



## 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 ( $50, 10^2, 10^3, 10^4, \text{ and } 10^5$  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),

once with saturated sodium chloride solution (200 mL) and then dried with magnesium sulfate. The mixture was filtered, and filtrate was evaporated to dryness on a rotary evaporator to afford 56.0 g (90%) of an oily liquid: bp 128–130 °C (4 mm) (lit. [18] oily liquid);  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  3.79 (s, 3H, Ar-OCH<sub>3</sub>), 3.91 (s, 3H, COOCH<sub>3</sub>), 6.87 (dd, 1H, Ar-H), 7.29 (d, 1H, Ar-H), and 7.51 ppm (d, 1H, Ar-H).

#### 2.10. 4,4'-Dimethoxydiphenic acid (**11**)

To a 500 mL, three-necked flask equipped with a mechanical stirrer and a reflux condenser were added methyl 2-bromo-5-methoxybenzoate (111 g, 0.453 mol), activated copper (55.5 g, 0.873 mol), and NMP (50 mL). The mixture was heated at 210 °C for 4 h. After NMP (120 mL) was added, the mixture was allowed to cool to room temperature. The mixture was filtered, and the filtrate was poured into a dilute hydrochloric acid/water solution with vigorous stirring. The brown precipitate was collected by filtration, and added to a 5 N sodium hydroxide aqueous solution (600 mL). The solution was stirred and heated at reflux until it became clear. Concentrated hydrochloric acid was used to neutralize the solution. The precipitate that formed was collected by filtration and recrystallized from ethanol/water to afford 60.0 g (88%) of white crystals: mp 250–252 °C (lit. [18] mp 245–248 °C);  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  3.82 (s, 3H, OCH<sub>3</sub>), 7.09 (m, 2H, Ar-H), and 7.36 ppm (d, 1H, Ar-H).

#### 2.11. 4,4'-Dihydroxydiphenic acid (**12**)

To a 500 mL, three-necked flask equipped with a mechanical stirrer and a reflux condenser were added 4,4'-dimethoxydiphenic acid (24.5 g, 0.0810 mol), glacial acetic acid (250 mL), and 48% hydrobromic acid (150 mL). The solution was heated at reflux overnight. After most of the solvent was removed by distillation under reduced pressure, water (150 mL) was added, and the mixture was heated at 100 °C until all the solids were dissolved. The solution was decolorized with charcoal and allowed to cool to afford 20.5 g (93%) of white crystals: mp > 300 °C (lit. [19] mp > 300 °C);  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  6.91 (m, 4H, Ar-H), 7.23 (s, 2H, Ar-H), 9.62 (s, 2H, ArOH), and 12.26 ppm (bs, 2H, ArCOOH).

#### 2.12. 4,4'-Dinitrodiphenic acid (**14** with 2,4'- and 2,2'- isomers)

After diphenic acid (63.0 g, 0.260 mol) was dissolved in sulfuric acid (500 mL), the solution was cooled to -15 °C in a dry-ice-acetone bath. A mixture of nitric acid (194 g), sulfuric acid (24 g) and water (7.0 g) was added dropwise so as to maintain the mixture below -10 °C. After the addition was complete, the solution was stirred at room temperature overnight and then poured into ice water (2000 mL). The mixture was stored in a freezer overnight. The precipitate that formed was collected by filtration and recrystallized from a 30% ethanol/water mixture to give 81.6 g (94%) of yellow crystals: mp 248–252 °C (lit [20] 258–259 °C).

#### 2.13. Dimethyl 4,4'-dinitro-2,2'-biphenyldicarboxylate (**15**)

4,4'-Dinitrodiphenic acid (21.0 g, 0.0632 mol) was dissolved in methanol (250 mL) containing sulfuric acid (2.0 mL). After the mixture was stirred and heated at reflux for 3 d, it was allowed to cool to room temperature. The white precipitate that formed was collected by filtration and dried under reduced pressure to afford 16.7 g (75%) of a white powder: mp 172–174 °C (lit [21] 174 °C); IR (KBr) 3080, 2958, 1726 (C=O), 1608, 1582, 1519, 1433, 1350, 1304, 1276, 1128, 972, 881, 818, and 744  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  3.63 (s, 6H, CH<sub>3</sub>), 7.60 (d, 2H, Ar-H), 8.51 (dd, 2H, Ar-H), and 8.68 ppm (d, 2H, Ar-H).

#### 2.14. Dimethyl 4,4'-diamino-2,2'-biphenyldicarboxylate (**16**)

To a 250 mL, three-necked flask equipped with a mechanical stirrer, a nitrogen inlet and a reflux condenser were added dimethyl 4,4'-dinitro-2,2'-biphenyldicarboxylate (9.00 g, 0.0250), 5% palladium on activated carbon (0.20 g) and ethanol (100 mL). Hydrazine monohydrate (5.2 mL) was added dropwise to mixture at reflux. After addition, 5% palladium on activated carbon (0.20 g) was added. After the mixture was stirred at reflux for 4 h, it was filtered while hot. The filtrate was concentrated to 50 mL, and stored in a freezer overnight to afford 6.0 g (80%) of light yellow crystals: mp 144–146 °C (lit [22] 148–150 °C). Anal. Calcd. for  $\text{C}_{16}\text{H}_{16}\text{N}_2\text{O}_4$ : C, 63.99%, H, 5.37%. Found: C, 63.67%, H, 5.38%; IR (KBr) 3468, 3370 (NH<sub>2</sub>), 3229, 2950, 1706 (C=O), 1632, 1609, 1564, 1488, 1434, 1323, 1231, 1071, 978, 827, and 789  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  3.46 (s, 6H, CH<sub>3</sub>), 5.24 (s, 4H, NH<sub>2</sub>), 6.69 (dd, 2H, Ar-H), 6.80 (d, 2H, Ar-H), and 6.95 ppm (d, 2H, Ar-H);  $^{13}\text{C NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  50.17, 113.11, 115.52, 128.66, 129.41, 130.35, 145.98, and 166.94 ppm.

#### 2.15. Dimethyl 4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**17**)

To a 250 mL, three-necked flask equipped with a mechanical stirrer and an addition funnel were added dimethyl 4,4'-diamino-2,2'-biphenyldicarboxylate (2.94 g, 0.0100 mol), concentrated hydrochloric acid (22 mL), and water (100 mL). The solution was cooled to 0 °C in an ice bath. A solution of sodium nitrite (1.45 g, 0.0210) in water (10 mL) was added at 0–5 °C. The resulting solution was poured into a cold solution of phosphoric acid (20 mL) in water (1.8 L). After stirring for 5 min, the orange mixture was heated at the boiling point for 10 min. The mixture was cooled and extracted with diethyl ether (3 × 200). The combined organic phase was extracted with 2 N sodium hydroxide solution (2 × 50 mL). The combined aqueous phase was acidified with concentrated hydrochloric acid, extracted with diethyl ether (3 × 100 mL), and dried with magnesium sulfate. The filtrate obtained by filtration was evaporated to dryness on a rotary evaporator. The residue was recrystallized from ethanol/water to afford 1.60 g (54%) of yellow crystals: mp 206–208 °C. Anal. Calcd. for  $\text{C}_{16}\text{H}_{14}\text{O}_6$ : C, 63.58%, H, 4.67%. Found: C, 63.67%, H, 4.61%; IR (KBr) 3394, 3350 (OH), 3005, 2949, 1698 (C=O), 1605, 1491, 1433, 1312, 1254, 1218, 1073, 836, and 790  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  4.76 (s, 6H, CH<sub>3</sub>), 6.92–6.94 (m, 4H, Ar-H), 7.18 (d, 2H, Ar-H), and 9.73 ppm (s, 2H, Ar-OH);  $^{13}\text{C NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  50.42, 114.57, 117.33, 129.63, 130.88, 131.71, 154.93, and 166.03 ppm.

#### 2.16. 4,4'-Dihydroxydiphenic acid (**12**)

To a 250 mL, three-necked flask equipped with a mechanical stirrer and a reflux condenser were added dimethyl 4,4'-dihydroxy-2,2'-biphenyldicarboxylate (3.02 g, 0.010 mol), sodium hydroxide (7.2 g, 0.180 mol), DMSO (45 mL), and water (20 mL) and were stirred at room temperature for 1 d. After the solution was neutralized with a dilute hydrochloric acid solution to pH = 1, water (100 mL) was added. The mixture was heated at 100 °C until all the solids were dissolved. The solution was decolorized with charcoal and allowed to cool to afford 2.5 g (91%) of white crystals: mp > 300 °C (lit [19] mp > 300 °C);  $^1\text{H NMR}$  ( $\text{DMSO}-d_6$ )  $\delta$  6.91 (m, 4H, Ar-H), 7.23 (s, 2H, Ar-H), 9.62 (s, 2H, ArOH), and 12.26 ppm (bs, 2H, ArCOOH).

#### 2.17. Tetramethylammonium salt of 4,4'-dihydroxydiphenic acid (**18**)

4,4'-Dihydroxydiphenic acid (2.74 g, 10.0 mol), 24% aqueous tetramethylammonium hydroxide (7.59 g, 0.0200 mol) and methanol (50 mL) were stirred until 4,4'-dihydroxydiphenic acid was



dissolved completely (slight heating was used if necessary). The solution was concentrated on a rotary evaporator to about 15 mL and then stored in a freezer ( $-10^{\circ}\text{C}$ ) overnight. The product was collected by filtration to afford 3.6 g (86%) of white crystals: mp  $> 300^{\circ}\text{C}$  (lit. [19] mp  $> 300^{\circ}\text{C}$ );  $^1\text{H NMR}$  ( $\text{D}_2\text{O}$ )  $\delta$  3.03 (s, 24H,  $\text{NCH}_3$ ), 6.75 (dd, 2H, Ar–H), 6.82 (d, 2H, Ar–H), and 7.04 ppm (d, 2H, Ar–H).

2.18. Bis[4-[3,4,5-tris(*n*-pentan-1-yloxy)benzyl]]-4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**19a**, C5BHBC)

To a 100 mL, three-necked flask equipped with a mechanical stirrer and a reflux condenser were added the tetramethylammonium salt of 4,4'-dihydroxydiphenic acid (2.94 g, 0.00700 mol), 3,4,5-tris(*n*-pentan-1-yloxy)benzyl chloride (5.40 g, 0.0140 mol), and hexamethylphosphoramide (30 mL). The mixture was stirred and heated at  $160^{\circ}\text{C}$  for 24 h. After the mixture was allowed to cool to room temperature, water (100 mL) was added. The solution was extracted with ether (400 mL). The ether extract was washed twice with water ( $2 \times 400$  mL), once with saturated sodium chloride solution (200 mL), and then dried with magnesium sulfate. The mixture was filtered, and filtrate was evaporated to dryness on a rotary evaporator. The solid residue was chromatographed on a silica gel column with chloroform as the eluent and then with ether as the eluent. The ether fraction was collected, and ether was removed on a rotary evaporator. The white residue was recrystallized from ethanol to afford 3.20 g (47%) of a white solid: mp  $120\text{--}122^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{58}\text{H}_{82}\text{O}_{12}$ : C, 71.72%, H, 8.51%. Found: C, 71.72%, H, 8.49%; IR (KBr) 3367 (OH), 2955, 2934, 2860, 1696 ( $\text{C}=\text{O}$ ), 1602, 1490, 1467, 1439, 1376, 1333, 1303, 1211, 1114, 963, and  $835\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 18H,  $\text{CH}_3$ ), 1.31 (m, 24H,  $(\text{CH}_2)_2$ ), 1.72 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.90 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.88 (s, 4H,  $\text{PhCH}_2\text{O}$ ), 5.78 (s, 2H, PhOH), 6.34 (s, 4H, Ar–H), 6.81 (dd, 2H, Ar–H), 6.89 (d, 2H, Ar–H), and 7.27 ppm (d, 2H, Ar–H).

2.19. Bis[4-[3,4,5-tris(*n*-hexan-1-yloxy)benzyl]]-4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**19b**, C6BHBC)

Compound **19b** was synthesized from the tetramethylammonium salt of 4,4'-dihydroxydiphenic acid (3.15 g, 0.00750 mol), and 3,4,5-tris(*n*-hexan-1-yloxy)benzyl chloride (6.41 g, 0.0150 mol) using the same procedure used for compound **19a** to afford 3.40 g (43%) of a white solid: mp  $82\text{--}84^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{64}\text{H}_{94}\text{O}_{12}$ : C, 72.83%, H, 8.98%. Found: C, 72.90%, H, 8.93%; IR (KBr) 3378 (OH), 2957, 2933, 2860, 1699 ( $\text{C}=\text{O}$ ), 1605, 1491, 1465, 1439, 1375, 1332, 1301, 1211, 1114, 965, and  $835\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.89 (t, 18H,  $\text{CH}_3$ ), 1.32 (m, 36H,  $(\text{CH}_2)_2$ ), 1.73 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.90 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.89 (s, 4H,  $\text{PhCH}_2\text{O}$ ), 5.86 (s, 2H, PhOH), 6.35 (s, 4H, Ar–H), 6.81 (dd, 2H, Ar–H), 6.89 (d, 2H, Ar–H), and 7.28 ppm (d, 2H, Ar–H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.18, 14.23, 22.79, 22.84, 25.93, 25.96, 29.58, 30.43, 31.78, 31.95, 67.35, 69.40, 73.79, 107.88, 117.22, 119.10, 130.82, 131.04, 132.03, 135.17, 138.22, 153.24, 155.04, and 167.38 ppm.

2.20. Bis[4-[3,4,5-tris(*n*-octan-1-yloxy)benzyl]]-4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**19c**, C8BHBC)

Compound **19c** was synthesized from the tetramethylammonium salt of 4,4'-dihydroxydiphenic acid (3.15 g, 0.00750 mol), and 3,4,5-tris(*n*-octan-1-yloxy)benzyl chloride (7.66 g, 0.0150 mol) using the same procedure used for compound **19a** to afford 4.50 g (49%) of a white solid: mp  $66\text{--}68^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{76}\text{H}_{118}\text{O}_{12}$ : C, 74.59%, H, 9.72%. Found: C, 74.72%, H, 10.14%; IR (KBr) 3372 (OH), 2921, 2852, 1717 ( $\text{C}=\text{O}$ ), 1597, 1506, 1467, 1441, 1377, 1337, 1306, 1239, 1117, 988, 822 and  $721\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.88 (t, 18H,  $\text{CH}_3$ ), 1.32 (m, 60H,  $(\text{CH}_2)_5$ ), 1.74 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.91 (m, 12H,

$\text{CH}_2\text{CH}_2\text{O}$ ), 4.89 (s, 4H,  $\text{PhCH}_2\text{O}$ ), 5.21 (s, 2H, PhOH), 6.35 (s, 4H, Ar–H), 6.82 (dd, 2H, Ar–H), 6.90 (d, 2H, Ar–H), and 7.28 ppm (d, 2H, Ar–H).

2.21. Bis[4-[3,4,5-tris(*n*-decan-1-yloxy)benzyl]]-4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**19d**, C10BHBC)

Compound **19d** was synthesized from the tetramethylammonium salt of 4,4'-dihydroxydiphenic acid (3.15 g, 0.00750 mol), and 3,4,5-tris(*n*-decan-1-yloxy)benzyl chloride (8.93 g, 0.0150 mol) using the same procedure used for compound **19a** to afford 4.10 g (39%) of a white solid: mp  $62\text{--}64^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{88}\text{H}_{142}\text{O}_{12}$ : C, 75.95%, H, 10.28%. Found: C, 76.22%, H, 10.34%; IR (KBr) 3387 (OH), 2953, 2932, 2860, 1689 ( $\text{C}=\text{O}$ ), 1602, 1491, 1465, 1438, 1375, 1333, 1303, 1211, 1114, 963, 822 and  $721\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.87 (t, 18H,  $\text{CH}_3$ ), 1.25 (m, 84H,  $(\text{CH}_2)_7$ ), 1.73 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.89 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.87 (s, 4H,  $\text{PhCH}_2\text{O}$ ), 5.76 (s, 2H, PhOH), 6.32 (s, 4H, Ar–H), 6.79 (dd, 2H, Ar–H), 6.91 (d, 2H, Ar–H), and 7.27 ppm (d, 2H, Ar–H);  $^{13}\text{C NMR}$  ( $\text{CDCl}_3$ )  $\delta$  14.27, 22.85, 26.33, 29.55, 29.65, 29.80, 29.87, 30.51, 32.10, 67.31, 69.39, 73.80, 107.97, 117.09, 118.93, 130.82, 131.11, 131.98, 135.06, 138.22, 153.18, 155.05, and 167.37 ppm.

2.22. Bis[4-[3,4,5-tris(*n*-dodecan-1-yloxy)benzyl]]-4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**78e**, C12BHBC)

Compound **19e** was synthesized from the tetramethylammonium salt of 4,4'-dihydroxydiphenic acid (1.60 g, 0.00380 mol), and 3,4,5-tris(*n*-dodecan-1-yloxy)benzyl chloride (5.00 g, 0.00760 mol) using the same procedure used for compound **19a** to afford 3.89 g (65%) of a white solid: mp  $72\text{--}74^{\circ}\text{C}$ . Anal. Calcd. for  $\text{C}_{100}\text{H}_{166}\text{O}_{12}$ : C, 76.97%, H, 10.72%. Found: C, 77.12%, H, 10.67%; IR (KBr) 3352 (OH), 2921, 2850, 1717 ( $\text{C}=\text{O}$ ), 1608, 1441, 1306, 1238, 1118, 990, and  $822\text{ cm}^{-1}$ ;  $^1\text{H NMR}$  ( $\text{CDCl}_3$ )  $\delta$  0.89 (t, 18H,  $\text{CH}_3$ ), 1.32 (m, 108H,  $(\text{CH}_2)_9$ ), 1.73 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 3.90 (m, 12H,  $\text{CH}_2\text{CH}_2\text{O}$ ), 4.89 (s, 4H,  $\text{PhCH}_2\text{O}$ ), 5.86 (s, 2H, PhOH), 6.35 (s, 4H, Ar–H), 6.81 (dd, 2H, Ar–H), 6.89 (d, 2H, Ar–H), and 7.28 ppm (d, 2H, Ar–H).

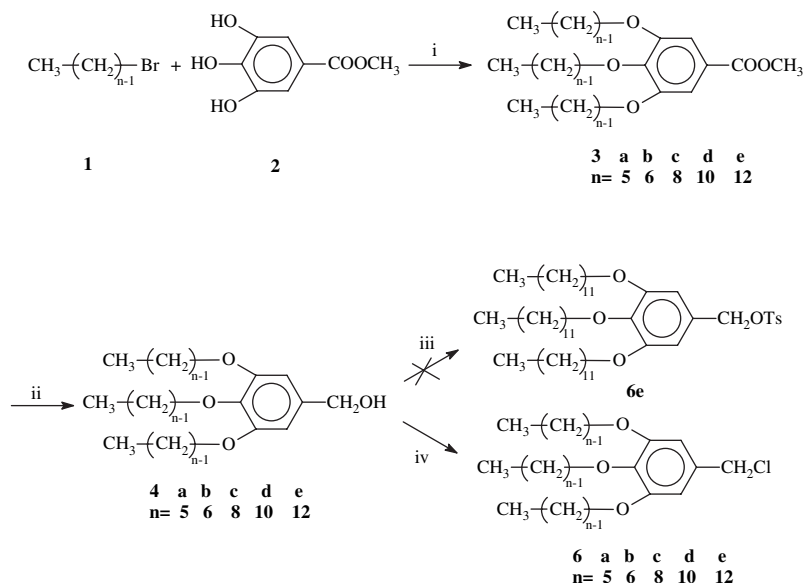
2.23. General procedure for the preparation of polyesters (**26a–e**, **28** and **29**)

A single-necked round-bottom flask containing a stir bar was dried and flushed thoroughly with  $\text{N}_2$ . Diol monomer **17** or **19** (1 equiv), 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid **25** or terephthalic acid **27** (1 equiv), 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS, 1 equiv) and diisopropylcarbodiimide (DiPC, 3 equiv) were charged to the flask. Dry methylene chloride (10 mL per gram of diol) was added via a syringe. The mixture was allowed to react at room temperature for 2 d, and then was poured into methanol (500 mL). The white precipitate that formed was collected and dissolved in methylene chloride. The mixture was poured into methanol. The polymer that precipitated was collected by filtration and dried under reduced pressure at  $80^{\circ}\text{C}$  for 48 h.

### 3. Results and discussion

#### 3.1. Monomer synthesis

3,4,5-Tris(*n*-alkan-1-yloxy)benzoates (**3**) were prepared by coupling *n*-alkyl bromides (**1**) with methyl 3,4,5-trihydroxybenzoate (**2**) using Williamson conditions according to the literatures (Scheme 1) [14c,23]. These intermediates were then reduced to 3,4,5-tris(*n*-alkan-1-yloxy)benzyl alcohols (**4a–e**) [14d,24]. An attempt to convert the hydroxyl group in compound **4e** to a tosyl group was unsuccessful. Only a very low yield ( $<5\%$  according to NMR results) of product **5** was obtained after water wash. The instability of benzyl tosylate has been recognized [25]. Researchers



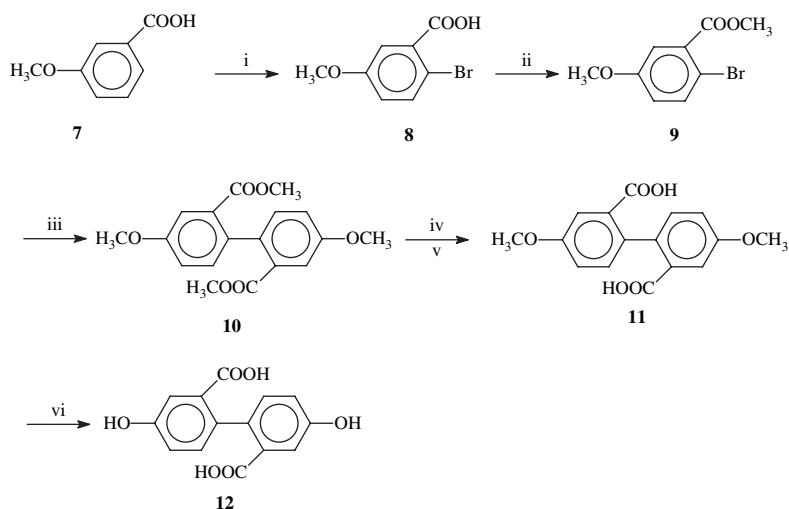
**Scheme 1.** Synthesis of side chains: (i) DMF,  $\text{K}_2\text{CO}_3$ ,  $\text{N}_2$ ,  $70^\circ\text{C}$ ; (ii)  $\text{LiAlH}_4$ , ether; (iii) *p*-toluenesulfonyl chloride, ether; (iv)  $\text{SOCl}_2$ ,  $\text{CH}_2\text{Cl}_2$ .

found that its preparations could not be successfully stored for prolonged periods. Since it was thought that water may catalyze the decomposition of this compound, it was prepared in an entirely anhydrous condition [26]. Thus, compounds **4a–e** were treated with thionyl chloride to give the 3,4,5-tris(*n*-alkan-1-yloxy)benzyl chlorides (**6a–e**), which were used in next-step esterification.

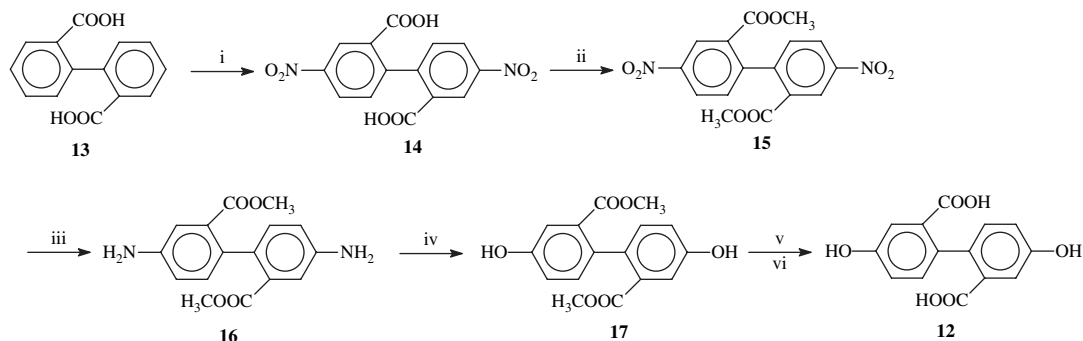
4,4'-Dihydroxydiphenic acid (**12**) had been synthesized previously and the yield was very low [27]. 4,4'-Dihydroxy-2,2'-biphenyldicarbonitrile was hydrolyzed either with strong acid or with base to give 4,4'-dihydroxydiphenic acid, which was difficult to isolate from the reaction mixtures. Thus, another published, 5-step route, which afforded higher yields and easier purification procedures, was used (Scheme 2) [18]. *m*-Anisic acid (**7**) was treated with bromine in acetic acid to afford 2-bromo-5-methoxybenzoic acid (**8**). The carboxylic acid group in compound **8** was protected by the conversion of **8** to methyl 2-bromo-5-methoxybenzoate (**9**). Compound **9** was dimerized using the Ullmann conditions to give compound **10**, which was used without further purification. Compound **10** was hydrolyzed with a sodium hydroxide solution to afford 4,4'-dimethoxydiphenic acid (**11**). Demethylation of

compound **11** with  $\text{HBr}$ /acetic acid gave 4,4'-dihydroxydiphenic acid (**12**). The overall 5-step yield of **12** was 57.5%.

4,4'-Dihydroxydiphenic acid (**12**) was also synthesized via a new 5-step route as shown in Scheme 3. Nitration of diphenic acid (**13**) gave 4,4'-dinitrodiphenic acid (**14**) plus some isomers (mainly 2,4'- and 2,2'-dinitrodiphenic acids). Unfortunately, neither recrystallization nor chromatography could afford the pure 4,4'-dinitrodiphenic acid (product). However, pure dimethyl 4,4'-dinitro-2,2'-biphenyldicarboxylate (**15**) was precipitated from solution when 4,4'-dinitrodiphenic acid (**14**) and its isomers were heated at reflux in methanol in the presence of an acid catalyst. Compound **15** was then reduced with hydrazine monohydrate and palladium on activated carbon to afford dimethyl 4,4'-diamino-2,2'-biphenyldicarboxylate (**16**). Compound **16** was converted to dimethyl 4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**17**) using a Sandmeyer reaction. Thus, compound **16** was treated with hydrochloric acid and sodium nitrite to form a diazonium salt, which was decomposed in phosphoric acid to afford compound **17**. After compound **17** was hydrolyzed using a sodium hydroxide solution the resulting product was acidified to afford



**Scheme 2.** Synthesis of 4,4'-dihydroxydiphenic acid **12**: (i)  $\text{Br}_2$ , acetic acid,  $\text{H}_2\text{O}$ , refluxing; (ii)  $\text{CH}_3\text{OH}$ , conc.  $\text{H}_2\text{SO}_4$ ; (iii)  $\text{Cu}$ ,  $\text{NMP}$ ; (iv)  $\text{NaOH}$ ,  $\text{H}_2\text{O}$ ; (v) conc.  $\text{HCl}$ ; (vi)  $\text{HBr}$ , acetic acid.



**Scheme 3.** Synthesis of 4,4'-dihydroxydiphenic acid **12**: (i)  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$ ; (ii)  $\text{CH}_3\text{OH}$ , conc.  $\text{H}_2\text{SO}_4$ ; (iii)  $\text{NH}_2\text{NH}_2$ , Pd/C; (iv)  $\text{HCl}$ ,  $\text{NaNO}_2$ ,  $\text{H}_3\text{PO}_4$ ; (v)  $\text{NaOH}$ ,  $\text{H}_2\text{O}$ ; (vi)  $\text{HCl}$ .

dihydroxydiphenic acid (**12**). However, the overall yield (27.8%) of **12** in this 5-step route was lower than the previous one (Scheme 2).

Ester linkages were to be used to connect alkyl chains to the two carboxylic acid groups in the 2- and 2'- position in compound **12**. There are two major ways to form esters (Scheme 4). The first involves treating carbonyl groups with alcohols or phenols using acid or base catalysts. In the second, the carboxyl group is converted to the carboxyl anion, which is used to displace halogen from alkyl halides. The presence of hydroxyl groups in the 4- and 4'-position of compound **12** ruled out the use of the first type of esterification reaction. Therefore, esterification reactions that use the carboxylic anion as a nucleophile were employed. Thus, compound **12** was treated with tetramethylammonium hydroxide in methanol/water to afford compound **18**. The nucleophilicity of the carboxylate anion

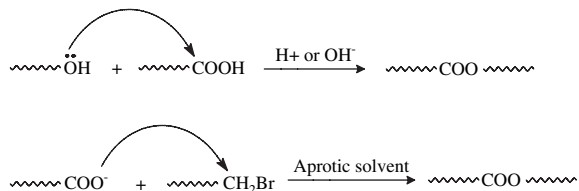
is enhanced in polar aprotic solvents due to the destruction of tight ion-pairs [28].

The desired alkyl-substituted diols (**19a–e**) were obtained by treating compound **18** with compounds **6a–e** in hexamethylphosphoramide (HMPA) at  $150^\circ\text{C}$  (Scheme 5). The IR spectrum of compound **19b** is shown in Fig. 1. The spectrum contains the characteristic absorption of aromatic phenols at  $3400\text{ cm}^{-1}$  and carbonyl groups at  $1717\text{ cm}^{-1}$ . All the diols were verified by elemental analysis, IR,  $^1\text{H}$  and  $^{13}\text{C}$  NMR.

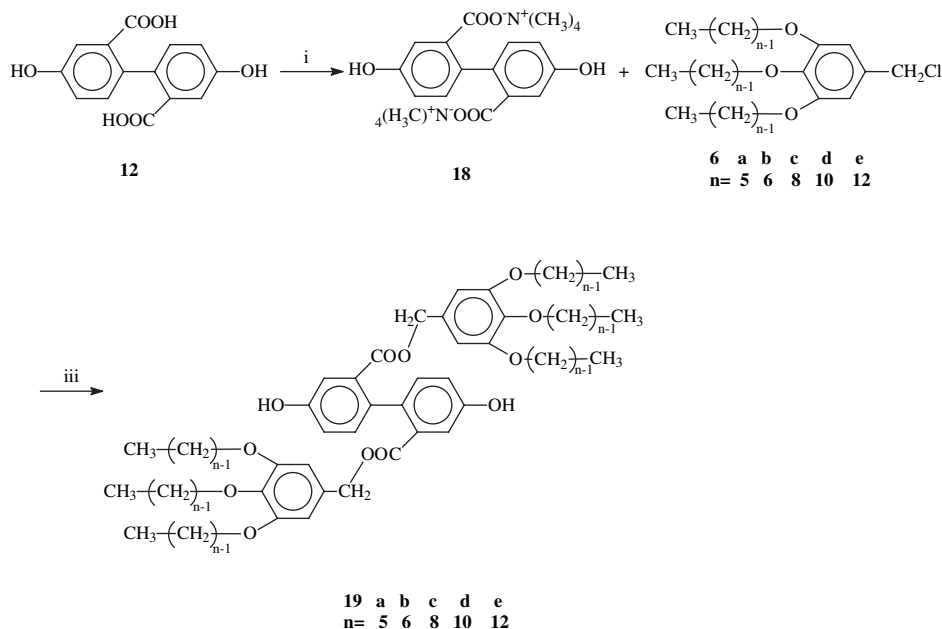
2,2'-Bis(trisfluoromethyl)-4,4'-biphenyldicarboxylic acid (**25**) was prepared by the known, 5-step synthetic route as shown in Scheme 6 [18]. The overall yield was about 32%.

### 3.2. Syntheses of polyesters

Polyesters can be synthesized by four methods: melt, interfacial, solution and direct polymerization. Melt polymerizations are generally carried out with a diacylated diol and a diacid at high temperature ( $>200^\circ\text{C}$ ) and in high vacuum in the last stage. With the monomers used in this study at that high temperature, transesterification would occur, which would result in the cleavage of the ester linkages. Interfacial polymerizations require the formation of phenoxide salts, which can be dissolved in an aqueous phase. Such monomers are polymerized with diacid chlorides at a water/organic phase interface. The phenoxide salts of the alkyl-substituted diols **19**



**Scheme 4.** Two methods of ester synthesis.



**Scheme 5.** Synthesis of alkyl-substituted diols **19a–e**: (i)  $(\text{CH}_3)_4\text{N}^+\text{OH}^-$ ,  $\text{H}_2\text{O}/\text{CH}_3\text{OH}$ ; (ii) HMPA,  $150^\circ\text{C}$ .

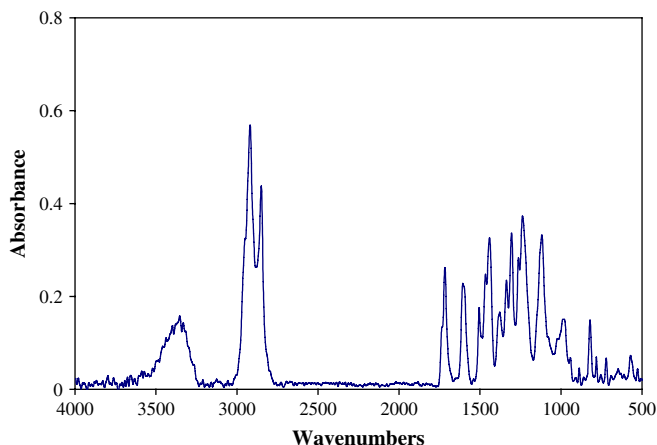
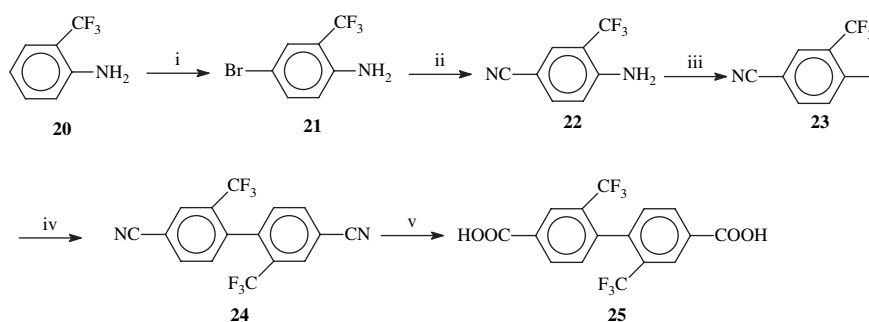


Fig. 1. IR spectrum of bis[4-[3,4,5-tris(*n*-hexan-1-yloxy)benzyl]]-4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**19b**, C6BHBC) (KBr).

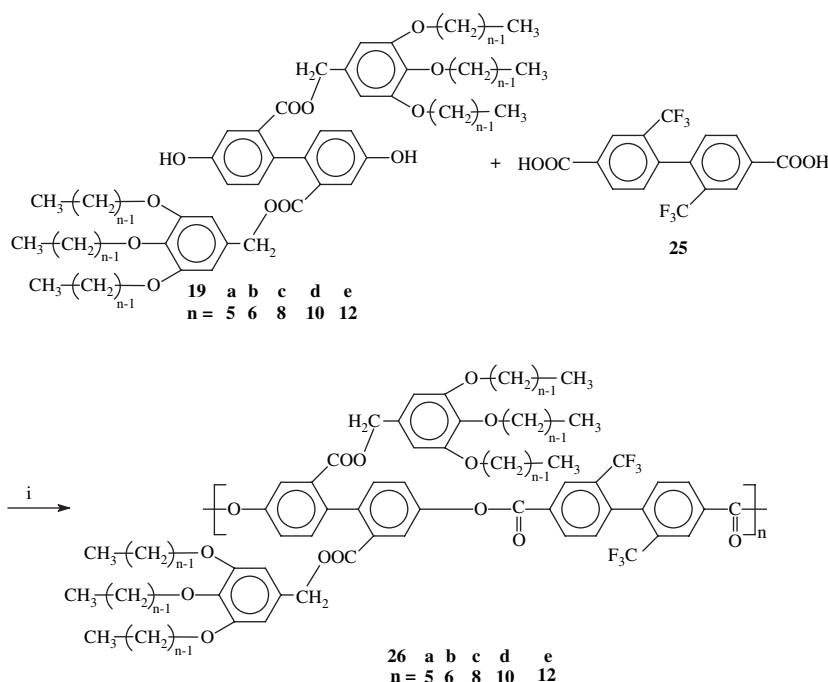
would not dissolve in water due to the six hydrophobic alkyl side chains. Initially, the polymerization of C12BHBC (**19e**) and 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbonyl chloride was carried out

in solution in 1,1,2,2-tetrachloroethane (TCE) containing pyridine. However, the intrinsic viscosity of the polyester obtained was only 0.22 dL/g. It is speculated that 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarbonyl chloride was so moisture sensitive that it was easily hydrolyzed to the corresponding acid, therefore, destroying the stoichiometry of the polymerization.

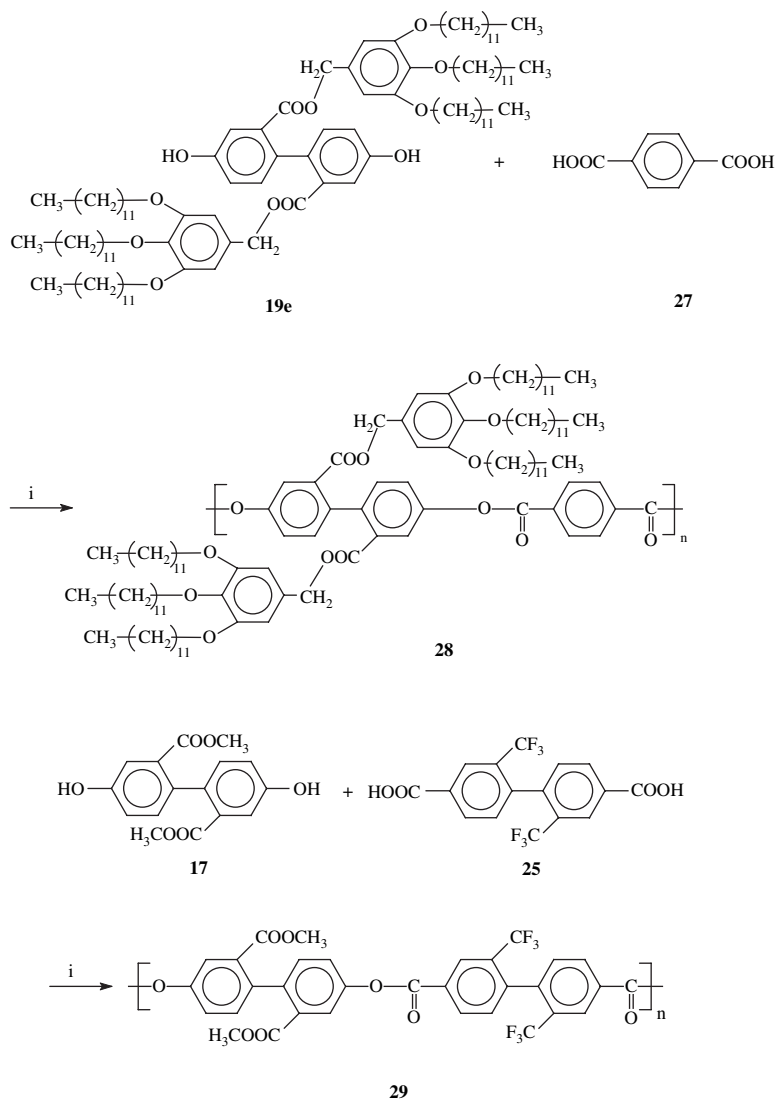
A convenient method to synthesize polyesters has been developed where a diacid is directly polymerized with a diol using diisopropylcarbodiimide (DiPC) as a dehydrating agent and 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) as a catalyst in methylene chloride at room temperature [15]. The direct condensation of the acid and the diol has several advantages. For example, preactivated acid derivatives, such as acid chlorides, are not required. Due to the fact that the reaction is carried out at room temperature and near neutral pH, it is useful in the polymerizations of thermal and chemically sensitive monomers. Thus, this method was used to prepare the polyesters containing alkyl side chains **26a–e** from the diols **19a–e** and 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid (**25**) in dry methylene chloride (Scheme 7). For comparison purpose, polyesters **28** were prepared from C12BHBC (**19e**) and terephthalic acid (**27**) and polyester **29** was prepared from dimethyl 4,4'-dihydroxy-2,2'-biphenyldicarboxylate (**17**) and compound **25** (Scheme 8).



Scheme 6. Synthesis of 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid **25**: (i) NBS, DMF; (ii) CuCN, NMP; (iii) H<sub>2</sub>SO<sub>4</sub>, H<sub>2</sub>O; NaNO<sub>2</sub>; KI; (iv) Cu, NMP; (v) NaOH, diethylene glycol.



Scheme 7. Synthesis of alkyl-substituted polyesters **26a–e**: (i) DiPC, DPTS, CH<sub>2</sub>Cl<sub>2</sub>.



**Scheme 8.** Synthesis of polyesters **28** and **29**: (i) DiPS, DPTS,  $\text{CH}_2\text{Cl}_2$ .

### 3.3. Solution properties

The intrinsic viscosities,  $\bar{M}_n$ s and  $\bar{M}_w$ s of polyesters **26a–e** and **28** are shown in Table 1. The intrinsic viscosities of the polymers, which ranged from 0.46 to 2.53 g/dL, were measured at  $30.0 \pm 0.1$  °C in chloroform. The number-average molecular weights ( $\bar{M}_n$ s), weight-average molecular weights ( $\bar{M}_w$ s), and molecular weight distributions (MWDs) of polyesters **26a–e** and **28** were determined with gel permeation chromatography (GPC) with THF as the eluent. The number- and weight-average molecular weights were in the range of 19,300–61,400 and 34,000–121,000, respectively. MWDs of **26a** and **b** were more than 2 while MWDs of **26c–e** and **28** were less than 2. We observed that similar results (MWDs < 2) in the polyimides containing multiple alkyl side chains due to their aggregation nature [14]. We believed that the aggregation of **26c–e** and **28** also contributed to narrow MWDs. Polyester **29** was not soluble in chloroform and THF. Its viscosity and molecular weights were not measured.

Similar to polyimides and polyetherimides as previously reported [14], polyesters **26** and **28** containing multiple alkyl side chains showed excellent solubility in common solvents. They were soluble in  $\text{CH}_2\text{Cl}_2$ ,  $\text{CHCl}_3$ , TCE, and THF (Table 2). They were not soluble in acetone and methanol. In contrast, polyester **29**, which

did not contain alkyl side chains, was only soluble in TCE. This polyester precipitated during the polymerization. Therefore, the alkyl side chains did improve the solubility.

**Table 1**  
Intrinsic viscosities and molecular weights of polyesters

Polyester	Diol	$[\eta]^a$ (dL/g)	$T_d$ (°C) <sup>b</sup>	$T_m$ (°C) <sup>c</sup>	$\bar{M}_n$ ( $\times 10^3$ ) <sup>d</sup>	$\bar{M}_w$ ( $\times 10^3$ ) <sup>d</sup>	MWD
<b>26a</b>	C5BHBC	0.68	306	ND	19.8	42.5	2.15
<b>26b</b>	C6BHBC	2.53	308	ND	57.2	121	2.12
<b>26c</b>	C8BHBC	0.75	322	ND	19.3	34.0	1.76
<b>26d</b>	C10BHBC	0.77	309	ND	31.8	59.7	1.88
<b>26e</b>	C12BHBC	1.58	335	−31	61.4	114	1.86
<b>28</b>	C12BHBC	0.46	327	−27	20.6	36.7	1.78
<b>29</b>	DMBHBC	– <sup>e</sup>	492	ND	– <sup>f</sup>	– <sup>f</sup>	– <sup>f</sup>

ND: Not detected.

<sup>a</sup> Intrinsic viscosity determined in chloroform at  $30.0 \pm 0.1$  °C.

<sup>b</sup> Temperature at which a 5% weight loss occurred in nitrogen when subjected to TGA with a heating rate of 10 °C/min.

<sup>c</sup> Minimum of melting point endotherm on DSC thermogram obtained with a heating rate of 10 °C/min.

<sup>d</sup> Number-average and weight-average molecular weight determined using GPC with a light scattering detector in THF at  $35.0 \pm 0.1$  °C with polystyrene standard.

<sup>e</sup> Insoluble in chloroform.

<sup>f</sup> Insoluble in THF.



**Table 2**  
Solubility of polyesters

Polyester	Diol	CH <sub>2</sub> Cl <sub>2</sub>	CHCl <sub>3</sub>	TCE	THF	Acetone	Methanol
<b>26a</b>	C5BHBC	+	+	+	+	–	–
<b>26b</b>	C6BHBC	+	+	+	+	–	–
<b>26c</b>	C8BHBC	+	+	+	+	–	–
<b>26d</b>	C10BHBC	+	+	+	+	–	–
<b>26e</b>	C12BHBC	+	+	+	+	–	–
<b>28</b>	C12BHBC	+	+	+	+	–	–
<b>29</b>	DMBHBC	–	–	+	–	–	–

+: Minimum solubility of 1 g/dL at room temperature; –: solubility less than 1 g/dL at room temperature; TCE: tetrachloroethane; THF: tetrahydrofuran.

### 3.4. Thermal properties

The thermal stability of **26** and **28** was much lower than that of **29** due to the presence of the alkyl side chains. Polyester **29** showed only 5% weight loss at 492 °C while the 5% weight loss temperatures of **26** and **28** decreased to 306–335 °C (Table 1). The  $T_g$ s of the rigid polymers could not be detected with DSC. Polyesters **26e** and **28**, which contained longer side chains, melted at –31 and –27 °C, respectively, due to C12 side chains. To our knowledge, it is the first time that the aromatic polyesters having melting points ( $T_m$ ) well below room temperature are reported.

Polyesters **26** were cast into films from TCE solutions. However, the films were opaque, indicating that the aromatic backbones and aliphatic side chains underwent phase separation.

## 4. Conclusion

4,4'-Dihydroxydiphenic acid was prepared from two different synthetic routes. It was treated with tetramethylammonium hydroxide to afford its tetramethylammonium salt. A series of alkyl-substituted diols 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. Thus, the alkyl-substituted diols were polymerized with 2,2'-bis(trifluoromethyl)-4,4'-biphenyldicarboxylic acid to afford a series of polyesters containing multiple alkyl side chains. The polyesters obtained were soluble in most chlorinated solvents and THF. The intrinsic viscosities of the polyesters ranged from 0.46 to 2.53 dL/g and their number-average molecular weights ranged from 19,300 to 61,400. The  $T_g$ s of the rigid polymers could not be detected with DSC. Polyesters containing C5–10 side chains were amorphous while the side chains of two C12 polyesters melted at –31 and –27 °C, respectively. The thermal stability of the polyesters decreased as a result of alkyl side chains. The films of polyester were opaque, indicating that the aromatic backbones and aliphatic side chains underwent phase separation.

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