Influence of shape on the reactivity and properties of dendritic, hyperbranched and linear aromatic polyesters*

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Previously described dendritic and hyperbranched polyesters and a new linear polyester obtained by polymerization of 3-hydroxy-5-(t-butyldimethylsilyloxy)benzoic acid, each based on the 3,5-dihydroxybenzoic acid building block, were used in the study of differences in chemical and physical properties between the three different polymer architectures. Comparison of the physical properties between the dendritic, hyperbranched and linear structures showed that thermal properties, such as glass transition temperature and thermogravimetric analysis, were independent of macromolecular architecture. However, the dendritic and hyperbranched materials demonstrated comparative solubilities which were much greater than that found for the linear polymer. Other differences were observed in chemical reactivities.

(Keywords: dendritic polyesters; hyperbranched polyesters; linear polyesters)

INTRODUCTION

The growing interest in highly branched, three-dimensional macromolecules is reflected in the large number of reports concerning the synthesis and properties of these structures[1–4]. These materials can be divided into two families, dendritic and hyperbranched macromolecules, that differ in their branching sequences. Dendritic macromolecules have highly regular or 'perfect' branching with at least one branch point per monomer unit, whereas hyperbranched macromolecules are randomly branched and contain varying amounts of linear segments. Interesting thermal[5], viscosity[6] and other properties[7–12] have been observed for dendritic and hyperbranched macromolecules and, in many cases, this behaviour is different from that of linear polymers. Possible reasons for these differences are the unique three-dimensional structures and the presence of a large number of chain ends in dendritic and hyperbranched macromolecules. This study will explore some of the differences in properties and behaviour that exist between dendritic, hyperbranched and linear macromolecules based on the same basic building block.

The syntheses of both the dendritic[13] **1** and hyperbranched[14,15] **2** polyesters based on 3,5-dihydroxybenzoic acid **3** have been reported. The hyperbranched structure was shown to have a degree of branching[14] of 60%, which implies that, on average, it contains approximately one branch point every second monomer unit, in contrast to the dendritic structure that has a degree of branching of 100%. Although the exact three-dimensional shapes of **1** and **2** are different, both structures are expected to be globular. We now report the synthesis of a linear polyester **4**, also based on 3,5-dihydroxybenzoic acid. *Figure 1* shows simplified, two-dimensional representations of the three architectures that illustrate only the differences in bonding sequence and relative positions of the phenolic chain ends, but cannot convey the shape differences.

EXPERIMENTAL

General directions

Glass transition temperatures were measured by differential scanning calorimetry (d.s.c.) using a Mettler DSC 30 low temperature cell coupled to a TC10A TA processor. The heating rate was 10 K min^{-1}. T_g was taken as the midpoint of the inflection tangent. Thermogravimetric analysis (t.g.a.) was performed on a Mettler TG50 thermobalance at a 20 K min^{-1} heating rate. Data analysis for both d.s.c. and t.g.a. was done with Mettler TA72 software. Infra-red (i.r.) spectra were recorded on a Perkin–Elmer spectrophotometer as thin films on NaCl discs. ^{1}H n.m.r. spectra were recorded on solutions in d_6-acetone or $CDCl_3$ on a Bruker AM 200 (200 MHz) or WM 300 (300 MHz) spectrometer with the solvent proton signal as standard. ^{13}C n.m.r. spectra were recorded at either 50 MHz or 75 MHz on a Bruker AM 200 (200 MHz) or AF 300 (300 MHz) spectrometer, respectively, with the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890

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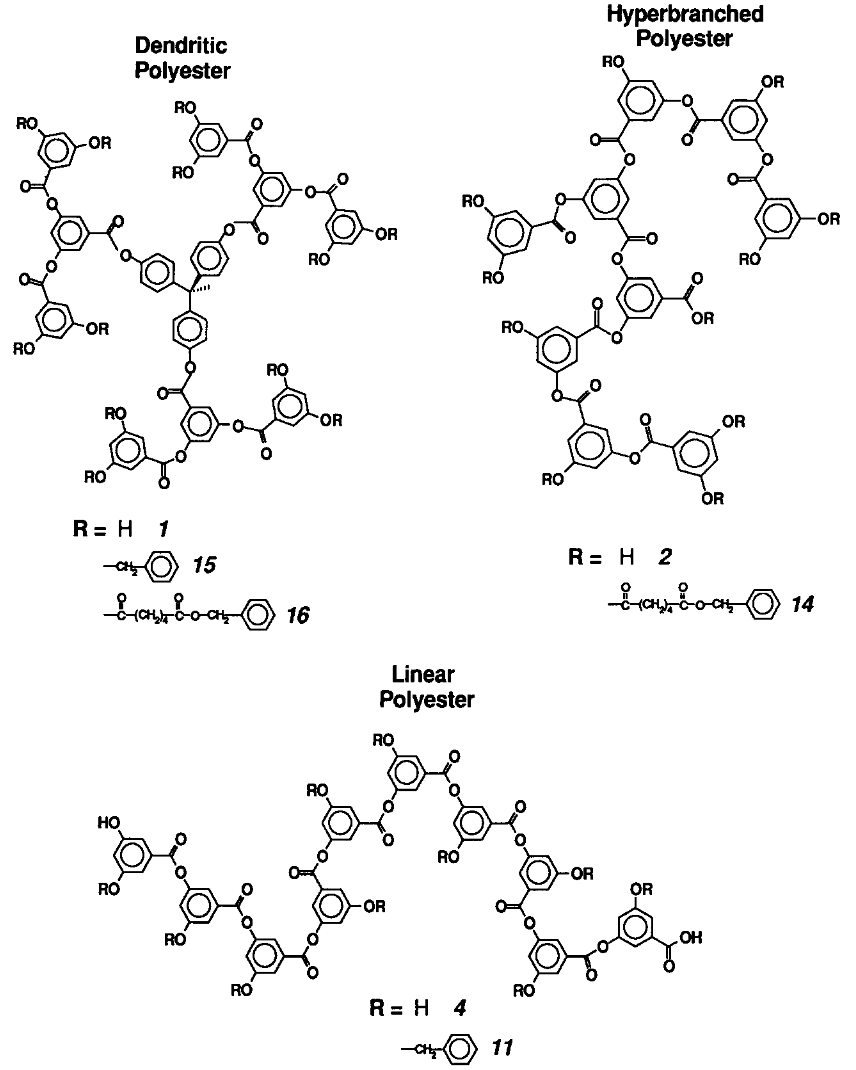


Figure 1 Oligomeric examples of the three types of architectures – dendritic, hyperbranched and linear – demonstrating the differences in branching sequences and structure

with EI ionization. Analytical thin layer chromatography (t.l.c.) was performed on commercial Merck plates coated with silica gel GF_{254} (0.25 mm thick). Silica for flash chromatography was Merck Kieselgel 60 (230–400 mesh). Size exclusion chromatography (s.e.c.) was carried out on an IBM LC/9560 chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector and data analysis was performed with GPC-PRO software, version 3.12 (Viscotek). Three 5 μm 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 tetrahydrofuran (THF) as solvent.

Methyl 3-benzyloxy-5-hydroxybenzoate 8

A mixture of methyl 3,5-dihydroxybenzoate **7** (3.50 g, 20.8 mmol), benzyl bromide **5** (3.39 g, 2.37 ml, 19.7 mmol), potassium carbonate (3.00 g) and 18-crown-6 (150 mg) dissolved in acetone (50 ml) was heated at reflux with vigorous stirring under nitrogen for 24 h. The reaction mixture was cooled, evaporated to dryness and partitioned between water (200 ml) and ether (200 ml). The aqueous layer was then extracted with ether (3 × 100 ml) and the combined organic layers dried and evaporated to dryness. The crude product was purified by flash chromatography, eluting with CH_2Cl_2 and gradually increasing to ether. The monophenol **8** was obtained as a white solid (2.95 g, 54%). I.r. (cm^{-1}) 1720, 1595, 1370 and 1165. ^1H n.m.r. (d_6-acetone) (ppm) 3.82 (s, 3H, OCH_3), 5.02 (s, 2H, OCH_2Ar), 6.73 (t, 1H, $J = 3$ Hz, ArH), 7.17 (d, 2H, $J = 3$ Hz, ArH), 7.22–7.43 (m, 5H, PhH) and 8.57 (br s, 1H, OH). ^{13}C n.m.r. (d_6-acetone) (ppm) 51.74, 69.78, 106.96, 107.05, 109.35, 127.38, 127.77, 128.35, 131.93, 136.73, 158.17, 159.84 and 166.53. Mass spectrum (EI) $m/z = 258$.

3-Benzyloxy-5-hydroxybenzoic acid 9

To a solution of the monophenol **8** (2.90 g, 11.2 mmol) in ethanol (25 ml) was added potassium hydroxide (1.40 g, 25.2 mmol) dissolved in water (5.0 ml) and the reaction mixture was heated at reflux for 6 h. The reaction mixture was then cooled and evaporated to dryness under reduced pressure. The residue was redissolved in water (100 ml) and acidified with 1 N HCl. A heavy white precipitate formed and this was collected and recrystallized from water–methanol to give the acid **9** as a white solid (2.42 g, 88%). I.r. (cm^{-1}) 3500–2500, 1690, 1595 and 1360. ^1H n.m.r. (d_6-acetone) (ppm) 5.10 (s, 2H, OCH_2Ar), 6.73 (t, 1H, $J = 3$ Hz, ArH), 7.14–7.21 (m, 2H, ArH) and 7.30–7.51 (m, 5H, PhH). ^{13}C n.m.r. (d_6-acetone) (ppm) 70.29, 107.32, 107.63, 109.88, 128.09, 128.35, 128.98, 133.13, 137.80, 159.06, 160.62 and 167.00. Mass spectrum (EI) $m/z = 244$.

Trimethylsilyl 3-benzyloxy-5-trimethylsilyloxybenzoate **10**

A solution of 3-benzyloxy-5-hydroxybenzoic acid **9** (4.88 g, 20.0 mmol) in hexamethyldisilazane (HMDS) (50 ml) was heated at reflux for 3 h, cooled, and evaporated to dryness. The crude product was purified by distillation, and the fraction boiling at 140–145°C (0.05 mmHg) was collected. The trimethylsilyl ester **10** was obtained as a colourless oil (5.42 g, 70%). I.r. (cm^{-1}) 2050, 1710, 1595 and 1170. ^{1}H n.m.r. ($CDCl_3$) (ppm) 0.25 (s, 9H, $OSi(CH_3)_3$), 0.39 (s, 9H, $OSi(CH_3)_3$), 5.05 (s, 2H, OCH_2Ar), 6.65 (t, 1H, $J = 3$ Hz, Ar*H*), 7.13 (dd, 1H, $J = 3$ Hz, Ar*H*), 7.27 (dd, 1H, $J = 3$ Hz, Ar*H*) and 7.30–7.44 (m, 5H, Ph*H*). ^{13}C n.m.r. ($CDCl_3$) (ppm) −0.20, 0.18, 70.24, 109.33, 111.94, 114.54, 127.56, 128.09, 128.62, 133.29, 136.56, 156.16, 159.59 and 166.31.

Poly(3-benzyloxy-5-oxybenzoate) **11**

To a solution of 3-benzyloxy-5-hydroxybenzoic acid **9** (2.44 g, 10.0 mmol) in dry dichloromethane (50 ml) was added 4-dimethylaminopyridinium toluene-4-sulfonate (DPTS) (3.52 g, 12.0 mmol) and the mixture was stirred at room temperature under nitrogen for 15 min. Dicyclohexylcarbodiimide (DCC) (2.47 g, 12.0 mmol) was then added and stirring was continued for 24 h. The resulting precipitate was then removed by filtration and the filtrate and washings were evaporated to dryness. The crude product was purified by precipitation (twice) into methanol (600 ml) and dried to give the polyester **11** as a white powder (1.94 g, 86%). I.r. (cm^{-1}) 1730, 1595, 1320, 1170 and 1120. ^{1}H n.m.r. ($CDCl_3$) (ppm) 5.11 (br s, 2H, OCH_2Ar), 7.12 (br t, 1H, Ar*H*), 7.26–7.50 (m, 5H, Ph*H*) and 7.62–7.70 (m, Ar*H*). ^{13}C n.m.r. ($CDCl_3$) (ppm) 70.58, 113.98, 114.47, 116.08, 127.56, 128.27, 128.66, 131.01, 135.83, 151.65, 159.67 and 163.77.

3-Hydroxy-5-(t-butyldimethylsilyloxy)benzoic acid **12**

To a solution of 3,5-dihydroxybenzoic acid **3** (5.00 g, 32.0 mmol) in dry dimethylformamide (DMF) (50 ml) was added t-butyldimethylsilyl chloride (9.63 g, 64.0 mmol) and imidazole (6.00 g, 90.0 mmol). The mixture was then heated at 60°C for 12 h, cooled, and evaporated to dryness. The crude silyl ester was redissolved in tetrahydrofuran (50 ml). Glacial acetic acid (100 ml) was added followed by water (50 ml) and the reaction was stirred at room temperature for 4 h and then poured into water (500 ml). The product was extracted with ether (4 × 75 ml) and the combined extracts were washed with water (2 × 150 ml), dried, and evaporated to dryness. The crude product was purified by flash chromatography (dry loading recommended), eluting with 1:9 ether–CH_2Cl_2 gradually increasing to 3:7 ether–CH_2Cl_2 to give the acid **12** as a white solid (3.89 g, 45%). I.r. (cm^{-1}) 3600–2500, 2050, 1690, 1600 and 1010. ^{1}H n.m.r. (d_6-acetone) (ppm) 0.21 (s, 6H, $OSi(CH_3)_2$), 0.96 (s, 9H, $C(CH_3)_3$), 6.62 (t, 1H, $J = 3$ Hz, Ar*H*), 7.06 (dd, 1H, $J = 3$ Hz, Ar*H*) and 7.19 (dd, 1H, $J = 3$ Hz, Ar*H*). ^{13}C n.m.r. (d_6-acetone) (ppm) −4.71, 18.28, 25.56, 110.44, 112.38, 113.02, 132.64, 157.11, 158.79 and 167.82.

Poly[3-oxy-5-(t-butyldimethylsilyloxy)benzoate] **13**

To a solution of 3-hydroxy-5-(t-butyldimethylsilyloxy)-benzoic acid **12** (1.50 g, 5.60 mmol) in dry dichloromethane (30 ml) was added DPTS (1.97 g, 6.70 mmol) and the mixture was stirred at room temperature under nitrogen for 15 min. DCC (1.40 g, 6.70 mmol) was then added and stirring was continued for 24 h. The resulting precipitate was then removed by filtration and the filtrate and washings were evaporated to dryness. The crude product was purified by precipitation (twice) into 1:1 water–methanol (600 ml) and dried to give the polyester **13** as a white powder (1.15 g, 82%). I.r. (cm^{-1}) 2050, 1720, 1600, 1340, 1190, 1160 and 1010. ^{1}H n.m.r. ($CDCl_3$) (ppm) 0.26 (s, 6H, $OSi(CH_3)_2$), 1.06 (s, 9H, $C(CH_3)_3$), 6.98 (t, 1H, $J = 3$ Hz, Ar*H*), 7.54 (m, 1H, $J = 3$ Hz, Ar*H*) and 7.65 (m, 1H, $J = 3$ Hz, Ar*H*). ^{13}C n.m.r. ($CDCl_3$) (ppm) −4.23, 18.16, 25.57, 116.49, 119.42, 130.98, 151.55, 156.78 and 163.84.

Poly(3-oxy-5-hydroxybenzoate) **4**

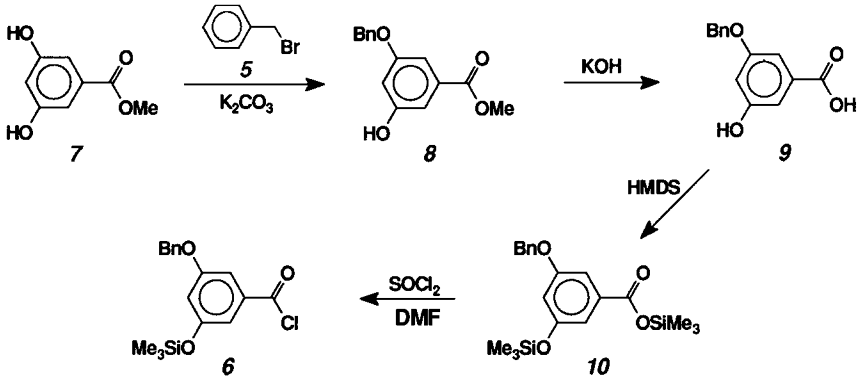
To a solution of poly[3-oxy-5-(t-butyldimethylsilyloxy)-benzoate] **13** (750 mg, 3.00 mmol equivalent) in tetrahydrofuran (30 ml) and acetone (10 ml) was added aqueous HCl (1 N, 5.0 ml) dropwise and the reaction mixture was stirred at 50°C for 24 h. The solution was then evaporated to dryness and the residue was redissolved in tetrahydrofuran (5 ml) and precipitated into dichloromethane (400 ml). The product was purified by precipitation (twice) into dichloromethane (600 ml) and dried to give the polyester **4** as a white powder (0.37, 91%). I.r. (cm^{-1}) 3600–2900, 1710, 1600, 1350, 1250 and 1170. ^{1}H n.m.r. (d_6-acetone) (ppm) 7.16 (br, t, 1H, Ar*H*) and 7.59 (m, 2H, Ar*H*). ^{13}C n.m.r. (d_6-acetone) (ppm) 114.66, 114.98, 115.19, 131.90, 152.71, 159.22 and 164.33.

RESULTS AND DISCUSSION

While a number of authors[16–21] have attempted comparisons between linear polymers and hyperbranched or dendritic macromolecules, their choices of linear polymers have hardly been optimized. This is because the linear polymers used for comparison were prepared from simple AB monomers containing only one B functionality instead of the two found in each repeating unit of dendritic or hyperbranched analogues. Therefore, the contributions from the numerous B functionalities that exist in the hyperbranched and dendritic polymers, derived from AB_2 monomers, are not taken into account. For example, any comparison of the linear polymer poly(3-oxybenzoate) prepared from 3-hydroxybenzoic acid with the dendritic and hyperbranched polyesters prepared from 3,5-dihydroxybenzoic acid **3** would not take into account the influence of the numerous additional phenolic groups present as chain ends in dendritic polymers or chain ends and unreacted side groups in hyperbranched structures. These phenolic groups are expected to have a dramatic effect on both the physical and chemical properties of the polymers.

Preparation of a linear polyester from an AB_2 monomer

To investigate further the influence of both structure and functionality, the linear polymer based on 3,5-dihydroxybenzoic acid, an AB_2 monomer, was prepared for comparative purposes. In order to obtain a perfectly linear material, the direct polymerization of **3** is not possible. One of its phenolic groups must be protected prior to polymerization, transforming it into an ABB′ monomer in which only A and B are mutually reactive. The chemistry employed in the synthesis of phenolic-terminated dendritic[13] and hyperbranched[14,15] polyesters suggested the preparation of linear polyester



Scheme 1

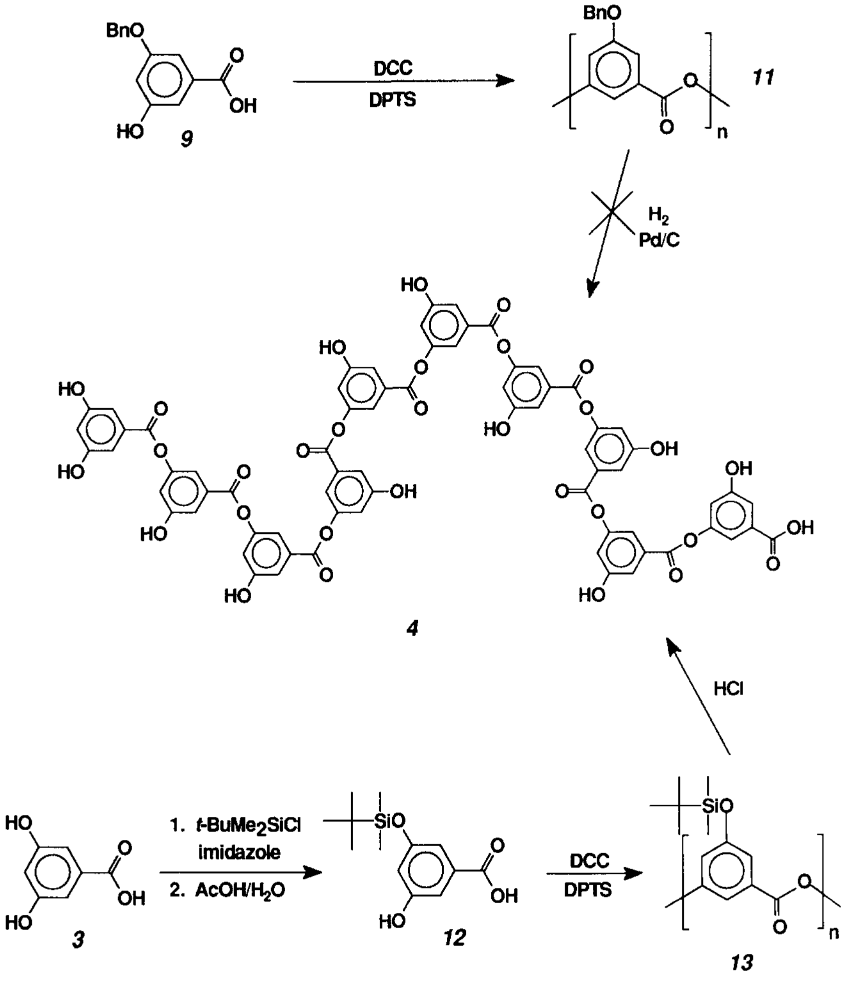
4 having free phenolic groups through a protection–deprotection strategy based on the catalytic hydrogenolysis of benzyl ethers coupled to a silicon-assisted polymerization[14,15,22]. As shown in *Scheme 1*, the synthesis of the required monomer unit, 3-benzyloxy-5-trimethylsilyloxybenzoyl chloride **6**, may be initiated from the commercially available methyl 3,5-dihydroxybenozate **7**. Monoalkylation with benzyl bromide **5** in the presence of potassium carbonate and 18-crown-6 gave the monophenolic derivative **8** in 54% yield after purification. Alkaline hydrolysis of **8** gave the corresponding acid **9**, which was protected with hexamethyldisilazane. This gave the trimethylsilyl ester **10** in which the two phenolic groups are differentiated by their protection as benzyl and trimethylsilyl ethers. Following the chemistry recently developed[15] for the synthesis and polymerization of 3,5-bis(trimethylsilyloxy)benzoyl chloride, **10** was treated with thionyl chloride in the presence of a catalytic amount of dimethylformamide. This gave the acid chloride **6**, as evidenced by changes in the infra-red, ^{1}H n.m.r. and ^{13}C n.m.r. spectra. However, attempts to purify **6** by distillation, even under high vacuum, were unsuccessful because of thermal decomposition. Polymerization of the crude acid chloride resulted in essentially complete conversion to an insoluble gel. Owing to the failure of the silicon-assisted acid chloride route, direct polymerization of the hydroxy acid **9** was explored.

While the polymerization of aromatic hydroxy acids usually leads to low molecular weight macromolecules, a recent report by Moore and Stupp[23] detailing the use of dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridinium toluene-4-sulfonate (DPTS) as condensing agents suggests that higher molecular weight materials can be obtained. Polymerization of **9** in the presence of DCC and DPTS in dichloromethane gave the desired polymer **11** ($M_w = 11\,000$, $M_w/M_n = 1.8$ by gel permeation chromatography (g.p.c.) with polystyrene standards) in 86% yield after purification (*Scheme 2*). Removal of the benzyl ether protecting groups to give the linear phenolic polymer **4** was initially attempted under standard catalytic hydrogenolysis conditions[24] with 10% Pd–C in tetrahydrofuran. However, even after prolonged stirring, no reaction was observed and **11** was recovered almost quantitatively. Increasing the pressure of hydrogen to 4 atm (1 atm = 101 325 Pa) did not lead to any reaction, nor did the addition of a variety of acids or bases. Owing to the decreased solubility of **11** in tetrahydrofuran when compared to the dendritic analogue, a number of different solvents and mixed solvent systems were employed, but no reaction was observed. The use of catalytic transfer hydrogenolysis conditions[25] was also found to cause no deprotection of the benzyl ethers. Attempts to cleave the benzyl ether groups under homogeneous conditions were not explored, owing to the relative instability of the phenyl ester bonds.

Therefore, the use of the t-butyldimethylsilyl protecting group instead of the benzyl group was explored. This required the use of the monosilyl-protected monomer **12**, which was prepared (*Scheme 2*) from 3,5-dihydroxybenzoic acid **3** in 45% yield after purification. The polycondensation reaction of **12** with DCC and DPTS in dichloromethane gave the t-butyldimethylsilyl-protected polymer **13** ($M_w = 20\,000$, $M_w/M_n = 1.9$ by g.p.c. with polystyrene standards) as a white powder. Miller *et al.*[16] have shown the deprotection of a t-butyldimethylsilyl-protected phenol in the presence of phenyl esters by treatment with 1 N HCl in acetone. However, owing to the insolubility of **13** in acetone, a mixed solvent system was used. Stirring **13** and 1 N HCl in a 3:1 mixture of tetrahydrofuran and acetone at 50°C for 24 h resulted in complete deprotection of the silyl groups to give the linear polyester **4** as a white powder. Both the ^{1}H and ^{13}C n.m.r. spectra of the linear polyester **4** were fully consistent with those expected from earlier model studies[14]. No resonances were observed for any branched units and, as expected, only very minor resonances were observed for the single diphenolic terminal unit. Attempts to calculate the molecular weight of the macromolecule **4** by end-group analysis proved unsuccessful owing to the very small size of the peaks.

Comparison of physical properties

It has been reported[16–19] that dendritic and hyperbranched polyphenylenes exhibit significantly enhanced solubilities (ca. 10^6 times) when compared to their linear *para*-linked polyphenylene analogues, although a more realistic comparison with the more soluble *meta*-linked polyphenylene has not been reported. While the reason for the increased solubility of these dendritic structures has not been explained, a similar behaviour has been reported for other systems. To try and understand this variation in solubility with changes in architecture, the solubility behaviour of dendritic, hyperbranched and linear polyesters was investigated. The dendritic and hyperbranched macromolecules proved to be highly soluble in solvents that are capable of solvating the numerous chain-end functional groups[26], with the



Scheme 2

dendritic macromolecules being slightly more soluble than their hyperbranched analogues. However, the linear polyesters showed marked decreases in the range of solvents in which they were soluble and also in the solubility in those solvents. For the materials containing free phenolic groups, the solubilities in acetone were 1.05 g ml^{-1} for **1**, 0.70 g ml^{-1} for **2** and only 0.02 g ml^{-1} for **4**. Similarly, the benzyl ether terminated dendritic polyester had a solubility of 1.15 g ml^{-1} in THF, while the benzyl ether terminated linear polyester **11** had a solubility of only 0.025 g ml^{-1} in THF. Comparison of the linear polyesters prepared from ABB′ and AB monomers also proved to be instructive. The linear polyester **4**, which contains a large number of phenolic groups, was much more soluble than the corresponding linear polyester based on 3-hydroxybenzoic acid (an AB monomer), which was insoluble in most solvents. Therefore, it appears that the high solubility of dendritic and hyperbranched macromolecules in comparison to linear polymers comes from a combination of the influence of architectural differences and the large number of chain-end functional groups.

The thermal properties of the three different polyester architectures were investigated under a nitrogen atmosphere. For the materials having phenolic functional groups, the glass transition temperature of the dendritic polyester with 48 phenolic groups at the chain ends was found to be 201°C[13]. For the hyperbranched phenol-terminated polyester **2**, values have been reported in the literature[14,15,23] ranging from 190 to 210°C. This range of values may come from imperfections in the structure caused by side reactions or entrapment of other molecules such as solvents. Using our standard conditions, a glass transition temperature of 197°C was observed, while for the linear analogue **4** a value of 204°C was found for the glass transition temperature. Thus it appears that, within experimental error, the glass transition temperature is independent of the architecture or shape of the macromolecule. Additional support for this finding is provided by results obtained with a variety of functionalized polymers. For example, the benzyl ether terminated dendritic polyester has a glass transition temperature of 73°C[13], while the corresponding value for the linear macromolecule **11** is 78°C. Similarly, the t-butyldimethylsilyl-protected linear polyester **13** has a glass transition temperature of 102°C, while the T_g for the hyperbranched analogue is 103°C[15]. The thermogravimetric behaviour for all three phenolic-terminated polyester architectures was also found to be essentially the same within experimental error. After a 30 min isotherm at 250°C, no decomposition was observed up to 400°C with a 10% weight loss occurring at 440 ± 10°C; rapid weight loss was then observed with 50% remaining at 575 ± 15°C.

Interestingly, the three different polymer architectures (dendritic, hyperbranched and linear) behaved differently in a process involving their interaction with a solid surface. It has recently been observed[15] that the benzyl ester chain ends of a modified hyperbranched polyester **14** showed little or no reactivity towards catalytic hydrogenolysis. A similar situation prevails with the benzyl ether groups of linear polyester **11** which are remarkably impervious to heterogeneous catalytic hydrogenolysis. As described earlier, these benzyl ether groups are fully resistant to catalytic hydrogenolysis under a variety of conditions. In contrast, both dendritic polyesters **15** and **16**, containing benzyl ether and benzyl ester chain ends, respectively, are readily and cleanly deprotected[13] under mild hydrogenolysis conditions to give phenol-terminated or carboxyl-terminated dendritic polyesters in 68–90% yields after purification.

Though it may be tempting to assign this unusual behaviour of **15** and **16** to their globular architecture, which may render their chain ends more accessible to the catalyst surface, alternative explanations cannot be excluded. For example, the higher solubility of the dendritic polymer may prevent fouling of the catalyst surface by partially reacted, insoluble polymer. Alternatively, the effect may be one of size exclusion as the active sites of the catalyst are located within the pores of the carbon support. However, the hydrodynamic volume of the unreactive linear polyester **11** ($M_w = 11\,000$ by g.p.c. with polystyrene standards) is not very different from that of **15** (nominal molecular weight of 10 829) or **16** (nominal molecular weight of 15 816), both of which react readily, while the unreactive hyperbranched polymer ($M_w = 53\,000$, $M_n = 20\,000$ by g.p.c. with polystyrene standards) is somewhat larger. Further experimentation is required to understand whether this reactivity difference is because of thermodynamic or steric reasons as the architecture progresses from dendritic to hyperbranched to linear. In earlier work, the sensitivity to catalytic hydrogenolysis of benzyl esters attached to linear polymers was shown[27] to be mainly dependent on the structure of the porous charcoal, the location of the Pd metal catalyst and the molecular weight and molecular weight distribution of the polymer. These effects were attributed to size exclusion effects, the preferential adsorption of smaller macromolecules onto the surface of the catalyst and/or surface affinity phenomena, which in some cases resulted in partially deprotected, blocky copolymers.

CONCLUSION

While traditional dendritic macromolecules contain no linear segments since they have at least one branch point at every repeat unit, the exact branching sequence and structure of hyperbranched macromolecules are unknown. Hyperbranched structures are intermediate between dendritic and linear structures in that they behave somewhat like dendrimers in terms of their solubility and low viscosity and they are similar to linear polymers in their reactivities, especially with a solid surface. These findings suggest that the more readily available hyperbranched materials may be used in place of the dendritic structures for some applications, especially those involving their unusual physical properties. However, their overall chemical reactivity may be very different. For example, both hyperbranched and dendritic materials should perform comparatively well in the area of rheology control for the accelerated processing of commodity polymers or as additives in lubricants. In contrast, while dendritic molecules carrying appropriate chain-end functional groups may provide excellent adhesion to substrates owing to their compact globular shape and the large number of 'attachment sites' in a very small area, the hyperbranched analogue may behave in a fashion similar to that of linear systems and provide no significant advantages. Future work will explore these issues.

There is considerable controversy as to the location of the chain ends of dendritic macromolecules. One model[28] predicts an extended structure with the chain ends on the periphery or surface of the structure, while another[29] predicts significant inward folding of chain-end groups to give a density maximum at the centre of the structure. Comparison of the reactivities of chain-end groups in dendritic, hyperbranched and linear materials with a solid surface confirms that the chain ends of dendritic structures are readily accessible, suggesting that each of the chain ends must be located at or near the surface of the macromolecule, at least for some of the time[30]. This applies especially to molecules in which the chain-end functional groups have a polarity or chemical composition that differs significantly from that of the building blocks leading to their segregation at the outer confines of the globular structure, or to a kind of micellization[26]. Therefore, we believe that while inward folding does occur, the chain ends are in a dynamic equilibrium that allows them to spend considerable periods of time at or near the outer surface of the macromolecule. The question as to the extent and depth of penetration of chain ends towards the centre of the structure still exists, and we have prepared dendritic macromolecules with a fully deuterated chain-end layer for the determination of their behaviour and structure by small-angle neutron-scattering experiments.

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