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Structural Variants of Hyperbranched Polyesters

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ABSTRACT: Hyperbranched polyesters based on 3,5-dihydroxybenzoic acid and its derivatives were prepared by self-condensation of the corresponding ester under standard trans-esterification conditions. The spacer segment length that connects the branching points was systematically varied by starting from the appropriate ethyl 3,5-bis(ω-hydroxyoligo(ethyleneoxy))benzoate. The thermal properties of the hyperbranched polyesters were studied using DSC, and they have been compared with those of the linear analogues prepared from the corresponding *p*-hydroxybenzoic acid derivatives and also with the molecularly "kinked" analogues prepared from the meta isomers. These hyperbranched polyesters were also terminally functionalized by using a potentially mesogenic 4-butoxybiphenylcarboxylic acid derivative in an attempt to prepare novel hyperbranched liquid crystalline polyesters. This was achieved by copolymerization of the AB_2 monomer with the mesogenic A-type capping unit. These polymers were found to be amorphous and did not exhibit any liquid crystalline phases, probably due to the random distribution of the mesogenic segments on the polymer framework, making it difficult to both crystallize and form mesophases.

Introduction

Highly branched, yet soluble, polymeric structures have attracted a lot attention from synthetic chemists and theoreticians, both because of their unique behavior and because of their potential applications.[1−3] Such highly branched polymers may be prepared by two distinct routes: (a) a stepwise procedure, in which the growth process is carried out one generation at a time, and (b) a one-step process, wherein the growth occurs randomly starting from an AB_2-type monomer, where A and B are functional groups that are reactive only toward each other. The former route, especially the convergent approach developed by Frechet and coworkers,[4−6] has been utilized extensively to generate perfectly branched structures with controlled variation of the peripheral functionality,[7] hybrid linear−dendritic block copolymers,[8−10] etc. This approach, while capable of generating perfect dendrimers, is rather tedious, often requiring chromatographic purification at every step of the growth process. The latter approach, being a one-pot approach, is more amenable to scaleup and, therefore, offers a wider scope for potential applications.

The one-step approach has been utilized to prepare a variety of hyperbranched polymers, such as polyesters,[11−14] polyethers,[15,16] polyurethanes,[17,18] poly(siloxysilanes),[19] polyphenylenes,[20] poly(ether ketones),[21] and polyamides.[22] Most of these reports have focused on the development of synthetic schemes for the preparation of the polymers and establishment of their structures. Little has been done by way of controlled structural variation to understand structure−property relationships in this class of hyperbranched polymers. Some recent efforts, however, have addressed the issues of the variation of terminal functionality[2] and the incorporation of mesogenic units.[15,23]

Hyperbranched polyesters (mostly wholly aromatic systems) have been prepared by two routes: (a) the trimethylsilyl ether−acid chloride approach[11,14] and (b) the acetate approach.[12,13] Both of these approaches generate high molecular weight polymers with a degree of branching of ca. 60%. Studies on the structural variation of the hyperbranched polyesters have essentially concentrated on the effect of terminal functional groups and monofunctional functional comonomers on the T_g of the resulting polymers.[13,14] In this paper, we report a systematic study of the variation of the spacer segment length between two branching junctions by using appropriately designed monomers that incorporate these segments and compare the thermal behavior of the resulting hyperbranched structures with those of the linear and kinked analogues. Further, we explore the possibility of preparing novel liquid crystalline polyesters by copolymerization of the AB_2 monomers with a potentially mesogenic A-type comonomer.

Experimental Section

General Procedures. ^1H NMR spectra were recorded on a Bruker ACF-200 spectrometer using the TMS/solvent signals as an internal reference. Solid state CP-MAS ^{13}C NMR spectra were recorded on a Bruker DSX-300 spectrometer. Differential scanning calorimetric studies were done using a Rheometric Scientific DSC Plus module, and TGA studies were done using a DuPont 910 module at a heating rate of 20 K/min under nitrogen. Polarizing light microscopic studies were carried out using a Leitz 12POL microscope and a Mettler FP82 HT hot stage. Viscosity measurements were made using an Ubellhode viscometer in a constant temperature bath.

Ethyl 3,5-Dihydroxybenzoate (2). 3,5-Dihydroxybenzoic acid (15 g, 97.4 mmol) was refluxed in 200 mL of absolute ethanol in the presence of 5 mL of concentrated sulfuric acid for 20 h. Ethanol was removed after neutralization of the sulfuric acid, and the residue was poured into excess water. The product was extracted into ether, and the ether layer was washed with water, dried over anhydrous sodium sulfate, and then concentrated to obtain a viscous liquid, which crystallized after being in the freezer for 3 h: yield 15.1 g (85%); mp 72−73 °C; ^1H NMR (acetone-d_6) δ 1.33 (t, 3H, $CH_2\mathbf{CH_3}$), 4.27 (q, 2H, $\mathbf{CH_2}CH_3$), 6.58 (t, 1H, **Ar**), 7.0 (d, 2H, **Ar**).

Ethyl 3,5-Bis(ω-hydroxyoligo(ethyleneoxy))benzoates (3a−c). Ethyl 3,5-dihydroxybenzoate (5 g, 27.5 mmol) was stirred at 90 °C for 24 h in the presence of 56 mmol of the appropriate monochlorooligoethyleneoxy glycol, 25 g of anhydrous potassium carbonate, and a few crystals of potassium iodide in 100 mL of DMF. The reaction mixture was poured into excess water and extracted with chloroform. The organic layer was washed with 5% aqueous sodium hydroxide (2 × 100 mL) and then with water, dried over sodium sulfate, and

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then concentrated to obtain the product. The product was dried in a vacuum oven at 100 °C for 1 day. **3a**: yield 57%; ^{1}H NMR (CDCl$_3$) δ 1.38 (t, 3H, CH$_2$**CH$_3$**), 2.47 (s, br, OH), 3.64 (t, 4H, HO**CH$_2$**CH$_2$), 4.18 (t, 4H, PhO**CH$_2$**CH$_2$), 6.72 (t, 1H, **Ar**), 7.22 (d, 2H, **Ar**). **3b**: yield 52%; ^{1}H NMR (CDCl$_3$) δ 1.38 (t, 3H, CH$_2$**CH$_3$**), 2.5 (s, broad, **OH**), 3.66 (t, 4H, HO**CH$_2$**), 3.77 (t, 4H, HOCH$_2$**CH$_2$**O), 3.85 (t, 4H, PhOCH$_2$**CH$_2$**O), 4.16 (t, 4H, PhO**CH$_2$**CH$_2$O), 4.35 (q, 2H, **CH$_2$**CH$_3$), 6.72 (t, 1H, **Ar**), 7.22 (d, 2H, **Ar**). **3c**: yield, 64.5%; ^{1}H NMR (CDCl$_3$) δ 1.30 (t, 3H, CH$_2$**CH$_3$**), 2.95 (s, br, **OH**), 3.54−3.79 (m, 20H, HOCH$_2$**CH$_2$CH$_2$OCH$_2$CH$_2$OCH$_2$**CH$_2$OPh), 4.07 (t, 4H, PhO**CH$_2$**CH$_2$), 4.26 (q, 2H, O**CH$_2$**CH$_3$), 6.65 (t, 1H, **Ar**), 7.11 (d, 2H, **Ar**).

Ethyl 4-Hydroxybenzoate (5). The same procedure was used as for **2**. The product was recrystallized from aqueous ethanol to obtain light gray crystals: yield, 9.6 g (85%); mp 190−191 °C; ^{1}H NMR (DMSO-d_6) δ 1.37 (t, 3H, **CH$_3$**), 1.95 (s, br, **OH**), 4.37 (q, 2H, **CH$_2$**CH$_3$), 6.98 (d, 2H, **Ar**), 7.1 (d, 2H, **Ar**), 8.04 (d, 2H, **Ar**).

Ethyl-4-(*ω*-Hydroxyoligo(ethyleneoxy))benzoate (6a−c). Ethyl *p*-hydroxybenzoate was stirred at 90 °C in 30 mL of DMF for 20 h in the presence of 25 mmol of monochlorooligoethyleneoxy glycols, 20 g of potassium carbonate, and a few crystals of potassium iodide. The reaction mixture was poured into excess water and extracted with chloroform. The organic layer was washed with 5% sodium hydroxide (2 × 100 mL) and then with water. It was then concentrated after drying over sodium sulfate to obtain the product. The product was dried in a vacuum oven at 100 °C for 1 day. **6a**: yield, 65%; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 3H, CH$_2$**CH$_3$**), 3.4 (s, br, **OH**), 3.98 (t, 2H, CH$_2$**CH$_2$**OH), 4.08 (t, 2H, PhO**CH$_2$**CH$_2$), 4.34 (q, 2H, **CH$_2$**CH$_3$), 6.9 (d, 2H, **Ar**), 7.96 (d, 2H, **Ar**). **6b**: yield, 65%; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 3H, CH$_2$**CH$_3$**), 3.64 (t, 2H, CH$_2$**CH$_2$**OH), 3.74 (t, 2H, **CH$_2$**CH$_2$OH), 3.85 (t, 2H, PhOCH$_2$**CH$_2$**), 4.14 (t, 2H, PhO**CH$_2$**CH$_2$), 4.31 (q, 2H, **CH$_2$**CH$_3$), 6.93 (d, 2H, **Ar**), 7.99 (d, 2H, **Ar**). **6c**: yield, 40%; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 3H, CH$_2$**CH$_3$**), 3.58 (t, 2H, CH$_2$**CH$_2$**OH), 3.72 (m, 6H, O**CH$_2$CH$_2$OCH$_2$**CH$_2$OH), 3.87 (t, 2H, PhOCH$_2$**CH$_2$**), 4.17 (t, 2H, PhO**CH$_2$**CH$_2$), 4.35 (q, 2H, **CH$_2$**CH$_3$), 6.94 (d, 2H, **Ar**), 7.99 (d, 2H, **Ar**).

Ethyl 3-Hydroxybenzoate (8). Same procedure as for **2** was used: yield, 90% mp 70−72 °C; ^{1}H NMR (CDCl$_3$) δ 1.37 (t, 3H, COOCH$_2$**CH$_3$**), 4.35 (q, 2H, COO**CH$_2$**CH$_3$), 7.05−7.1 (m, 1H, **Ar**), 7.26−7.32 (m, 1H, **Ar**), 7.56−7.63 (m, 2H, **Ar**).

Ethyl 3-(*ω*-Hydroxyoligo(ethyleneoxy))benzoate (9a−c). Same procedure as for **6a−c** was used. **9a**: yield, 76%; mp 47−48 °C; ^{1}H NMR (CDCl$_3$) δ 1.34 (t, 3H, CH$_2$**CH$_3$**), 2.7 (s, br, **OH**), 3.95 (t, 2H, CH$_2$**CH$_2$**OH), 4.1 (t, 2H, PhO**CH$_2$**CH$_2$), 4.33 (q, 2H, **CH$_2$**CH$_3$), 7.06−7.85 (m, 4H, **Ar**). **9b**: yield, 69%; ^{1}H NMR (CDCl$_3$) δ 1.36 (t, 3H, CH$_2$**CH$_3$**), 3.65 (t, 2H, CH$_2$**CH$_2$**OH), 3.76 (t, 2H, **CH$_2$**CH$_2$OH), 3.91 (t, 2H, PhOCH$_2$**CH$_2$**), 4.17 (t, 2H, PhO**CH$_2$**CH$_2$), 4.41 (q, 2H, **CH$_2$**CH$_3$), 4.49 (t, 1H, **OH**), 7.06−7.85 (m, 4H, **Ar**). **9c**: yield, 66%; ^{1}H NMR (CDCl$_3$) δ 1.38 (t, 3H, CH$_2$**CH$_3$**), 3.6 (t, 2H, CH$_2$**CH$_2$**OH), 3.70 (m, 6H, PhOCH$_2$CH$_2$O**CH$_2$CH$_2$OCH$_2$**CH$_2$OH), 3.87 (t, 2H, PhOCH$_2$**CH$_2$**), 4.17 (t, 2H, PhO**CH$_2$**CH$_2$), 4.33 (q, 2H, **CH$_2$**CH$_3$), 4.49 (t, 1H, **OH**), 7.06−7.86 (m, 4H, **Ar**).

4-(4-Acetoxyphenyl)acetophenone (11). The synthesis was carried out starting from 4-phenylphenol as described by Tanagaki et al.[24] (yield, 97%; mp. 124.5−125.5 °C).

4-(4-Butoxyphenyl)acetophenone (12). 4-(4-Acetoxyphenyl)acetophenone (**11**) (2 g, 9.4 mmol) was refluxed in 50 mL of water containing 3 g (75.2 mmol) of sodium hydroxide until the initially insoluble starting material dissolved (ca. 6 h). Butyl bromide (1.37 g, 9.45 mmol) in 25 mL of ethanol was then added dropwise and the mixture was refluxed for another 21 h. The precipitate that formed was filtered, washed with water, and recrystallized from ethanol: yield, 85%; mp 195−97 °C (dec); ^{1}H NMR δ 0.85 (t, 3H, OCH$_2$CH$_2$CH$_2$**CH$_3$**), 1.2−1.43 (h, 2H, OCH$_2$CH$_2$**CH$_2$**CH$_3$), 1.47−1.71 (p, 2H, OCH$_2$**CH$_2$**CH$_2$CH$_3$), 2.45 (s, 3H, CO**CH$_3$**), 3.9 (t, 2H, O**CH$_2$**CH$_2$CH$_2$CH$_3$), 6.93 (d, 2H, **Ar**), 7.5−7.66 (m, 4H, **Ar**), 7.95 (d, 2H, **Ar**).

4-(4-Butoxyphenyl)benzoic Acid (13). The oxidation of 4-(4-butoxyphenyl)acetophenone was carried out as described by Dauben et al.[25] for 4-(4-methoxyphenyl)acetophenone. The product was recrystallized from dioxane: yield, 89%; mp 210−215 °C (dec); ^{1}H NMR (acetone-d_6) δ 0.85 (t, 3H, **CH$_3$**), 1.2−1.43 (h, 2 H, OCH$_2$CH$_2$**CH$_2$**CH$_3$), 1.47−1.71 (p, 2H, OCH$_2$**CH$_2$**CH$_2$CH$_3$), 3.92 (t, 2H, PhO**CH$_2$**), 6.91 (d, 2H, **Ar**), 7.55 (d, 2H, **Ar**), 7.64 (d, 2H, **Ar**), 7.95 (d, 2H, **Ar**).

Ethyl 4-(4-Butoxyphenyl)benzoate (14). 4-(4-Butoxyphenyl)benzoic acid (2 g, 7.19 mmol) was refluxed in 50 mL of absolute alcohol and 3 mL of concentrated sulfuric acid for 18 h. The product crystallized on cooling. It was then filtered, washed with water, and dried in an oven to obtain 1.9 g (86% yield) white crystals: mp 127.5−128.5 °C; ^{1}H NMR (CDCl$_3$) δ 0.9−2.0 (m, 10H, **CH$_3$CH$_2$CH$_2$O**, COOCH$_2$**CH$_3$**), 4.04 (t, 2H, PhO**CH$_2$**), 4.41 (q, 2H, COO**CH$_2$**CH$_3$), 6.95 (d, 2H, **Ar**), 7.52−7.62 (m, 4H, **Ar**), 8.10 (d, 2H, **Ar**).

Polymerization of 3a−c. Dried monomer (500 mg) was heated gradually to 200 °C, under dry nitrogen, in the presence of ca. 1 mol % of titanium 1−methylethoxide catalyst for 30 min. This viscous mass was further heated under dynamic vacuum for 3 h to obtain high molecular weight rubbery polymers **P3a-c**. The polymers were purified by dissolving them in *p*-chlorophenol and precipitating in ether. All of the polymers were washed with acetone before drying in a vacuum oven at 100 °C for 1 day. **P3a**: ^{1}H NMR (TFA/DMSO-d_6) δ 3.7−4.5 (m, 8H, **CH$_2$'s**) 6.7 (s, 1H, **Ar**), 7.1 (s, 2H, **Ar**). **P3b**: ^{1}H NMR (TFA/DMSO-d_6) δ 3.7−4.5 (m, 16H, **CH$_2$'s**), 6.7 (s, 1H, **Ar**), 7.1 (s, 2H, **Ar**). **P3c**: ^{1}H NMR (TFA/DMSO-d_6) δ 3.7−4.4 (m, 24H, **CH$_2$'s**), 6.7 (s, 1H, **Ar**), 7.1 (s, 2H, **Ar**).

Polymerization of 6a−c and 9a−c. Polymerizations of **6a−c** and **9a−c** were done in a similar fashion as **3a−c** but were heated for longer times (18 h) under dynamic vacuum to obtain the higher molecular weight polymers **P6a−c** and **P9a−c**. Polymers were purified by precipitation in methanol from *p*-chlorophenol for **P6a** and **P9a**, and **P6b**,**c** and **P9b**,**c** were dissolved in chloroform and reprecipitated into methanol. **P6b**: ^{1}H NMR (CDCl$_3$) δ 3.9 (m, 4H, COOCH$_2$**CH$_2$OCH$_2$**CH$_2$OPh), 4.2 (t, 2H, PhO**CH$_2$**), 4.4 (t, 2H, COO**CH$_2$**), 6.9 (d, 2H, **Ar**), 8.0 (d, 2H, **Ar**). **P6c**: ^{1}H NMR (CDCl$_3$) δ 3.6−3.9 (m, 8H, COOCH$_2$**CH$_2$OCH$_2$CH$_2$OCH$_2$**CH$_2$OPh), 4.2 (t, 2H, PhO**CH$_2$**), 4.4 (t, 2H, COO**CH$_2$**), 6.9 (d, 2H, **Ar**), 8.0 (d, 2H, **Ar**). **P9b**: ^{1}H NMR (CDCl$_3$) δ 3.5−3.8 (m, 4H, COOCH$_2$**CH$_2$OCH$_2$**CH$_2$OPh), 4.13 (s, 2H, **CH$_2$**OPh), 4.46 (s, 2H, COO**CH$_2$**), 7.0−7.1 (m, 1H, **Ar**), 7.26−7.33 (m, 1H, **Ar**), 7.56−7.65 (m, 2H, **Ar**). **P9c**: ^{1}H NMR (CDCl$_3$) δ 3.7−3.84 (m, 8H, COOCH$_2$**CH$_2$OCH$_2$OCH$_2$**CH$_2$OPh), 4.13 (s, 2H, **CH$_2$**OPh), 4.46 (s, 2H, COO**CH$_2$**), 7.0−7.1 (m, 1H, **Ar**), 7.26−7.33 (m, 1H, **Ar**), 7.56−7.65 (m, 2H, **Ar**).

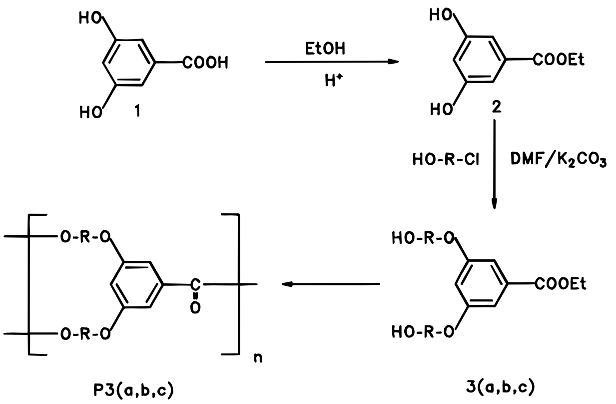
Preparation of HPE-PMa−c. In a typical procedure, 1.5 mmol of **3a**, **3b**, or **3c** was taken along with 1.5 mmol of ethyl 4-(4-butoxyphenyl)benzoate (**14**) in a reaction vessel and heated to 200 °C in the presence of ca. 1 mol % of titanium 1-methylethoxide for about 2−3 h, during which time a solid mass formed. The polymerization was continued for an additional 12−16 h under dynamic vacuum at 220 °C. The polymer was dissolved in *p*-chlorophenol at 90 °C (∼2 days), repreciptated into diethyl ether, washed thoroughly, and dried in a vacuum oven. The percentage yields of the different polymers are given in Table 3.

Results and Discussion

The monomers **3a−c** were prepared from ethyl 3,5-dihydroxybenzoate by coupling with the appropriate oligoethylene glycol monochlorohydrin, using the standard DMF/K$_2$CO$_3$ approach (Scheme 1). The AB-type analogues (both para isomers **6a−c** and meta isomers **9a−c**) were prepared by using similar reaction conditions (Scheme 2).

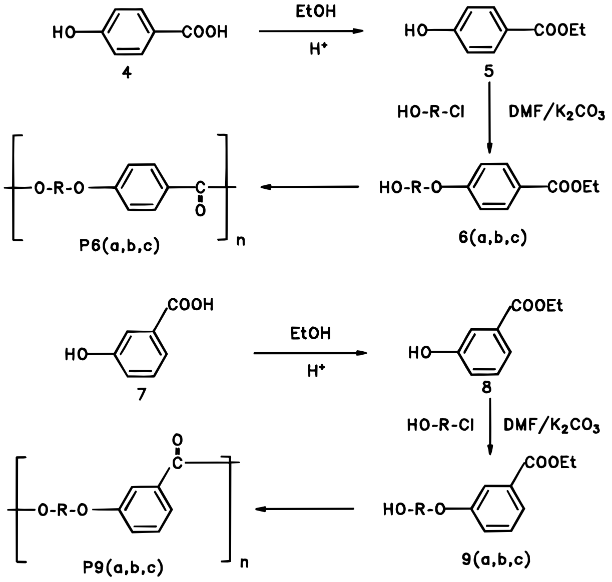
The polymerization of the AB$_2$ monomers, **3a−c**, was carried out neat under standard trans-esterification conditions using titanium 1-methylethoxide as the catalyst. The polymerization was first carried out under a dry nitrogen flow at 200 °C for 30 min, after which time a dynamic vacuum (0.05 mbar) was applied to remove the ethanol generated and to ensure the formation of high molecular weight polymers **P3a−c**. The

Scheme 1



	a	b	c
R	$(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2O(CH_2)_2$

Scheme 2



	a	b	c
R	$(CH_2)_2$	$(CH_2)_2O(CH_2)_2$	$(CH_2)_2O(CH_2)_2O(CH_2)_2$

polymers were purified by reprecipitating a *p*-chlorophenol solution into ether. The linear analogues (para, **P6a**−**c** and meta, **P9a**−**c** isomers) were also prepared similarly, but were heated for longer times under dynamic vacuum to obtain high molecular weight polymers. The linear polymers were purified similarly by reprecipitation of a *p*-chlorophenol/chloroform solution into methanol.

The hyperbranched polyesters, **P3a**−**c**, were found to be soluble only in solvents like trifluoroacetic acid and *p*-chlorophenol. Contrary to our expectation that a high level of branching should enhance the solubility, we found that the linear analogues were more readily soluble even in solvents like chloroform. This may be due to the presence of strong intermolecular hydrogen-bonding interactions between the large number of terminal hydroxyl groups in these hyperbranched polyesters and/or due to their higher molecular weights.

The ^{1}H NMR spectra of the monomer **3b** and the polymer **P3b** are shown in Figure 1. The signals corresponding to the ethyl ester in the monomer (at 4.2 and 1.3 ppm) are essentially absent from the polymer spectrum, while a new peak corresponding to the methylene ester protons (**CH_2**OOC) is seen at 4.4 ppm. This suggests that the conversion is rather high, implying the formation of high molecular weight polymers. Unlike the case of wholly aromatic polyesters,[11] where the degree of branching is easily established from the relative intensities of signals belonging to the dendritic, defective, and terminal segments, in our case, where a spacer segment is incorporated, it is not possible to distinguish the various types of segments by using NMR, and therefore the degree of branching could not be estimated. The ^{1}H NMR spectra of the linear analogues, both para- and meta-linked isomers, exhibit features similar to those described for the hyperbranched structures, but the end group methyl proton signals are visible in some cases, the relative intensities of which suggest the formation of reasonably high molecular weight polymers. The inherent viscosity of the polymers varies from 0.4 to 0.8 dL/g (Table 1), which also indicates that the samples are of reasonable molecular weights. The inherent viscosity of the hyperbranched polyesters, **P3a**−**c**, appears to increase with increasing length of the spacer segment. However, conclusions regarding their molecular weights may be difficult to make as the variation in branching density is also likely to effect their solution viscosity. In the case of the wholly aromatic hyperbranched polyesters reported by Turner et al.,[13] inherent viscosity values of 0.3 dL/g (at a concentration of 0.5 g/L) represent molecular weights in the range of 100 000. Although a direct comparison of these solution viscosities with those of the spacer containing hyperbranched polyesters (Table 1) is not strictly valid, it suggests that the molecular weights of our polymers are certainly high enough that comparison of their physical properties is reasonable.

The DSC thermograms (Figure 2) of the hyperbranched polymers **P3a**−**c** indicate that the samples are all amorphous and they exhibit only a glass transition. As expected, the T_g's decreased (from 353 to 269 K) upon increasing the length of the spacer segment from a monoethyleneoxy to a triethyleneoxy unit. To compare the behavior of such hyperbranched structures, we have synthesized two series of linear analogues containing the same spacer segments: (a) linear analogues starting from *p*-hydroxybenzoic acid derivatives and (b) molecularly “kinked” analogues starting from the corresponding meta isomer. We may expect the meta isomers to have a greater structural similarly to the backbone of the hyperbranched polymer than the para isomers. We note that, for a given spacer length, the meta isomers always have lower T_g's than the other two. In an attempt to rationalize the glass transition temperatures of highly branched polymeric structures, Stutz[26] recently suggested that the number of branching points and the number of chain ends are two factors that contribute in an opposite fashion to the glass transition temperatures. While the chain ends tend to lower the T_g, branching would increase it, and oftentimes these effects cancel each other, leading to the observed invariance in T_g with branching. It was also noted that variation from the general trend can occur when specific interactions between chain ends lower the mobility and, hence, increase the T_g.

In the series of hyperbranched polyesters examined in this paper, we notice that the T_g of the wholly aromatic phenol-terminated hyperbranched polyesters[11] (**P3**) drastically decreased upon the introduction of an

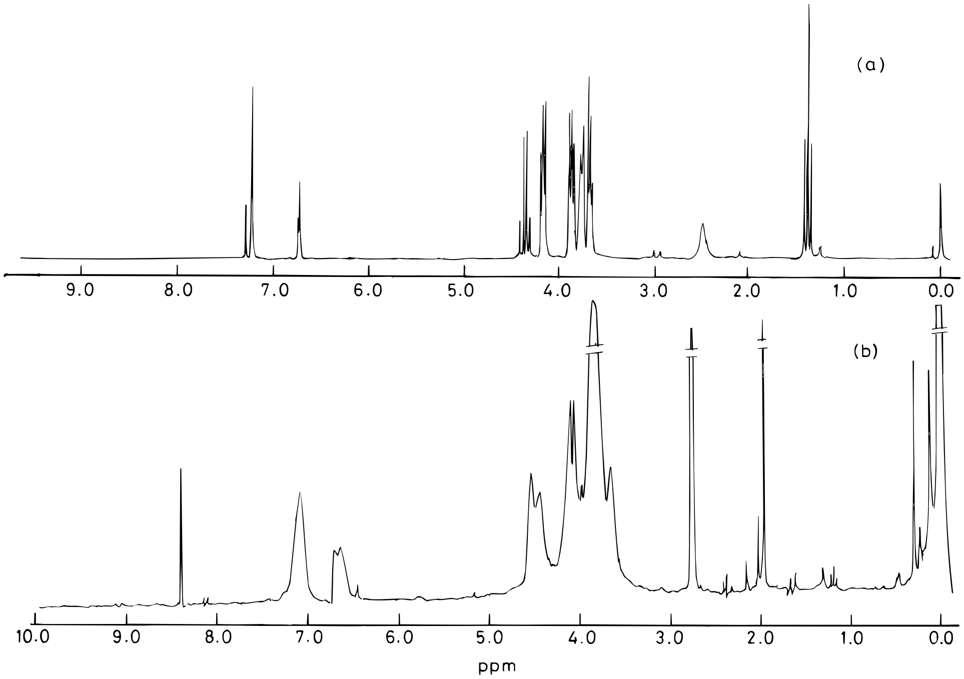


Figure 1. ^{1}H NMR spectra of **3b** in $CDCl_3$ (a) and of **P3b** in TFA/DMSO-d_6 (b).

Table 1

polymer	% yield	η inh (dL/g)	T_g (K)	T_m (K)
P3a	72	0.43[a]	353	
P3b	85	0.65[a]	288	340
P3c	70	0.82[a]	269	374
P6a	86	0.53[a]	344	478
P6b	85	0.45[b]	301	394
P6c	79	0.68[b]	276	350
P9a	88	0.42[a]	320	428
P9b	90	0.35[b]	282	
P9c	86	0.54[b]	266	

[a] 0.2% solution in *p*-chlorophenol at 50 °C. [b] 0.2% solution in chloroform at 30 °C.

aliphatic spacer from 473 K for **P3** to 353 K for **P3a**. Further reduction in the T_g's is noticed when the length and flexibility of the spacer segment increase. One further interesting observation is that while the T_g's of the linear meta polyesters **P9a**−**c** are consistently lower than those of their hyperbranched analogues **P3a**−**c**, the difference between their T_g's for a given spacer length decreases with increasing spacer length, i.e., the difference in T_g's of **P3a** and **P9a** is 33 K, while that between **P3c** and **P9c** is only 3 K. If one assumes that the two factors, namely, number of chain ends and degree of branching, remain constant with increasing spacer length, then it appears that the effect of branching on the T_g becomes weaker as one increases the spacer length between the branching points. This, of course, is a qualitative conclusion based on only three data points and needs to be confirmed in other hyperbranched systems where a larger variation in spacer length can be investigated. The assumption regarding the number of chain ends and degree of branching, we believe, is reasonable for high molecular weight hyperbranched structures, as the degree of branching in such polymers, prepared via the AB_2 self-polycondensation route, was found to be invariant (ca. 50−60%) with the type of polymer.[11,12,18]

In an attempt to further rationalize this behavior, we have considered the basic polymer structure to be a copolymer of the wholly aromatic polyester and poly(ethylene oxide). By using the standard Fox equation:[27]

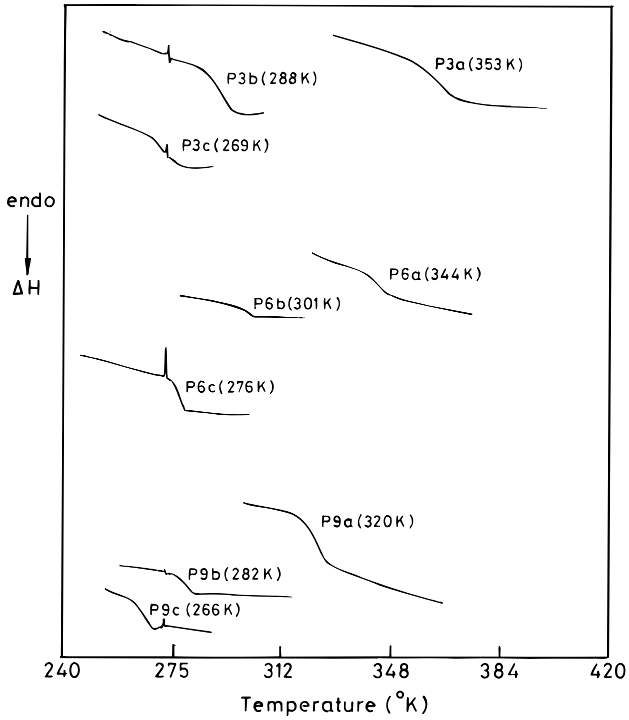


Figure 2. DSC curves of the polymers. The small peak at 273 K is due to ice.

$$\frac{1}{T_g} = \frac{w_1}{T_{g_1}} + \frac{w_2}{T_{g_2}} \tag{1}$$

which describes the variation in T_g with the composition of random copolymers, where w_1 and w_2 are the weight fractions of the two monomers and T_{g1} and T_{g2} are the glass transition temperatures of the corresponding homopolymers, we have calculated the T_g's of the various linear meta and para polyesters and those of the hyperbranched polyesters. The T_g value of 434 K was taken for the wholly aromatic para polyester[28] and

Table 2

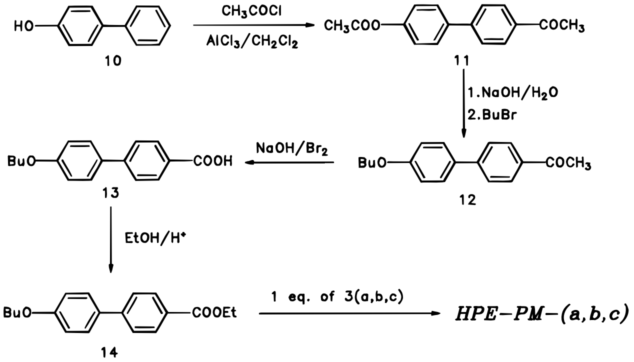
polymer	w_1	T_g (obs) (K)	T_g (calc) (K)	$\Delta T_g{}^a$
P3	0.00	473		
P3a	0.39	353	322	−31
P3b	0.57	288	281	−7
P3c	0.66	269	264	−5
P6	0.00	434		
P6a	0.27	344	340	−4
P6b	0.42	301	304	3
P6c	0.52	276	284	8
P9	0.00	428		
P9a	0.27	320	338	18
P9b	0.42	282	302	20
P9c	0.52	266	283	17
PEO	1.00	215		

[a] $\Delta T_g = T_g(\text{calc}) - T_g(\text{obs})$.

that of 328 K for the corresponding meta polyester.[29] The T_g of poly(ethylene oxide) (M_n = 60 000) was measured to be 215 K. These calculated values are listed in Table 2. It is seen that, in the case of the linear meta polyesters, the calculated values are considerably higher than the observed ones, while in the hyperbranched systems they are lower than the observed values. Furthermore, the T_g's of these linear polyesters predicted by eq 1 are higher by almost a constant value (ΔT_g is ca. 18°). But in the hyperbranched polymers, the ΔT_g value decreases with increasing spacer length. This behavior may be qualitatively interpreted in the following manner. First, since eq 1 is strictly valid only for random linear copolymers, the presence of branching, as expected, will cause the observed T_g's to be higher than those predicted by the equation. Second, the decrease in ΔT_g with an increase in spacer length can be rationalized by the fact that increasing the spacer length amounts to decreasing the branching density and, hence, a diminished effect on the T_g. Thus, we may anticipate that continually increasing the length of the spacer segment will cause these hyperbranched polymers to exhibit essentially the same T_g's as their linear analogues. It must be noted that we have chosen to neglect the effect of chain ends, as we expect both the nature and the number of chain ends to have remained the same in the series of hyperbranched polyesters. In the linear para polyesters, although the variation in ΔT_g is slightly larger than in the meta analogues, the calculated values are in general closer to the observed ones, suggesting that the Fox equation appears to be more applicable to the linear systems.

The effect of branching and molecular kinks on the melting temperatures T_m and also on the propensity of the system to crystallize appears to be significant. All of the linear para polyesters undergo crystallization upon annealing at temperatures between the T_g and T_m. The T_m decreased with an increase in spacer length, as expected. **P6a** and **P6b** show multiple melting transitions, the relative intensities of which varied with annealing temperatures and times, probably due to the presence of different crystal forms. **P6c** shows a single, but slightly broad transition. The temperatures reported in all cases (Table 1) are those of the highest melting transitions. The linear meta polyesters (**P9a**−**c**), however, were found to be very sluggish to crystallize. While the annealing of sample **P9a** for 1 h at 371 K resulted in two weak melting transitions at 413 and 428 K, prolonged annealing of both **P9b** and **P9c** above their T_g's did not result in any crystallinity in them, as confirmed by the absence of any melting transitions. Here it should be noted that the wholly aromatic meta polyester also does not crystallize, even upon prolonged annealing, but does so only by solvent-induced crystallization.[29] Thus, it is interesting to note that while the wholly aromatic polyester and the polyesters with longer spacers do not crystallize, the polyesters with intermediate spacer lengths do. In hyperbranched systems, on the other hand, the wholly aromatic polyesters and the polyesters with short spacer segments (**P3a**) do not crystallize, but the ones with longer spacer segments crystallize very slowly upon prolonged annealing. Since both **P3b** and **P3c** have T_g's below room temperature, prolonged annealing (10−20 days) at room temperature yields partially crystalline samples with T_m's of 374 and 340 K, respectively. Annealing of **P3a** at 373 K for about 21 h does not, however, result in any crystallinity. Further prolonged annealing may, however, lead to crystallization. It should be noted that, unlike in linear polyesters, in hyperbranched systems a single broad transition was observed. The high degree of randomness in the structure and the rather broad molecular weight distributions typically observed in such hyperbranched structures[12] may explain the rather broad melting transition. The degradation temperature as observed from TGA studies was found to be 643 K for all of the polyesters and was independent of the hyperbranched or linear nature of the polymers.

Scheme 3



Incorporation of Mesogenic Segments. AB_2-type monomers can be copolymerized with molecules containing a single A-type functional group up to a molar ratio of 1:1 without, in principle, expecting any reduction in molecular weight, as the functional group equivalence is still maintained. Thus, copolymerization of an AB_2-type monomer with an A-type comonomer can serve as a novel method for the introduction of functional units, such as mesogens. This approach of utilizing an A-type comonomer as a capping agent to prevent cross-linking has been utilized in hyperbranched polyurethanes[17] and also in hyperbranched polyesters.[12,14] We have explored the possibility of using this approach to generate novel liquid crystalline polymers.

The potentially mesogenic unit (a promesogen) ethyl 4-(4-butoxyphenyl)benzoate (**14**) was prepared according to Scheme 3. Although this ester is unlikely to exhibit liquid crystallinity, we anticipate that, upon copolymerization with the monomers **3a**−**c**, the ester linkage formed with the aliphatic spacer in the AB_2-type monomer will lead to a mesogenic segment with a longer axial ratio due to the inclusion of the spacer segment of the AB_2-type monomer. Two extreme structures (Figure 3) can result when such a copolymerization is carried out: (a) the A-type monomers can react first with an AB_2-type monomer to form a simple AB monomer, which can further polymerize to give a linear polymer with pendant mesogenic units (Case I), and (b) a perfect dendritic structure may be generated first, after which the

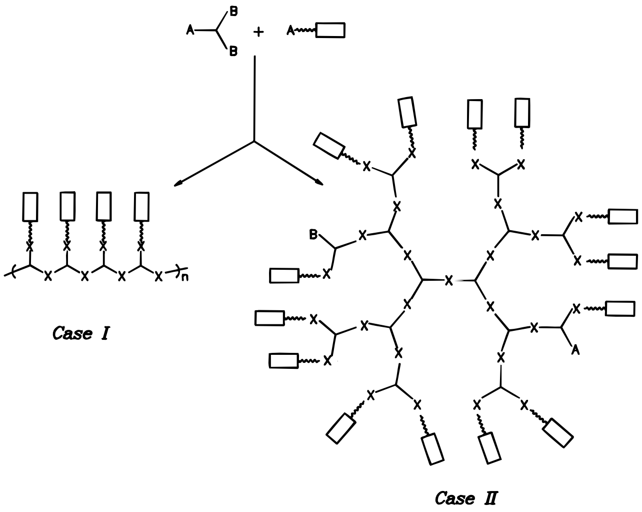


Figure 3. Schematic representation of the 1:1 copolymerization of an AB_2-type monomer with an A-type monomer.

Table 3

polymer	% yield	η inh[a] (dL/g)	T_g (K)
HPE-PMa	79	0.73	350
HPE-PMb	86	0.58	324
HPE-PMc	81	0.79	290

[a] 0.2% solution in *p*-chlorophenol at 50 °C.

terminal B groups may react with the A-type monomer to give a structure with the mesogenic units at the periphery (case II). In practice, we may expect an intermediate structure between the two extreme cases.

Copolymerization of the promesogenic unit with the AB_2 monomers **3a**−**c** was carried out by using equimolar ratios of the two monomers under standard transesterification conditions. The resulting polymers HPE-PMa−c with varying spacer segment lengths were all soluble in *p*-chlorophenol. Their inherent viscosities (Table 3) indicate the formation of moderately high molecular weight polymers. As a suitable solvent for recording the solution NMR spectra of these polymers was not found, their solid state CP-MAS ^{13}C NMR spectra were recorded. Representative CP-MAS ^{13}C NMR spectra of HPE-PMb (with a diethyleneoxy spacer) and of the parent hyperbranched polyester without the pendant mesogen (**P3b**) are shown in Figure 4. The spectrum of HPE-PMb clearly shows the presence of the pendent mesogenic unit; the signals due to the butoxy group carbons are seen in the region betwen 14 and 32 ppm, and additional aromatic signals around 111 and 127 ppm due to the biphenyl unit are also visible. One further confirmation for the capping of the terminal hydroxyl groups comes from the absence of the peak at 61 ppm due to the **CH2**OH carbons in the spectrum of HPE-PMb, which is clearly seen in the spectrum of the parent hyperbranched polyester. Upon esterification, this signal is shifted slightly downfield and gets buried under the signal due to ethyleneoxy spacers.

The T_g's of these polymers (Table 3) decrease with increasing spacer length from 350 to 290 K. While the T_g of HPE-PMa is almost the same as that of the parent hyperbranched polyester **P3a** with hydroxy end groups, the T_g's of the remaining two polymers are considerably higher than those of the parent hyperbranched polymers. This effect, due to the incorporation of biphenyl-containing end groups, is rather interesting and suggests that in more flexible systems the relative rigidity of the biphenyl unit contributes more significantly to the T_g than in less flexible systems. The DSC traces of these polymers indicate that they do not exhibit liquid crystallinity and that they were also completely amorphous, exhibiting only a T_g even after prolonged annealing at temperatures above their T_g's. This was further confirmed by the absence of birefringence in the polarized light optical microscopic studies up to 573 K. Thus, despite the incorporation of flexible spacers to link the mesogens to these polymers, these mesogens are unable to organize to form ordered mesophases. This may be due to the completely random placement of these mesogens on the hyperbranched polymer framework and also is probably due to the restricted mobility of these mesogenic units in such hyperbranched structures. This is in contrast to the work reported by Percec et al.,[15] where incorporation of mesogens in the backbone of hyperbranched structures resulted in the realization of liquid crystallinity. Controlled generation of two extreme structures (case I and case II) may help to analyze the problem in a bit more detail.

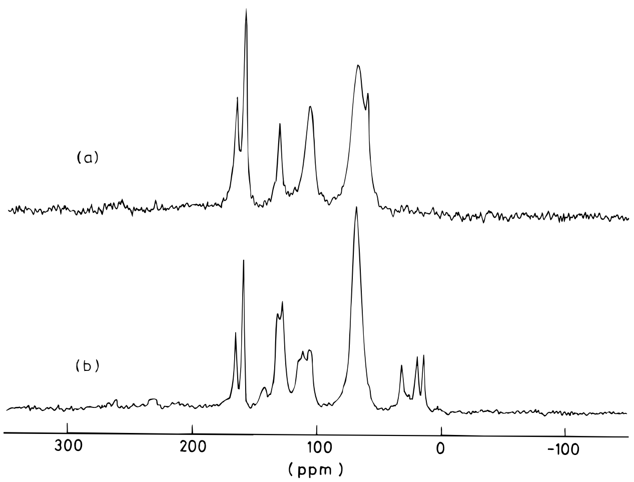


Figure 4. CP-MAS ^{13}C NMR spectra of the parent hyperbranched polyester **P3b** (a) and the corresponding 1:1 mesogen containing copolymer HPE-PMb (b).

Conclusions

A series of hyperbranched polyesters with varying oligo(ethyleneoxy) spacer segments between branching points was prepared by trans-esterification of the appropriate ethyl 3,5−bis(hydroxyoligo(ethyleneoxy))-benzoates. Linear analogues of these polyesters starting from the appropriate *p*- and *m*-hydroxybenzoic acid derivatives were also prepared for comparison of their thermal behavior. The T_g's of the linear meta polyesters were found to be lower than those of the hyperbranched analogues, but the difference in their T_g's decreased with increasing spacer length. By considering these polyesters to be copolymers of the corresponding wholly aromatic polyesters and poly(ethylene oxide), we have used the Fox equation to calculate T_g's for the different systems. The results indicate that, in the hyperbranched polyesters, the agreement with the calculated values is better in systems with longer spacer segments, i.e., lower branching density. Further, potentially mesogenic biphenyl units have been incorporated into hyperbranched systems by copolymerization of the AB_2 monomers with the appropriate promesogenic A-type monomer. The resulting copolymers, however, did not exhibit liquid cystallinity, despite the incorporation of long spacer segments. This is probably due to the random incorporation of the mesogenic segments and may also be inherent to the hyperbranched framework itself, which makes the formation of ordered mesophases difficult.

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