



## Synthesis and characterization of aromatic polyesters containing multiple *n*-alkyl side chains

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### ABSTRACT

A series of 2,2'-disubstituted-4,4'-dihydroxybiphenyl monomers was prepared from 3,4,5-tris(*n*-alkoxy)-benzyl chlorides ( $n = 5, 6, 8, 10, 12$ ) and tetramethylammonium salt of 4,4'-dihydroxydiphenic acid, which was synthesized from two different 5-step routes. 2,2'-Bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid was synthesized via 5-step route. A series of aromatic polyesters containing multiple alkyl side chains was prepared from the 2,2'-disubstituted-4,4'-dihydroxybiphenyl monomers and 2,2'-bis-(trifluoromethyl)-4,4'-biphenyldicarboxylic acid using diisopropylcarbodiimide as a dehydrating agent and 4-(dimethylamino)pyridinium 4-toluenesulfonate as a catalyst at room temperature. Their thermal and solution properties were measured and compared with the polyester without multiple alkyl side chains. The polyesters displayed better solubility in common solvents such as chlorinated solvents and THF but lower thermal stability than the polyester without multiple alkyl side chains. The intrinsic viscosities of the polyesters ranged from 0.68 to 2.53 dL/g and their number-average molecular weights ranged from 19,300 to 61,400. Polyesters containing C5–10 side chains were amorphous while the two polyesters containing C12 side chains crystallized at  $-27$  and  $-31$  °C, respectively. The thermal stability of the polyesters decreased as a result of alkyl side chains. The films of polyesters were opaque, indicating that the aromatic backbones and aliphatic side chains underwent phase separation.

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### 1. Introduction

Many aromatic, rod-like polymers, such as polyimides, polyamides, and polyesters have been synthesized during the last five decades. Because of the high aromatic content, all of the polymers display excellent thermal stability. They also have excellent mechanical and physical properties and good chemical resistance. They are used as structural materials in car and aerospace applications. They are also used as load-bearing fibers and as insulating and packaging materials in microelectronics [1].

The high regularity and high rigidity of the backbones of rod-like polymers result in strong chain–chain interaction, high crystallinity, high melting points, and low solubility. Thus, processing of rod-like polymers is often impossible. In order to increase the processibility and systematically understand rod-like polymers, a wide variety of modified rod-like polymers have been synthesized. Alkyl side chains have been attached to rigid polymers such as aromatic polyesters and polyimides to decrease their melting points and glass transition temperatures and to increase their

solubilities [2–6]. These types of polymers are referred to as hairy-rod polymers. The attachment of alkyl side chains also results in changes in liquid-crystalline behavior. Poly(1,4-phenylene 2,5-dialkoxyterephthalate)s with short side chains exhibit nematic mesophases, while longer side chains lead to novel layered mesophases [7,8]. Polyimides containing two side chains per repeat unit were prepared to increase the solubility of aromatic polymers and to maintain the rigidity of the backbone [9,10]. Photoalignable aromatic polyesters containing phenylenediacrylate units in their backbones and *n*-alkyl moieties in their side groups showed the excellent properties which make them promising candidate materials for use as liquid crystal (LC) alignment layers in advanced LC display devices [11]. Low-density liquid-crystalline polyesters with *n*-alkyl side chains, were synthesized from the 1,4-di-(*n*-alkyl ester) of 1,2,4,5-benzenetetracarboxylic acid and 4,4'-biphenol, to clarify the effect of side chain length on higher ordered structure in the solid state and gas sorption and diffusion properties of these polyesters [12]. Hairy-rod polyfluorene was synthesized as a material used in backlighting system of liquid crystal displays (LCDs) [13]. The branched-side-chain containing polyfluorene formed a systematic intermolecular self-assembly and liquid-crystalline phase behavior in combination with uniaxial and biaxial alignments.

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Polyimides and polyetherimides containing multiple *n*-alkyl side chains, in which the length of the alkyl side chains was varied from 5 to 18 methylene units, were prepared [14]. Most of the polymers exhibited good solubility in chlorinated solvents. As part of our continuing effort, one series of biphenyl diols containing multiple *n*-alkyl side chains was prepared. They were polymerized with 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid to afford a series of polyesters containing multiple *n*-alkyl side chains. The thermal and solution properties of the polyesters were measured and compared with the polyester without multiple alkyl side chains. The objective of this research was to synthesize a series of diols containing multiple alkyl side chains and polymerize them with diacids to improve the solubility and processibility of aromatic polyesters.

## 2. Experimental section

### 2.1. Materials

4-(Dimethylamino)pyridinium 4-toluenesulfonate (DPTS) was synthesized from *p*-toluenesulfonic acid and 4-(dimethylamino)pyridine according to Ref. [12] [15]. Hydrochloric acid, nitric acid and conc. sulfuric acid were purchased from Fisher Scientific Co. and used as received. All the other reagents and solvents were purchased from Aldrich as reagent grade and used as received.

### 2.2. Instrumentation

Proton and carbon nuclear magnetic ( $^1\text{H}$  and  $^{13}\text{C}$  NMR) spectra were measured at 200 MHz on a Varian Gemini-200 spectrometer. Infrared (IR) spectra were obtained with an ATI Mattson Genesis Series Fourier transform infrared spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN. All melting points were determined on a Mel-Temp melting point apparatus and were uncorrected. Intrinsic viscosities were determined with a Cannon Ubbelohde No. 50 viscometer using chloroform as the solvent at  $30.0 \pm 0.1$  °C. Thermogravimetric analyses (TGA) were performed in nitrogen and air using a TA Hi-Res TGA 2950 thermogravimetric analyzer with a heating rate of 10 °C/min. Differential scanning calorimetry (DSC) analyses were carried out on a Du Pont 9900 thermal analysis system and a Perkin-Elmer DSC-7 with a heating rate of 10 °C/min. Gel permeation chromatography (GPC) analyses were carried out using a Waters 510 HPLC pump, a Waters 410 differential refractometer, and a series of ultrastaygel columns ( $50, 10^2, 10^3, 10^4,$  and  $10^5$  nm) with tetrahydrofuran as the eluent at 35 °C.

### 2.3. 3,4,5-Tris(*n*-pentan-1-yloxy)benzyl chloride (**6a**)

To a 125 mL, one-necked flask equipped with a magnetic stirrer were added 3,4,5-tris(*n*-pentan-1-yloxy)benzyl alcohol (5.70 g, 0.0149 mol), and methylene chloride (50 mL). After the solution was cooled to 0–5 °C in an ice bath, thionyl chloride (3.15 g, 0.0268 mol) was added dropwise. The solution was allowed to warm up to room temperature and stirred for an additional 3 h. It was washed twice with water (50 mL), once with 2% sodium bicarbonate solution (50 mL), once with water (50 mL), and then dried with magnesium sulfate. The methylene chloride was removed on a rotary evaporator to afford 5.60 g (94%) of a light yellow liquid (lit. [16] bp not reported); IR (KBr) 2955, 2921, 2848, 1594, 1466, 1440, 1335, 1247, 1125, 723, 701, and 668 ( $\text{CH}_2\text{-C1}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.87 (t, 9H,  $\text{CH}_3$ ), 1.26 (m, 12H,  $(\text{CH}_2)_2$ ), 1.77 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.95 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.50 (s, 2H,  $\text{CH}_2\text{C1}$ ), and 6.55 ppm (s, 2H, Ar-H);  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.18, 22.83, 26.26, 29.51, 29.55, 29.73, 29.79, 29.85, 30.54, 32.08, 47.43, 69.64, 73.88, 107.72, 132.81, 138.75, and 153.59 ppm.

### 2.4. 3,4,5-Tris(*n*-hexan-1-yloxy)benzyl chloride (**6b**)

Compound **6b** was synthesized from 3,4,5-tris(*n*-hexan-1-yloxy)benzyl alcohol (7.20 g, 0.0176 mol) using the same procedure used for compound **6a** to afford 7.40 g (98%) of a light yellow liquid (lit. [16] bp not reported); IR (KBr) 2954, 2920, 2848, 1593, 1467, 1441, 1335, 1246, 1124, 724, 700, and 668 ( $\text{CH}_2\text{-C1}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 9H,  $\text{CH}_3$ ), 1.26 (m, 18H,  $(\text{CH}_2)_3$ ), 1.77 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.96 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.51 (s, 2H,  $\text{CH}_2\text{C1}$ ), and 6.56 ppm (s, 2H, Ar-H).

### 2.5. 3,4,5-Tris(*n*-octan-1-yloxy)benzyl chloride (**6c**)

Compound **6c** was synthesized from 3,4,5-tris(*n*-octan-1-yloxy)benzyl alcohol (14.8 g, 0.0300 mol) using the same procedure used for compound **6a** to afford 15.0 g (98%) of a colorless liquid (lit. [16] bp not reported); IR (KBr) 2954, 2920, 2848, 1593, 1467, 1441, 1335, 1246, 1124, 723, 703, and 668 ( $\text{CH}_2\text{-C1}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 9H,  $\text{CH}_3$ ), 1.28 (m, 30H,  $(\text{CH}_2)_5$ ), 1.76 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.97 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.51 (s, 2H,  $\text{CH}_2\text{C1}$ ), and 6.57 ppm (s, 2H, Ar-H).

### 2.6. 3,4,5-Tris(*n*-decan-1-yloxy)benzyl chloride (**6d**)

Compound **6d** was synthesized from 3,4,5-tris(*n*-decan-1-yloxy)benzyl alcohol (17.3 g, 0.0300 mol) using the same procedure used for compound **6a** to afford 17.2 g (96%) of a colorless liquid (lit. [16] bp not reported); IR (KBr) 2954, 2920, 2848, 1593, 1467, 1441, 1335, 1246, 1124, 725, 701, and 668 ( $\text{CH}_2\text{-C1}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 9H,  $\text{CH}_3$ ), 1.28 (m, 42H,  $(\text{CH}_2)_7$ ), 1.76 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.97 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.51 (s, 2H,  $\text{CH}_2\text{C1}$ ), and 6.57 ppm (s, 2H, Ar-H).

### 2.7. 3,4,5-Tris(*n*-dodecan-1-yloxy)benzyl chloride (**6e**)

Compound **6e** was synthesized from 3,4,5-tris(*n*-dodecan-1-yloxy)benzyl alcohol (16.5 g, 0.0250 mol) using the same procedure used for compound **6a** with following modification: the product was recrystallized from acetone to afford 16.9 g (95%) of a white solid: mp 56–58 °C (lit. [17] 60 °C); IR (KBr) 2953, 2920, 2849, 1593, 1505, 1465, 1440, 1392, 1334, 1245, 1124, 829, 723, 700, and 672 ( $\text{CH}_2\text{-C1}$ )  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 9H,  $\text{CH}_3$ ), 1.26 (m, 54H,  $(\text{CH}_2)_9$ ), 1.77 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.96 (m, 6H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.51 (s, 2H,  $\text{CH}_2\text{C1}$ ), and 6.56 ppm (s, 2H, Ar-H).

### 2.8. 2-Bromo-5-methoxybenzoic acid (**8**)

To a 1 L, three-necked flask equipped with a mechanical stirrer, a reflux condenser and an addition funnel were added *m*-anisic acid (50.0 g, 0.328 mol) and acetic acid (300 mL). A solution of bromine (53.0 g, 0.332 mol) in acetic acid (300 mL) and water (600 mL) was added slowly through the additional funnel. The resulting solution was stirred, heated at reflux for 2 h, and allowed to cool to afford 59.4 g (78%) of white needles: mp 158–159 °C (lit. [18] mp 159–160 °C);  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  3.79 (s, 3H,  $\text{OCH}_3$ ), 6.90 (dd, 1H, Ar-H), 7.47 (d, 1H, Ar-H), and 7.53 ppm (d, 1H, Ar-H).

### 2.9. Methyl 2-bromo-5-methoxybenzoate (**9**)

To a 1 L, three-necked flask equipped with a mechanical stirrer and a reflux condenser were added 2-bromo-5-methoxybenzoic acid (58.4 g, 0.253 mol), methanol (600 mL) and concentrated sulfuric acid (4 mL). The resulting solution was stirred and heated at reflux for 24 h. After the volume of the solution was reduced to about 200 mL on a rotary evaporator, it was extracted with ether (500 mL). The ether extract was washed twice with water (500 mL),

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