

(ArC-3,3'',5,5''), 143.50 (ThiC-2',5'), 152.92 (ArC-4,4''); MS (25 eV)  $m/z$  (rel intensity) 636 ( $M^+$ , 100); UV ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 242 (4.16), 342 (4.50). Anal. Calcd for  $\text{C}_{38}\text{H}_{60}\text{O}_2\text{SSi}$ : C, 71.64; H, 9.49; S, 5.03. Found: C, 71.32; H, 9.60; S, 4.95.

**2,5-Bis(3,5-di-*tert*-butyl-4-hydroxyphenyl)thiophene (7c).** To a solution of **6c** (2.00 g, 3.139 mmol) in acetonitrile (440 mL) were added 12 M HCl (40 mL) and  $\text{H}_2\text{O}$  (8 mL) at room temperature. After stirring for 5 h, the reaction mixture was concentrated under reduced pressure. Water was added, and the mixture was extracted with ether. After usual workup and chromatographic separation ( $\text{SiO}_2$ -98:2 hexane- $\text{CH}_2\text{Cl}_2$ ) of the reaction products, pure **7c** was isolated as colorless crystals (1.61 g, 99.8%): mp 91-93 °C; IR (KBr) 3640 (s), 2960-2875 (s), 1436 (s), 1236 (s), 1154 (m), 880 (w), 798 (w), 700 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.49 (s, 36 H, *t*-Bu), 5.25 (s, 2 H, OH), 7.11 (s, 2 H, ThiH-3',4'), 7.43 (s, 4 H, ArH-2,2'',6,6'');  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ )  $\delta$  30.28 (Me), 34.40 (CMe), 122.54 (ThiC-3',4'), 122.78 (ArC-2,2'',6,6''), 126.17 (ArC-1,1''), 136.32 (ArC-3,3'',5,5''), 143.70 (ThiC-2',5'), 153.53 (ArC-4,4''); EI-MS (70 eV)  $m/z$  (rel intensity) 494 ( $M^+$  + 2, 11), 493 ( $M^+$  + 1, 36), 492 ( $M^+$ , 100), 410 (27); UV (MeCN)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 242 sh (4.16), 342 (4.50). Anal. Calcd for  $\text{C}_{32}\text{H}_{44}\text{O}_2\text{S}$ : C, 78.00; H, 9.00; S, 6.51. Found: C, 77.88; H, 9.15; S, 6.47.

**2,5-Bis(3,5-di-*tert*-butyl-4-oxo-2,5-cyclohexadien-1-ylidene)-2,5-dihydrothiophene (2c).** In a manner similar to **2a**, a solution of **7c** (1.45 g, 2.942 mmol) in benzene (240 mL) was treated with a 0.1 M aqueous KOH solution (480 mL) and potassium ferricyanide (9.63 g, 29.42 mmol) at room temperature for 5 h. Pure **2c** was obtained as shining green or black fine crystals (1.318 g, 91.4%) after chromatography ( $\text{SiO}_2$ -95:5 hexane-ether) and recrystallization (MeCN): mp 270-273 °C; IR (KBr) 2960-2845 (w), 1630 (vw), 1591 (vs), 1556 (w), 1510 (w), 1454 (w), 1360 (m), 1332 (w), 1257 (w), 1146 (w), 1088 (w), 1030 (m), 991 (w), 893 (w), 852 (m), 818 (w), 785 (w)  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ )  $\delta$  1.36 (s, 18 H, *t*-Bu), 1.38 (s, 18 H, *t*-Bu), 7.28 (d, 2 H,  $J$  = 2.5 Hz, ArH-2,2''), 7.43 (d, 2 H,  $J$  = 2.5 Hz, ArH-6,6''), 7.69 (s, 2 H, ThiH-3',4');  $^{13}\text{C}$  NMR (50.3 MHz,  $\text{CDCl}_3$ )  $\delta$  29.68 (Me), 35.63 and 35.89 (CMe), 125.35 (ArC-6,6''), 127.28 (ArC-1,1''), 128.04 (ArC-2,2''), 133.94 (ThiC-3',4'), 147.71 (ArC-3,3''), 150.32 (ArC-5,5''), 152.64 (ThiC-2',5'), 185.81 (ArC-4,4''); EI-MS (70 eV)  $m/z$  (rel intensity) 494

( $M^+$  + 4, 11), 493 ( $M^+$  + 3, 36), 492 ( $M^+$  + 2, 100), 491 ( $M^+$  + 1, 10), 490 ( $M^+$ , 21); UV-vis (MeCN)  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) 272 (3.72), 282 (3.71), 294 (3.68), 349 (3.85), 558 (4.90). Anal. Calcd for  $\text{C}_{32}\text{H}_{42}\text{O}_2\text{S}$ : C, 78.32; H, 8.63; S, 6.53. Found: C, 77.99; H, 8.63; S, 6.68.

**Single-Crystal X-ray Structure Determination of 2c.** The crystals of **2c** belong to a monoclinic system with cell dimensions  $a = 19.918$  (5) Å,  $b = 24.394$  (9) Å,  $c = 5.971$  (2) Å,  $\beta = 92.93$  (2)°, and  $V = 2897.4$  (17) Å<sup>3</sup>. The space group is  $P2_1/a$  and  $Z = 4$ . The empirical formula is  $\text{C}_{32}\text{H}_{42}\text{O}_2\text{S}$ , molecular weight is 490.72, and calculated density is 1.125  $\text{g}/\text{cm}^3$ . The three-dimensional X-ray data were collected by the use of graphite-monochromated Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) on a Syntex R3 automatic four-circle diffractometer up to a maximum  $2\theta$  of 50°. The intensity data of 5222 independent reflections were collected and 1884 with  $|F_o| > 4\sigma|F_o|$  were used in the present X-ray analysis. The structure was solved by the direct method (MULTAN 78). All non-hydrogen atoms were located on the initial E synthesis. Remaining hydrogens were located by the difference Fourier map and included in the further calculations. Block-diagonal least-squares refinements with anisotropic 35 non-hydrogen atoms and 42 isotropic hydrogens have converged to a conventional  $R$  factor of 0.078. All the calculations were done on a HITAC M-680H computer of Hiroshima University by using a structure analysis program system UNICS3 [Sakurai, T.; Kobayashi, K. *Rep. Inst. Phys. Chem. Res.* 1979, 56, 69].

**Acknowledgment.** This work was supported by a Grant-in-aid from the Ministry of Education, Science and Culture, Japan. We thank Professor Masaaki Yoshifuji for his encouragement to our study. We also thank Mr. Kazuo Sasaki and Takeyoshi Kondo of Tohoku University, Instrumental Analysis Center for Chemistry, for measurement of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.

**Supplementary Material Available:** Tables of hydrogen atom coordinates, fractional coordinates, anisotropic thermal parameters, mean square displacement tensor of atoms, and bond angles and bond distances (5 pages). Ordering information is given on any current masthead page.

## One-Step Synthesis of Hyperbranched Dendritic Polyesters

C. J. Hawker,<sup>†</sup> R. Lee, and J. M. J. Fréchet\*

Contribution from the Department of Chemistry, Baker Laboratory, Cornell University, Ithaca, New York 14853-1301. Received December 20, 1990

**Abstract:** The one-step synthesis of a hyperbranched polyester possessing a dendritic structure has been achieved by thermal self-condensation of 3,5-bis(trimethylsiloxy)benzoyl chloride. The hyperbranched polyesters are obtained in yields of 80% or greater and with polystyrene equivalent weight average molecular weights in the range 30 000 to almost 200 000. The polydispersity and the molecular weights of the polyesters were found to vary greatly with the temperature of the polymerization. Characterization of the polymers was readily accomplished by NMR spectroscopy with the help of model compounds. The degree of branching of the polyesters as determined from NMR experiments was between 55 and 60%. The polyesters, which contain reactive functional groups at all chain extremities, are glassy materials that show a very high thermal stability comparable to that of analogous linear materials. In contrast, the excellent solubility properties of the hyperbranched polyesters influenced by their shape and functionalization are at variance with those of their linear polyester analogues.

### Introduction

Polycondensation reactions leading to highly branched polymers, with branches at almost every repeating unit, have been a neglected subject until recently. Initial interest dates back to the early 1950s with publication of a theoretical paper by Flory<sup>1</sup> on polymers made from  $\text{AB}_x$ -type monomers containing a single reaction group A and at least  $x$  reactive groups B ( $x \geq 2$ ). In such systems, growth occurs through direct reactions involving the two different functionalities without requiring separate activation or deprotection

steps. Early examples of such processes include the Friedel-Crafts condensation of benzyl halides<sup>2</sup> and the condensation of 2,5,6-tribromophenol under basic conditions.<sup>3</sup> These  $\text{AB}_x$  polycondensation reactions generally led to the formation of highly irregular and frequently ill-characterized structures,<sup>1-3</sup> with few reports of purposeful attempts to control molecular architecture found in the literature until recently. The preparation of polybenzyl has been reinvestigated<sup>4,5</sup> and remains largely unexploited

<sup>†</sup> Current address: Department of Chemistry, University of Queensland, St. Lucia, 4072 Queensland, Australia.

(1) Flory, P. J. *J. Am. Chem. Soc.* 1952, 74, 2718.

(2) Jacobson, R. A. *J. Am. Chem. Soc.* 1932, 54, 1513.

(3) Hunter, W. H.; Woollett, G. H. *J. Am. Chem. Soc.* 1921, 43, 135.

due to the lack of structural control and poor properties of the materials that are obtained. In contrast, preliminary reports<sup>6,7</sup> of the preparation of a hyperbranched dendritic polyphenylene by catalyzed aryl-coupling reactions appear to be much more promising. The first approach, by Kim and Webster,<sup>6,7</sup> utilizes (3,5-dibromophenyl)boronic acid as the monomer unit with Pd(0) as the catalyst. The polymerization is a simple coupling process, a modification of the Suzuki reaction,<sup>8</sup> that affords a 60% yield of a polyphenylene containing phenyl rings linked through their 1-, 3-, and 5-positions and carrying reactive aromatic bromide functionalities at the chain extremities. The polyphenylenes obtained by this procedure typically have molecular weights in the range 3000–6000 (by GPC with polystyrene calibration) with a broad molecular weight distribution and a degree of branching near 70%. These highly branched polymers showed some very interesting physical properties, such as increased solubility, and enhanced mechanical properties when blended with some commodity polymers. It is particularly interesting to compare the solubility of this type of highly branched polyphenylene with those of the linear polyphenylenes, which are usually largely insoluble. Of further significance is the fact that chemical modification of the remaining aromatic bromide functionalities located at the outer extremities of the branches could be achieved readily to afford, for example, a water-soluble polyphenylene that has been referred to as a unimolecular micelle.<sup>7</sup> A second approach to hyperbranched polyphenylene by the same researchers<sup>6</sup> involved the Ni(II)-catalyzed polycondensation of (3,5-dibromophenyl)magnesium bromide; however, the material obtained by this technique had both a low molecular weight and a low degree of branching.

While our work was in progress, another interesting approach<sup>9</sup> to a similar rigid polymer with unusual solubility properties has involved a slightly different reaction scheme with stepwise rather than one-step growth. This process involves the three-step preparation of a dendritic arylboronic acid moiety containing seven phenyl rings with a 1,3,5 substitution pattern. Condensation of 3 mol of this arylboronic acid with 1 mol of 1,3,5-tribromobenzene in the presence of a catalytic amount of Pd catalyst<sup>8</sup> affords a symmetrical 1,3,5-linked oligophenylene consisting of exactly 22 phenyl rings devoid of surface functionality. Despite its symmetry and the aromatic nature of its building blocks, this oligophenylene is remarkably soluble in common solvents.

Although these results are of much significance, the achievement of high molecular weights by the reported methods is not possible. High molecular weight hyperbranched polymers with reactive functionalities at chain extremities would be of particular interest if they could be obtained in a one-step process from readily available starting materials, thereby facilitating their use in the study of the novel properties derived from hyperbranching in polymer systems. Our approach to such materials involves a one-step condensation of an AB<sub>2</sub> monomer derived from 3,5-dihydroxybenzoic acid.

## Results and Discussion

The procedure we used for the one-step synthesis of a hyperbranched polymer with reactive surface functionalities is derived from a reaction developed by Kricheldorf<sup>10,11</sup> for the preparation of linear or slightly branched polyesters, polyamides, etc. In this reaction, polyesters are prepared by heating (trimethylsilyl)

## Scheme 1

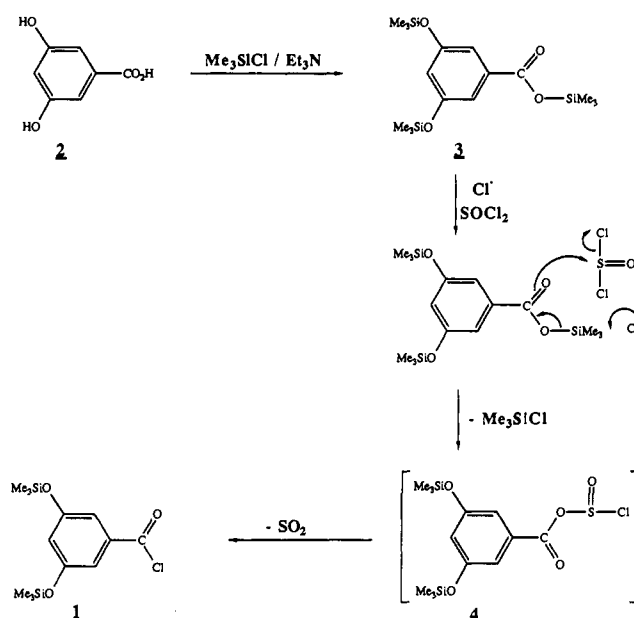


Table I. Polymerization of 3,5-Bis(trimethylsilyloxy)benzoyl Chloride

temp (°C)	time (h)	yield (%)	M <sub>w</sub> (GPC) <sup>a</sup>	M <sub>n</sub> (GPC) <sup>a</sup>	M <sub>w</sub> /M <sub>n</sub>
190	1	83	164 000	55 000	2.9
200	1	96	158 000	44 000	3.5
200	2	91	184 000	48 000	3.8
230	2	84	42 000	18 000	2.3
240	1	63	39 000	19 000	2.1
250	1	88	64 000	26 000	2.5
250	2	83	44 000	21 000	2.1
260	1	60	31 000	16 000	1.9
275	1	86	48 000	26 000	1.9

<sup>a</sup> Polystyrene equivalent molecular weight.

oxy)benzoyl chlorides to temperatures of 250 °C or greater. This results in the release of gaseous trimethylsilyl chloride as the only side product and gives polyester macromolecules with yields of 89% or greater and molecular weights significantly higher than those obtained via other methods.<sup>12,13</sup>

The preparation<sup>10</sup> of 3,5-bis(trimethylsilyloxy)benzoyl chloride (1) from commercially available 3,5-dihydroxybenzoic acid (2) is outlined in Scheme 1. The acid 2 is protected as the tris(trimethylsilyl) derivative 3 by reaction with trimethylsilyl chloride and triethylamine; 3 was obtained in 90% yield after distillation under reduced pressure. Reaction of 3 with thionyl chloride in refluxing dichloromethane proved to be undependable. Consideration of the reaction mechanism reveals that a catalytic amount of chloride ion is required to activate the reaction and give the thionyl chloride adduct 4. However, in reactions using purified 3, there is no available chloride ion to activate 3 and form the adduct 4, which may explain the inconsistent nature of the reaction. To overcome this, a catalytic amount of trimethylamine hydrochloride was added to the reaction mixture as a source of chloride ion. Therefore, reaction of the trimethylsilyl ester 3 with thionyl chloride and 0.05 equiv of trimethylamine hydrochloride reproducibly gave the desired acid chloride 1 in near quantitative yields.

Bulk polymerization of crude 1 at 250 °C gave an insoluble material: Presumably trace amounts of impurities cause cross-linking to occur; similar observations were made by Kricheldorf.<sup>10</sup> Short-path distillation of 1 at 0.3 mmHg and 175 °C gave pure 1; however, the yield was reduced to ca. 60% due to a significant amount of polymerization during distillation. Heating the neat

(4) Kuo, J.; Lenz, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1976**, *14*, 2749. Pinkus, A. G.; Lin, W. H. *J. Macromol. Sci. Chem.* **1979**, *A13*, 133.

(5) Tsonis, C. P. *J. Mol. Catal.* **1990**, *57*, 313. Stöver, H. D. H.; Matuszczak, S.; Willson, C. G.; Fréchet, J. M. J. *Macromolecules* **1991**, *24*, in press.

(6) Kim, Y. H.; Webster, O. W. *ACS Polym. Prepr.* **1988**, *29* (2), 310. Kim, Y. H. U.S. Patent 4,857,630, 1989.

(7) Kim, Y. H.; Webster, O. W. *J. Am. Chem. Soc.* **1990**, *112*, 4592.

(8) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513.

(9) Miller, T. M.; Neenan, T. X. *Chem. Mater.* **1990**, *2*, 346.

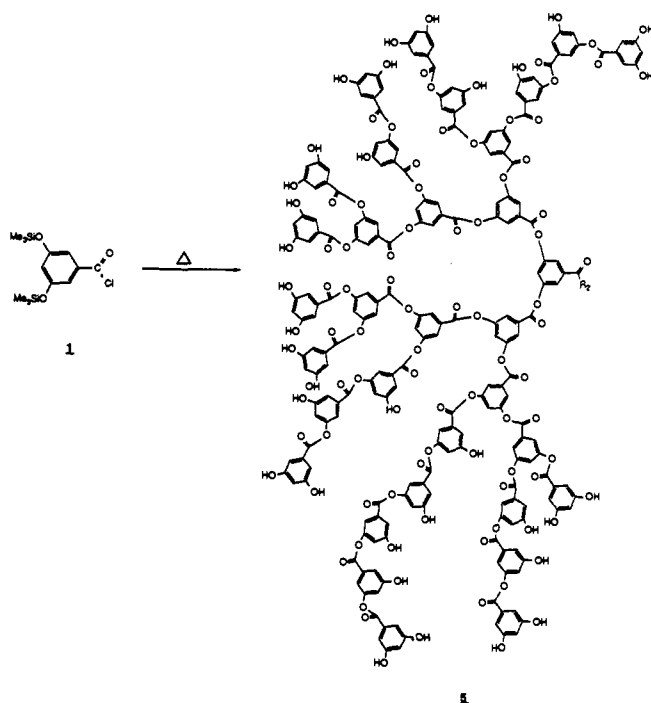
(10) Schwarz, G.; Alberts, H.; Kricheldorf, H. R. *Liebigs Ann. Chem.* **1981**, 1257. Kricheldorf, H. R.; Zeng, Q. Z.; Schwarz, G. *Polymer* **1982**, *23*, 1821.

(11) Kricheldorf, H. R.; Lübbers, D. *Makromol. Chem., Rapid Commun.* **1990**, *11*, 261.

(12) Gilkey, R.; Caldwell, J. R. *J. Appl. Polym. Sci.* **1959**, *2*, 198.

(13) Higashi, F.; Kubota, K.; Sekizuka, M.; Goto, M. *J. Polym. Sci., Polym. Chem. Ed.* **1980**, *18*, 2879.

Scheme II



purified acid chloride **1** at various temperatures under a stream of nitrogen, as outlined in Table I, resulted in vigorous effervescence and subsequent solidification of the reaction mixture. Dissolution of this in the minimum amount of pyridine/benzene (1:1) and precipitation into methanol gave the hyperbranched polyester **5** (Scheme II) as a tan solid. The polystyrene equivalent molecular weights and yields are shown in Table I; these demonstrate that the condensation reaction is efficient in terms of both molecular weight and yield of purified macromolecule. Surprisingly, even the high molecular weight polymers proved to be highly soluble in a variety of solvents such as acetone, tetrahydrofuran, dimethylformamide, aqueous NaOH, etc. This enhanced solubility when compared to that of linear polyesters is undoubtedly due to the dendritic shape of the molecule, which prevents close packing and crystallization of the various polymer segments. It is also influenced by the presence of numerous surface functional groups as shown, for example, by the aqueous base solubility of polymer **5**, which contains a large number of free phenolic groups at both chain extremities and within those repeating units that have remained unbranched.

The proposed representative structure **5** was confirmed by normal spectroscopic techniques. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra are shown in Figure 1. For the 300-MHz  $^1\text{H}$  NMR spectrum of the hyperbranched polyester **5**, four distinct regions are present, a broad peak at 6.60–6.68 ppm, a number of peaks in the regions 7.05–7.30 and 7.50–7.85 ppm, and a broad set of resonances at 8.05–8.25 ppm. Similarly, resonances are observed in distinct regions of the  $^{13}\text{C}$  NMR spectra corresponding to structure **5**; surprisingly the peaks show only slight broadening and reveal a degree of fine structure.

The thermal properties of the hyperbranched polyester **5** were investigated under nitrogen atmosphere. Thermogravimetric analysis showed essentially no decomposition to 400 °C with a 10% weight loss at  $435 \pm 5$  °C after annealing to 250 °C for 5 min. This is followed by rapid decomposition with 50% weight loss near 560 °C, and a glass transition temperature of 190 °C was also observed. These values are close to those found for the linear polyester based on 3-hydroxybenzoic acid<sup>10</sup> and demonstrate that the large number of end groups present in **5** has little effect on the overall thermal properties.

**Characterization of the Polyesters and Determination of Their Degree of Branching.** In the absence of a regular mode of generation growth via sequential activation-coupling steps, the one-step dendritic growth techniques described herein produce

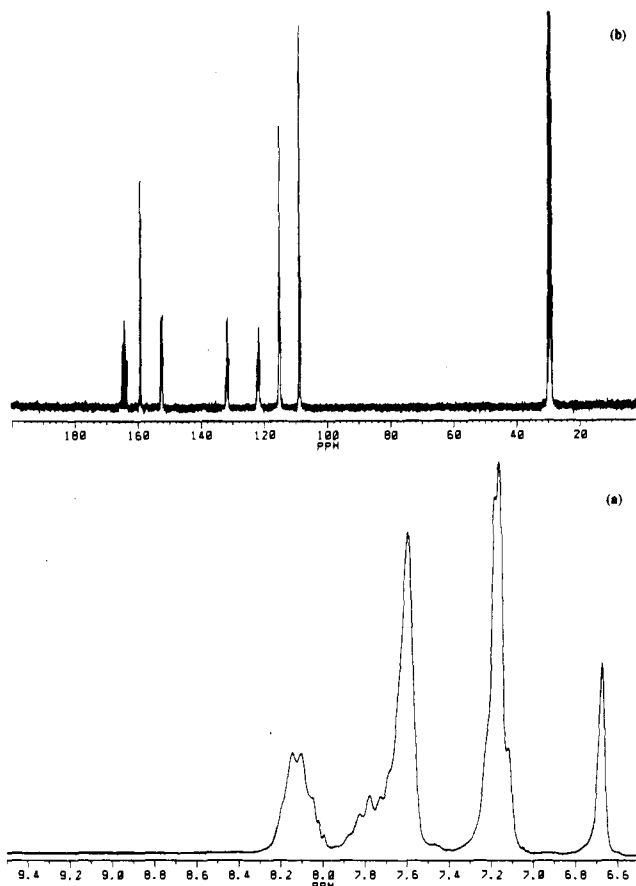


Figure 1. 300-MHz  $^1\text{H}$  NMR (a) and 75-MHz  $^{13}\text{C}$  NMR (b) spectra of hyperbranched polyester **5**.

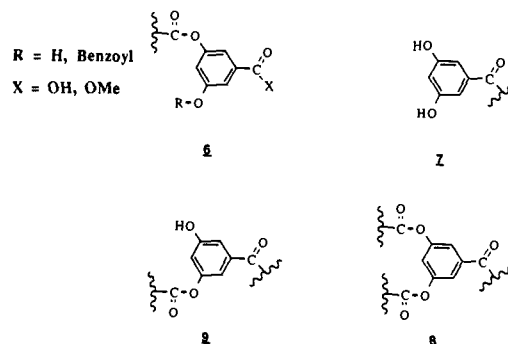


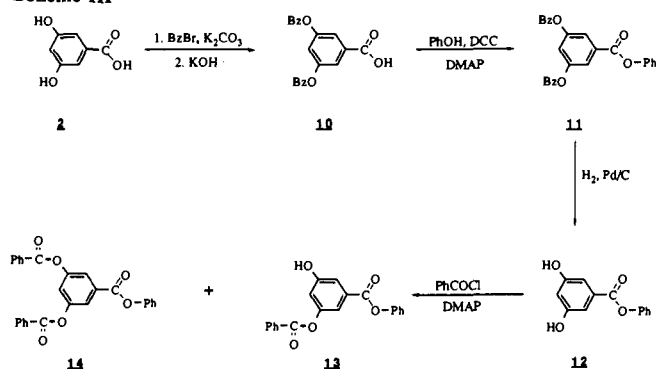
Figure 2. Structure of possible monomer units in macromolecule **5**.

irregular dendritic structures with a lower degree of branching than would be achieved through the use of the stepwise convergent growth<sup>14,15</sup> method, for example. Consideration of the structure of dendritic macromolecule **5** (Scheme II) reveals that four different types of subunits may be present as shown in Figure 2. These include the unique monomer unit at the focal point **6**, the "terminal" monomer units **7**, which have two phenolic groups, the "dendritic" monomer units **8**, which have no free phenolic groups and two benzyloxy groups, and finally the "linear" monomer units **9**, which have one phenolic and one benzyloxy group. Of these, the single monomer unit at the focal point can be ignored since it may be difficult to observe for the type of high molecular weight

(14) Fréchet, J. M. J.; Jiang, Y.; Hawker, C. J.; Philippides, A. E. *Prepr. IUPAC Int. Symp. Funct. Polym., Seoul 1989*, 19. Hawker, C. J.; Fréchet, J. M. J. *J. Chem. Soc., Chem. Commun.* **1990**, 1010.

(15) Hawker, C. J.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1990**, *112*, 7638. Hawker, C. J.; Fréchet, J. M. J. *Macromolecules* **1990**, *23*, 4726. Wooley, K.; Hawker, C.; Fréchet, J. M. J. *J. Chem. Soc., Perkin Trans. 1* **1991**, in press. Wooley, K.; Hawker, C.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **1991**, *113*, in press.

## Scheme III



polymer we have obtained and its influence becomes insignificant as molecular weight increases. Therefore, we define the degree of branching (DB) and the percent of branching as follows:

$$DB = \frac{(\text{no. of dendritic units}) + (\text{no. of terminal units})}{\text{total no. of units}}$$

$$\% \text{ branching} = (DB) 100$$

Both the dendritic and terminal units, in this case 7 and 8, contribute to the "perfect" or "fully" hyperbranched character of the macromolecule, while the linear units 9 decrease the degree of branching. In all cases, DB is between 0 and 1. When the end units are neglected, the value of DB for a linear polymer would be 0, while a perfect dendritic macromolecule<sup>15</sup> would have a degree of branching equal to 1.

As the NMR spectrum of macromolecule 5 exhibits much fine structure related to its state of branching, a number of model compounds useful for NMR characterization of 5 were prepared as shown in Scheme III. The phenolic groups of 3,5-dihydroxybenzoic acid (2) are protected as their benzyl ethers by reaction of 2 with benzyl bromide, potassium carbonate, and 18-crown-6 followed by saponification with potassium hydroxide. This affords the acid 10 in 65% yield after purification. Esterification of 10 with phenol, in the presence of DCC and DMAP, gives the phenyl ester 11 in 78% yield after purification. Hydrogenolysis of 11 gives the diphenol 12 in 90% yield. Reaction of 12 with 1 equiv of benzoyl chloride gives a mixture of monoacylated 13 and diacylated 14 phenyl esters, which were purified by flash chromatography and obtained in 39 and 49% yields, respectively. The diphenolic phenyl ester 12 was used as a model for the terminal unit 7, while the dibenzoyl derivative 14 was used as a model for the dendritic unit 8. The model for the linear units 9 was the monophenol 13.

The 300-MHz <sup>1</sup>H NMR spectra for 12, 13, and 14 are shown in Figure 3; partial decoupling experiments revealed that, for 12, the C-4 proton appears as a triplet at 6.77 ppm, while the C-2 and C-6 protons of 14 are observed as a doublet at 8.06 ppm. The complex resonance at 8.25 ppm in the spectra of 13 and 14 is due to the benzyl group; this functionality is absent in our hyperbranched macromolecule 5 and, therefore it does not affect our calculations. The other resonances due to the aromatic rings derived from 3,5-dihydroxybenzoic acid of the terminal, 12, and dendritic, 14, models are in the region 7.17–7.75 ppm as are all the resonances of the linear unit 13. It is therefore possible to determine the amount of 12 or 14 and by default the amount of 13 in any mixture of <sup>1</sup>H NMR spectroscopy.

Examination of the <sup>1</sup>H NMR spectrum of the hyperbranched polyester 5 reveals good correlation between the C-4 proton of the model unit 12 and the broad resonance observed at 6.68 ppm. Similarly, the C-2 and C-6 protons of the model 14 are observed in the same region as the broad set of resonances at 8.05–8.25 ppm. The relative percentages of each type of monomer unit can be determined by assigning these resonances to the corresponding protons of the terminal unit 7 and the dendritic unit 8, respectively, and by assuming that all other resonances in the spectra are due to the remaining protons of 7 and 8 and all protons of the linear unit 9. Integration of each region of the <sup>1</sup>H NMR spectrum then

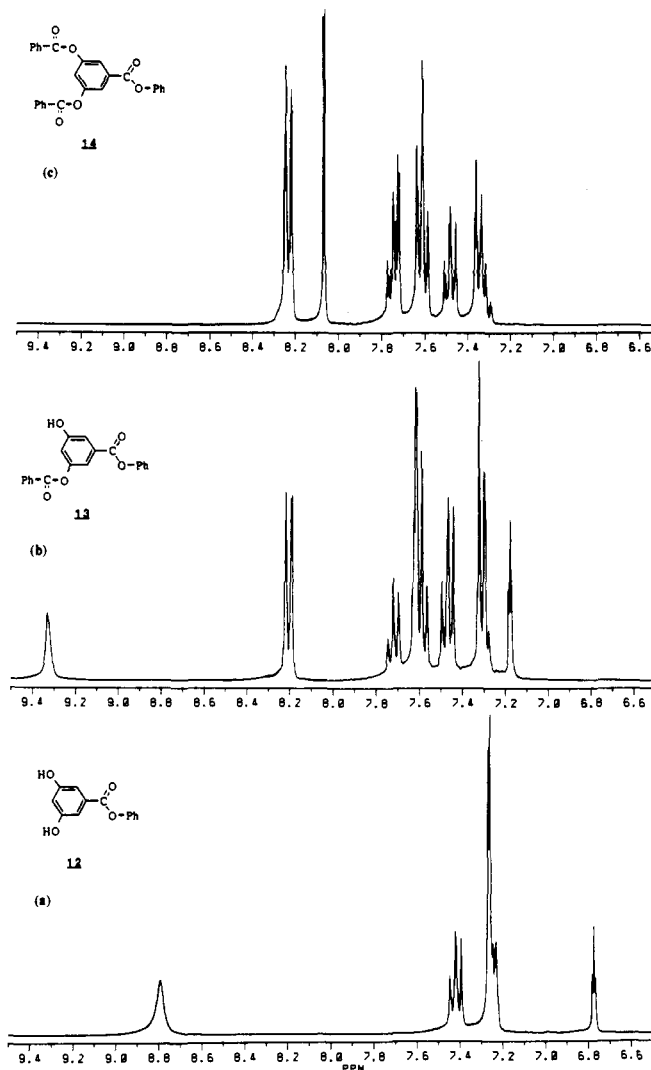


Figure 3. 300-MHz <sup>1</sup>H NMR spectra of model compounds 12 (a), 13 (b), and 14 (c).

allows the relative percentage of each monomer unit to be determined. Use of the above formulae allows us to determine that the DB for these hyperbranched polyesters is generally in the range 0.55–0.60. It is not overly surprising to find that all of the samples we have studied have 55–60% branching since the steric inhibition to full dendritic growth (100% branching) is not expected to be affected by the modest differences in reaction conditions we have studied.

Similarly the <sup>13</sup>C NMR spectra of the model compounds showed unique resonances depending on the substitution pattern of the aromatic nucleus derived from 3,5-dihydroxybenzoic acid (Figure 4). The most prominent difference is for the C-2, -4, and -6 carbon atoms. These occur at 108.32 and 108.83 ppm for the dihydroxy model 12. For the monohydroxy model 13, three resonances are observed at 114.73, 115.04, and 115.10 ppm, while two resonances are seen at 121.48 and 122.07 ppm for the dibenzoyl model 14. These resonances are well-separated from each other and from others in the spectra of both the models and the actual hyperbranched macromolecule 5. Accumulation of the <sup>13</sup>C NMR spectra for the macromolecule 5 with a relaxation delay of 15 s (*T*<sub>1</sub> < 10 s) allowed the set of resonances at 108.5–109.0, 114.79–115.45 and 121.64–122.30 ppm to be integrated. These experiments indicate that the degree of branching is 0.57 (57% branching), in good agreement with the value determined earlier by <sup>1</sup>H NMR spectroscopy.

## Conclusion

We have demonstrated that the synthesis of hyperbranched polyester macromolecules from the AB<sub>2</sub> monomer, 3,5-bis(tri-

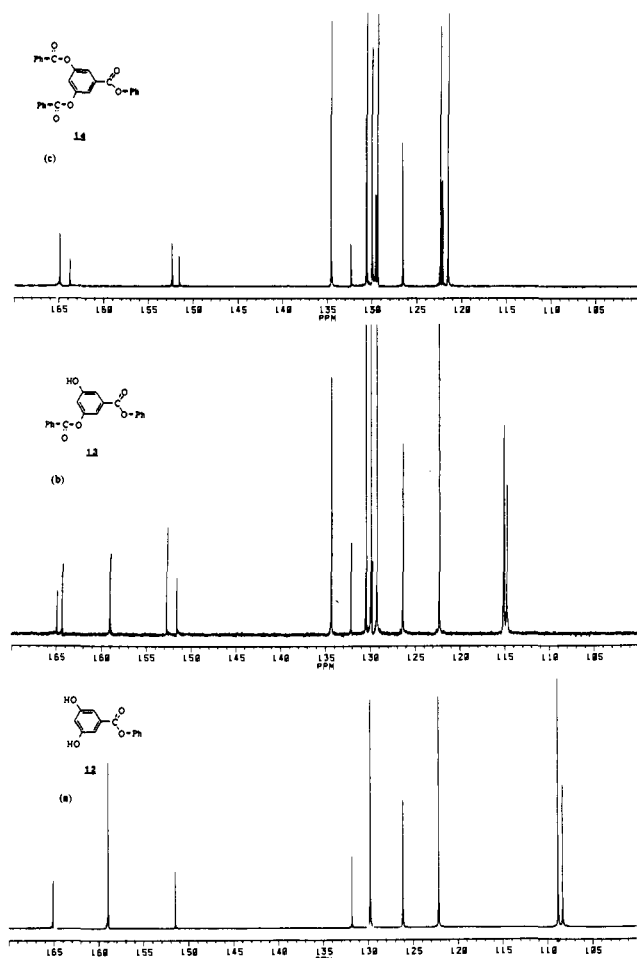


Figure 4. 75-MHz  $^{13}\text{C}$  NMR spectra of model compounds 12 (a), 13 (b), and 14 (c).

methylsiloxy)benzoyl chloride (1), is both viable and practical. Very high molecular weight dendritic macromolecules are obtained in high yields with some control over molecular weight and polydispersity through modifications in reaction conditions. The polymers have good thermal stability and excellent solubility in common organic solvents. Their degree of branching (55–60%) as measured by spectroscopic techniques with the use of model compounds is not as high as that which is obtained by either the classical divergent (or “starburst”) synthesis<sup>16</sup> or the convergent growth approach.<sup>15</sup> However, in contrast to these techniques that involve a tedious but significantly more precise stepwise approach, this one-step synthesis can provide access to large amounts of a material with unusual properties resulting from its hyperbranched structure. While such molecules obtained through one-step processes will never replace their more perfect 100% branched analogues for the *accurate* determination of the ultimate properties of dendritic or spherical macromolecules, their availability through simple processes will make further research in this area more attractive. We are currently refining the synthesis both of monomer 1 and of polymer 5 and also testing new approaches designed to provide better control over variables such as molecular weight, polydispersity, and degree of branching. In addition, the availability of “surface” functional groups in compounds such as 5 allows considerable latitude in terms of their possible chemical modification using both reactive low molecular weight compounds or end-reactive polymers. This is being explored while the polycondensation of other  $\text{AB}_2$  monomers to form hyperbranched dendritic macromolecules is also actively pursued.<sup>17</sup>

(16) Tomalia, D. A.; Naylor, M.; Goddard, W. A., III. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 138.

(17) Uhrich, K. E.; Hawker, C. J.; Fréchet, J. M. J.; Turner, S. R. *Polym. Mater. Sci. Eng.* **1991**, *64*, 137.

## Experimental Section

**General Directions.** Melting points were determined on a Kofler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet IR/44 spectrophotometer as thin films on NaCl disks.  $^1\text{H}$  NMR spectra were recorded on solutions in  $\text{CDCl}_3$  or acetone- $d_6$  on a Bruker WM 300 (300 MHz) spectrometer with use of the solvent proton signal as standard.  $^{13}\text{C}$  NMR spectra were recorded at 75 MHz on a Bruker WM300 spectrometer by using  $\text{CDCl}_3$  or acetone- $d_6$  as the solvent and the solvent carbon signal as internal standard. Mass spectra were obtained on a Kratos MS890 by using EI.

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 a Nicolet LC/9560 liquid chromatograph connected to a Milton Roy refractoMonitor IV refractive index detector; data analysis was performed with use of Viscotek GPC-PRO software. Five 10- $\mu\text{m}$  GPC/SEC columns (300  $\times$  7.7 mm, Polymer Laboratories) connected in series in order of decreasing pore size were used with THF as solvent, and column calibration involved the use of narrow dispersity polystyrene standards. The following abbreviations are used below: Ph refers to the phenyl ring derived from phenol; Ar refers to the aromatic ring derived from 3,5-dihydroxybenzoic acid (2); and Ar' refers to the aromatic ring(s) derived from benzoyl chloride. Elemental analyses were performed by MHW Laboratories, Phoenix, AZ.

**Trimethylsilyl 3,5-Bis(trimethylsiloxy)benzoate (3).** To a solution of 3,5-dihydroxybenzoic acid (2) (50.0 g, 0.32 mol) and trimethylsilyl chloride (113 g, 1.04 mol) in dry toluene (500 mL) was added dropwise triethylamine (108 g, 1.07 mol). The mixture was then heated at reflux for 3 h under nitrogen, cooled, filtered, and evaporated to dryness. The crude product was purified by distillation, and the fraction boiling at 121–126  $^\circ\text{C}$  (0.45 mmHg) being collected, the trimethyl silyl ester 3 was obtained as a colorless oil (111 g, 90%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.23 (s, 18 H,  $(\text{CH}_3)_3\text{SiOAr}$ ), 0.33 (s, 9 H,  $(\text{CH}_3)_3\text{SiOCO}$ ), 6.51 (t, 1 H,  $J = 3$  Hz, ArH), and 7.13 (d, 2 H,  $J = 3$  Hz,  $J = 3$  Hz, ArH); mass spectrum (EI)  $m/z$  372.

**3,5-Bis(trimethylsiloxy)benzoyl Chloride (1).** To a solution of the trimethylsilyl ester 3 (42.0 g, 114 mmol) in dry dichloromethane (60 mL) containing trimethylammonium chloride (190 mg, 2.1 mmol) was added freshly distilled thionyl chloride (16.2 g, 136 mmol) dropwise under nitrogen. After addition was complete, the solution was heated at reflux for 3 h, cooled, and evaporated to dryness at room temperature. The crude product was purified by short-path distillation at 175  $^\circ\text{C}$  (0.3 mmHg) to give the acid chloride 1 as a pale yellow oil (20.6 g, 65%):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.28 (s, 18 H,  $(\text{CH}_3)_3\text{SiO}$ ), 6.62 (t, 1 H,  $J = 3$  Hz, ArH), and 7.20 (d, 2 H,  $J = 3$  Hz, ArH);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.14, 110.60, 116.23, 119.11, 134.89, 137.72, and 156.46.

**Polymerization of 3,5-Bis(trimethylsiloxy)benzoyl Chloride (1). Example 1.** The purified acid chloride 1 (6.0 g, 19.0 mmol) was heated with stirring under nitrogen in an oil bath at 200  $^\circ\text{C}$  for 1 h. Vigorous effervescence was observed initially, and the reaction mixture solidified after ca. 30 min. After cooling, the residue was dissolved in the minimum amount of pyridine/benzene (1:1, ca. 10 mL) at 50  $^\circ\text{C}$  and precipitated into methanol (ca. 1000 mL). The precipitated polymer was collected by filtration and dried at 80  $^\circ\text{C}$  under high vacuum for 3 days and obtained as a light brown solid (91% yield). GPC that the polymer thus obtained had a polystyrene equivalent weight average molecular weight  $M_w$  of approximately 150 000 and a polydispersity of 3.0: IR 3600–3000, 1720, 1595, 1300, and 1195  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (acetone- $d_6$ )  $\delta$  6.60–6.68 (m, ArH), 7.05–7.30 (m, ArH), 7.60–7.85 (m, ArH), and 8.05–8.25 (m, ArH);  $^{13}\text{C}$  NMR (acetone- $d_6$ )  $\delta$  108.5–109.0, 114.79–115.45, 121.64–122.30, 131.27–132.08, 152.25–152.82, 159.07–159.29, 163.48, 164.10, 164.12, 164.77, and 164.87.

**Example 2.** The purified acid chloride 1 (6.0 g, 19.0 mmol) was heated with stirring under nitrogen in an oil bath at 250  $^\circ\text{C}$  for 1 h. Vigorous effervescence was observed initially, and the reaction mixture solidified after ca. 15 min. After cooling, the residue was dissolved in the minimum amount of pyridine/benzene (1:1, ca. 10 mL) at 50  $^\circ\text{C}$  and precipitated into methanol (ca. 1000 mL). The precipitated polymer was collected by filtration and dried at 80  $^\circ\text{C}$  under high vacuum for 3 days and obtained as a light brown solid (80% yield). The polymer thus obtained had a polystyrene equivalent GPC  $M_w$  of ca. 50 000 and a polydispersity of 2.0.

**3,5-Bis(benzyloxy)benzoic Acid (10).** A mixture of benzyl bromide (35.5 g, 24.6 mL, 208 mmol), 3,5-dihydroxybenzoic acid (2) (10.0 g, 64.9 mmol), potassium carbonate (20.0 g, 150.0 mmol), and 18-crown-6 (530 mg, 2.0 mmol) in dry acetone (250 mL) was heated at reflux under nitrogen for 24 h. The mixture was then cooled and evaporated to dryness. The crude material was then dissolved in 95% ethanol (100 mL) and  $\text{H}_2\text{O}$  (30 mL), and potassium hydroxide was (20.0 g) added. The mixture was heated at reflux for 24 h, cooled, and concentrated (to ca.

50 mL). Water (400 mL) was added and the mixture acidified with glacial acetic acid and then extracted with dichloromethane (6 × 100 mL). The combined extracts were dried, evaporated to dryness, and purified by flash chromatography eluting with dichloromethane gradually increasing to 1:4 ether/dichloromethane to give **10** as colorless crystals: yield 65% (14.2 g); mp 210–211 °C (EtOH); IR 3400–2400, 1705, 1595, and 1170 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.18 (s, 4 H, CH<sub>2</sub>O), 6.93 (t, 1 H, *J* = 3 Hz, *ArH*), 7.27 (d, 2 H, *J* = 3 Hz, *ArH*), and 7.28–7.51 (m, 10 H, 2 × Ph); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 70.46, 107.23, 108.99, 128.16, 128.42, 129.10, 133.17, 137.67, 160.58, and 167.20; mass spectrum (EI) *m/z* 334. Anal. Calcd for C<sub>21</sub>H<sub>18</sub>O<sub>4</sub>: C, 75.43; H, 5.43. Found: C, 75.36; H, 5.70.

**Phenyl 3,5-Bis(benzyloxy)benzoate (11).** To a solution of the acid **10** (4.60 g, 13.8 mmol) in dry tetrahydrofuran was added phenol (1.55 g, 16.5 mmol) followed by DCC (3.40 g, 16.5 mmol) and 4-(dimethylamino)pyridine (200 mg, 1.65 mmol). The reaction mixture was stirred at room temperature under nitrogen for 6 h and then evaporated to dryness. The crude product was purified by flash chromatography eluting with dichloromethane to give **11** as colorless needles: yield 78% (4.42 g); mp 72–74 °C (MeOH); IR 3020, 1710, and 1220 cm<sup>-1</sup>; <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 5.08 (s, 4 H, PhCH<sub>2</sub>O), 6.78 (t, 1 H, *J* = 2 Hz, *ArH*), 7.10–7.37 (m, 17 H, 3 × PhH, 2 × *ArH*); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 70.36, 107.80, 108.94, 121.64, 125.89, 127.57, 128.15, 128.63, 129.43, 131.43, 136.37, 150.92, 159.89, and 164.81; mass spectrum (EI) *m/z* 410. Anal. Calcd for C<sub>27</sub>H<sub>22</sub>O<sub>4</sub>: C, 79.00; H, 5.40. Found: C, 79.36; H, 5.70.

**Phenyl 3,5-Dihydroxybenzoate (12).** A mixture of the dibenzyl ester **11** (2.00 g, 4.88 mmol), 10% Pd/C (200 mg), and sodium carbonate (300 mg) in dry tetrahydrofuran (30 mL) was stirred vigorously under an atmosphere of hydrogen until the theoretical amount of hydrogen had been consumed. The reaction mixture was then filtered and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:9 ether/dichloromethane to give **12** as colorless crystals: yield 90% (1.01 g); mp 174–176 °C (MeOH/H<sub>2</sub>O); IR 3600–3100, 1705, 1600, 1340, 1220, and 1190 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 6.77 (t, 1 H, *J* = 3 Hz, *ArH*), 7.22–7.27 (m, 5 H, *ArH*), 7.40–7.45 (m, 2 H, *ArH*), and 8.79 (br s, 2 H, *ArOH*); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 108.32, 108.83, 122.13, 126.11, 129.75, 131.81, 151.51, 158.52, and 165.07; mass spectrum (EI) *m/z* 230. Anal. Calcd for C<sub>13</sub>H<sub>10</sub>O<sub>4</sub>: C, 67.82; H, 4.40. Found: C, 67.64; H, 4.73.

**Phenyl 3,5-Bis(benzyloxy)benzoate (14).** Benzoyl chloride (403 mg, 2.87 mmol, 1.20 equiv) was dissolved in dry tetrahydrofuran (10 mL) and

cooled to 0 °C under nitrogen pyridine (0.25 mL) and 4-(dimethylamino)pyridine (40 mg) were added, and stirring was continued for 15 min at 0 °C. The dihydroxy ester **12** (550 mg, 2.39 mmol), dissolved in dry tetrahydrofuran (10 mL), was added dropwise and stirring continued for 1 h at 0 °C and then at room temperature for 16 h. The reaction mixture was evaporated to dryness, redissolved in dichloromethane (50 mL), washed with water (3 × 25 mL), and evaporated to dryness. The crude product was purified by flash chromatography eluting with 1:3 hexane/dichloromethane to give the triester **14** as a white solid: yield 49% (514 mg); mp 137–139 °C; IR 3100–2900, 1720, and 1220 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 7.33–7.37 and 7.46–7.51 (m, 5 H, PhH), 7.59–7.64 and 7.72–7.75 (m, 7 H, 6 × *Ar'H* and *ArH*), 8.06 (d, 2 H, *J* = 2 Hz, *ArH*), and 8.22–8.25 (m, 4 H, 4 × *Ar'H*); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 121.48, 122.07, 122.31, 126.55, 129.36, 129.59, 129.82, 130.31, 132.36, 134.55, 151.58, 152.35, 163.75, and 164.88; mass spectrum (EI) *m/z* 438. Anal. Calcd for C<sub>27</sub>H<sub>18</sub>O<sub>6</sub>: C, 73.96; H, 4.14. Found: C, 73.69; H, 4.28.

**Phenyl 3-Hydroxy-5-(benzyloxy)benzoate (13).** Increasing the eluent to dichloromethane and then to 1:19 ether/dichloromethane gave the monophenol **13** as a white solid: yield 39% (310 mg); mp 151–155 °C; IR 3600–3200, 1720, 1700, 1260, and 1190 cm<sup>-1</sup>; <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>) δ 7.17 (t, 1 H, *J* = 2 Hz, *ArH*), 7.27–7.32 and 7.39–7.46 (m, 5 H, PhH), 7.56–7.63 and 7.69–7.74 (m, 5 H, 3 × *Ar'H* and 2 × *ArH*), 8.20–8.22 (m, 4 H, 4 × *Ar'H*), and 9.33 (br s, 1 H, *ArOH*); <sup>13</sup>C NMR (acetone-*d*<sub>6</sub>) δ 114.73, 115.04, 115.10, 122.27, 126.35, 129.24, 129.79, 129.90, 130.44, 132.14, 134.32, 151.11, 152.72, 159.03, and 164.36; mass spectrum (EI) *m/z* 334. Anal. Calcd for C<sub>20</sub>H<sub>14</sub>O<sub>5</sub>: C, 71.85; H, 4.22. Found: C, 71.62; H, 4.54.

**Acknowledgment.** Financial support of this research through unrestricted gifts from the Eastman Kodak Co. and IBM Corp. (Materials and Processing Science Program) is gratefully acknowledged. Continuing support of related work on dendritic macromolecules by the National Science Foundation (Grant DMR-8913278) is also acknowledged with thanks.

**Registry No.** 1, 75750-29-7; **1** (homopolymer), 133551-53-8; **2**, 490-79-9; **3**, 79314-27-5; **10**, 28917-43-3; **11**, 28917-43-3; **12**, 133551-50-5; **13**, 133551-52-7; **14**, 133551-51-6; Me<sub>3</sub>SiCl, 75-77-4; PhOH, 108-95-2; PhCOCl, 98-88-4.

## Mechanisms for the Uncatalyzed and Hydrogen Ion Catalyzed Reactions of a Simple Quinone Methide with Solvent and Halide Ions

John P. Richard

Contribution from the Department of Chemistry, University of Kentucky, Lexington, Kentucky 40506-0055. Received November 2, 1990

**Abstract:** The quinone methide 4-[bis(trifluoromethyl)methylene]cyclohexa-2,5-dienone (**1**) has been prepared in situ from the solvolysis of 4-MeOArC(CF<sub>3</sub>)<sub>2</sub>OTs in 50:50 (v/v) trifluoroethanol/water, and its reactions with solvent and halide ions have been studied. Rate constants for the uncatalyzed and hydrogen ion catalyzed reactions of solvent, Cl<sup>-</sup>, Br<sup>-</sup>, and I<sup>-</sup> with **1** to form the respective phenols 4-HOArC(CF<sub>3</sub>)<sub>2</sub>Y, equilibrium constants for the addition of HI and HBr, and solvent deuterium isotope effects are reported. The equilibrium constant for the addition of HI to **1** is 17-fold larger than for the addition of HBr. The reactions of **1** have been compared with the reactions of the O-methylated analogue 4-MeOArC(CF<sub>3</sub>)<sub>2</sub><sup>+</sup>. Methylation of the carbonyl oxygen causes a ~10<sup>19</sup>-fold increase in *K*<sub>eq</sub> for the addition of Br<sup>-</sup> to the electrophile and a large decrease in the selectivity for the addition of solvent and halide ions. Rate constants for the capture of the highly unstable O-methylated carbocation by nucleophilic reagents do not obey the *N*<sub>s</sub> equation, which requires that carbocation selectivity be independent of electrophile reactivity. The solvent deuterium isotope effects on the uncatalyzed addition of water and bromide ion are (*k*<sub>o</sub>)<sub>HOH</sub>/*(k*<sub>o</sub>)<sub>DOD</sub> = 2.0 and (*k*<sub>Br</sub>)<sub>HOH</sub>/*(k*<sub>Br</sub>)<sub>DOD</sub> = 1.0, respectively. The difference in the isotope effects on these two reactions may be explained by considering the changes in the interaction of solvent with the water and bromide ion nucleophiles that occur on moving to the reaction transition states. The solvent deuterium isotope effects on the hydrogen ion catalyzed addition of water and bromide ion are *k*<sub>H</sub>/*k*<sub>D</sub> = 0.68 and *k*<sub>HBr</sub>/*k*<sub>DBr</sub> = 1.0, respectively. The difference in the isotope effects on these reactions and several other experimental observations are consistent with a stepwise mechanism for the H<sup>+</sup>-catalyzed addition of solvent and a concerted mechanism for the H<sup>+</sup>-catalyzed reactions of halide ions in which protonation of the carbonyl oxygen and carbon–bromine bond formation occur in a single step.

Quinone methides are of considerable interest as the reactive intermediates formed upon reductive activation of mitomycin C<sup>1</sup>

and anthracyclines,<sup>2</sup> in the biosynthesis of neolignan,<sup>3</sup> and as a product of tyrosinase-catalyzed oxidation of α-methyl dopa methyl