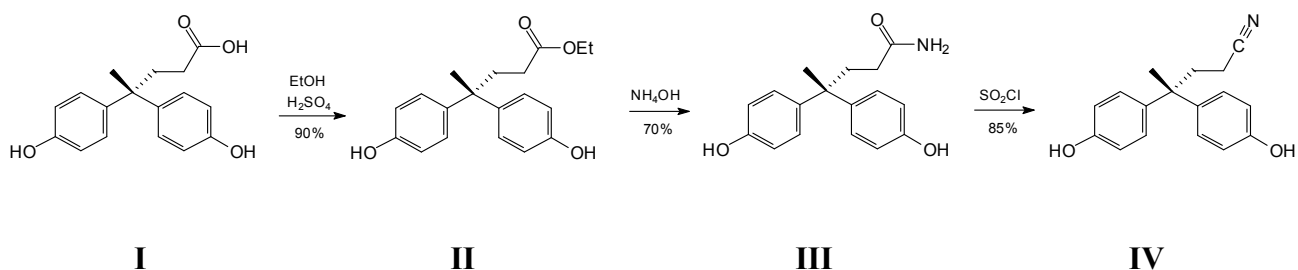


## Supporting Information: Synthesis of CN-PC

The CN-PC was synthesized as follows. The three-step synthetic strategy for the nitrile BPA monomer from commercially available 4,4-bis(4-hydroxyphenyl)pentanoic acid (diphenolic acid) **I**, is illustrated in **Scheme 1**. Synthesis of 4,4-bis(4-hydroxyphenyl)pentanenitrile, **IV**, was previously reported in 1990 by Schmidhauser<sup>7</sup> who converted the corresponding diphenolic ester **II** to the amide **III** with subsequent dehydration using acetic anhydride and 10% HCl to afford the corresponding nitrile **IV**. A modified procedure for synthesis of **IV** from **III** was employed.

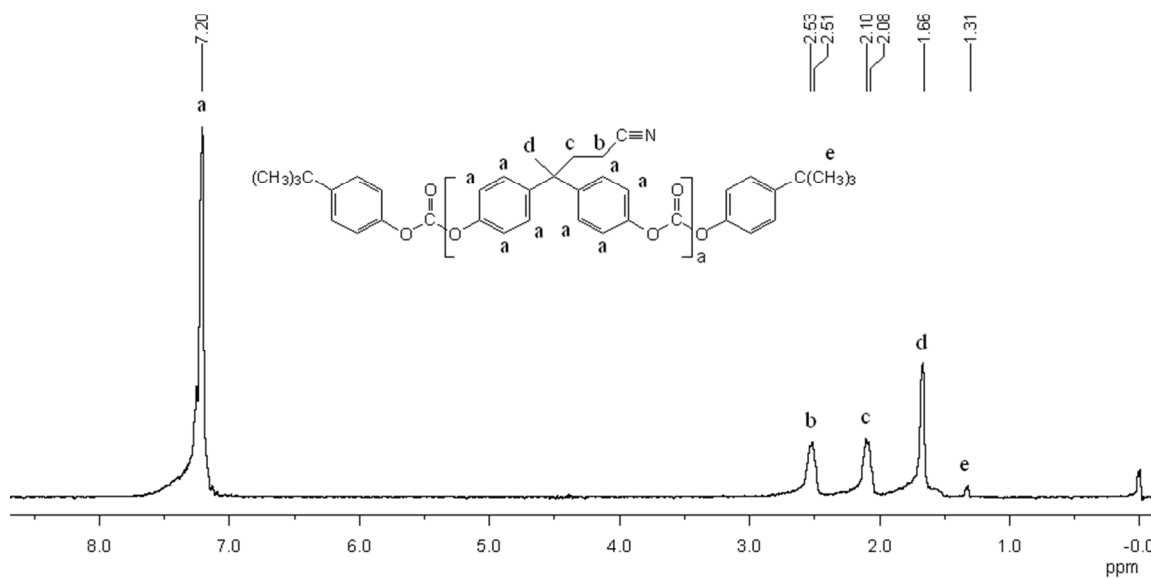
Esterification of **I** successfully produced a high yield of ethyl 4,4-bis(4-hydroxyphenyl)pentanoate **II** which was subsequently converted to the corresponding amide using the Schmidhauser procedure.<sup>7</sup> Rather than acetic anhydride and 10% HCl, excess thionyl chloride (SOCl<sub>2</sub>) was employed as dehydrating agent to afford the crude nitrile, **IV**. This compound was purified using flash chromatography to afford white crystals in an overall yield of 54%.



**Scheme 1.** Synthesis of 4,4-bis(4-hydroxyphenyl)pentanenitrile, **IV**

The nitrile bisphenol **IV** was reacted under conditions of interfacial polymerization using phosgene gas in a biphasic aqueous NaOH-CH<sub>2</sub>Cl<sub>2</sub> system with a phase transfer agent. *Para-t*-butylphenol was used as a chain-terminator.<sup>14</sup> The nascent homopolycarbonate CN-PC, **V**, was

washed with dilute HCl to protonate phenolate end groups with subsequent, successive washings of deionized water. The final water wash was analyzed by atomic absorption spectrometry (AAS). The concentration of sodium ions was below the limits of detection ( $< 1.0 \times 10^{-6}$  mg/mL). The isolated polymer product was characterized by  $^1\text{H}$  NMR spectroscopy. The results with peak assignments are shown in Figure 1.



**Figure 1.**  $^1\text{H}$  NMR spectrum of CN-PC homopolycarbonate (CN-PC, V)

Polycarbonate **V** was characterized for absolute molecular weight (MW) and polydispersity (PDI) after first manual injections of the homopolymer in THF at multiple concentrations using the software described in the Instrumentation section of this Supporting Information. These data are reported in **Table 1** with the glass transition temperature obtained from differential scanning calorimetry (DSC). Data for commercial purified BPA-PC (Lexan® 101 pellets) is included for comparison.

**Table 1.** Physical and Thermal Characteristics of Homopolymer CN-PC and BPA-PC.

PC	$dn/dc$ mL.g <sup>-1</sup>	$M_w$ g.mol <sup>-1</sup>	$M_n$ g.mol <sup>-1</sup>	PDI	$T_g$ °C
BPA-PC	0.184	26,410	17,310	1.53	148
CN-PC	0.186	24,630	13,400	1.84	167

### Instrumentation

The NMR spectrum was recorded with a GE-QE300 operating at 300 MHz. <sup>1</sup>H chemical shifts were reported as  $\delta$  values (ppm) relative to CDCl<sub>3</sub> (7.24). A Waters Atomic Absorption Spectrometer (AAS) Analyst 100 was used for detection of sodium ions. The values of refractive index increment ( $dn/dc$ ) in THF at 25°C were determined using a Wyatt Optilab DSP differential refractive index detector at 690 nm. Wyatt Technology's Windows®-based DNDC™ software was used to measure the  $dn/dc$ . Molecular weights were measured using a Shimadzu HPLC-GPC system. Differential Scanning Calorimetry (DSC) was performed with a DSC Q100 in aluminum pans at heating and cooling rates of 10 °C/min.  $T_g$ s are given by the midpoint of the heat capacity jump of the third heating scan.

**Synthesis of ethyl 4,4-bis(4-hydroxyphenyl)pentanoate, II.** Diphenolic acid, I, (20.00 g, 69.85 mmol) and ethanol (250 mL, 4.281 mol) were added to a 500 mL round bottom flask with a stir bar and a reflux condenser. Sulfuric acid (10 drops) was added to the reaction mixture and the reaction mixture was refluxed for 72 hours. Reaction completion was confirmed by thin layer chromatography (TLC). The reaction mixture was cooled to room temperature, neutralized using a dilute solution of NaHCO<sub>3</sub> and subsequently extracted with ethyl acetate (3x60 mL). The

combined organic layers were dried over sodium sulfate and concentrated under reduced pressure to afford the crude target compound (19.65 g, 90.0%) as light yellow crystals.

**Synthesis of 4,4-bis(4-hydroxyphenyl)pentanamide, III.** Amide **III** was prepared as previously reported in the literature.<sup>6</sup> Intermediate **II**, (19.45 g, 62.16 mmol) was stirred with aqueous ammonium hydroxide (141.9 g, 4.031 mol) at room temperature for 96 h. The resulting brown solution was diluted with water and extracted with ethyl acetate (3x50 mL), washed with water (100 mL), dried over sodium sulfate, and concentrated under reduced pressure to afford the crude compound **III** (12.40 g, 70.0%) as a tan powder.

**Synthesis of 4,4-bis(4-hydroxyphenyl)pentanenitrile, IV.** Amide, **III**, (5.00 g, 17.3 mmol) and thionyl chloride (24.5 g, 0.206 mol) were added to a 50 mL round bottom flask with a stir bar, a reflux condenser, and a calcium chloride tube. The reaction was refluxed for 1 h. After cooling to room temperature, the reaction mixture was poured slowly over ice with continuous stirring during which time a pale, yellow-orange gum separated. After the ice melted the mixture was neutralized with dilute sodium bicarbonate, extracted with ethyl acetate (3x30 mL), washed with water (2x30 mL), and dried over sodium sulfate. The organic solution was concentrated under reduced pressure during which precipitation occurred, affording 3.98 g (85.0%) of light yellow powder. Additional purification by flash chromatography (methylene chloride/acetone) on silica gel afforded pure monomer, **IV**, as white crystals.

**Homopolymer of 4,4-bis(4-hydroxyphenyl)pentanenitrile, CN-PC.** A mixture of 4,4-bis(4-hydroxyphenyl)pentanenitrile monomer (5.20 mmol), water (80 mL), methylene chloride (100

mL), 1.2 mL of 5% w/v triethylamine solution in methylene chloride and 0.3 mL of a 10% w/v solution of *p-t*-butylphenol in methylene chloride was prepared. The pH was adjusted to 12 by addition of 10% aqueous sodium hydroxide solution, stirred 5 minutes, then cooled to 0-5 °C. Phosgene was bubbled in during 5 minutes keeping the pH between 8 and 9 by dropwise addition of sodium hydroxide solution. The methylene chloride layer was washed with 5% aq. HCl solution (2x200 mL), deionized water (6x400 mL), then concentrated and precipitated by pouring into methanol. The resulting polymer was dried *in vacuo* to afford powdery material. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.18-7.28 (m, 8H, ArH), 2.51-2.53 (m, 2H, CH<sub>2</sub>), 2.08-2.10 (m, 2H, CH<sub>2</sub>), 1.66 (s, 3H, CH<sub>3</sub>).