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Synthesis of stretchable polyetherimides containing multiple alkyl side chains

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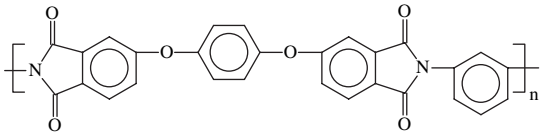
Abstract

Two series of diamine monomers, i.e., 4-[3,4,5-tris(*n*-alkan-1-yloxy)benzyl]-3,5-diaminobenzoate and 2,2′-bis{4-[3,4,5-tris(*n*-alkan-1-yloxy) benzoate]}-4,4′-biphenyldiamines containing multiple alkyl side chains, were synthesized in which the length of the alkyl side chains was varied from 5 to 18 ethylene units. Polyetherimides (PEIs) were prepared from these two diamines and bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydrides (BisADA) using a one-step method in 1-chloronaphthalene. All the polymers possessed good solubility in chlorinated solvents. The high-molecular weight PEIs could be solution cast into transparent, tough films. The polymers containing the side chains which were at least 16 methylene units could be crystallized. The melting points of the crystals increased as the length of the side chains increased. The glass transition temperatures (T_gs) of the PEIs decreased as the length of the side chains increased due to an internal plasticizing effect of the alkyl side chains. The PEIs containing multiple alkyl side chains showed excellent drawability with much higher elongations but lower tensile strengths and moduli compared with the commercial PEI, Ultem® 1000. The film's in-plane refractive index parallel to the drawing direction ($n_{//}$) increased and its in-plane refractive index perpendicular to the drawing direction ($n_{\perp}$) decreased during drawing mainly due to the orientation of main chains in the drawing direction. The film's in-plane birefringence increased with the drawing ratios.

Keywords: Polyetherimides; Alkyl side chains; Birefringence

1. Introduction

Polyetherimides (PEIs) have been prepared via aromatic nucleophilic substitution reactions [1]. Polymerization was carried out in dimethyl sulfoxide (DMSO)/toluene, *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc) or 1-methyl-2-pyrrolidinone (NMP) using moderate reaction conditions. PEIs were also synthesized from the diamine–dianhydride reaction. The majority of PEIs are non-crystalline and their glass transition temperatures (T_gs) range from 200 to 280 °C [2]. PEIs are injection moldable and exhibit high strengths and moduli, good ductility, excellent thermal stability, and flame resistance as well as good electrical properties. These basic properties make them outstanding high performance engineering thermoplastics. Ultem® 1000 is the most important PEI being sold by the General Electric Co. [3]. The polymer has also been used as a graphite–fiber–composite matrix resin.



Ultem® 1000

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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 [4–8]. These types of polymers are referred to as hairy-rod polymers. The attachment of alkyl side chains often induces liquid-crystalline behavior [9,10]. Introduction of alkyl side chains to aromatic polyimides decreases their T_gs, which results in lower processing temperatures [11]. Soluble polyimides containing long alkyl side chains have been used to prepare Langmuir–Blodgett films [12]. 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 [13,14]. The attachment of alkyl side chains to polyimides was used in the development of alignment layers for liquid crystal displays (LCDs) [15]. Hairy-rod polyfluorene was synthesized as a material used in backlighting system of LCDs [16]. The branched-side-chain containing polyfluorene formed a systematic intermolecular self-assembly and liquid-crystalline phase behavior in combination with uniaxial and biaxial alignments. PEIs and coPEIs containing fluorinated side chains were prepared and showed lower T_gs compared with Ultem® 1000 [17].

Polyimides and copolyimides containing multiple alkyl side chains, in which the length of the alkyl side chains was varied from 5 to 18 methylene units, were prepared [18]. Most of the polymers exhibited good solubility in chlorinated solvents. As part of our continuing effort, two series of PEIs containing multiple alkyl side chains were prepared from bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydrides (BisADA) using a one-step imidization method in 1-chloronaphthalene. The thermal, solution, mechanical and optical properties were measured and compared with commercially available Ultem® 1000. The objective of this research was to investigate the effect of introducing multiple alkyl side chains on the thermal, mechanical and optical properties of aromatic polyetherimides. Those polymers show high elongations under stress and can be used as stretchable elastomers, birefringence films and for other applications.

2. Experimental section

2.1. Materials

2,2′-Bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (GE Co.) was recrystallized from acetic anhydride and dried at 120 °C under reduced pressure overnight. 1-Chloronaphthalene (Aldrich) was distilled under reduced pressure after drying with calcium hydride. 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 resonance (^{1}H and ^{13}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 ± 0.1 °C. Thermogravimetric analyses (TGA) were performed in nitrogen and air with a TA Hi-Res TGA 2950 thermogravimetric analyzer using a heating rate of 10 °C/min. Differential scanning calorimetric (DSC) analyses were carried out on a Du Pont 9900 thermal analysis system and a Perkin–Elmer DSC-7 using a heating rate of 10 °C/min. Polymer thin films were solution cast from 10 to 15 wt% of 1,1,2,2-tetrachloroethane solutions. Thin film tensile properties were determined on a Model 5567 Instron with a crosshead separation speed of 1 mm/min at room temperature. Refractive index and birefringence measurements were carried out using a Metricon Model 2010 Prism Coupler. This equipment uses a high refractive index rutile prism and a 10 mW He–Ne laser operating at a wavelength of 633 nm.

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

A suspension of lithium aluminum hydride (1.20 g, 0.0320 mol) in anhydrous ethyl ether (50 mL) was cooled to 0–5 °C in an ice bath. A solution of methyl 3,4,5-tris(*n*-pentan-1-yloxy)benzoate (7.88 g, 0.0200 mol) in ethyl ether (50 mL) was added dropwise. The resulting mixture was stirred at 0–5 °C for 1 h. After the mixture was stirred and allowed to warm to room temperature over 2 h, water (5 mL) was added dropwise until the generation of hydrogen ceased. Dilute hydrochloric acid was added to the mixture until two phases formed. The organic phase was separated, washed three times with water (100 mL), once with a saturated sodium chloride aqueous solution (50 mL), and then dried with magnesium sulfate. The filtrate obtained by filtration was evaporated to dryness under reduced pressure to afford 6.6 g (89%) of a white solid: mp 44–46 °C. IR (KBr): 3327 (br, OH), 2919, 2852, 1589, 1507, 1468, 1439, 1383, 1337, 1227, 1124 (C–O–Ph), and 752 cm^{-1}. ^{1}H NMR ($CDC1_3$) δ: 0.87 (t, 9H, CH_3), 1.27 (m, 12H, $(CH_2)_2$), 1.78 (m, 6H, CH_2CH_2O), 3.95 (m, 6H, CH_2CH_2O), 4.58 (s, 2H, CH_2OH), and 6.54 ppm (s, 2H, Ar–H). ^{13}C NMR ($CDC1_3$) δ: 14.18, 22.83, 26.26, 29.51, 29.53, 29.73, 29.79, 29.85, 30.54, 32.08, 65.82, 69.64, 73.88, 105.52, 136.67, 137.95, and 153.59 ppm.

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

Compound **4b** was synthesized from methyl 3,4,5-tris(*n*-hexan-1-yloxy)benzoate (24.0 g, 0.0550 mol) using the same procedure used for compound **4a** to afford 20.6 g (92%) of a white solid: mp 47–48 °C. IR (KBr): 3326 (br, OH), 2918, 2852, 1590, 1507, 1467, 1439, 1383, 1337, 1227, 1124 (C–O–Ph), and 750 cm^{-1}. ^{1}H NMR ($CDC1_3$) δ: 0.87 (t, 9H, CH_3), 1.26 (m, 18H, $(CH_2)_3$), 1.77 (m, 6H, CH_2CH_2O), 3.95 (m, 6H, CH_2CH_2O), 4.58 (s, 2H, CH_2OH), and 6.54 ppm (s, 2H, Ar–H). Anal. Calcd for $C_{25}H_{44}O_4$: C, 73.49%; H, 10.85%. Found: C, 73.56%; H, 10.83%.

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

Compound **4c** was synthesized from methyl 3,4,5-tris(*n*-octan-1-yloxy)benzoate (26.7 g, 0.0513 mol) using the same procedure used for compound **4a** to afford 23.8 g (94%) of a white solid: mp 47–48 °C (lit. [19] mp not reported). IR (KBr): 3326 (br, OH), 2918, 2852, 1590, 1507, 1467, 1439, 1383, 1337, 1227, 1124 (C–O–Ph), and 750 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.87 (t, 9H, CH_3), 1.26 (m, 30H $(CH_2)_5$), 1.77 (m, 6H, CH_2CH_2O), 3.95 (m, 6H, CH_2CH_2O), 4.58 (s, 2H, CH_2OH), and 6.54 ppm (s, 2H, Ar–H).

2.6. 3,4,5-Tris(n-dodecan-1-yloxy)benzyl alcohol (**4d**)

Compound **4d** was synthesized from methyl 3,4,5-tris-(*n*-dodecan-1-yloxy)benzoate (36.6 g, 0.0530 mol) using the same procedure used for compound **4a** with the following modification: the product was recrystallized from acetone to afford 32.1 g (97%) of a white solid: mp 49–50 °C (lit. [20] mp 50 °C). IR (KBr): 3313 (br, OH), 2918, 2852, 1591, 1506, 1469, 1437, 1383, 1337, 1226, 1125 (C–O–Ph), 1015, 828, and 750 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.87 (t, 9H, CH_3), 1.26 (m, 54H, $(CH_2)_9$), 1.77 (m, 6H, CH_2CH_2O), 3.95 (m, 6H, CH_2CH_2O), 4.58 (s, 2H, CH_2OH), and 6.54 ppm (s, 2H, Ar–H).

2.7. 3,4,5-Tris(n-pentan-1-yloxy)benzoic acid (**5a**)

To a 125 mL Erlenmeyer flask containing a Teflon-coated magnetic stir bar were added methyl 3,4,5-tris(*n*-pentan-1-yloxy)benzoate (6.1 g, 0.015 mol), 95% ethanol (50 mL) and potassium hydroxide (5.8 g, 0.10 mol). The mixture was heated at 78 °C for 2 h with stirring and allowed to cool to room temperature. The solution was acidified with dilute hydrochloric acid and added to water (ca. 100 mL). The solid that precipitated was collected by filtration to yield 5.4 g (95%) of a white solid: mp 46–48 °C (lit. [21a] mp 51 °C, DSC, 20 °C/min). IR (KBr): 3078, 2920, 2850, 2640 (br, COOH), 1685 (C=O), 1587, 1505, 1466, 1433, 1391, 1333, 1231, 865, 765 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.88 (t, 9H, CH_3), 1.27 (m, 12H, $(CH_2)_2$), 1.78 (m, 6H, CH_2CH_2OPh), 4.01 (m, 6H, CH_2CH_2OPh), and 7.24 ppm (s, 2H, Ar–H).

2.8. 3,4,5-Tris(n-octan-1-yloxy)benzoic acid (**5b**)

Compound **5b** was synthesized from methyl 3,4,5-tris(*n*-octan-1-yloxy)benzoate (26.0 g, 0.0500 mol) using the same procedure used for compound **5a** to afford 25.3 g (96%) of a white solid: mp 59–61 °C (lit. [21b] mp 53 °C). ^1H NMR ($CDC1_3$) δ: 0.94 (t, 9H, CH_3), 1.40 (m, 30H, $(CH_2)_5$), 1.78 (m, 6H, CH_2CH_2OPh), 4.01 (m, 6H, CH_2CH_2OPh), and 7.24 ppm (s, 2H, Ar–H).

2.9. 3,4,5-Tris(n-dodecan-1-yloxy)benzoic acid (**5c**)

To a 500 mL Erlenmeyer flask containing a Teflon-coated magnetic stir bar were added methyl 3,4,5-tris(*n*-dodecan-1-yloxy)benzoate (20.4 g, 0.0294 mol), 95% ethanol (160 mL) and potassium hydroxide (14.5 g, 0.204 mol). The mixture was heated at 78 °C for 2 h with stirring and then allowed to cool to room temperature. The resulting solid was collected by filtration, transferred to a 500 mL Erlenmeyer flask, and then dissolved in THF (300 mL). The solution was acidified with dilute hydrochloric acid to pH = 1 and then added into water (ca. 500 mL). The precipitate that formed was collected by filtration and recrystallized from acetone to yield 17.8 g (90%) of a white solid: mp 59–60 °C (lit. [21a] mp 64 °C, DSC, 20 °C/min). IR (KBr): 2955, 2919, 1850, 2643 (br, COOH), 1683 (C=O), 1586, 1504, 1468, 1431, 1383, 1333, 1275, 1226, 1121, 994, and 767 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.88 (t, 9H, CH_3), 1.27 (m, 54H, $(CH_2)_9$), 1.78 (m, 6H, CH_2CH_2OPh), 4.01 (m, 6H, CH_2CH_2OPh), and 7.24 ppm (s, 2H, Ar–H). ^{13}C NMR ($CDC1_3$) δ: 14.18, 22.83, 26.26, 29.51, 29.55, 29.73, 29.79, 29.85, 30.54, 32.08, 69.64, 73.88, 109.30, 125.11, 142.95, 153.29, and 172.62 ppm.

2.10. 3,4,5-Tris(n-hexadecan-1-yloxy)benzoic acid (**5d**)

Compound **5d** was synthesized from methyl 3,4,5-tris-(*n*-hexadecan-1-yloxy)benzoate (26.0 g, 0.0300 mol) using the same procedure as compound **5c** to afford 24.0 g (95%) of a white solid: mp 78–80 °C (lit [22] mp 78–80 °C). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 9H, CH_3), 1.27 (m, 78H, $(CH_2)_{13}$), 1.78 (m, 6H, CH_2CH_2OPh), 4.01 (m, 6H, CH_2CH_2OPh), and 7.24 ppm (s, 2H, Ar–H).

2.11. 3,4,5-Tris(n-octadecan-1-yloxy)benzoic acid (**5e**)

Compound **5e** was synthesized from methyl 3,4,5-tris-(*n*-octadecan-1-yloxy)benzoate (9.4 g, 0.010 mol) using the same procedure used for compound **5c** to afford 8.3 g (93%) of a white solid: mp 85–86 °C (lit. [23] mp 83–85 °C). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 9H, CH_3), 1.27 (m, 90H, $(CH_2)_{15}$), 1.78 (m, 6H, CH_2CH_2OPh), 4.01 (m, 6H, CH_2CH_2OPh), and 7.24 ppm (s, 2H, Ar–H).

2.12. 4-[3,4,5-Tris(n-pentan-1-yloxy)benzyl]-3,5-dinitrobenzoate (**7a**)

3,5-Dinitrobenzoic acid (5.08 g, 0.0240 mol), 3,4,5-tris(*n*-pentan-1-yloxy) benzyl alcohol (8.80 g, 0.0240 mol), dicyclohexylcarbodiimide (DCC, 5.0 g, 0.024 mol), dimethylaminopyridine (DMAP, 0.20 g), and methylene chloride (50 mL) were stirred at room temperature for 2 d. The mixture was filtered, and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in hexane (50 mL) and filtered. The filtrate was evaporated to dryness. The residue was chromatographed on a basic aluminum oxide column with methylene chloride as the eluent. The solvent was removed and the residue was recrystallized from acetone to yield 4.63 g (85%) of yellow crystals: mp 53–55 °C. IR (KBr): 3120, 3097, 2953, 2921, 2872, 1722 (C=O), 1628, 1593, 1547, 1534, 1440, 1344, 1275, 1249, 1166, 1113, 972, 836, and 720 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.92 (t, 9H, CH_3), 1.42

(m, 12H, $(CH_2)_2$), 1.81 (m, 6H, CH_2CH_2O), 3.99 (m, 6H, CH_2CH_2OAr), 5.35 (s, 2H, Ar–CH_2OPh), 6.65 (s, 2H, Ar–H), 9.17 (d, 2H, Ar–H), and 9.20 ppm (d, 1H, Ar–H). ^{13}C NMR ($CDC1_3$) δ: 14.15, 14.21, 22.60, 22.70, 28.41, 29.23, 30.14, 69.25, 69.48, 73.65, 108.01, 122.66, 129.81, 134.26, 139.24, 148.98, 153.72, and 162.74 ppm. Anal. Calcd for $C_{29}H_{40}N_2O_9$: C, 62.13%; H, 7.19%. Found: C, 61.85%; H, 7.15%.

2.13. 4-[3,4,5-Tris(n-hexan-1-yloxy)benzyl]-3,5-dinitrobenzoate (**7b**)

Compound **7b** was synthesized from 3,5-dinitrobenzoic acid (6.18 g, 0.0290 mol) and 3,4,5-tris(*n*-hexan-1-yloxy) benzyl alcohol (11.83 g, 0.0290 mol) using the same procedure used for compound **7a** to afford 13.8 g (79%) of yellow crystals: mp 46–48 °C. IR (KBr): 3100, 2953, 2921, 2872, 1723 (C=O), 1626, 1595, 1543, 1534, 1441, 1346, 1280, 1249, 1166, 1115, 972, 837, and 721 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.92 (t, 9H, CH_3), 1.41 (m, 18H, $(CH_2)_3$), 1.77 (m, 6H, CH_2CH_2O), 3.99 (m, 6H, CH_2CH_2OAr), 5.35 (s, 2H, Ar–CH_2OPh), 6.65 (s, 2H, Ar–H), 9.17 (d, 2H, Ar–H), and 9.21 ppm (d, 1H, Ar–H). Anal. Calcd for $C_{32}H_{46}N_2O_9$: C, 63.77%; H, 7.69%. Found: C, 63.58%; H, 7.64%.

2.14. 4-[3,4,5-Tris(n-octan-1-yloxy)benzyl]-3,5-dinitrobenzoate (**7c**)

Compound **7c** was synthesized from 3,5-dinitrobenzoic acid (5.08 g, 0.0240 mol) and 3,4,5-tris(*n*-octan-1-yloxy) benzyl alcohol (11.83 g, 0.0240 mol) using the same procedure used for compound **7a** to afford 13.5 g (82%) of yellow crystals: mp 56.5–57.5 °C. IR (KBr): 3101, 2955, 2924, 2872, 1724 (C=O), 1624, 1595, 1543, 1534, 1441, 1346, 1280, 1249, 1166, 1116, 972, 837, and 721 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.92 (t, 9H, CH_3), 1.41 (m, 30H, $(CH_2)_5$), 1.77 (m, 6H, CH_2CH_2O), 3.99 (m, 6H, CH_2CH_2OAr), 5.35 (s, 2H, Ar–CH_2OPh), 6.65 (s, 2H, Ar–H), 9.17 (d, 2H, Ar–H), and 9.21 ppm (d, 1H, Ar–H). Anal. Calcd for $C_{38}H_{58}N_2O_9$: C, 66.45%; H, 8.51%. Found: C, 66.22%; H, 8.45%.

2.15. 4-[3,4,5-Tris(n-dodecan-1-yloxy)benzyl]-3,5-dinitrobenzoate (**7d**)

Compound **7d** was synthesized from 3,5-dinitrobenzoic acid (2.54 g, 0.0120 mol) and 3,4,5-tris(*n*-dodecan-1-yloxy) benzyl alcohol (7.90 g, 0.0120 mol) using the same procedure used for compound **7a** to afford 8.70 g (85%) of yellow crystals: mp 76–77 °C. IR (KBr): 3101, 2955, 2920, 2849, 1719 (C=O), 1627, 1595, 1541, 1534, 1466, 1441, 1346, 1285, 1249, 1168, 1121, 938, 837, and 729 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.92 (t, 9H, CH_3), 1.41 (m, 54H, $(CH_2)_9$), 1.77 (m, 6H, CH_2CH_2O), 3.99 (m, 6H, CH_2CH_2OAr), 5.35 (s, 2H, Ar–CH_2OPh), 6.65 (s, 2H, Ar–H), 9.17 (d, 2H, Ar–H), and 9.21 ppm (d, 1H, Ar–H). Anal. Calcd for $C_{50}H_{82}N_2O_9$: C, 70.22%; H, 9.60%. Found: C, 70.15%; H, 9.58%.

2.16. 4-[3,4,5-Tris(n-pentan-1-yloxy)benzyl]-3,5-diaminobenzoate (**8a**, C5DAB)

4-[3,4,5-Tris(*n*-pentan-1-yloxy)benzyl]-3,5-dinitrobenzoate (2.4 g, 0.0043 mol), hexane (100 mL) and 5% palladium on activated carbon (0.40 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with hexane and then filtrate was evaporated to dryness under reduced pressure. The white residue was recrystallized from ethanol/water to give 1.6 g (75%) of white crystals: mp 57.5–59 °C. IR (KBr): 3423, 3370, 3340 (NH_2), 2955, 2935, 2870, 1694 (C=O), 1624, 1598, 1508, 1466, 1439, 1383, 1353, 1235, 1116, 990, 852, and 770 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.89 (t, 9H, CH_3), 1.32 (m, 12H, $(CH_2)_3$), 1.77 (m, 6H, CH_2CH_2O), 3.65 (br s, 4H, NH_2), 3.97 (m, 6H, CH_2CH_2OAr), 5.18 (s, 2H, Ar–CH_2OPh), 6.17 (d, 1H, Ar–H), 6.60 (s, 2H, Ar–H), and 6.79 ppm (d, 1H, Ar–H). ^{13}C NMR ($CDC1_3$) δ: 14.12, 14.17, 22.54, 22.65, 28.35, 29.17, 30.08, 67.11, 69.29, 73.53, 105.89, 107.11, 107.26, 131.31, 132.24, 138.39, 147.79, 153.43, and 167.04 ppm. Anal. Calcd for $C_{29}H_{44}N_2O_5$: C, 69.57%; H, 8.86%. Found: C, 69.29%; H, 8.81%.

2.17. 4-[3,4,5-Tris(n-hexan-1-yloxy)benzyl]-3,5-diaminobenzoate (**8b**, C6DAB)

Compound **8b** was synthesized from 4-[3,4,5-tris(*n*-hexan-1-yloxy)benzyl]-3,5-dinitrobenzoate (3.0 g, 0.0050 mol) using the same procedure used for compound **8a** to afford 2.4 g (86%) of white crystals: mp 48–50 °C. IR (KBr): 3428, 3375, 3339 (NH_2), 2923, 2853, 1698 (C=O), 1623, 1599, 1507, 1467, 1443, 1379, 1354, 1233, 1116, 978, 852, and 770 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.89 (t, 9H, CH_3), 1.32 (m, 18H, $(CH_2)_3$), 1.75 (m, 6H, CH_2CH_2O), 3.66 (br s, 4H, NH_2), 3.97 (m, 6H, CH_2CH_2OAr), 5.18 (s, 2H, Ar–CH_2OPh), 6.17 (d, 1H, Ar–H), 6.60 (s, 2H, Ar–H), and 6.79 ppm (d, 1H, Ar–H). Anal. Calcd for $C_{32}H_{48}N_2O_5$: C, 71.08%; H, 8.95%. Found: C, 71.05%; H, 9.69%.

2.18. 4-[3,4,5-Tris(n-octan-1-yloxy)benzyl]-3,5-diaminobenzoate (**8c**, C8DAB)

Compound **8c** was synthesized from 4-[3,4,5-tris(*n*-octan-1-yloxy)benzyl]-3,5-dinitrobenzoate (2.5 g, 0.0036 mol) using the same procedure used for compound **8a** to afford 1.6 g (71%) of white crystals: mp 74–75 °C. IR (KBr): 3422, 3370, 3339 (NH_2), 2932, 2857, 1696 (CO), 1624, 1597, 1508, 1466, 1439, 1383, 1352, 1233, 1117, 971, 852, and 770 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.87 (t, 9H, CH_3), 1.28 (m, 30H, $(CH_2)_5$), 1.75 (m, 6H, CH_2CH_2O), 3.55 (br s, 4H, NH_2), 3.96 (m, 6H, CH_2CH_2OAr), 5.18 (s, 2H, Ar–CH_2OPh), 6.17 (d, 1H, Ar–H), 6.60 (s, 2H, Ar–H), and 6.79 ppm (d, 1H,

Ar–H). Anal. Calcd for $C_{40}H_{72}N_2O_5$: C, 72.80%; H, 9.97%; N, 4.47%. Found: C, 72.89%; H, 9.90%; N, 4.44%.

2.19. 4-[3,4,5-Tris(n-dodecan-1-yloxy)benzyl]-3,5-diaminobenzoate (**8d**, C12DAB)

Compound **8d** was synthesized from 4-[3,4,5-tris(*n*-dodecan-1-yloxy)benzyl]-3,5-dinitrobenzoate (3.5 g, 0.0042 mol) using the same procedure used for compound **8a** to afford 2.8 g (84%) of white crystals: mp 65–68 °C. IR (KBr): 3425, 3370, 3340 (NH_2), 2935, 2870, 1694 (C=O), 1624, 1599, 1508, 1466, 1439, 1383, 1355, 1235, 1117, 973, 852, and 770 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.87 (t, 9H, CH_3), 1.26 (m, 54H, $(CH_2)_9$), 1.80 (m, 6H, CH_2CH_2O), 3.66 (br s, 4H, NH_2), 3.96 (m, 6H, CH_2CH_2OAr), 5.18 (s, 2H, Ar–CH_2OPh), 6.18 (d, 1H, Ar–H), 6.60 (s, 2H, Ar–H), and 6.80 ppm (d, 1H, Ar–H). Anal. Calcd for $C_4oH_{72}N_2O_5$: C, 75.72%; H, 10.82%. Found: C, 75.52%; H, 10.90%.

2.20. 4-Iodo-3-methoxynitrobenzene (**10**)

Concentrated sulfuric acid (200 mL) was added slowly to a mixture of 2-methoxy-4-nitroaniline (100.8 g, 0.3000 mol) and water (400 mL). The solution was heated until all the solids dissolved and then cooled to 0 °C in an ice bath. A solution of sodium nitrite (49.2 g, 0.720 mol) in water (160 mL) was added dropwise, so that the mixture was maintained between 0 and 5 °C. After the addition was complete, the solution was stirred for 30 min at 0 °C and then filtered. The filtrate was added slowly to a vigorously stirred solution of potassium iodide (199.2 g, 1.200 mol) in the water (2000 mL). The solid was collected by filtration and washed first with a dilute aqueous sodium bisulfite solution and then with water. The product was recrystallized from acetone/methanol to afford 128.0 g (77%) of brown crystals: mp 133–135 °C (lit. [24] mp 127–128 °C). ^1H NMR ($CDC1_3$): 8 3.96 (s, 3H, CH_3), 7.54–7.61 (m, 2H, Ar–H), and 7.91 ppm (d, 1H, Ar–H).

2.21. 2,2′-Dimethoxy-4,4′-dinitrobiphenyl (**11**)

To a 250 mL, three-necked flask equipped with a condenser and a mechanical stirrer were added 4-iodo-3-methoxynitrobenzene (33.4 g, 0.120 mol), activated copper (38.1 g, 0.600 mol) and DMF (80 mL). After the solution was stirred and heated at reflux for 16 h, DMF (80 mL) was added. The resulting solution was heated to reflux and then filtered while hot. The filtrate was stored in a freezer (−10 °C) overnight. The solid that formed was collected by filtrated and washed with methanol to afford 10.8 g (61%) of yellow crystals: mp 255–257 °C (lit. [25] mp 253–254 °C). ^1H NMR ($CDC1_3$) δ: 3.86 (s, 6H, CH_3), 7.34 (d, 2H, Ar–H), 7.82 (d, 2H, Ar–H), and 7.88 ppm (dd, 2H, Ar–H).

2.22. 4,4′-Dinitro-2,2′-biphenyldiol (**12**)

2,2′-Dimethoxy-4,4′-dinitrobiphenyl (10.0 g, 0.0333 mol) and pyridine hydrochloride (100 g) were stirred and heated at 210 °C for 2 h and then poured into water (800 mL). The solid that formed was collected by filtration and recrystallized from acetone/water to give 8.24 g (90%) of yellow crystals: mp 254–255 °C (lit. [25] mp 253–254 °C). ^1H NMR (DMSO-d_6) δ: 7.44 (dd, 2H, Ar–H), and 7.69–7.75 ppm (m, 4H, Ar–H).

2.23. 2,2′-Bis{4-[3,4,5-tris(n-pentan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (**13a**)

4,4′-Dinitro-2,2′-biphenyldiol (0.80 g, 0.0030 mol), 3,4,5-tris(*n*-pentan-1-yloxy)benzoic acid (2.28 g, 0.00600 mol), dicyclohexylcarbodiimide (1.24 g, 0.00600 mol), 4-dimethylaminipyridine (0.22 g) and methylene chloride (50 mL) were stirred at room temperature for 24 h. The resulting precipitate was filtered, and the methylene chloride was evaporated. The residue was dispersed in hexane (50 mL) and then filtered. The filtrate was evaporated to dryness under reduced pressure. THF (25 mL) was added, and the solution was poured into water (200 mL) that was slightly acidified with hydrochloric acid. After the mixture was stirred for 24 h, methylene chloride (75 mL) was added. The organic layer was separated, dried over magnesium sulfate, and the methylene chloride was evaporated. The solid was recrystallized from ethanol to yield 2.3 g (77%) of a white solid: mp 77–78 °C. IR (KBr): 2917, 2850, 1738 (C=O), 1337, and 1123 cm^{-1} (C–O–Ph). ^1H NMR ($CDC1_3$) δ: 0.85 (t, 18H, CH_3), 0.95–1.43 (m, 24H, $(CH_2)_2$), 1.69 (m, 12H, CH_2CH_2O), 3.80–4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar–H *ortho* to C=O), 7.58 (d, 2H, Ar–H *meta* to O–C=O), 8.20 (dd, 2H, Ar–H *para* to O–C=O), and 8.26 ppm (d, 2H, Ar–H *ortho* to O–C=O). ^{13}C NMR ($CDC1_3$) δ: 14.09, 14.15, 22.51, 22.60, 28.24, 28.30, 29.04, 30.10, 69.23, 73.75, 108.56, 118.64, 121.11, 122.25, 131.83, 135.77, 143.94, 148.90, 153.30, and 163.91 ppm. Anal. Calcd for $C_{62}H_{76}N_2O_{14}$: C, 67.18%; H, 7.65%. Found: C, 67.34%; H, 7.86%.

2.24. 2,2′-Bis{4-[3,4,5-tris(n-octan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (**13b**)

Compound **13b** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (3.45 g, 0.0125 mol) and 3,4,5-tris(*n*-octan-1-yloxy)benzoic acid (12.7 g, 0.0250 mol) using the same procedure used for compound **13a** to afford 12.4 g (77%) of a white solid: mp 49–51 °C. IR (KBr): 2917, 2850, 1738 (C=O), 1337, and 1123 cm^{-1} (C–O–Ph). ^1H NMR ($CDC1_3$) δ: 0.85 (t, 18H, CH_3), 0.95–1.43 (m, 60H, $(CH_2)_5$), 1.69 (m, 12H, CH_2CH_2O), 3.80–4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar–H *ortho* to C=O), 7.58 (d, 2H, Ar–H *meta* to O–C=O), 8.20 (dd, 2H, Ar–H *para* to O–C=O), and 8.26 ppm (d, 2H, Ar–H *ortho* to O–C=O). Anal. Calcd for

$C_{74}H_{112}N_2O_{14}$: C, 70.90%; H, 9.00%. Found: C, 71.01%; H, 8.96%.

2.25. 2,2′-Bis{4-[3,4,5-tris(n-dodecan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (**13c**)

Compound **13c** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (1.1 g, 0.0040 mol) and 3,4,5-tris(*n*-dodecan-1-yloxy)benzoic acid (5.4 g, 0.0080 mol) using the same procedure used for compound **13a** with the following modification: the product was recrystallized from acetone to afford 5.91 g (91%) of a white solid: mp 58–59 °C. IR (KBr): 3084, 2955, 2919, 2850, 1711 (C=O), 1586, 1529, 1501, 1467, 1437, 1345, 1284, 1238, 1148, 1105 (C–O–Ph), 961, and 721 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.85 (t, 18H, CH_3), 0.95–1.43 (m, 108H, CH_2s), 1.69 (m, 12H, CH_2CH_2O), 3.80–4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar–H *ortho* to C=O), 7.58 (d, 2H, Ar–H *meta* to O–C=O), 8.20 (dd, 2H, *Ar–H para* to O–C=O), and 8.26 ppm (d, 2H, Ar–H *ortho* to O–C=O). Anal. Calcd for $C_{98}H_{160}N_2O_{14}$: C, 74.01%; H, 10.14%. Found: C, 74.37%; H, 10.25%.

2.26. 2,2′-Bis{4-[3,4,5-tris(n-hexadecan-1-yloxy)-benzoate]}-4,4′-dinitrobiphenyl (**13d**)

4,4′-Dinitro-2,2′-biphenyldiol (2.76 g, 0.0100 mmol), 3,4,5-tris(*n*-hexadecan-1-yloxy)benzoic acid (16.8 g, 0.0200 mmol), dicyclohexylcarbodiimide (4.20 g, 0.0200 mol), 4-dimethylaminipyridine (0.40 g) and methylene chloride (300 mL) were stirred at room temperature for 6 h and then heated at reflux for 24 h. The mixture was filtered while hot. After the solution was allowed to cool to room temperature, a precipitate formed. The precipitate was removed by filtration and the filtrate was stored in a refrigerator (0 °C). The solid that formed was collected by filtration, and recrystallized from acetone to give 16.90 g (88%) of a white powder: mp 77–79 °C. IR (KBr): 3069, 2955, 2918, 2850, 1723 (C=O), 1586, 1524, 1467, 1438, 1349, 1281, 1243, 1116 (C–O–Ph), 966, 833, and 720 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.85 (t, 18H, CH_3), 0.95–1.43 (m, 156H, CH_2s), 1.69 (m, 12H, CH_2CH_2O), 3.80–4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar–*H ortho* to O–C=O), 7.58 (d, 2H, Ar–H *meta* to O–C=O), 8.20 (dd, 2H, Ar–H *para* to O–C=O), and 8.26 ppm (d, 2H, Ar–H *ortho* to O–C=O). Anal. Calcd for $C_{122}H_{208}N_2O_{14}$: C, 75.87%; H, 11.04%. Found: C, 76.04%; H, 10.88%.

2.27. 2,2′-Bis{4-[3,4,5-tris(n-octadecan-1-yloxy)-benzoate]}-4,4′-dinitrobiphenyl (**13e**)

Compound **13e** was synthesized from 4,4′-dinitro-2,2′-biphenyldiol (1.22 g, 0.00440 mol) and 3,4,5-tris(*n*-octadecan-1-yloxy)benzoic acid (8.20 g, 0.00887 mol) using the same procedure used for compound **13d** to afford 8.10 g (86%) of a white powder: mp 61–62 °C. IR (KBr): 2917, 2850, 1738 (C=O), 1337, and 1123 cm^{-1} (C–O–Ph). ^1H NMR ($CDC1_3$) δ: 0.85 (t, 18H, CH_3), 0.95–1.43 (m, 180H, CH_2s), 1.69 (m, 12H, CH_2CH_2O), 3.80–4.01 (overlapped t, 12H, CH_2O), 7.12 (s, 4H, Ar–H *ortho* to C=O), 7.58 (d, 2H, Ar–H *meta* to O–C=O), 8.20 (dd, 2H, Ar–H *para* to O–C=O), and 8.26 ppm (d, 2H, Ar–H *ortho* to O–C=O). Anal. Calcd for $C_{134}H_{232}N_2O_{14}$: C, 76.81%; H, 11.16%. Found: C, 76.91%; H, 11.11%.

2.28. 2,2′-Bis{4-[3,4,5-tris(n-pentan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**14a**, *C5BBPA*)

2,2′-Bis{4-[3,4,5-tris(*n*-pentan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (5.5 g, 0.0055 mol), hexane (150 mL), and 5% palladium on activated carbon (0.70 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with hexane and then the filtrate was evaporated to dryness under reduced pressure. The yellow residue was recrystallized from ethanol/water, which was stored in a freezer, to give 4.20 g (76%) of yellow crystals: mp 90–92 °C. IR (KBr): 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C=O), 1625, 1586, 1496, 1430, 1336, 1201, and 1117 cm^{-1} (C–O–Ph). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 18H, CH_3), 1.15–1.35 (m, 24H, $(CH_2)_2$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89–3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar–H *para* to O–C=O), 6.60 (d, 2H, Ar–H *ortho* to O–C=O), 7.08 (d, 2H, Ar–H *meta* to O–C=O), and 7.27 ppm (s, 4H, Ar–H *ortho* to C=O). ^{13}C NMR ($CDC1_3$) δ: 14.15, 14.18, 22.54, 22.64, 28.29, 28.33, 29.10, 30.11, 69.13, 73.61, 108.37, 108.96, 113.13, 120.88, 124.36, 132.43, 142.71, 146.90, 149.50, 153.07, and 164.91 ppm. Anal. Calcd for $C_{56}H_{80}N_2O_{10}$: C, 71.87%; H, 8.73%; N, 2.89%. Found: C, 71.48%; H, 8.45%; N, 2.97%.

2.29. 2,2′-Bis{4-[3,4,5-tri(n-octan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**14b**, *C8BBPA*)

Compound **14b** was synthesized from 2,2′-bis{4-[3,-4,5-tri(*n*-octan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0020 mol) using the same procedure used for compound **14a** with the following modification: the product was recrystallized from ethanol to afford 2.2 g (89%) of yellow crystals: mp 88–89 °C. IR (KBr): 3465 (NH_2), 3372 (NH_2), 2926, 2855, 1726 (C=O), 1626, 1586, 1496, 1430, 1336, 1199, and 1115 cm^{-1} (C–O–Ph). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 18H, CH_3), 1.15–1.35 (m, 60H, $(CH_2)_5$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89–3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar–H *para* to O–C=O), 6.60 (d, 2H, Ar–H *ortho* to O–C=O), 7.08 (d, 2H, Ar–H *meta* to O–C=O), and 7.27 ppm (s, 4H, Ar–H *ortho* to C=O). Anal. Calcd for $C_{74}H_{116}N_2O_{10}$: C, 74.46%; H, 9.79%; N, 2.35%. Found: C, 74.68%; H, 9.80%; N, 2.30%.

2.30. 2,2′-Bis{4-[3,4,5-tri(n-dodecan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**14c**, C12BBPA)

2,2′-Bis{4-[3,4,5-tris(*n*-dodecan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (5.0 g, 0.0031 mol), hexane/ethyl acetate (150/45 mL), and 5% palladium on activated carbon (0.40 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with ethyl acetate and then the filtrate was evaporated to dryness under reduced pressure. The residue was recrystallized from acetone, which was stored in a freezer, to afford 3.50 g (71%) of a white powder: mp −14 and 44 °C (DSC). IR (KBr): 3453 (NH_2), 3366 (NH_2), 2957, 2920, 2854, 1715 (C═O), 1622, 1592, 1496, 1465, 1440, 1375, 1331, 1230, 1114 (C−O−Ph), 825, and 721 cm^{-1}. ^1H NMR ($CDC1_3$) δ: 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 108H, $(CH_2)_9$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). Anal. Calcd for $C_{98}H_{168}N_2O_{10}$: C, 76.91%; H, 10.80%; N, 1.83%. Found: C, 77.32%; H, 10.66%; N, 1.75%.

2.31. 2,2′-Bis{4-[3,4,5-tris(n-tetradecan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**14d**, C14BBPA)

2,2′-Bis{4-[3,4,5-tris(*n*-tetradecan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0014 mol), toluene (150 mL), and 5% palladium on activated carbon (0.40 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with toluene and then the filtrate was evaporated to dryness under reduced pressure. The solid was recrystallized from acetone to give 2.3 g (95%) of a white powder: mp 35 and 55 °C (DSC). IR (KBr): 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336, 1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 132H, $(CH_2)_{11}$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C−O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to C═O). Anal. Calcd for $C_{110}H_{188}N_2O_{10}$: C, 77.78%; H, 11.15%; N, 1.65%. Found: C, 77.76%; H, 11.39%; N, 1.63%.

2.32. 2,2′-Bis{4-[3,4,5-tris(n-hexadecan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**14d**, C16BBPA)

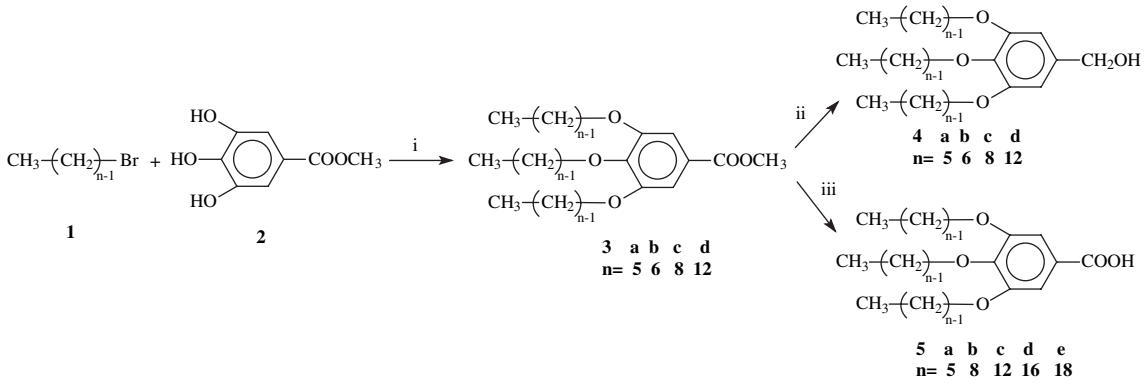
2,2′-Bis{4-[3,4,5-tris(*n*-hexadecan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.5 g, 0.0013 mol), toluene (150 mL), and 5% palladium on activated carbon (0.40 g) were added to a hydrogenation bottle. The bottle was secured on a Parr hydrogenation apparatus, flushed three times with hydrogen, and then pressurized to 16 psi. After the mixture was agitated at room temperature for 12 h under the hydrogen pressure of 16 psi, it was filtered through Celite. The filter cake was washed with toluene and then the filtrate was evaporated to dryness under reduced pressure. The solid was recrystallized from acetone to give 2.3 g (95%) of a white powder: mp 59 °C (DSC). IR (KBr): 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336, 1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 156H, $(CH_2)_{13}$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{122}H_{212}N_2O_{10}$: C, 78.49%; H, 11.44%; N, 1.56%. Found: C, 78.74%; H, 11.16%; N, 1.56%.

2.33. 2,2′-Bis{4-[3,4,5-tris(n-octadecan-1-yloxy)benzoate]}-4,4′-biphenyldiamine (**14e**, C18BBPA)

Compound **14e** was synthesized from 2,2′-bis{4-[3,4,5-tris(*n*-octadecan-1-yloxy)benzoate]}-4,4′-dinitrobiphenyl (2.68 g, 0.00128 mol) using the same procedure used for the compound **14d** to afford 2.46 g (95%) of a white powder: mp 62 °C (DSC). IR (KBr): 3455 (NH_2), 3371 (NH_2), 2923, 2853, 1723 (C═O), 1625, 1586, 1496, 1430, 1336, 1201, and 1117 cm^{-1} (C−O−Ph). ^1H NMR ($CDC1_3$) δ: 0.88 (t, 18H, CH_3), 1.15−1.35 (m, 180H, $(CH_2)_{15}$), 1.72 (m, 12H, CH_2CH_2O), 3.74 (br s, 4H, NH_2), 3.89−3.99 (overlapped t, 12H, CH_2O), 6.56 (dd, 2H, Ar−H *para* to O−C═O), 6.60 (d, 2H, Ar−H *ortho* to O−C═O), 7.08 (d, 2H, Ar−H *meta* to O−C═O), and 7.27 ppm (s, 4H, Ar−H *ortho* to O−C═O). Anal. Calcd for $C_{134}H_{236}N_2O_{10}$: C, 79.08%; H, 11.69%; N, 1.38%. Found: C, 79.12%; H, 11.77%; N, 1.30%.

2.34. General procedure for the preparation of PEIs (**16a–d** and **17a–e**)

The diamine with alkyl side chains (0.001000 mol), the BisADA (0.001000 mol) and 1-chloronaphthalene (20–30 mL) were added to a three-necked resin kettle equipped with a mechanical stirrer, a nitrogen inlet, and a distillation head. Isoquinoline (5 drops) was added to the resin kettle. After the mixture was stirred and heated at 80 °C for 1 h, it was heated to 180–200 °C for 24 h. Water was continuously distilled from the reaction mixture. The solution was poured into methanol (1 L). The polymer that precipitated was collected by filtration and dried under reduced pressure at 200 °C for 6–8 h.



Scheme 1. Synthesis of side chains. (i) DMF, K_2CO_3, N_2, 70 °C; (ii) $LiAlH_4$, ether; (iii) KOH, EtOH.

3. Results and discussion

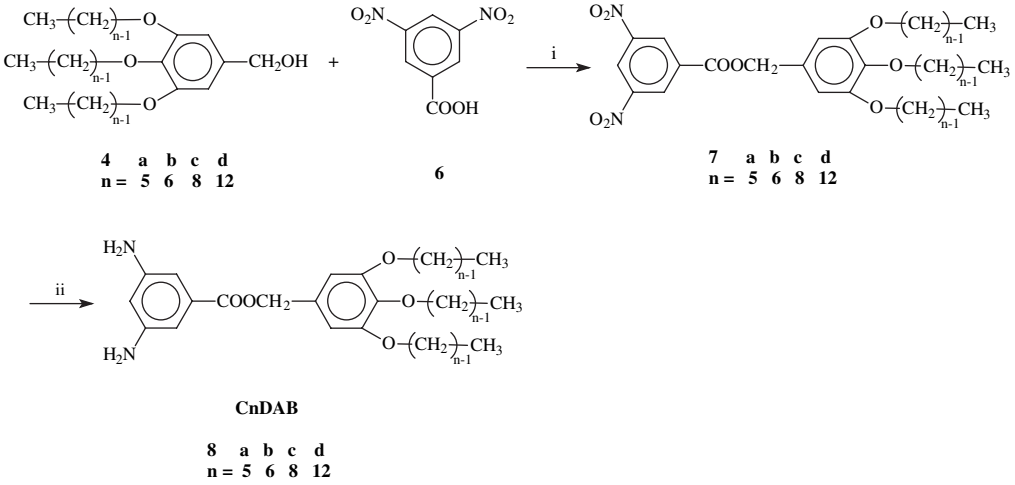
3.1. Monomer synthesis

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 [18,21]. These intermediates were either reduced to 3,4,5-tris(*n*-alkan-1-yloxy)benzyl alcohols (**4a–d**) or hydrolyzed to 3,4,5-tris(*n*-alkan-1-yloxy)benzoic acids (**5a–e**) as shown in Scheme 1. 3,5-Dinitrobenzoic acid (**6**) was esterified with 3,4,5-tris(*n*-alkan-1-yloxy)benzyl alcohols (**4a–d**) to afford a series of alkyl-substituted dinitro compounds **7a–d** using DCC as the dehydration agent and DMAP as a catalyst. The next step in the reaction sequence required the selection of a suitable method to reduce the nitro groups to amino groups. The use of acids as hydrogen sources was not feasible in the reduction of **7** because of the possibility of hydrolysis of the ester groups. $LiAlH_4$ could not be used because it could also reduce the ester groups to benzyl alcohol groups. The use of hydrazine monohydrate resulted in the cleavage of the ester groups. Catalytic hydrogenation affords clean products in high yields when carried out in non-polar solvents. The use of the polar solvents, such as ethyl acetate, resulted in the cleavage of the ester groups. Thus, the dinitro compounds **7** were hydrogenated to the alkyl-substituted diamines (**8a–d**, CnDAB) containing side chain lengths of 5 to 12 carbon atoms in hexane (Scheme 2).

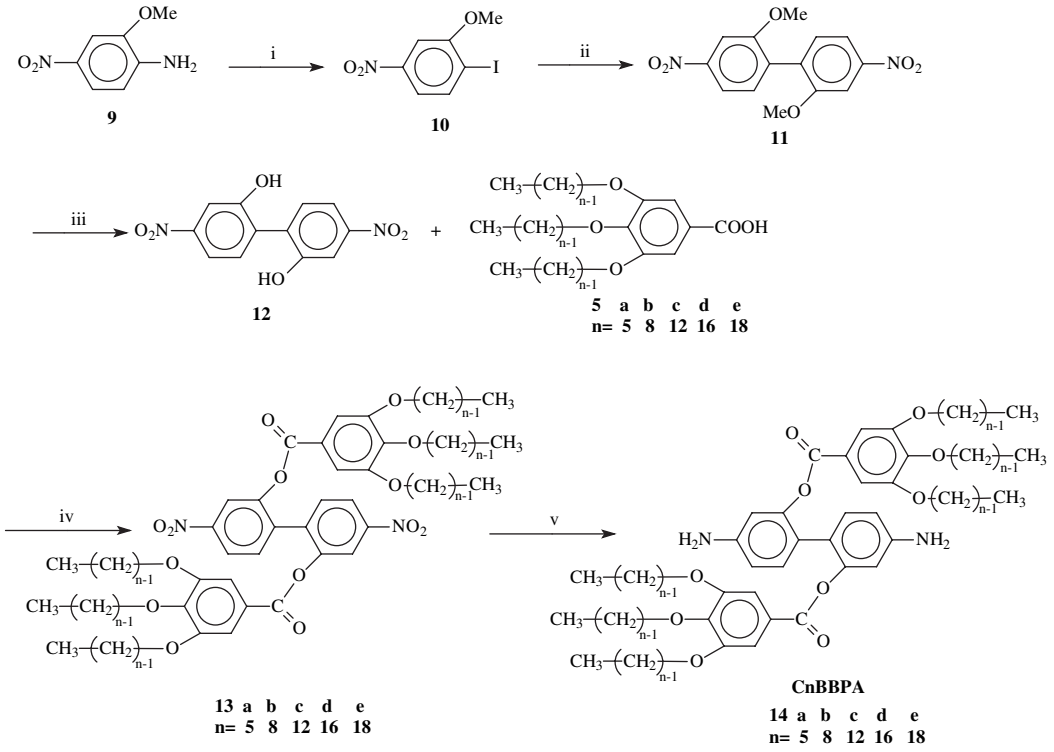
In Scheme 3, 2-methoxy-4-nitroaniline (**9**) was converted to 4-iodo-3-methoxynitrobenzene (**10**) using a Sandmeyer reaction. Ullmann conditions were then used to dimerize compound **10** to give 2,2′-dimethoxy-4,4′-dinitrobiphenyl (**11**). Demethylation of compound **11** in pyridine hydrochloride at 200 °C gave 4,4′-dinitro-2,2′-biphenyldiol (**12**). Compound **12** was esterified with 3,4,5-tris(*n*-alkan-1-yloxy)benzoic acids (**5a–e**) to afford the alkyl-substituted dinitro compounds **13a–g** using dicyclohexylcarbodiimide (DCC) as the dehydration agent. Then the alkyl-substituted dinitro compounds **13** were successfully reduced to the alkyl-substituted diamines (**14a–e**) using palladium on activated carbon in hexane or toluene.

3.2. Syntheses of polyetherimides

The preparation of the PEIs was carried out in 1-chlorophthalene by the same procedure used for the polyimides [18]. As shown in Scheme 4, 2,2′-bis[4-(3,4-dicarboxyphenoxy)-phenyl]propane dianhydride (BisADA, **15**) was polymerized



Scheme 2. Synthesis of diamines containing multiple alkyl side chains CnDAB. (i) DCC, DMAP, CH_2Cl_2; (ii) H_2, Pd/C, hexane.

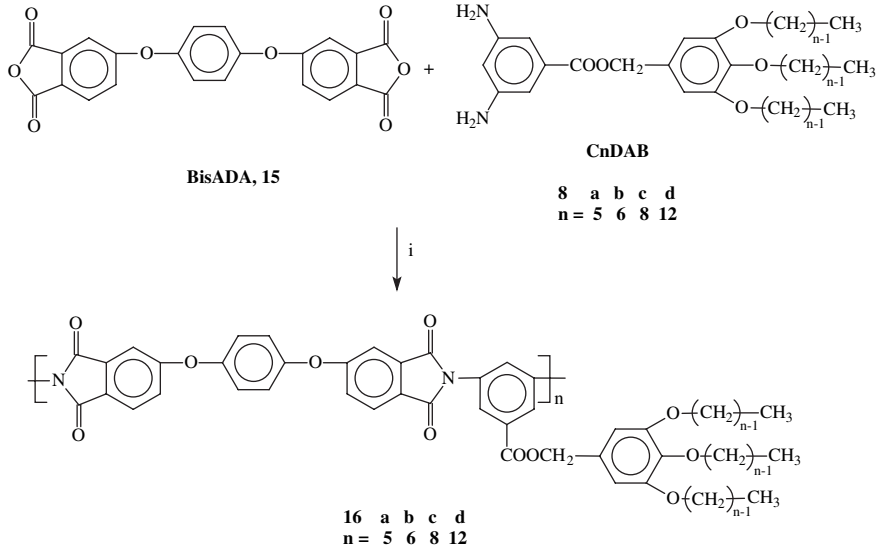


Scheme 3. Synthesis of diamines containing multiple alkyl side chains CnBBPA. (i) H_2SO_4, $NaNO_2$; KI; (ii) Cu, DMF; (iii) pyridine hydrochloride; (iv) DCC, DMAP, CH_2Cl_2; (v) H_2, Pd/C, hexane/toluene.

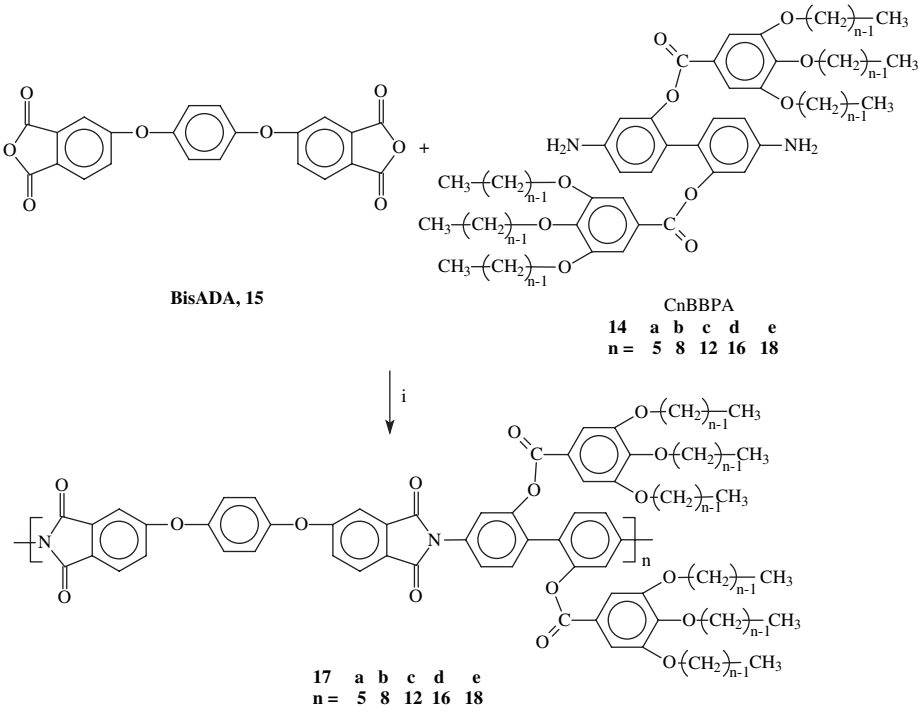
with diamines **8a–d** to afford a series of polyetherimides (**16a–d**), which have a backbone of Ultem® 1000. Another series of diamines (**14a–e**), i.e., 2,2′-bis{4-[3,4,5-tris(*n*-alkan-1-yloxy)benzoate]}-4,4′-biphenyldiamines (CnBBPA), were also polymerized with BisADA to afford another series of PEIs (**17a–e**) containing side chain lengths of 5 to 18 carbon atoms (Scheme 5). In both cases 1-chloronaphthalene was used as the polymerization solvent. Similar to the preparation of polyimides [18] the ester linkages of PEIs were cleaved when *m*-cresol was used as a polymerization solvent due to its acidic nature at high temperature. The two series of PEIs **16** and **17** were obtained in nearly quantitative yields.

3.3. Solution and thermal properties

The intrinsic viscosities and thermal properties of the PEIs **16** and **17** are shown in Table 1. The polymers **16** belong to the



Scheme 4. Synthesis of polyetherimides **16a–d** containing multiple alkyl side chains. (i) Chloronaphthalene, isoquinoline, 180–200 °C.



Scheme 5. Synthesis of polyetherimides **17a–e** containing multiple alkyl side chains. (i) Chloronaphthalene, isoquinoline, 180–200 °C.

same family of PEIs as Ultem® 1000. The intrinsic viscosity and thermal properties of Ultem® 1000 are also shown in Table 1 [1]. The intrinsic viscosity of Ultem® 1000 is 0.50 dL/g. The intrinsic viscosities of **16** and **17**, which were measured in chloroform at 30 °C, range from 0.34 to 0.93 dL/g. The thermal stability of **16** and **17** is less than that of Ultem® 1000 due to the presence of the alkyl side chains. Ultem® 1000 shows only 1% weight loss at 480 °C while the 5% weight loss temperatures of **16** and **17** decrease to 335–368 °C. The T_g of Ultem® is 217 °C. Because of the plasticizing effect of the alkyl side chains, the T_gs of **16** and **17** are also much lower than that of Ultem®. As the length of side chains increases, the T_gs decrease gradually from 106 °C for **16a** to 61 °C for **17d**. The number of side chains per repeat unit also has an effect on the T_gs. PEIs **16** only contain three alkyl side chains per repeat unit while PEIs **17** contain six alkyl side chains per repeat unit. The T_gs of PEIs **17** are lower than PEIs **16** with the same lengths of side chains. For example the side chains of **16a** and **17a** both contain five carbon atoms. The T_g of **17a** is 96 °C, 10 °C lower than **16a**. However, the T_g of PEI **17e** is 5 °C higher than **17d** although the length of **17e** is two carbon atoms longer than **17d**. Since **17d** and **e** have similar viscosity, the higher T_g of **17e** can be attributed to its side chain melting point and crystallinity. In fact, both **17d** and **e** display side chain melting temperatures. This temperature increases as the length of the side chains increases.

Table 1
Intrinsic viscosities and thermal properties of polyetherimides **16**, **17** and Ultem®

PEI	$[\eta]$[a] (dL/g)	T_d[b] (°C) in N_2	T_g[c] (°C)	T_m[d] (°C)
16a	0.61	363	106	ND[e]
16b	0.47	354	102	ND
16c	0.51	335	94	ND
16d	0.34	367	87	ND
17a	0.40	364	96	ND
17b	0.59	363	74	ND
17c	0.41	366	65	ND
17d	0.93	368	61	−1
17e	0.80	357	66	18
Ultem®	0.50	480[f]	217	ND

[a] Intrinsic viscosity determined in chloroform at 30.0 ± 0.1 °C.
[b] Temperature at which a 5% weight loss occurred when subjected to TGA with a heating rate of 10 °C/min.
[c] Mid-point of change in slope on DSC thermogram obtained with a heating rate of 10 °C/min.
[d] Minimum of melting point endotherm on DSC thermogram obtained with a heating rate of 10 °C/min.
[e] ND: not detected.
[f] Temperature at which a 1% weight loss occurred when subjected to TGA with a heating rate of 10 °C/min.

Six solvents, i.e., CH_2Cl_2, $CHCl_3$, tetrachloroethane (TCE), *o*-dichlorobenzene (DCB), 1-chloronaphthalene (CN), and toluene, were used to test the solubilities of PEIs **16** and **17**. The polymers were considered soluble if a solution containing 1 g/dL could be prepared. The results are shown in Table 2. The PEIs are soluble in the chlorinated solvents. PEIs **17d** and **e**, which were prepared from the C16 and C18 diamines, are soluble in the non-polar solvent toluene. Both PEIs become insoluble in polar solvents such as methylene chloride. These observations can be attributed to the high aliphatic content of the polymers. These facts also lead to speculation that these polyetherimides may associate in polar solvents. This would also explain the gels that formed in these solvents at high concentrations and at room temperature.

Table 2
Solubility of polyetherimides **16a–d** and **17a–e**

PEI	CH_2Cl_2	$CHCl_3$	TCE	DCB	CN	Toluene
16a	+	+	+	+	+	−
16b	+	+	+	+	+	−
16c	+	+	+	+	+	−
16d	+	+	+	+	−	−
17a	+	+	+	+	+	−
17b	+	+	+	+	+	−
17c	+	+	+	+	+	−
17d	−	+	+	+	+	+
17e	−	+	+	+	+	+

+: Minimum solubility of 1 g/dL at room temperature; −: solubility less than 1 g/dL at room temperature; TCE: tetrachloroethane; DCB: *o*-dichlorobenzene; CN: 1-chloronaphthalene.

Table 3
Mechanical properties of thin films of polyetherimides **16**, **17** and Ultem®

PEI	Dianhydride/diamine	σ[a] (MPa)	E[a] (MPa)	ε[a] (%)
16a	BisADA/C5DAB	42.0 ± 2.0	704 ± 21	80.8 ± 4.3
16b	BisADA/C6DAB	38.2 ± 2.5	641 ± 14	96.8 ± 13
16c	BisADA/C8DAB	30.3 ± 1.5	519 ± 10	125 ± 2.0
16d	BisADA/C12DAB	23.6 ± 1.3	248 ± 21	236 ± 22
17a	BisADA/C5BBPA	57.8 ± 3.7	550 ± 23	134 ± 7.0
17b	BisADA/C8BBPA	38.0 ± 7.1	394 ± 69	258 ± 21
17c	BisADA/C12BBPA	27.2 ± 1.5	176 ± 10	366 ± 20
17d	BisADA/C16BBPA	19.2 ± 0.5	92.7 ± 6.8	478 ± 7.0
Ultem®	BisADA/MPD[c] [1]	105[b]	3000	60

[a] Determined according to ASTM Test D638 on a Model 5567 Instron with a crosshead separation speed of 1 mm/min.
[b] Tensile strength at yield.
[c] MPD: *m*-phenylene diamine.

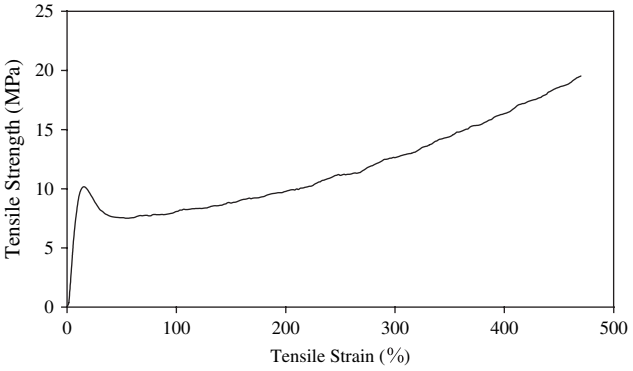


Fig. 1. Tensile strength vs. tensile strain plot for a thin film of polyetherimide **17d**.

3.4. Mechanical properties

Polymer thin films were cut into dog bone specimens (38 mm × 15 mm overall in size, 5 mm × 22 mm in the gauge area). Thin film tensile properties were determined on a Model 5567 Instron with a crosshead separation speed of 1 mm/min at room temperature. Specimens were placed in the grips of the Instron at a specified grip separation and pulled until failure. Tensile strengths at break (σ), tensile moduli (E) and percent elongations at break (ε) were measured (Table 3). The mechanical properties of Ultem® are also shown in the table [1]. Compared with Ultem® 1000, polymers **16** and **17** have lower tensile strengths (σ) and tensile moduli (E), but much higher elongations. A tensile strength vs. strain plot for a thin film of the PEI **17d** is shown in Fig. 1. The film displays

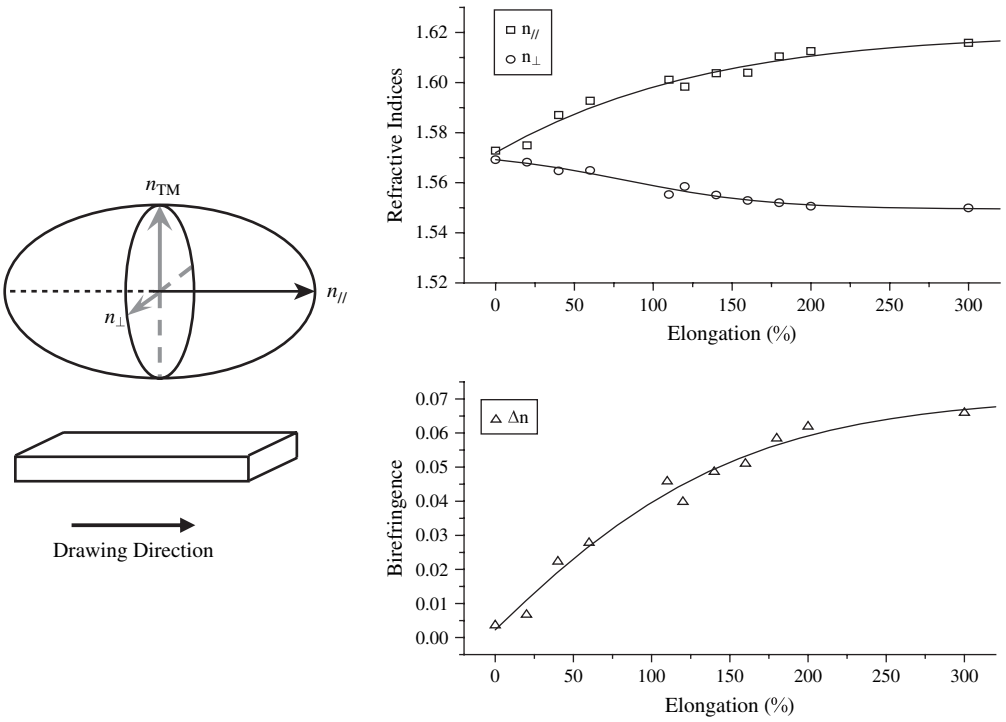


Fig. 2. Optical properties of **17b** (BisADA/C8BBPA). (a) Refractive index vs. drawing ratio and (b) birefringence vs. drawing ratio.

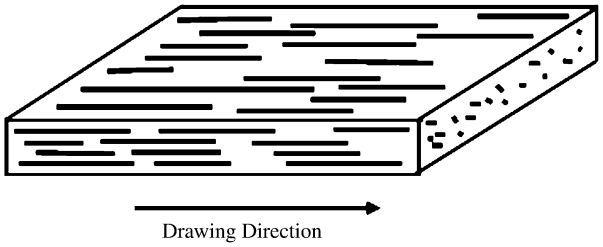


Fig. 3. PEI backbone alignment along drawing direction.

a yield strength of 10 MPa. The ultimate strength is 19.2 MPa. The elongation at break is as high as 470%, almost eight times higher than Ultem® 1000. This is attributed to the alkyl side chains acting as internal plasticizers. In both series, as the length of the side chains increases, the tensile strengths and tensile moduli decrease, but the elongations increase.

3.5. Optical properties

All the PEIs can be solution cast into transparent, tough films. In order to investigate the optical properties of PEIs under a stress we stretched PEI **17b** (BisADA/C8BBPA) under force above its T_g at 85 °C. Then its in-plane indices parallel to the drawing direction ($n_{//}$) and in-plane refractive indices perpendicular to the drawing direction ($n_{\perp}$) were measured at different drawing ratios as shown in Fig. 2(a). The wavelength of the laser beam for the measurements is 633 nm. The birefringence was calculated based on the difference between $n_{//}$ and $n_{\perp}$ as shown in Fig. 2(b). The birefringence of **17b** is negligible (<0.01) due to large amount of amorphous alkyl chains as the dominant component. As elongations increase its $n_{//}$ increases while its $n_{\perp}$ decreases. After the film was stretched to 300% at elevated temperature its $n_{//}$ increases from 1.57 to 1.61 and its $n_{\perp}$ decreases from 1.57 to 1.55, which result in a birefringence of 0.06. The film's birefringence results from the alignment of PEI's rigid backbones as shown in Fig. 3.

4. Conclusions

In summary, two series of PEIs were prepared from the diamines containing multiple alkyl side chains and bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydrides (BisADA) using a one-step method in 1-chloronaphthalene. All the polymers have good solubility in chlorinated solvents. The high-molecular weight PEIs could be solution cast into transparent, tough film. The side chains that contain at least 16 carbon atoms crystallize. The melting points of the crystalline regions increase as the length of the side chains increases. The T_gs of the PEIs decrease as the length of the side chains increases due to the internal plasticizing effect of alkyl side chains. The PEIs containing multiple alkyl side chains show much higher elongations but lower tensile strengths and moduli than the commercial Ultem® 1000. The film's in-plane index parallel to the drawing direction increases and in-plane refractive index perpendicular to the drawing direction decreases during drawing due to the orientation of the main chains in the drawing direction. The film's in-plane birefringence increases with the drawing ratios. The potential applications include stretchable, birefringence optical films.

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