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Polyketone Synthesis Involving Nucleophilic Substitution via Carbanions Derived from Bis(α-amino nitrile)s. 2.[1] Wholly Aromatic Polyketones without Ether Linkages

Jinlian Yang and Harry W. Gibson*

Chemistry Department and NSF Science and Technology Center for High Performance Polymeric Adhesive and Composites, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

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ABSTRACT: To address the insolubility problem of polyketones, we used a new approach to high molecular weight wholly aromatic polyketones without ether linkages via soluble precursors derived from isophthaldehyde-based amino nitriles.[1] High molecular weight, soluble poly(amino nitrile)s **2** were synthesized from the anions of these bis(amino nitrile)s **1** and 4,4′-difluorobenzophenone using sodium hydride as base under mild reaction conditions. Hydrolysis of the poly(amino nitrile)s under acidic conditions yielded the corresponding polyketone, poly(*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl) (**3**). This all aromatic polyketone, with an absence of ether linkages in the polymer backbone, displays excellent thermal properties and solvent resistivity. It is infusible and insoluble in most common organic solvents.

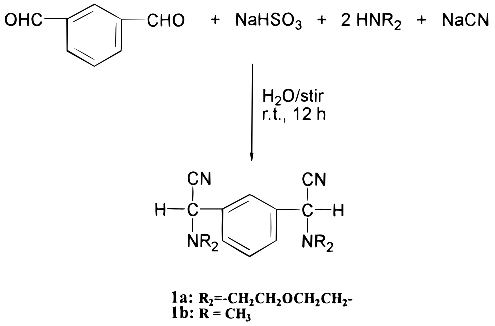
Introduction

Aromatic poly(ether ketone)s are an important class of thermoplastic polymers because of their unique properties such as thermal stability, toughness, and chemical and solvent resistance.[2−4] One of the important properties of aromatic poly(ether ketone)s such as poly(ether ether ketone) (PEEK) and poly(ether ketone) (PEK) is the crystallinity contributed, at least in part, by the keto functionality in the polymer backbone. In contrast to amorphous engineering plastics such as poly(ether sulfone)s, poly(ether ketone)s are usually crystalline and resistant to chemical solvents. However, it is the crystallinity and the resulting insolubility combined with high melting points that lead to synthetic and processing difficulties.

Poly(ether ketone)s are usually synthesized by the nucleophilic aromatic substitution of activated dihalides and bisphenolates, or by the electrophilic aromatic substitution (Friedel−Crafts acylation) of arylene ethers. The major problem with these two synthetic routes is the insolubility of the polymeric product, which requires the use of harsh reaction conditions in order to obtain a high molecular weight. To address the solubility problem, several approaches by soluble precoursor polymers have been reported.[5−8] Nucleophilic ring-opening polymerization of macrocyclic oligomers and nickel-catalyzed coupling of the aromatic diketo ether dichlorides were also reported to produce poly(ether ketone)s.[9−13] A new polymerization reaction based on the cross coupling of bis(stannane)s and diacid chlorides was reported to produce high molecular weight aromatic polyketones without ether linkages; however, alkyl substituents in the aromatic rings had to be used to address the solubility problem and to obtain high molecular weight polymers.[14]

In the previous paper,[1] we reported a new approach to synthesize high molecular weight poly(ketone sulfone)s via soluble precursors derived from bis(α-amino nitrile)s under mild reaction conditions. In this paper we will discuss the first synthesis of a high molecular weight wholly aromatic polyketone without ether linkages or alkyl substituents in the aromatic rings.

Scheme 1



Results and Discussion

A. Bis(α-amino nitrile)s from Dialdehydes. α-Amino nitriles can be easily synthesized from aldehydes and secondary amines in high yields by the Strecker reaction.[15] The cabanions of α-amino nitriles are selective and powerful nucleophiles that can displace activated halides to form carbon−carbon bonds.[15] Hydrolysis of amino nitriles under acidic conditions reforms the carbonyl group. Isophthalamino nitriles **1a** and **1b** were synthesized by the aqueous one-pot method of the Strecker synthesis in high yields (Scheme 1). The proton NMR spectrum of compound **1b** showed a methyl singlet at 2.35 ppm, the methine proton signal at 4.83 ppm in the aliphatic region, and three signals in the aromatic region (Figure 1). The IR spectrum and elemental analysis were consistent with the structure. The ^{13}C NMR spectrum of compound **1a** showed two signals for every carbon due to its diastereomeric nature.[1] However, the ^{13}C NMR spectrum of purified compound **1b** showed only one signal for each carbon, probably as a result of fractionation during purification by recrystallization. Each carbon was assigned according to the APT (*A*ttached *P*roton *T*est) and ^{1}H−^{13}C HETCOR (*HET*eronuclear *COR*relation) spectra.

B. Poly(amino nitrile) Synthesis. Bis(amino nitrile) **1a** was polymerized via its dianion with 4,4′-difluorobenzophenone in dimethylformamide (DMF)

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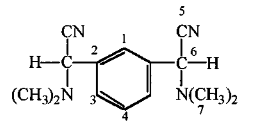


1b

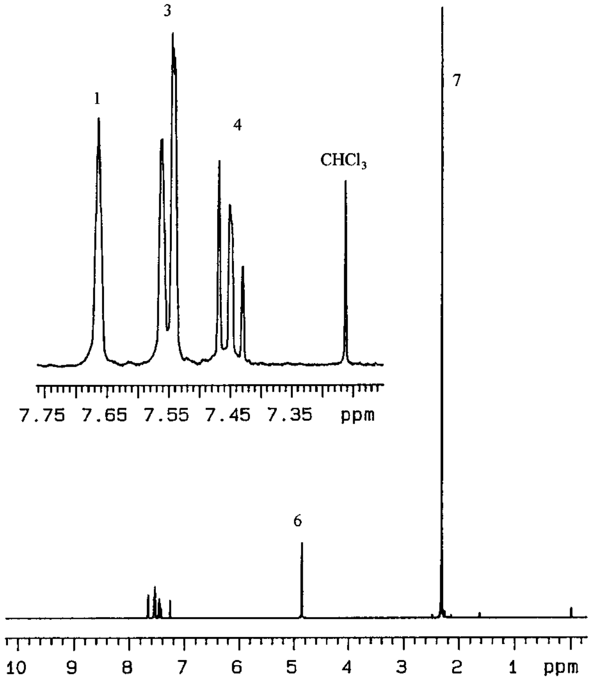
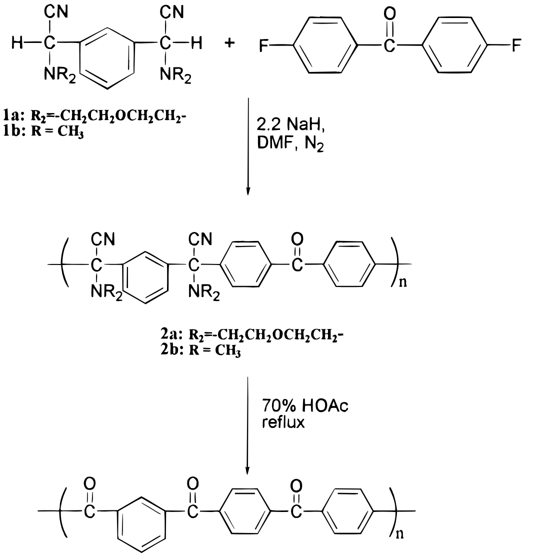


Figure 1. 400 MHz ^{1}H NMR spectrum of compound **1b** in CDCl$_3$.

Scheme 2



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using sodium hydride as base at room temperature (Scheme 2). The resultant polymer **2a** was soluble in common organic solvents such as THF, chloroform, acetone, etc. GPC analysis indicated a bimodal distribution (absolute GPC, NMP, 60 °C, Figure 2). The low molecular weight fraction is possibly due to cyclic species favored by the meta linkage of the isophthalamino nitrile. The number average molecular weight, M_n, and the weight average molecular weight, M_w, estimated for the polymer not including the low molecular fraction were 43.2k and 89.8k, respectively. The calculations including the low molecular fraction indicated an M_n of 16.7k and an M_w of 59.1k, with a polydispersity of 3.54. Most of the low molecular weight fraction was removed by Soxhlet extraction with ethanol. GPC analysis of this polymer after extraction indicated an M_n of 27.0k and an M_w of 63.1k, with a polydispersity of 2.34 (Figure 2). According to the elemental analysis results of this polymer, the average number of repeat units (Scheme 2) is approximately 50, which corresponds to a number average molecular weight of 25.2 k, in good agreement with the GPC result.

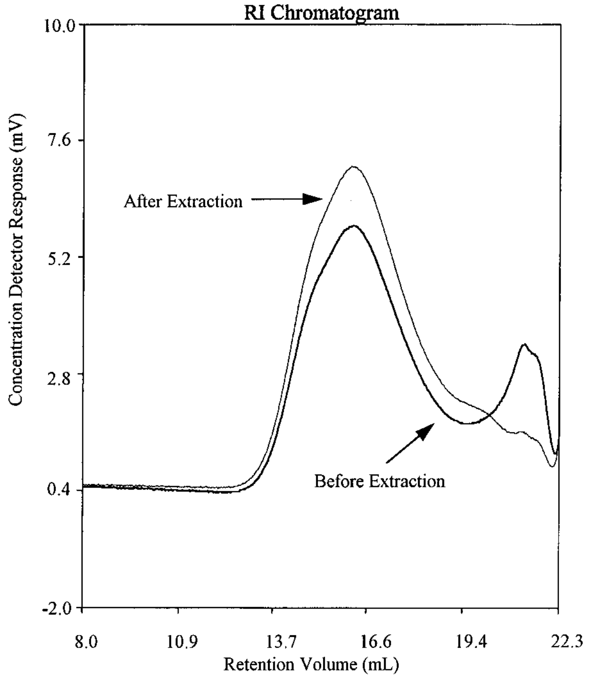

Figure 2. GPC traces of polymer **2a** (NMP, 60 °C).

The IR spectrum of poly(amino nitrile) **2a** showed aliphatic C−H stretches at 2963 and 2851 cm^{-1}, a strong carbonyl absorbance at 1668 cm^{-1}, and the C−O−C stretches of the morpholino groups at 1118 cm^{-1} (Figure 3). The proton NMR spectrum of **2a** showed only two broad signals in the aliphatic region at about 2.5 and 3.8 ppm corresponding to the methylene protons of the morpholino units. No methine proton signal (4.8 ppm) was detected (Figure 4). The protons in the aromatic region were assigned by the 2D-COSY spectrum. The ^{13}C NMR (APT) spectrum showed a carbonyl signal at 194.32 ppm, nitrile carbon signal at 115.84 ppm, and three signals in the aliphatic region corresponding to the morpholino and quaternary carbons. The rest of the carbon atoms in the aromatic region were assigned according to the ^{1}H−^{13}C HETCOR spectrum (Figure 5). The doubling of C-1 is consistent with the presence of both *meso* and *racemic* structures.

Bis(amino nitrile) **1b** was polymerized with 4,4′-difluorobenzophenone at lower temperatures (0−10 °C) and higher concentrations (Scheme 2). Compared with polymer **2a**, polymer **2b** had a smaller low molecular weight fraction and the low molecular weight fraction was easier to remove by Soxhlet extraction using ethanol as solvent. According to GPC (absolute, NMP, 60 °C), an M_n of 16.1k and an M_w of 32.9k were obtained after extraction. The elemental analysis results of this polymer agree well with the structure and the molecular weight data. Polymerization of **1b** with 4,4′-difluorobenzophenone using a 1:0.995 mole ratio, respectively, under the same conditions gave similar results; GPC

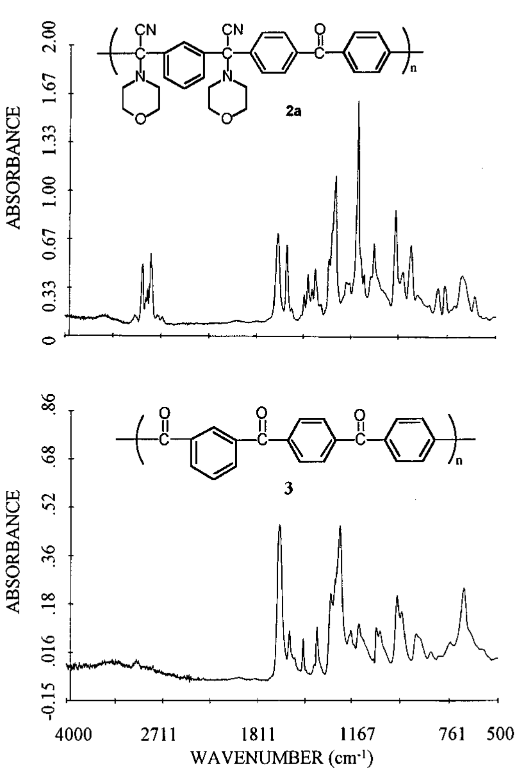

Figure 3. FTIR spectra of polymers **2a** and **3** (KBr).

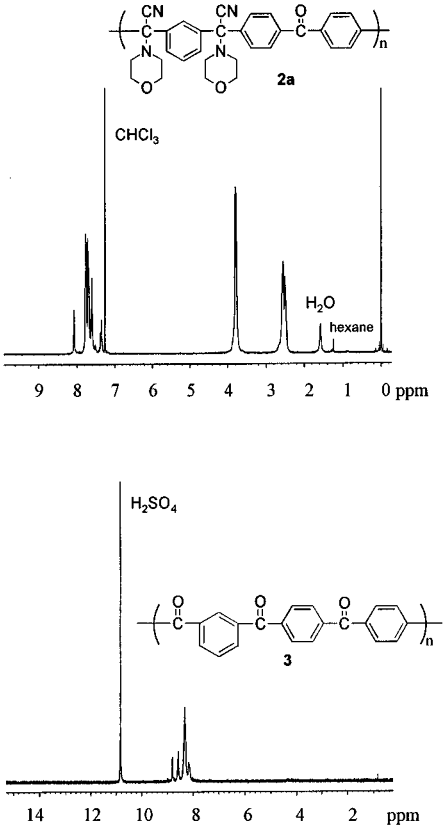

Figure 4. 400 MHz ^{1}H NMR spectra of polymer **2a** in $CDCl_3$ and polymer **3** in D_2SO_4.

analysis gave an M_n of 15.8k and an M_w of 28.0k after extraction.

C. Hydrolysis: A Wholly Aromatic Polyketone without Ether Linkages. Hydrolysis of polymer **2a** with 70% aqueous acetic acid and HCl afforded wholly aromatic polyketone **3** (Scheme 2). In contrast to precursor polymer **2a**, this polyketone was not soluble in common organic solvents such as THF, chloroform, DMSO, DMAc, NMP, etc. It was only soluble in very strong acids, such as concentrated sulfuric acid. The main reason for the dramatic difference in solubility between polymers **2** and **3** is due to the amorphous nature of **2** caused in part by the atacticity arising from the chiral centers at the carbon atoms of the amino nitrile units and the disorder of **2** versus the more rigid, polar, planar carbonyl moieties in **3**, which promote crystallinity.

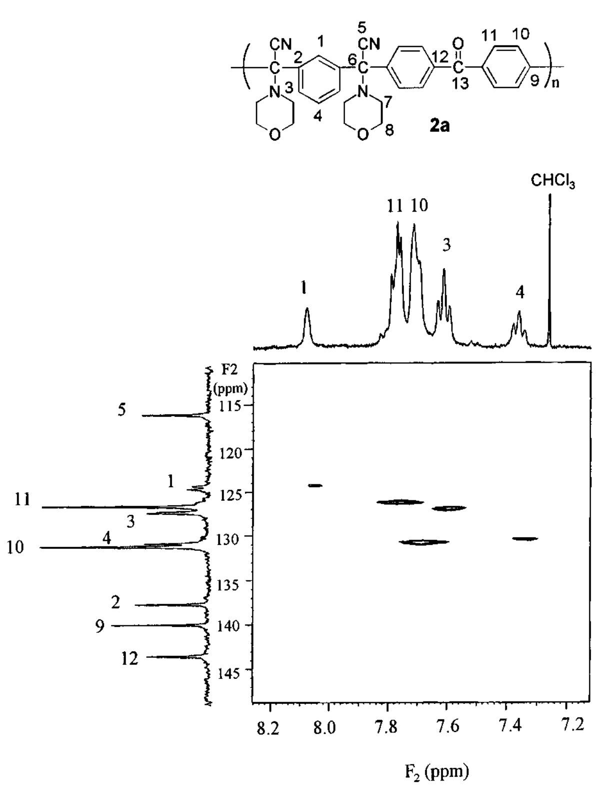

Figure 5. 400 MHz ^{1}H–^{13}C HETCOR spectrum of polymer **2a** in $CDCl_3$.

The hydrolysis of amino nitrile units to carbonyl units was complete, as shown by the proton NMR and IR spectra. The IR spectrum of polymer **3** showed very strong carbonyl absorbance at 1662 cm^{-1} and the absence of aliphatic C–H stretches and C–O–C modes due to the removal of morpholino groups (Figure 3). The proton NMR spectrum of polymer **3** in concentrated D_2SO_4 showed no signals in the aliphatic region, which also indicated the removal of the morpholino groups (Figure 4). All the proton signals were shifted downfield due to the protonation of the carbonyl groups under the strongly acidic conditions. The COSY spectrum is consistent with the structure of polymer **3**. Hydrolysis of polymer **2b** also gave polyketone **3**. The ^{1}H NMR spectrum of the product was the same as that from polymer **2a**.

Thermogravimetric analysis of poly(amino nitrile) **2a** in air shows a 5% weight loss at 263 °C. Polyketone **3** shows a 5% weight loss at 501 °C (Figure 6). The DSC trace of polymer **3** showed no T_g either in the first heating or the second heating. No melting transition was observed up to 500 °C. However, the wide angle X-ray diffraction pattern of polymer **3** shows sharp peaks due to the crystallinity of the polymer (Figure 7). The melting point must be >500 °C.

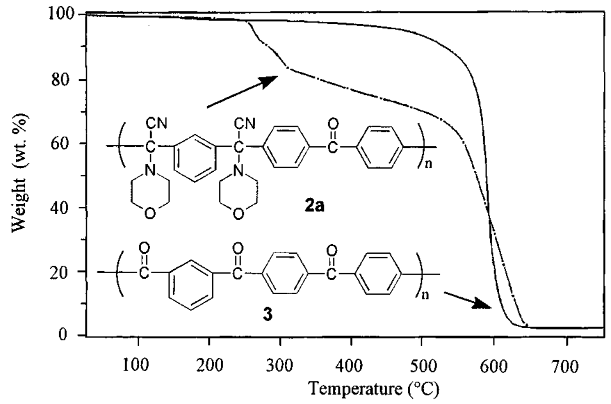

Figure 6. TGA of polymers **2a** and **3** in air.

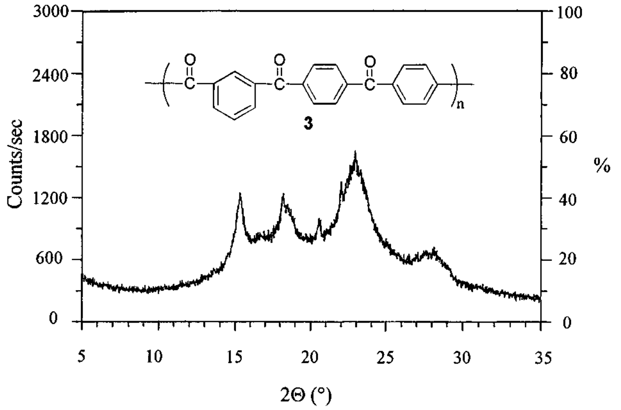

Figure 7. Wide angle X-ray diffraction pattern of polymer **3**.

Conclusions

We have presented a polymerization reaction to synthesize wholly aromatic polyketones based on condensation of bis(amino nitrile)s and activated dihalides. High molecular weight soluble poly(amino nitrile)s were successfully synthesized by condensation of the anions of bis(amino nitrile)s **1a** and **1b** with 4,4′-difluorobenzophenone under mild reaction conditions. Hydrolysis of the poly(amino nitrile)s yielded the corresponding polyketone **3**, which displays excellent thermal stability and chemical resistance. This polymerization method has successfully addressed the solubility problem associated with conventional polyketone syntheses. Moreover, wholly aromatic polyketones without ether linkages or alkyl substituents can be synthesized by this approach under mild reaction conditions.

Experimental Section

Materials and Instrumentation. The monomers were recrystallized at least three times to a constant melting point range and dried under vacuum at 60 °C for 36 h prior to use. Sodium hydride (60% dispersion in light mineral oil) and anhydrous DMF were purchased from Aldrich and used as received. Melting points were determined using a Haake-Buchler apparatus and are corrected. The proton NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 399.95 MHz and reported in δ units. Tetramethylsilane was used as the internal standard. All ^{1}H COSY (*CO*rrelated *S*pectroscop*Y*) spectra were obtained using a 16-step phase cycle. The spectral window was centered. A 90° pulse (177.5 μs) was used for both dimensions (F_1 and F_2); 128 increments of 512 point FID's (acquisition time 247 ms) with 16 scans were accumulated. Zero filling, multiplication by the sine window function, Fourier transformation, and symmetrization were applied. The ^{13}C NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 100.60 MHz. Spectra were proton-decoupled and recorded in deuteriochloroform (76.9) as solvent and internal standard. FTIR spectra were recorded on a Nicolet MX-1 with KBr pellets. GPC analyses were done with a Waters 150C ALC/GPC system with Permagel 10^2–10^6 Å polystyrene–divinylbenzene columns. This instrument was equipped with a Viscotek 100 differential viscometer and differential refractive index detectors. The viscometric data by the universal calibration yielded absolute molecular weights. Thermogravimetric analyses were carried out on a Perkin-Elmer 7700 thermal analysis system at a heating rate of 10 °C/min. Differential scanning calorimetric analyses were performed on a Perkin-Elmer DSC-4 at a scan rate of 10 °C/min in a nitrogen atmosphere. Wide angle X-ray diffraction was carried out on an XDS-200 diffractometer using a PAD V diffraction system.

α,α′-Dicyano-α,α′-bis(dimethylamino)-*m*-xylene (1b). To a 1 L three-necked round bottom flask equipped with a mechanical stirrer were added 25.97 g (193.6 mmol) of isophthalaldehyde, 40.30 g (387.2 mmol) of sodium bisulfite, and 600 mL of distilled water. The mixture was stirred until it became homogeneous. Then 43.65 g (387.2 mmol) of 40% dimethylamine in water was added to the flask and the stirring was continued until it became homogeneous. A solution of 18.98 g (387.2 mmol) of NaCN in water (100 mL) was added dropwise by a dropping funnel. A light yellow gummy material was formed; it solidified after ca. 2 days. The solid was suction filtered off, washed with water, and air dried to give 42.23 g (98%) of crude product, with a melting point of 63.0–91.0 °C (diastereomers). Purification was done by dissolving it in 200 mL of methylene chloride, and the solution was passed through a short silica gel column. Upon removing the methylene chloride on a rotary evaporator, the oil was washed with a small amount of hexane to give white crystals, which were recrystallized from hexane/ethyl acetate three times to give long white needles, mp 96.4–97.1 °C (27.87 g, 66%). FTIR (KBr): 3100–2800 (C–H stretches), 2235 (nitrile) cm^{-1}. ^{1}H NMR (CDCl$_3$, Figure 1): δ 7.66 (s, 1 H, H-1), 7.55 (m, diastereomeric protons, 2 H, H-3), 7.45 (m, 1 H, H-4), 4.86 (s, 2 H, H-6), 2.32 (s, 12 H, H-7). ^{13}C NMR (CDCl$_3$): δ 134.67 (C-2), 129.10 (C-1), 128.27 (C-3), 127.34 (C-4), 114.72 (C-5), 62.78 (C-6), 41.70 (C-7). Anal. Calcd (found) for $C_{14}H_{18}N_4$: C, 69.39 (69.42); H, 7.48 (7.46); N, 23.12 (23.10).

α,α′-Dicyano-α,α′-bis(*N*-morpholino)-*m*-xylene (1a). See ref 1 for procedural details and analytical data.

Polymerization of Compound 1a with 4,4′-Difluorobenzophenone To Form Polymer 2a. To a flame-dried 100 mL round bottom flask were added 2.4480 g (7.5000 mmol) of compound **1a**, 1.6365 g (7.5000 mmol) of 4,4′-difluorobenzophenone, and 25 mL of anhydrous DMF under nitrogen. NaH (0.75 g, 19 mmol, 60% in light mineral oil) was added to the flask. A vigorous bubbling and an immediate color change to yellowish green and then dark brown were observed. The mixture was stirred at room temperature under nitrogen for 14 days until the color of the solution faded to light yellow. The solution was then quenched into 600 mL of cold water. The pale yellow precipitate was filtered, washed with methanol, and air dried, 3.95 g (99%). Purification was done by precipitation from DMF into water using a high-speed blender and then from THF into hexane to remove the light mineral oil from the NaH. FTIR (KBr, Figure 3): 2963, 2851 (C–H stretches), 1668 (carbonyl), 1064 (phenyl), 1118 (C–O–C), 1270 cm^{-1}. ^{1}H NMR (CDCl$_3$, Figure 4): δ 8.07 (br s, 1 H, H-1), 7.76 (br m, 4 H, H-11), 7.68 (br m, 4 H, H-10), 7.58 (m, 2 H, H-3), 7.35 (m, 1 H, H-4), 3.70–3.93 (br, m, 8 H, H-8), 2.42–2.74 (br, m, H-7). ^{13}C NMR (CDCl$_3$): δ 194.32 (C-13), 143.19 (C-12), 139.69 (C-9), 137.39 (C-2), 130.90 (C-10), 130.55 (C-4), 127.13 (C-3), 127.01 (C-10), 125.37, 124.40 (C-1), 115.85 (C-5), 75.64 (C-6), 66.80 (C-8), 49.57 (C-7). Anal. Calcd (found) for $[F(C_{31}H_{28}N_4O_3)_{50}H]$: C, 73.73 (72.94); H, 5.59 (5.64); N, 11.09 (11.04), F, 0.08 (0.09).

Polymerization of Compound 1b with 4,4′-Difluorobenzophenone To Form Polymer 2b. The procedural details were the same as polymer **1a** with following modification: The temperature was controlled between 0 and 10 °C using an ice bath. The reaction time was 6 days. The yield was 97%. Most of the low molecular weight species were removed by Soxhlet extraction with ethanol over 3 days. FTIR (KBr): 2996, 2958, 2894, 2875, 2791 (C−H stretches), 1666 (carbonyl), 1062 (phenyl), 1404, 1275, 1038, 930, 708 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 8.14, 8.10 (br s, 1 H, H-1), 7.78 (br m, 4 H, H-11), 7.71 (br m, 4 H, H-10), 7.57 (m, 2 H, H-3), 7.30 (m, 1 H, H-4), 2.31 (s, 12 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 194.57 (C═O), 144.39 (C-12), 140.71 (C-9), 137.15 (C-2), 130.69 (C-10), 129.63 (C-4), 126.73, 126.58 (C-3), 126.09 (C-10), 123.82, 123.47 (C-1), 115.83 (C-5), 41.38 (CH_3). Anal. Calcd (found) for $[F(C_{27}H_{24}N_4O)_{35}H]$: C, 77.01 (76.97); H, 5.75 (5.72); N, 13.31 (12.94); F, 0.13 (0.16).

Polymerization of Compound 1b with 4,4′-Difluorobenzophenone To Form Polymer 2b Using 99.5 mol % of 4,4′-Difluorobenzophenone. The procedural details are the same as above. Compound **1b** (2.4232 g, 10.000 mmol), 2.1711 g (9.9500 mmol) of 4,4′-difluorobenzophenone, and 15 mL of anhydrous DMF were used. The yield was 4.15 g (99%). Most of the low molecular weight species were removed by Soxhlet extraction with ethanol over 3 days. The NMR and IR spectra were almost the same as above.

Poly(phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl) (3). In a 100 mL round bottom flask, 0.50 g of polymer **2a** (ground) was suspended in 20 mL of 70% aqueous acetic acid and 5 mL of concentrated HCl. The mixture was heated at reflux for 3 h and then quenched into 500 mL of distilled water. The white powder was suction filtered and washed with water and then methanol. It was dried in a vacuum oven at 140 °C for 30 h. The product weighed 0.31 g (100%). Polymer **3** was insoluble in $CHCl_3$, THF, acetone, ethyl acetate, DMF, DMSO, DMAc, NMP, etc. It was only soluble in very strong acids such as concentrated sulfuric acid. FTIR (KBr, Figure 3): 1662 (carbonyl), 1596 (phenyl), 1309, 1245, 930 cm^{-1}. ^{1}H NMR (D_2SO_4, Figure 4): δ 10.90 (s, H_2SO_4, reference), 8.90 (br s, 1 H), 8.67 (br m, 2 H), 8.38 (br m, 8 H), 8.23 (br m, 1 H). Anal. Calcd (found) for $[F(C_{21}H_{12}O_3)_{50}H]$: C, 80.66 (79.84); H, 3.87 (4.04); F, 0.12 (0.20).

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