

## A Versatile New Method for Structure Determination in Hyperbranched Macromolecules

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A novel degradative procedure for the determination of the degree of branching in hyperbranched macromolecules is presented, and its versatility and scope are demonstrated with the synthesis and characterization of hyperbranched polyesters based on 4,4-bis(4'-hydroxyphenyl)pentanoic acid.

Two emerging themes in polymer chemistry are the synthesis of macromolecules with new architectures and the accurate control and determination of polymeric structure.<sup>1</sup> Both of these themes are driven by the desire for materials with new and/or improved properties.<sup>2</sup> An increasing amount of interest has recently been shown in a new class of polymeric material, termed hyperbranched macromolecules, with structures ranging from polyesters<sup>3</sup> to polyphenylenes.<sup>4</sup> These macromolecules are prepared by the one-step polymerization of AB<sub>2</sub> monomers which results in a branched structure that would be expected to assume a globular shape if the degree of branching was sufficiently high. The physical properties of these hyperbranched macromolecules have been shown to be different from linear polymers. For example, the solubility of hyperbranched macromolecules has been shown to be dramatically increased<sup>5</sup> while their viscosity is substantially decreased<sup>6</sup> when compared with linear polymers. However structure-property relationships are not well understood and the factors determining these property changes are not known. In order to establish a relationship between degree of branching and physical properties and to fully characterize these unique materials, determination of the degree of branching is essential. Currently there is only a single method available which relies on differences in the <sup>1</sup>H and/or <sup>13</sup>C NMR resonances for the different types of building blocks present in hyperbranched macromolecules.<sup>3,4,7</sup> However this method is limited and is practical only for specific types of monomer units that give rise to distinct resonances depending on their substitution pattern and for hyperbranched macromolecules with sufficiently resolved NMR spectra. Thus the degree of branching has not been determined for a large number of systems and the question as to whether these materials resemble linear polymers or highly branched globular systems cannot be answered.<sup>8-12</sup> Therefore the development of a more versatile method for determining the degree of branching is required. We report a new approach to the determination of degree of branching for hyperbranched macromolecules which not only complements, but has the potential to be more versatile than, the existing method.

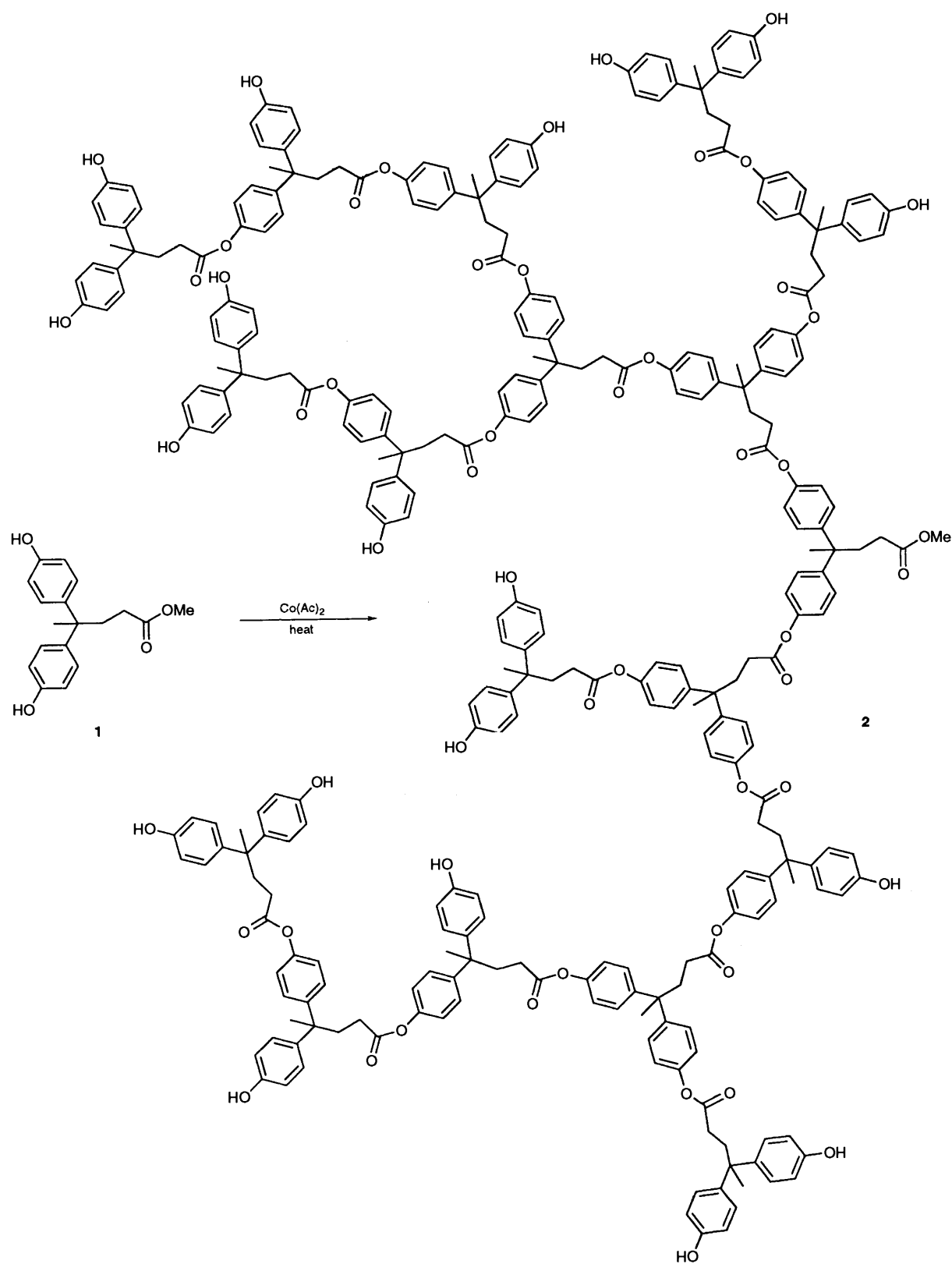
### Results and Discussion

To demonstrate this new approach, the polymerization of methyl 4,4-bis(4'-hydroxyphenyl)pentanoate **1** and structural elucidation of the resultant hyperbranched polyester was investigated. The polymerization of **1** was initially conducted at 120 °C, 10 mmHg, on a melt of the neat monomer in the presence of cobalt acetate (*ca.* 5%). This resulted in effervescence and a subsequent increase in the viscosity of the melt.<sup>13</sup> After 2 h the temperature was increased to 210 °C, 0.5 mmHg, and the viscous melt heated for an extra 3 h. The reaction mixture was allowed to cool and the solid dissolved in the minimum amount of tetrahydrofuran (THF). Purification of the crude polymer

was by initial precipitation into water, followed by reprecipitation into ether, and finally hexane. This gave the phenolic-terminated hyperbranched polyester **2** as a white solid in 90% yield, which was shown by gel permeation chromatography to have a polystyrene equivalent molecular weight, *M<sub>w</sub>*, of 47 000 (Scheme 1). As has been found previously<sup>5</sup> for other systems, the polyester **2** proved to be highly soluble in a range of solvents such as acetone, THF, methanol, dimethyl sulfoxide, *etc.* However, due to the uncontrolled and irregular nature of the polymerization reaction, compound **2** is obtained with a polydispersity of 2.1. More importantly the structure itself is not regular or 'perfect' and contains defects. Consideration of the structure for compound **2** reveals that there are only four different types of subunits or building blocks present. These include the single unique subunit at the focal point which can be neglected due to the high molecular weight of the polymer, the 'terminal' subunits which have two phenolic groups, the 'dendritic' subunits which have no free phenolic groups, and finally the 'linear' subunits which have one single phenolic group. In previous studies one would rely on these subunits having discrete resonances in the <sup>1</sup>H or <sup>13</sup>C NMR spectra to determine the degree of branching. However since the phenolic groups are on different aromatic rings, and both the <sup>1</sup>H and <sup>13</sup>C NMR spectra were broad and undefined, no distinction between resonances for the different subunits could be observed. Therefore this technique gives no information and the degree of branching could not be determined (Fig. 1).

The presence of three different types of subunits was used to advantage in the development of a new degradative technique for the determination of degree of branching. This technique involves initial modification of the chain ends of the hyperbranched macromolecule followed by chemical degradation of the polymeric linkages. Two fundamental requirements are that the chemistry used for degradation does not affect the modified chain ends and that degradation results in complete conversion into the elementary subunits. Therefore the B functionalities of the AB<sub>2</sub> monomer are chemically differentiated depending on the nature of the original polymeric subunit which allows for identification of the relative amounts of each subunit and hence the degree of branching.

To demonstrate this concept suitable modification and degradation reactions, which satisfied the above criteria, were required. The chemical degradation of linear polyester copolymers by hydrolysis is a well known reaction and it was decided to apply it to the above problem. Therefore the choice of modification reaction was governed by the stability of the resultant functional group to hydrolysis conditions. A suitable modification reaction is alkylation since the ethers obtained are stable to even vigorous hydrolysis conditions. For simplicity methylation was chosen as the modification reaction. However treatment of compound **2** with diazomethane under a variety of conditions<sup>14</sup> failed to give complete functionalization. Reaction



of compound **2** with methyl iodide in the presence of potassium carbonate<sup>15</sup> resulted in degradation to lower molecular weight oligomers. A mild, non-basic methylation procedure based on a silver oxide has been reported.<sup>16</sup> Therefore treatment of the phenolic polyester **2** with an excess of methyl iodide and silver oxide was found to give the methylated derivative **3**. A combination of size exclusion chromatography, model studies,

IR, <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy showed that methylation proceeded with complete conversion and no evidence of side reactions such as C-alkylation or degradation was observed. The resultant methyl ether chain ends are stable to base and treatment of **3** with an excess of potassium hydroxide in a mixture of THF and water results in cleavage. Only three products were observed and on comparison with independently

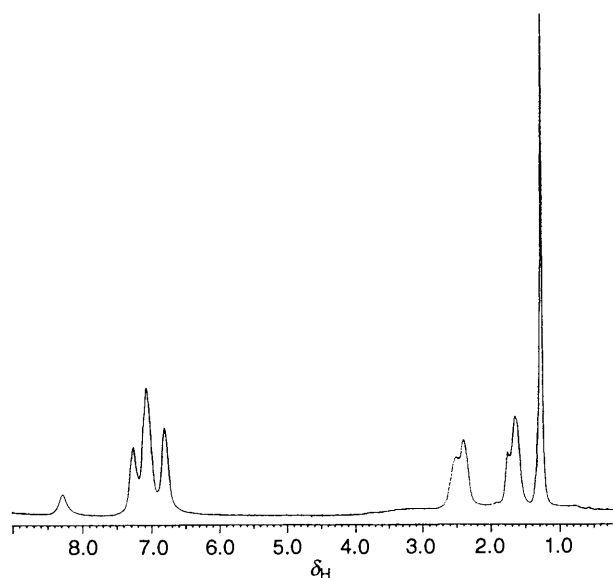


Fig. 1  $^1\text{H}$  NMR spectrum of phenolic-terminated polyester 2

synthesized model compounds, these degradation products were shown to be the dimethylated 4, monomethylated 5, and diphenolic 6 derivatives by capillary gas chromatography and HPLC (Scheme 2). They were obtained in 24, 51 and 25% respectively. These products are directly related to the three different types of building blocks present in the initial phenolic-terminated hyperbranched polyester, 2. Therefore from the relative percentages of each the degree of branching of 2 can be calculated to be 49%.

In conclusion, we have demonstrated a new degradative approach for the determination of the degree of branching for hyperbranched macromolecules. This approach is both complementary to, and more widely applicable and versatile than, the existing method based on NMR spectroscopy. The effect of catalyst and nature of the monomer unit on the degree of branching in the above system is currently being studied using this technique as is its extension to other hyperbranched polymers by the use of different modification and degradation reactions.

## Experimental

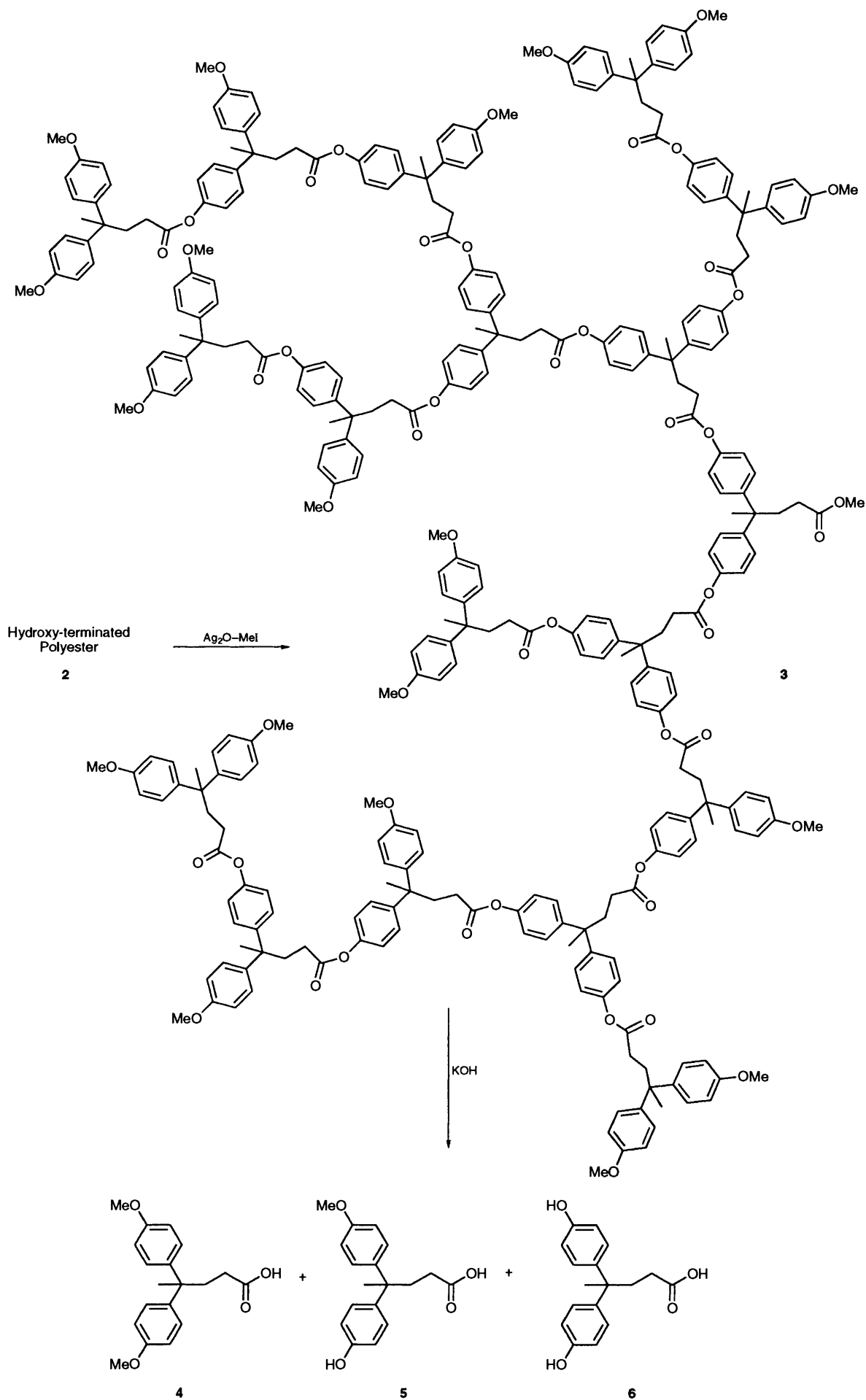
**General.**—M.p.s were determined on a Kofler hot-stage apparatus and are uncorrected. IR spectra were recorded on a Perkin-Elmer spectrophotometer as thin films on NaCl disks.  $^1\text{H}$  NMR spectra were recorded on solutions in  $\text{CDCl}_3$ , unless otherwise noted, on a Bruker AM 200 (200 MHz) spectrometer with the solvent proton signal as standard.  $^{13}\text{C}$  NMR spectra were recorded at 50 MHz on a Bruker AM 200 (200-MHz) spectrometer, with the solvent carbon signal as internal standard. Mass spectra were obtained on either a Kratos MS890 with EI ionization or a Hewlett Packard 5970 mass spectrometer. Analytical TLC was performed on commercial Merck plates coated with silica gel GF<sub>254</sub> (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Size exclusion chromatography was carried out on an IBM LC/9560 chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed with GPC-PRO software, version 3.12 (Viscotek Corp.). Three 5 micron Hewlett Packard columns (300 × 7.7 mm) connected in series in order of increasing pore size (500 Å, 1000 Å, mixed bed C) were used with THF as solvent. Capillary gas chromatography was performed on a Hewlett Packard 5890 gas chromatograph.

**Polymerization of Methyl 4,4-Bis(4'-hydroxyphenyl)pentanoate 1.**—To a round-bottom flask was added methyl 4,4-bis(4'-hydroxyphenyl)pentanoate 1 (2.00 g, 6.67 mmol) followed by cobalt(II) acetate (100 mg, 0.4 mmol). The mixture was heated at 120 °C under reduced pressure (10 mmHg) for 2 h, the temperature was then increased to 210 °C and the pressure decreased to 0.5 mmHg for 3 h. During this time the reaction mixture became progressively more viscous and eventually solidified. After cooling, the reaction mixture was dissolved in THF and precipitated into water, ether and finally hexane. The phenolic-terminated polyester 2 was obtained as a white solid (1.61 g, 90%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3500–2900, 1735, 1610, 1510, 1200 and 830;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.27 (s, 3 H,  $\text{CH}_3$ ), 1.55–1.80 (br m, 2 H,  $\text{CH}_2$ ), 2.30–2.60 (br m, 2 H,  $\text{CH}_2$ ), 6.79, 7.06 and 7.25 (each br s, 8 H, ArH) and 8.25 (br s, 1 H, OH);  $\delta_{\text{C}}(\text{CDCl}_3)$  25.78, 27.68, 37.05, 45.18, 115.27, 121.66, 128.60, 139.51, 140.45, 146.39, 147.31, 149.48, 155.75 and 172.26 [Found: C, 76.35; H, 5.85.  $(\text{C}_{17}\text{H}_{16}\text{O}_3)_n$  requires C, 76.1; H, 6.01%].

**Methylation of Phenolic-terminated Polyester 2.**—The phenolic-terminated polyester 2 (2.00 g, 7.5 mmol equiv.) was dissolved in dry acetone (15  $\text{cm}^3$ ) and methyl iodide (3.00 g, 1.32  $\text{cm}^3$ , 21.1 mmol) added followed by silver oxide (1.80 g). The reaction, which was initially exothermic, was stirred at 60 °C under nitrogen for 18 h. The reaction mixture was then filtered, the filtrate evaporated to dryness and the crude polymer purified by precipitation from THF into methanol. The methyl ether-terminated polyester 3 was obtained as a white solid (1.81 g, 86%);  $\nu_{\text{max}}/\text{cm}^{-1}$  2970, 1750, 1610, 1510, 1290, 1205 and 830;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.40–1.50 (br s, 3 H,  $\text{CH}_3$ ), 2.20–2.60 (br m, 4 H,  $\text{CH}_2$ ), 3.60 (br s, 3 H,  $\text{CH}_3$ ) and 6.80–6.85, 6.90–7.00 and 7.05–7.15 (each br s, 8 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.60, 29.80, 30.25, 36.30, 44.22, 44.30, 44.65, 54.87, 113.23, 120.80, 127.98, 139.90, 140.64, 145.36, 146.18, 148.59, 157.41, 172.02 and 173.98 [Found: C, 76.7; H, 6.65.  $(\text{C}_{18}\text{H}_{18}\text{O}_3)_n$  requires C, 76.6; H, 6.43%].

**Hydrolysis of Methyl Ether-terminated Polyester 3.**—The methyl ether-terminated polyester 3 (0.50 g, 1.77 mmol equiv.) was dissolved in THF (10  $\text{cm}^3$ ), and aqueous sodium hydroxide solution (15  $\text{cm}^3$ , 1  $\text{mol dm}^{-3}$ ) was added. Sufficient ethanol (*ca.* 5  $\text{cm}^3$ ) was then added to make a one-phase solution and the reaction mixture was heated at reflux for 18 h. The solution was cooled and evaporated to dryness, dissolved in water (50  $\text{cm}^3$ ) and acidified with 5% HCl. The hydrolysis products were then extracted with ether (3 × 30  $\text{cm}^3$ ), combined extracts dried and evaporated to dryness. The mixture of hydrolysis products were analysed by either capillary gas chromatography or HPLC after treatment with diazomethane or *N,O*-bis(trimethylsilyl)-acetamide.

**Synthesis of 4,4-Bis(4'-methoxyphenyl)pentanoic Acid 4 and (4'-Hydroxyphenyl)-4-(4''-methoxyphenyl)pentanoic Acid 5.**—To methyl 4,4-bis(4'-hydroxyphenyl)pentanoate (4.00 g, 13.3 mmol) dissolved in acetone (30  $\text{cm}^3$ ) was added methyl iodide (1.89 g, 0.89  $\text{cm}^3$ , 13.3 mmol) and potassium carbonate (2.00 g). The reaction mixture was then heated at reflux under nitrogen for 18 h, cooled and filtered, and the filtrate was evaporated to dryness. The crude product was dissolved in THF (50  $\text{cm}^3$ ), and aqueous sodium hydroxide (50  $\text{cm}^3$ , 1  $\text{mol dm}^{-3}$ ) was added followed by sufficient ethanol to give a one-phase mixture. The solution was then heated at reflux for 6 h and evaporated to dryness. The residue was dissolved in water (100  $\text{cm}^3$ ), acidified with 5% HCl and extracted with ether (4 × 50  $\text{cm}^3$ ). The combined extracts were dried, evaporated to dryness, and purified by flash chromatography eluting with 1:4 hexane-ether to give the dimethylated derivative 4 as a colourless oil (0.79 g, 18.1%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3500–2600, 1710, 1610, 1510, 1290, 1250,



Scheme 2

1190 and 830;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.58 (s, 3 H,  $\text{CH}_3$ ), 2.15 and 2.40 (each t, 4 H,  $\text{CH}_2$ ), 3.77 (s, 6 H,  $\text{CH}_3$ ) and 6.79 and 7.10 (ABq, 8 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.64, 20.05, 36.32, 44.34, 55.07, 113.33, 128.11, 140.80, 157.47 and 179.91;  $m/z$  314 ( $\text{M}^+$ , 20%) (Found: C, 72.4; H, 6.89%;  $\text{M}^+$ , 314.1518.  $\text{C}_{18}\text{H}_{20}\text{O}_4$  requires C, 72.6; H, 7.06%;  $M$ , 314.1519).

Continued elution with ether gave the monomethylated derivative **5** as a colourless oil (1.74 g, 43.6%);  $\nu_{\text{max}}/\text{cm}^{-1}$  3500–2600, 1705, 1610, 1510, 1250 and 830;  $\delta_{\text{H}}(\text{CDCl}_3)$  1.54 (s, 3 H,  $\text{CH}_3$ ), 2.12 and 2.37 (each t, 4 H,  $\text{CH}_2$ ), 3.75 (s, 3 H,  $\text{CH}_3$ ), 6.70 and 7.01, and 6.79 and 7.09 (each ABq, 8 H, ArH);  $\delta_{\text{C}}(\text{CDCl}_3)$  27.63, 30.04, 36.36, 44.34, 55.14, 113.36, 114.89, 128.14, 128.26, 140.53, 140.95, 153.78, 157.35 and 179.54;  $m/z$  300 ( $\text{M}^+$ , 25%) (Found: C, 71.7; H, 6.54%;  $\text{M}^+$ , 300.1362.  $\text{C}_{18}\text{H}_{20}\text{O}_4$  requires C, 72.0; H, 6.72%;  $M$ , 300.1332).

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