	154
P-4[c]	0.08	9300	26 000	2.79	154
P-4[d]	0.08	6903	20 200	2.93	154
P-5[e]	0.08	8667	21 300	2.45	153

[a] Concentration of monomer. [b] GPC data were obtained using the RI detector. [c] GPC data were obtained using the viscometric detector and RI detector. [d] GPC data were obtained using the MALLS and RI detector. [e] Reaction time was 48 h, and GPC data were obtained using MALLS and RI detector.

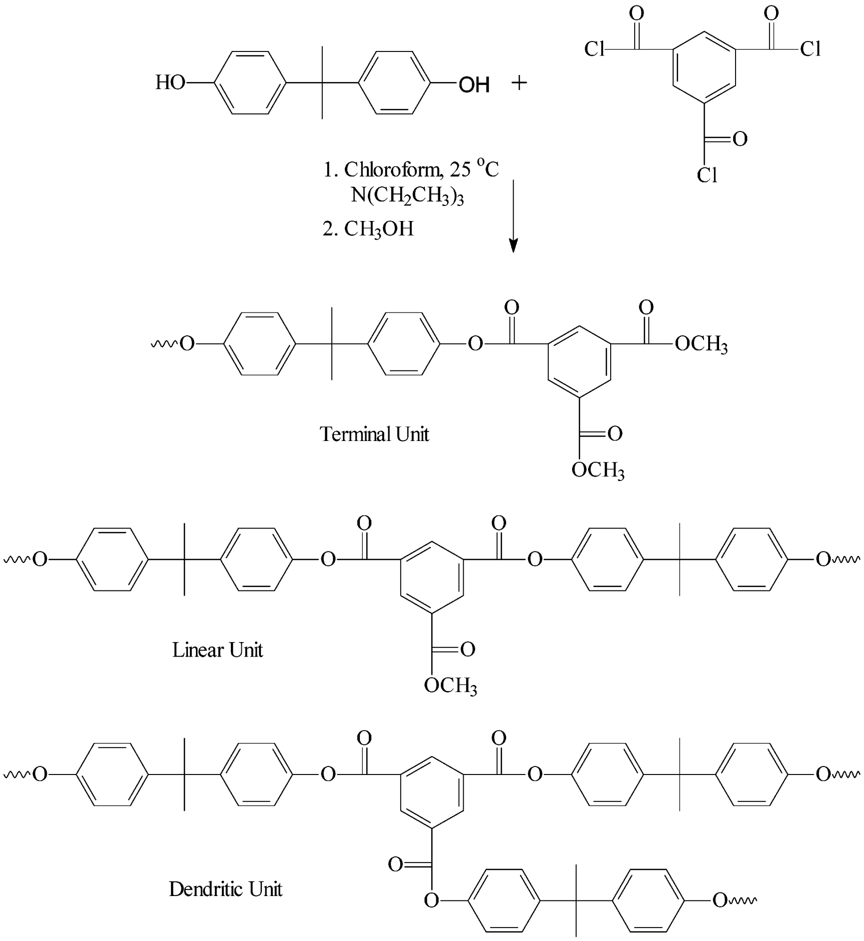
Synthesis of 1,3-Methyl-5-phenylbenzenetricarboxylate (1). Phenol (4.71 g, 0.05 mol), 13.27 g (0.05 mol) of BTC, and 5.06 g (0.05 mol) of TEA were dissolved in 100 mL of chloroform in a thoroughly dried, three-necked flask with a magnetic stir bar and reflux condenser and allowed to react at room temperature for 24 h. The solution was poured into methanol to precipitate the product. The crude product was a viscous oil, and TLC indicated three compounds. The compounds were separated using column chromatography with a 2:1 v/v mixture of dichloromethane and hexane. ^{1}H NMR spectroscopy and mass spectroscopy indicated that the second fraction was the targeted model compound. The product was a crystalline white solid with a melting point of 82.3 °C. ^{1}H NMR (chloroform-*d*, ppm): δ 3.98 (s, 6H, $-\mathrm{OCH_3}$), 7.23−7.32 (m, 3H, aromatic protons from phenol), 7.51−7.43 (m, 2H, aromatic protons from phenol), 8.93 (s, 1H, aromatic proton from BTC), 9.02 (s, 2H, aromatic protons from BTC). ^{13}C NMR (chloroform-*d*, ppm): δ 53.0 ($-\mathrm{OCH_3}$), 121.7 (phenol), 126.5 (phenol), 129.5 (phenol), 130.8 (BTC), 131.7 (BTC), 135.6 (BTC), 150.8 (BTC), 163.8 (C=O), 165.6 (C=O). MS(CI): 377 *m*/*z* (MH$^+$, calcd 377 *m*/*z*). Anal. Calcd for $C_{22}O_6H_{16}$: C, 64.96; H, 4.49. Found: C, 64.66; H, 4.63.

Synthesis of 1-Methyl-3,5-phenylbenzenetricarboxylate (2). The synthetic method was similar to the preparation of compound **1** except that the molar ratio of BTC to phenol was 1:2. The crude product was a viscous oil, and TLC indicated four compounds. The compounds were separated using column chromatography with a 2:1 v/v mixture of dichloromethane and hexane. ^{1}H NMR spectroscopy and mass spectroscopy indicated that the third fraction was the targeted compound. The product was a crystalline white solid with a melting point of 93.5 °C. ^{1}H NMR (chloroform-*d*, ppm): δ 4.02 (s, 3H, $-\mathrm{OCH_3}$), 7.23−7.34 (m, 6H, aromatic protons from phenol), 7.43−7.48 (m, 4H, aromatic protons from phenol), 9.10 (s, 2H, aromatic protons from BTC), 9.21 (s, 1H, aromatic proton from BTC). ^{13}C NMR (chloroform-*d*, ppm): δ 53.0 ($-\mathrm{OCH_3}$), 121.7 (phenol), 126.5 (phenol), 129.9 (phenol), 131.2 (phenol), 132.1 (phenol), 136.0 (BTC), 150.8 (BTC), 163.8 (C=O), 165.6 (C=O). MS(CI): 315 *m*/*z* (MH$^+$, calcd 315 *m*/*z*). Anal. Calcd for $C_{27}O_6H_{29}$: C, 70.21; H, 4.28. Found: C, 69.95; H, 4.39.

Confirmation of the Absence of Phenol Terminal Groups on Methyl Ester-Terminated Hyperbranched Poly(aryl ester)s. P-4 (0.50 g, 1.30 mmol) and TEA (0.10 g, 1.00 mmol) were dissolved in 20 mL of freshly distilled chloroform in a 100 mL, thoroughly dried, three-necked flask. Acetyl chloride (0.08 g, 1.10 mmol) was added slowly using a syringe, and the reaction was maintained at 23 °C for 24 h. The solution was poured slowly into methanol to precipitate the product. The white powder was filtered and dried in a vacuum oven at 40 °C for 24 h. The product was redissolved in chloroform. The solution was washed with water and reprecipitated. The ^{1}H NMR spectrum of the product was identical to the starting materials and confirmed the absence of phenyl acetates due to the presence of residual phenol end groups.

Characterization. ^{1}H and ^{13}C NMR analyses were performed on a Varian Unity 400 MHz spectrometer at ambient

Scheme 1. Synthesis of Methyl Ester-Terminated Hyperbranched Poly(aryl ester)s via Polymerization of A_2 and B_3 Monomers



temperature. Two gel permeation chromatography (GPC) instruments equipped with different detectors were used to measure the molecular weights. GPC measurements were conducted on a Waters 2690 chromatograph equipped with a differential refractive index detector (Viscotek laser refractometer) and an on-line differential viscometric detector (Viscotek 100) coupled in parallel, using polystyrene standards. A Waters styragel HR0.5, HR2, HR3, and HR4 column bank was used. The flow rate was 1.0 mL/min, the injection volume was 100 μL, and the column temperature was 40 °C. Additional GPC measurements were performed on a Waters SEC (515 pump, 717 autosampler) with an external 410 refractive index detector. Multiangle laser light scattering (MALLS) was also performed using an in-line Wyatt Minidawn. A Polymer Laboratories PLgel, 5 μm MIXED-C column with a length of 300 mm and inner diameter of 7.5 mm was used. The flow rate was 1.00 mL/min, and the temperature was 40 °C. Thermal transition temperatures were determined using a Perkin-Elmer DSC-7 at 10 °C/min, and all reported data were obtained from the second heating. Thermogravimetric analysis (TGA) was performed on a Perkin-Elmer TGA 7 under a nitrogen atmosphere at a heating rate of 10 °C /min.

Results and Discussion

The common products that result from polycondensation of A_2 and B_3 monomers are networks, and hyperbranched products are only obtained under highly restricted reaction conditions.[12−19] Thus, it is essential to select suitable reaction conditions that avoid gelation, and the specific conditions for polymerization of bisphenol A and 1,3,5-benzenetricarbonyl trichloride for the preparation of hyperbranched poly(aryl ester)s without gelation are discussed in this report. Furthermore, it is also important to define the chemical structure, such as the degree of branching (DB) and the terminal groups of this family of polymers.

Polymerization. Poly(aryl ester)s with tailored architectures are typically prepared using a variety of interfacial or melt methodologies.[24,26] Linear, high molecular weight poly(aryl ester)s are commonly synthesized using interfacial methods that employ weakly basic aqueous bisphenolate solutions and organic diacid chloride solutions.[24,26] However, this method leads to cross-linked products if A_2 and B_3 monomers are used. One approach for preparing hyperbranched poly(aryl ester)s from A_2 and B_3 monomers that avoids gelation is to conduct solution polymerizations wherein a dilute solution of one monomer is slowly added to a dilute solution of the other monomer (Scheme 1). The order of addition of the monomer solution will significantly influence the structures of the final poly(aryl ester)s. When the A_2 dilute solution was slowly added to the B_3 dilute solution, gelation was avoided and hyperbranched polymers were obtained in a high yield (>90%). In contrast, when the dilute B_3 solution was added to the dilute A_2 solution (irrespective of the rate of B_3 addition), only cross-linked products were obtained. It was presumed that a high local concentration of B functional groups during the addition promoted cross-linking.

Specific reaction conditions for the polycondensation of A_2 and B_3 monomers in the absence of gelation were determined. Chloroform was able to dissolve low levels of the monomers and hyperbranched products and was used as the polymerization solvent. The polymerizations

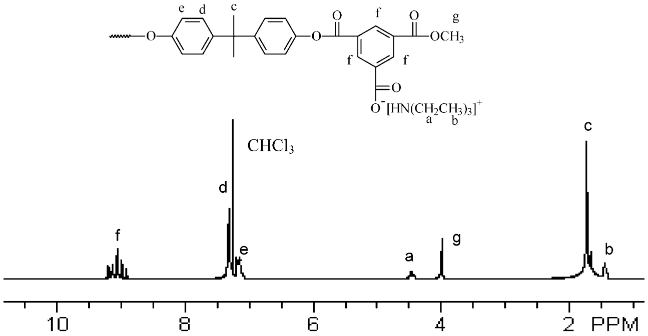


Figure 1. ^{1}H NMR spectrum of a methyl ester-terminated hyperbranched poly(aryl ester) (P-2, 400 MHz, $CDCl_3$).

were conducted at ambient temperature due to the high reactivity of acid chlorides. Bisphenol A (Bis A) and 1,3,5-benzenetricarbonyl trichloride (BTC) were used as the A_2 and B_3 monomers, but structural variations are achievable using other bisphenols. The final molar ratio of A_2 to B_3 monomers was maintained at 1:1, in an effort to generate similar hyperbranched architectures to those derived from traditional AB_2 monomers. It was determined that the final concentration of monomers should not exceed 0.08 M to avoid gelation. The reaction completion was expected in several hours; however, to ensure quantitative reaction, the reactions were allowed to proceed for 24 h. Although the polymerization times were typically 24 h, significantly longer times were investigated (>72 h) and gelation was not observed.

The stoichiometric ratio of A groups (phenols) to B groups (acid chlorides) was 2:3, and various reagents were used to react with the remaining acid chlorides for the introduction of peripheral functionality. One process involved simply quenching the terminal acid chlorides with water in the presence of triethylamine as an acid scavenger to produce peripheral carboxylic acid functionalities (P-1). However, ^{1}H NMR spectroscopy disclosed a large amount of residual TEA-based ammonium salt even after the polymer was extensively washed using various pH value aqueous solutions. Water-soluble hyperbranched polymers derived from 5-acetoxyisophthalic acid with carboxylic ammonium or sodium salts as terminal groups were reported earlier.[22,23] However, the P-1 salt was not water-soluble, and only swelling occurred. Compared to the earlier water-soluble hyperbranched poly(aryl ester)s, P-1 has a repeat unit consisting of three phenyl rings. Thus, the charge density of the obtained poly(aryl ester)s was lower than the previous water-soluble poly(aryl ester)s and not high enough to result in a fully water-soluble polymer. Methanol was alternatively used to consume terminal acid chloride groups in the hyperbranched poly(aryl ester)s. ^{1}H NMR spectroscopy (Figure 1) confirmed the presence of methyl ester terminal groups in addition to minor levels (1−2 mol %) of residual TEA salts. An interesting area for further study involves the use of alcohols containing chiral or fluoro alkyls for the preparation of hyperbranched poly(aryl ester)s with an extended range of tailored functional terminal groups.

Branched Structures. The structures of the polymeric products that are derived from A_2 and B_3 monomers are not well-understood, and it remains difficult to describe them using one or two parameters. Several concepts, such as the definition of repeat units (linear, dendritic, and terminal) and branching degree, were borrowed from the traditional hyperbranched polymers prepared from AB_n monomers. In this section, the structures of the hyperbranched poly(aryl ester)s will be defined on the basis of the available NMR spectroscopy data.

In theory, each molecule of hyperbranched polymers prepared from AB_n monomers will have only one A left functional group, which is termed the focal unit (Figure 2). In practice, however, most hyperbranched polymers derived from AB_n monomers do not have the focal unit due to intramolecular cyclization side reactions (Figure 2).[7,28] Moreover, to increase the degree of branching, the methodology for the copolymerization of AB_n and B_n monomers was developed, and the products from this synthetic method do not have a focal unit. For hyperbranched products from the polycondensation of A_2 and B_3 monomers, defining the structure was more complicated because the number of residual A functional groups depended on the ratio of charged functional groups (Figure 2). In theory, when the ratio of A to B is larger than 2:3, one molecule may bear one or more A functional groups. However, when the ratio of A to B is 2:3, in theory, the terminal groups will be exclusive B groups.[21] The terminal groups played an important role in the thermal stability of the poly(aryl ester)s. If the terminal groups were reactive groups such as carboxylic acid or alcohol, or A and B functional groups existed simultaneously, continued polycondensation would result in poor thermal stability at high temperature (>200 °C).[29] In this study, the ratio of A_2 and B_3 monomers was 1:1, and the A functional group, phenol, was presumed to be completely consumed during the reaction. Two methodologies, ^{1}H NMR spectroscopy and derivatization of terminal groups, were used to confirm the hypothesis. A detectable resonance that was related to the phenol group (A functionality) was not observed in the ^{1}H NMR spectra of hyperbranched poly(aryl ester)s. In addition, the attempted derivatization of any phenol end groups with acetyl chloride did not result in the appearance of new ^{1}H NMR resonances that are associated with a phenyl acetate. These results indicated that when the ratio of two monomers was 1:1, the hyperbranched poly(aryl ester)s did not contain residual phenol groups. The derivatives with methyl ester terminal groups did not have reactive terminal groups (<0.10 mol %) and were expected to exhibit a higher thermal stability.

Unlike dendrimers with a perfect structure, hyperbranched polymers have highly irregular structures due to the one-step process. Hyperbranched polymers prepared form AB_n monomers contain three types of units including terminal units with two end groups, linear units with one end group, internal dendritic units, and possibly a cyclic structure.[36] To better define the chemical structures of hyperbranched polymers, Fréchet and co-workers quantified the degree of branching (DB) using eq 1:[3,36]

$$DB = (D + T)/(D + T + L) \tag{1}$$

where D, T, and L refer to the numbers of dendritic, terminal, and linear units in the hyperbranched polymers, respectively. Experimentally, DB is usually determined using ^{1}H NMR spectroscopy and a comparison of the integrals of the resonances of the respective units in the hyperbranched polymers.

For hyperbranched polymers that are obtained via the polycondensation of A_2 and B_3 monomers, it is more complicated since the products may contain more than

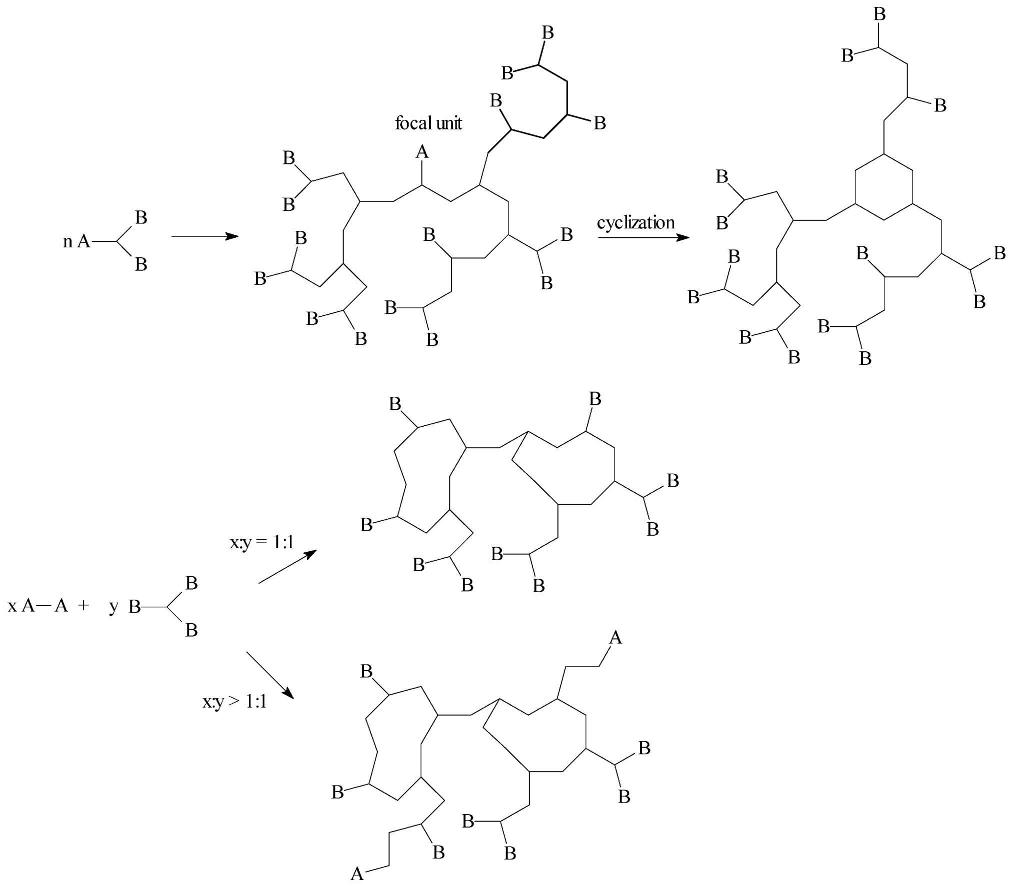
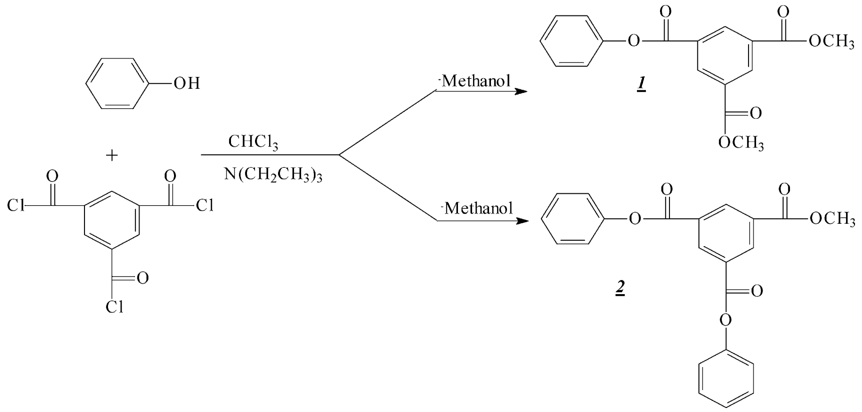


Figure 2. Schematic representation of hyperbranched polymers obtained from one-step polycondensation of AB_n monomers and polycondensation of A_2 and B_3 monomers.

Scheme 2. Synthesis of Model Compounds 1 and 2



one cyclic structure. However, the definitions of three units (dendritic, terminal, and linear) of basic structures are still applicable. The ^{1}H NMR spectra of hyperbranched poly(aryl ester)s showed that the resonances from the hydrogens in the D, L, and T units had different shifts due to the difference in their chemical environments (Figure 3). Model compounds **1** and **2** were synthesized (Scheme 2) to establish ^{1}H NMR assignments for quantifying the relative percentages of the different types of units. The assignment of ^{1}H NMR resonances of hydrogens in linear, dendritic, and terminal units is depicted in Figure 3. The calculated DBs based on the relative percentages of those units ranged between 45% and 55%. Hyperbranched poly(aryl ester)s that were derived from AB_n monomers (5-acetoxyisophthalic acid and 5-(2-hydroxyethoxy)isophthalic acid) and hyperbranched polyamides from diamines (A_2) and trimesic acid (B_3) also had DBs near 50%.[21,29−30] Thus, the hyperbranched poly(aryl ester)s prepared via polycondensation of A_2 and B_3 monomers exhibited comparable branching degrees to products from AB_n monomers and other families of hyperbranched polymers derived from A_2 and B_3 monomers.

Another important parameter that further defines structures of hyperbranched products from the polycondensation of A_2 and B_3 monomers is the number of cyclic structures in each molecule, and perhaps a novel parameter, the average number of cyclic structures should be developed. In fact, it is still a technological difficulty to precisely determine the average number of cyclic structures. In most cases, MALDI−TOF MASS was able to provide the identify of the low molecular weight cyclic products, and Kricheldorf and co-workers successfully determined the number of cyclic structures

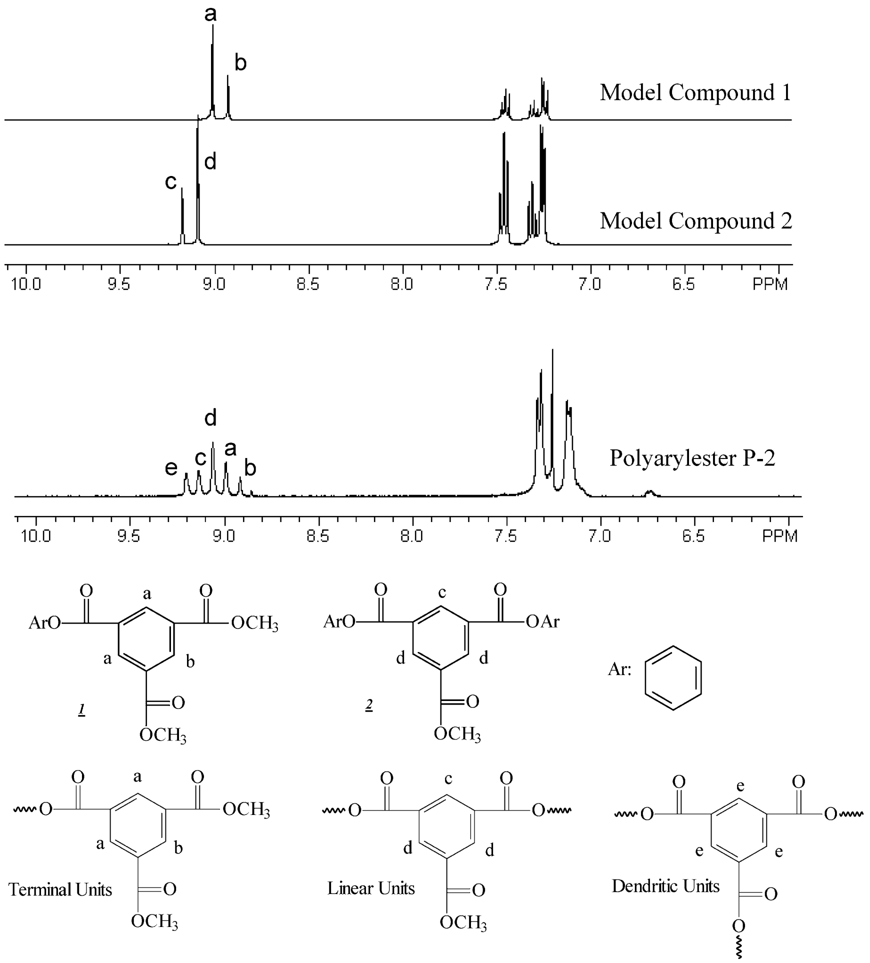


Figure 3. Comparison of ^{1}H NMR spectra (400 MHz, $CDCl_3$) of model compounds (1 and 2) and a methyl ester-terminated hyperbranched poly(aryl ester) (P-2).

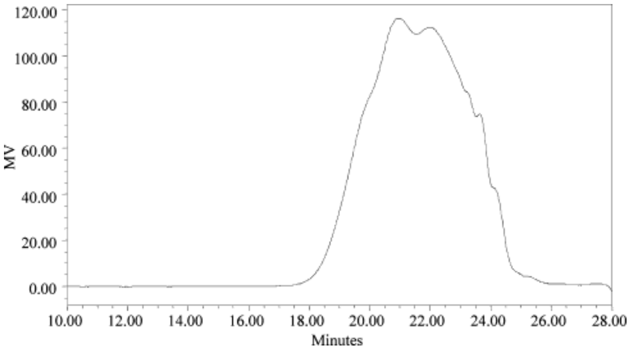


Figure 4. Characteristic polymodal GPC trace of a methyl ester-terminated hyperbranched poly(aryl ester) (P-4).

in the low molar mass hyperbranched poly(arylene ether)s from polycondensation of A_2 and B_3 monomers.[23] However, for our hyperbranched polymers, a suitable matrix was not successfully identified to ionize these aromatic polymers and obtain reliable signals; further work continues in our laboratories.

Molar Mass Characterization. Two GPC instruments equipped with different detectors (DRI, MALLS, and viscometer) were used to measure the molecular weights of hyperbranched poly(aryl ester)s. As expected on the basis of the prior literature, the GPC traces exhibited multimodal character due to the existence of different molecular weight products with highly irregular structures (Figure 4).[8,29,30] The use of a light scattering detector required the determination of a specific refractive index increment, d*n*/d*c*, which was measured using a differential refractometer. The d*n*/d*c* value for the hyperbranched poly(aryl ester)s in chloroform was approximately 0.14 mL/g. The measured molecular weights of a P-4 sample using three different detectors and calibration approaches were in a good agreement (Table 1). This was attributed to the moderate weight-average molecular weights that resulted in small differences in measured values using different detectors.

Several families of hyperbranched polymers derived from AB_n monomers exhibited a maximum number-average molecular weight due to intramolecular cyclization.[7−8,29,30] The number-average molecular weights of P-4 and P-5 were ~9000 g/mol, which are comparable to the maximum value for several of the families of hyperbranched polymers prepared from AB_n monomers (Table 1).[7,29,30] In fact, weight-average molecular weights are preferred for the characterization of hyperbranched polymers,[37] and the weight-average molecular weights of the hyperbranched poly(aryl ester)s were moderate and ranged between 10 000 and 22 000. During the polymerization of AB_n monomers, the weight-average molecular weights continually increased with the reaction time.[7] However, in the present work, the longer reaction times did not have a significant effect on the weight-average molecular weights. P-4 (maintained reaction for 24 h) and P-5 (maintained reaction for 48 h) had similar weight-average molecular weights (Table 1).

It is also interesting to compare the GPC results of the hyperbranched poly(aryl ester)s to earlier hyperbranched products derived from AB_n monomers. In a fashion similar to the polymerization of AB_n monomers, molecular weights of hyperbranched poly(aryl ester)s that were obtained from the polymerization of A_2 and B_3 monomers increased with the monomer concentration prior to the critical point.[7,8,29,30] However, in contrast to previous reports dealing with the synthesis of hyperbranched polymers from AB_n monomers or A_2 and B_3 monomers, the molecular weight distribution of the poly(aryl ester)s did not increase with an increase in molecular weight and remained relatively constant (Table 1).[7,14] In our studies, the slow addition of a highly reactive monomer was used, and previous research demonstrated that this technology resulted in narrower molecular weight distribution products.[11] The development of the molar mass of this described dilute system was certainly not compared fully with previous systems in the melt or even other A_2 and B_3 systems. In this system, because of the slow addition of a highly reactive monomer, a relatively fast reaction occurred at the beginning, but later on there was no driving force (compared to high functionality density, high temperature, and applied vacuum), which served to drive the conversion higher. Thus, a long reaction time did not lead to a higher conversion, which would result in a broad molecular weight distribution.

The relationship between intrinsic viscosity and molecular weight was measured across the molecular weight distribution in the GPC viscometric experiment and was analyzed using the Mark−Houwink equation $[\eta] = kM^{\alpha}$. The value of α approaches 0.5 at a θ condition and is generally between 0.65 and 0.75 for linear random coils in a good solvent. However, α values for P-4 and P-5 were approximately 0.25, which is a typical value for many families of hyperbranched polymers.[8,29,30] These small values are consistent with highly branched, compact, and globular structures. The α values for P-1, P-2, and P-3 were close to zero due to relatively low molecular weights as described earlier.[29,30]

Thermal Properties. Although the hyperbranched poly(aryl ester)s from polycondensation of AB_n and $A_2 + B_3$ monomers have different repeat unit structures, their derivatives with nonpolar terminal groups (methyl esters for $A_2 + B_3$ and acetyl esters for AB_2) exhibited similar glass transition temperatures (approximately 150 °C). Moreover, the glass transition temperature of both families of poly(aryl ester)s increased with increasing molecular weight. The hyperbranched products exhibited lower glass transition temperatures relative to their linear analogues derived from bisphenol A and isophthaloyl chloride via interfacial polymerization (~200 °C), and this was presumed to be due to irregular branching and a high concentration of end groups.[26] P-1 with carboxylic acid terminal groups did not exhibit a much higher glass transition temperature as expected. It was presumed that the large amount of residual TEA salts (20 wt %) plasticized P-1.

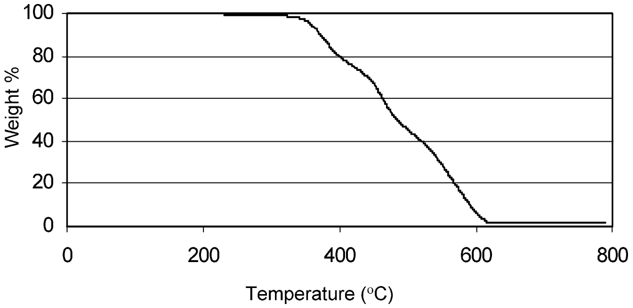


Figure 5. Thermogravimetric analysis of a methyl-terminated hyperbranched poly(aryl ester) (P-2) under nitrogen.

The earlier hyperbranched poly(aryl ester)s prepared using melt polymerization of AB_2 monomers exhibited poor thermal stability due to continued polycondensation at high temperatures (>200 °C).[29,30] However, the hyperbranched poly(aryl ester)s via this novel methodology exhibited excellent thermal stability, and no weight loss was observed before the onset of polymer degradation (390 °C, Figure 5). The improved thermal stability was ascribed to the lack of reactive terminal groups (only methyl esters), which excluded the continued polycondensation at high temperatures. As a result, these novel hyperbranched poly(aryl ester)s may potentially be used as additives in a melt process.

Conclusions

Hyperbranched poly(aryl ester)s were prepared via adding a dilute bisphenol A (A_2) solution to a dilute 1,3,5-benzenetricarbonyl trichloride (B_3) solution. The order of addition and solution concentrations were important reaction parameters to avoid gelation, and concentration changes within the dilute regime did not affect molecular weight distributions (~3.00). These hyperbranched poly(aryl ester)s had structures similar to those prepared from more common AB_n monomers in terms of the degree of branching (47−55%) and exclusive B terminal functionality. The hyperbranched polymers exhibited lower solution viscosities, which were characteristic of hyperbranched polymers (Mark−Houwink constants (α) were 0.25), and glass transition temperatures ranged from 130 to 150 °C depending on molecular weight.

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