A Polyketone Synthesis Involving Nucleophilic Substitution via Carbanions Derived from Bis(α-aminonitrile)s. 4.[1−3] Aromatic Poly(ether ketone)s

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ABSTRACT: To address the insolubility problem of polyketones, we used an approach to high molecular weight wholly aromatic polyketones without ether linkages via soluble precursors derived from isophthaldehyde-based bis(aminonitrile)s. Polymerization of bis(α-aminonitrile)s with activated dihalides using NaH as base in DMF yielded soluble, high molecular weight poly(aminonitrile)s, which were hydrolyzed in acidic conditions to produce the corresponding aromatic polyketones without ether linkages or alkyl substituents in the polymeric backbones. These polyketones displayed excellent thermal properties and solvent resistance. For the synthesis of poly(aminonitrile)s and polyketones containing ether linkages in the polymeric backbone, only low to medium molecular weight polymers were obtained. Model studies proved that the carbanions of the aminonitriles reacted with ether linkages to form more stable phenoxide anions and cause the termination of the polymerization.

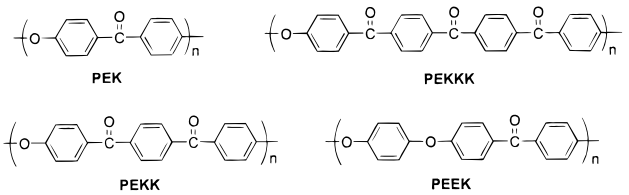
Introduction

Poly(arylene ether ketone)s (PAEKs), such as PEK, PEKK, PEKKK, and PEEK (Scheme 1), are an important class of high-performance engineering thermoplastics displaying a unique combination of thermal stability, chemical and solvent resistance, good mechanical properties over a wide temperature range, good fire resistance, and good electrical performance.[4−7] Compared to poly(arylene ether sulfone)s, which are usually amorphous polymers and thus subject to attack by solvents, PAEKs are semicrystalline polymers and therefore resistant to solvents, which is a critical factor in an aerospace environment. However, because of their crystallinity and the resulting insolubility, together with melting points generally above 300 °C, these polymers are also difficult to prepare with sufficiently high molecular weight unless extreme reaction conditions are used.

PAEKs are generally synthesized by an aromatic nucleophilic substitution reaction of activated aryl dihalides with aromatic diphenolates in a dipolar aprotic solvent or by electrophilic (Friedel−Crafts) acylation of aryl ethers.[4−7] 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 high molecular weight. To address the solubility problem, several approaches by soluble precursor polymers have been reported to produce high molecular weight PAEKs.[8−11] Nucleophilic ring-opening polymerization of macrocyclic oligomers[12−15] and nickel-catalyzed coupling of the aromatic diketo ether dichlorides[16,17] were also reported to produce poly(ether ketone)s.

In the previous papers,[1−3] we reported a new approach to synthesize high molecular weight poly(ketone sulfone)s and polyketones via soluble precursors derived from bis(α-aminonitrile)s under mild reaction conditions. In this paper we will discuss the synthesis of other aromatic polyketones without ether linkages, as well as polymerization and model studies of bis(α-aminonitrile)s containing ether linkages.

Scheme 1



Results and Discussion

1. Synthesis of Aromatic Polyketones without Ether Linkages. α-Aminonitriles can be easily synthesized from aldehydes and secondary amines in high yields by the Strecker reaction.[18] The carbanions of α-aminonitriles are selective and powerful nucleophiles which can displace activated halides to form carbon−carbon bonds.[18] Hydrolysis of aminonitriles under acidic conditions reforms the carbonyl group. Isophthalaminonitrile **1** was synthesized by the aqueous one-pot method of the Strecker synthesis in high yield.[1]

Poly(aminonitrile)s **3a**−**c** were synthesized in high molecular weight by the condensation of bis(aminonitrile) **1** with activated aromatic difluorides **2a**−**c** in DMF using sodium hydride as base at room temperature, as shown in Scheme 2. The poly(aminonitrile)s **3a**−**c** contain two chiral centers per repeat unit. These atactic polymers are generally amorphous and soluble in many common organic solvents, such as THF, acetone, DMSO, DMAc, etc. These polymers were characterized by GPC, FTIR, ^{1}H NMR, COSY, ^{13}C NMR, and HETCOR spectroscopies. The molecular weight data of these polyaminonitriles are listed in Table 1.

Hydrolysis of poly(aminonitrile)s **3a**−**c** in refluxing aqueous acetic acid and hydrochloric acid solution gave the corresponding polyketones **4a**−**c**, as previously

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Scheme 2

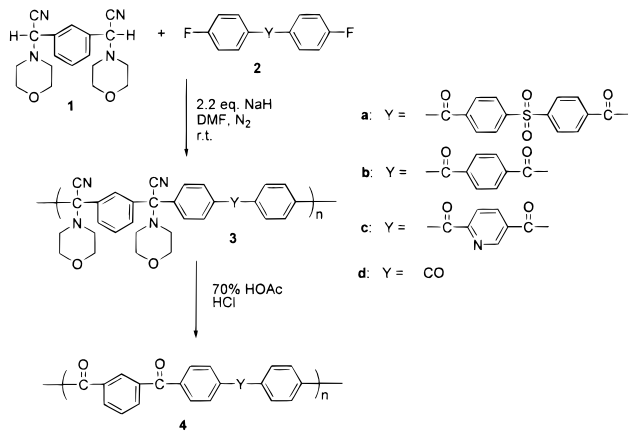


Table 1. GPC Data of Poly(aminonitrile)s (NMP, 60 °C)

polymer	M_n[a] (kg/mol)	M_w[a] (kg/mol)	M_w/M_n
3a	17.0	57.1	3.35
3b	22.7	31.4	1.38
3c	11.6	19.5	1.68

[a] Absolute values determined by use of a viscometric detector and the universal calibration.

Table 2. Thermal Properties (TGA and DSC) of Aromatic Polyketones

polymer	T_g (°C)	T_m (°C)	5% weight loss in air (°C)[c]
4a	198[a]	>500	495
4b	195[a]	>500	514
4c	177[b]	386[b]	493

[a] First heating at 10 °C/min. [b] Second heating at 10 °C/min. [c] Heating rate: 10 °C/min.

reported,[1−3] even though the reaction was heterogeneous. In contrast to the poly(aminonitrile)s **3a**−**c**, the hydrolysis products **4a**−**c** are insoluble in most common organic solvents such as THF, $CHCl_3$, DMF, NMP, etc. They are only soluble in very strong acids such as concentrated sulfuric acid. The complete hydrolysis was confirmed by FTIR, ^{1}H NMR, and ^{13}C NMR spectra according to the removal of morpholino groups of the aminonitrile moieties and the formation of the carbonyl group.[2] According to the TGA analysis, these polyketones also display high thermal stability. The TGA and DSC data are summarized in Table 2.

2. Polymerization and Model Studies of Bis(α-aminonitrile)s Containing Ether Linkages. To further explore the scope and limitations of this polymerization, known aromatic polyketones containing ether linkages such as PEKKK[19] were prepared by this aminonitrile approach and then compared with those made by the conventional nucleophilic and electrophilic approaches.

2.1. Synthesis of Bis(α-aminonitrile)s Containing Ether Linkages. Dialdehydes **5a**−**b**[20] were synthesized in 96−99% yield using 10 mol % excess 4-fluorobenzaldehyde and diphenols in toluene and DMAc (Scheme 3). Bis(α-aminonitrile)s **6a**−**b** were synthesized in good yields using an excess of trimethylsilyl cyanide (TMSCN) and morpholine in refluxing methylene chloride (Scheme 3).[21] The ^{1}H NMR spectrum of **6a** showed three signals in the aliphatic region corresponding to the aminonitrile units and four signals in the aromatic region for a typical AA′BB′ coupling pattern (Figure 1). The ^{13}C NMR spectrum and elemental analysis of **6a** also agree well with the expected structure. The FTIR spectrum of **6a** showed aliphatic C−H stretches at about 2900 cm^{-1}, a nitrile absorbance at 2220 cm^{-1}, and a C−O−C stretch at 1163 cm^{-1}. The NMR and FTIR spectra and elemental analysis of bis(α-aminonitrile) **6b** also agree well with the structure shown.

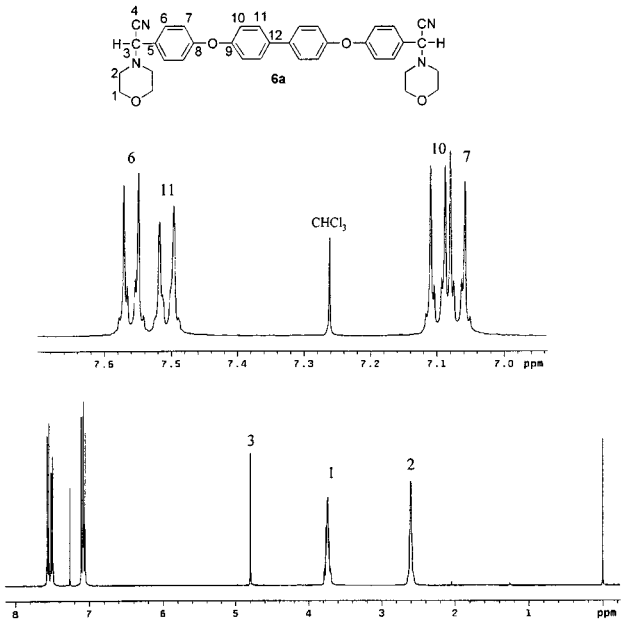
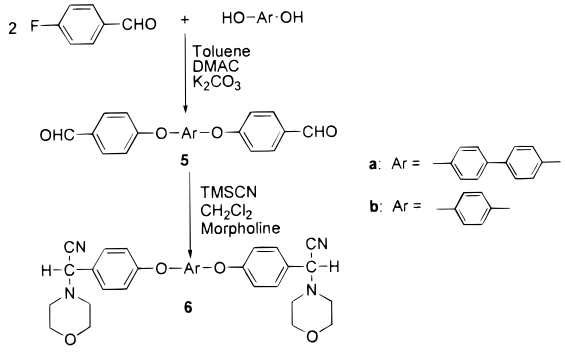
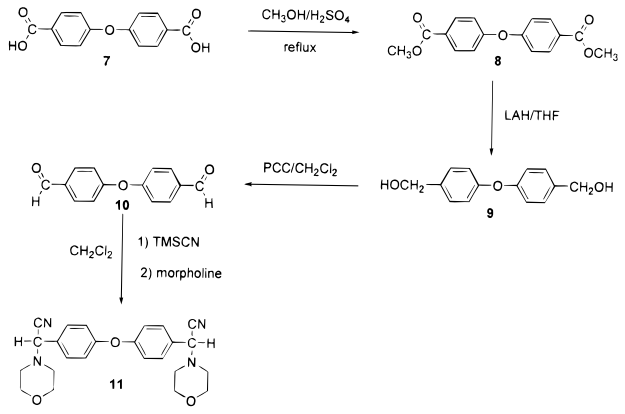


Figure 1. The 400 MHz ^{1}H NMR spectrum of compound **6a** in $CDCl_3$.

Scheme 3



Scheme 4



Bis(aminonitrile) **11** was synthesized from 4,4′-oxybis(benzoic acid) (**7**) by a four-step synthesis procedure (Scheme 4). **7** was converted to the corresponding dimethyl ester **8** in 95% yield. Reduction of **8** with lithium aluminum hydride (LAH) gave 4,4′-oxybis-

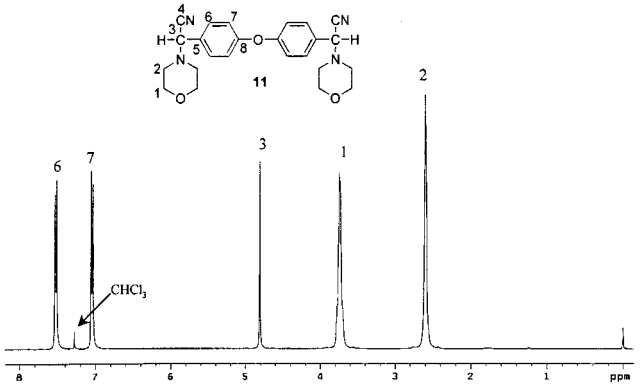


Figure 2. The 400 MHz ^{1}H NMR spectrum of compound **11** in $CDCl_3$.

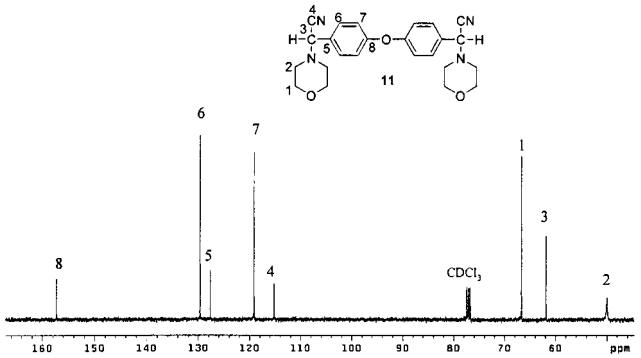
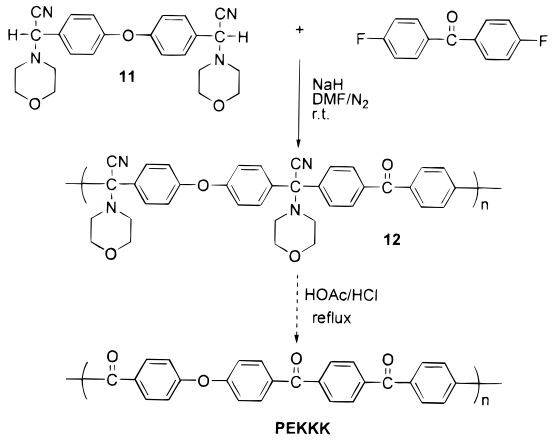


Figure 3. The 100 MHz ^{13}C NMR spectrum of compound **11** in $CDCl_3$.

Scheme 5



(benzyl alcohol) (**9**) in 83% yield. Oxidation of **9** with pyridinium chlorochromate (PCC) yielded the corresponding dialdehyde **10** in 87% yield. Bis(α-aminonitrile) **11** was synthesized in 97% yield by reaction of **10** with TMSCN and morpholine.[21] Monomer **11** was purified by recrystallization form ethanol. The structure of this new monomer was further confirmed by ^{1}H, ^{13}C NMR (Figure 2 and Figure 3), and FTIR spectra and elemental analysis.

2.2. Synthesis of Poly(aminonitrile)s Containing Ether Linkages. To prepare the known aromatic poly(ether ketone) PEKKK (Scheme 1), bis(α-aminonitrile) **11** was polymerized with 4,4′-difluorobenzophenone in DMF at room temperature using NaH as base (Scheme 5). After 24 h reaction time, the color of the solution was still dark brown. However, according to the ^{1}H NMR spectrum of the product after quenching, all methine protons of the aminonitrile units (4.81 ppm)

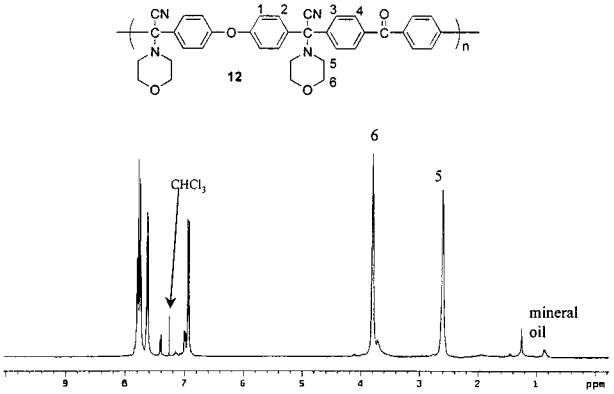


Figure 4. The 400 MHz ^{1}H NMR spectrum of crude polymer **12** (24 h reaction) in $CDCl_3$.

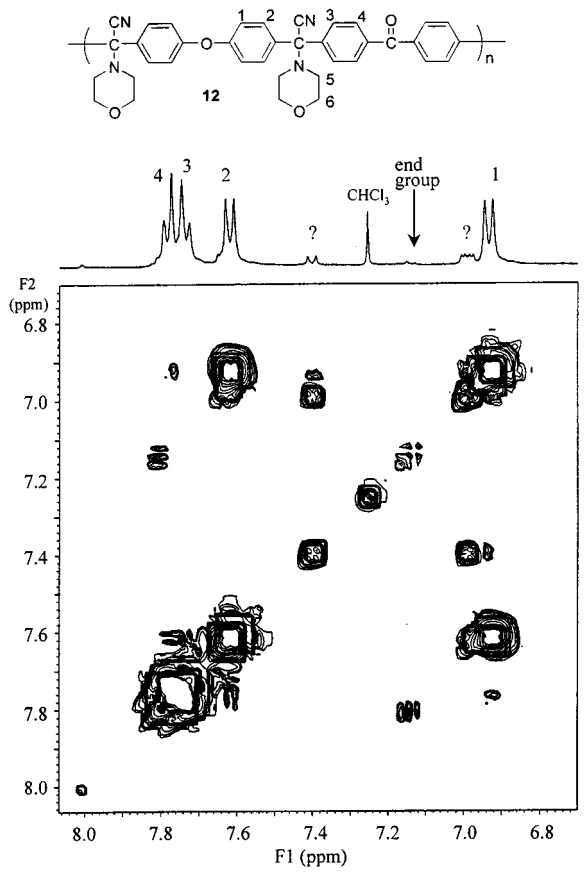


Figure 5. The 400 MHz COSY spectrum of polymer **12** in $CDCl_3$.

were consumed (Figure 4). No significant changes were observed after 48 h reaction time; the color of the solution remained dark brown even after 1 week. The COSY spectrum (Figure 5) of product polymer **12** (24 h) in the aromatic region showed two pairs of doublets coupled to each other (1−2, 3−4), which agrees with the structure of polymer **12**. Several small doublets coupled with each other (labeled "?") were also observed. Significant end group signals for aromatic protons ortho to fluoro substituents (labeled "end group") were also detected. According to the GPC traces (Figure 6) of polymer **12** at different reaction times, there were no significant changes in molecular weight after 24 h reaction. The molecular weight data are summarized in Table 3. Polymerization of **11** with 4,4′-difluorobenzophenone at 0 °C for 72 h also gave low molecular weight polymer **12** (**M_n** = 5.21 kg/mol and **M_w** = 11.5

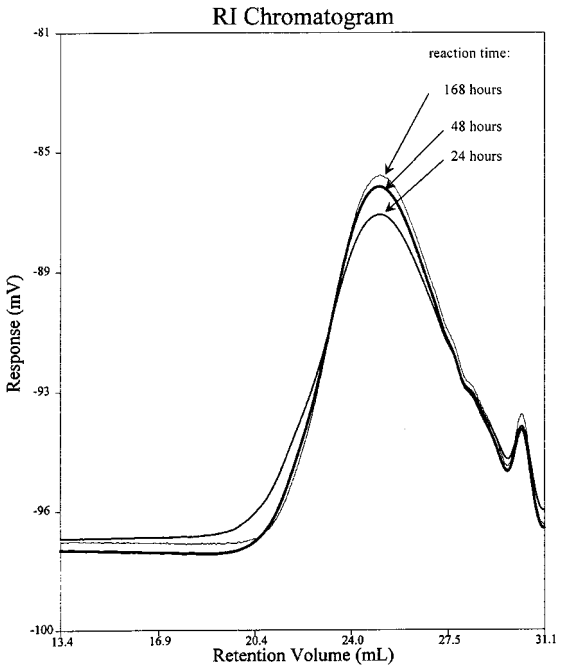


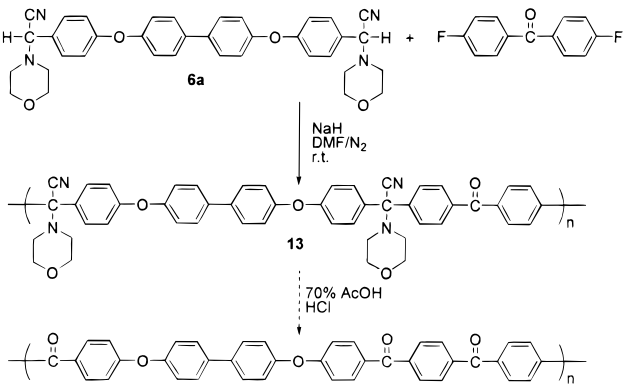
Figure 6. GPC traces of polymer **12** (NMP, 60 °C).

Table 3. GPC Data of Poly(aminonitrile) 12 (NMP, 60 °C)

reaction time (h)[a]	M_n[b] (kg/mol)	M_w[b] (kg/mol)	M_w/M_n
24	5.22	9.10	1.74
48	5.11	7.81	1.53
168	4.96	7.78	1.57

[a] At ambient temperature. [b] Absolute values determined by use of a viscometric detector and the universal calibration.

Scheme 6

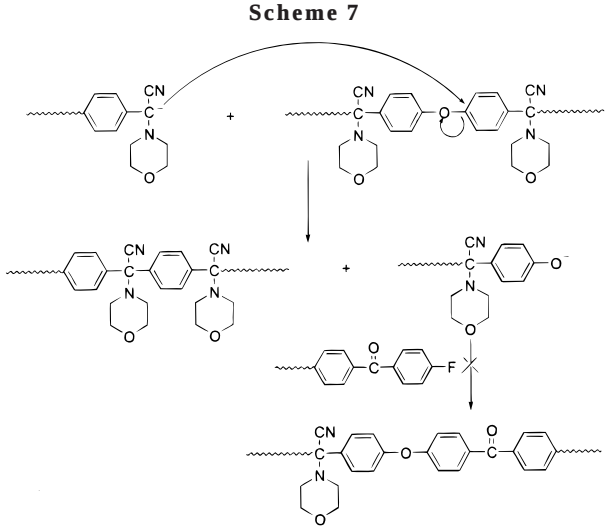


kg/mol). The ^{1}H NMR spectrum was about the same as that of polymer **12** made at room temperature.

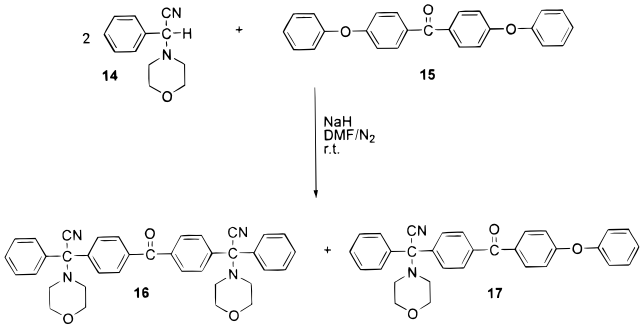
Bis(aminonitrile) **6a** was also polymerized with 4,4′-difluorobenzophone in DMF at room temperature using NaH as base (Scheme 6). After 36 h reaction, a small portion of solution was withdrawn and precipitated into water and then washed with MeOH. Results similar to those of poly(aminonitrile) **12** were obtained. GPC analysis (NMP, 60 °C) indicated an M_n of 5.98 kg/mol and an M_w of 26.9 kg/mol for polymer **13**.

2.3. Model Studies. All poly(aminonitrile)s containing ether linkages synthesized from bis(aminonitrile)s and activated dihalides are only low to medium molecular weight polymers. For systems from both aminonitriles containing ether linkages and activated dihalides containing ether linkages, the number-average molecular weights are less than 10 kg/mol. Significant

Scheme 7



Scheme 8



amounts of end groups can be observed in ^{1}H NMR spectra of these poly(aminonitrile)s. One of the possible explanations for low molecular weight is the formation of cyclic species; indeed, in our previous synthesis of **3d**, we observed low molecular weight byproducts believed to be cyclic oligomers.[2] However, cyclic species do not have end groups, which is contrary to the present NMR results. The other possible explanation for low molecular weight is that the carbanion of the aminonitrile attacked the ether linkage to form a phenoxide anion, which cannot further react with the activated fluoro chain end at room temperature (Scheme 7). The dark brown color is possibly due to the color of the phenoxide anion. This reaction would cause the cessation of the polymerization reaction. To test the stability of ether linkages in the presence of the carbanions of the aminonitriles, several model reactions were performed.

2.3a. The Stability of Activated Ether Linkages in the Presence of Carbanions. To address the problem of the stability of activated arylene ether linkages, monofunctional model compounds **14** and **15** were synthesized. Benzalaminonitrile **14** was synthesized from benzaldehyde by Strecker synthesis.[1] Compound **15** was synthesized from difluorobenzophenone and phenol in toluene and DMAc. To see whether the carbanion of the aminonitrile could react with activated ether linkages under standard polymerization conditions, 2 equiv of **14** was mixed with 1 equiv of compound **15** in DMF at room temperature using 2.2 equiv of NaH as base (Scheme 8). After 24 h, the solution was precipitated into water, and the crude product was isolated. The TLC of this crude product in 3:1 hexane:EtOAc showed four spots. Two of them were the starting materials **14** and **15**. The other possible products are

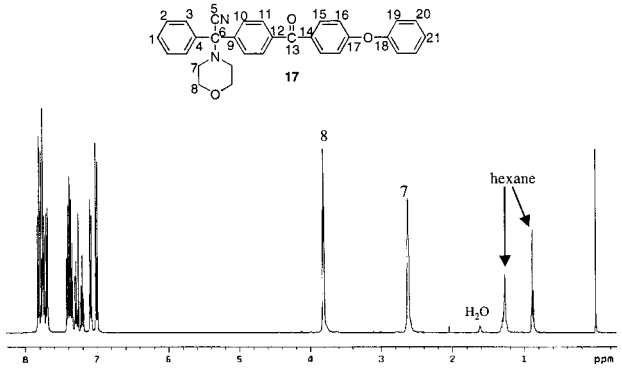


Figure 7. The 400 MHz ^{1}H NMR spectrum of compound **17** in $CDCl_3$.

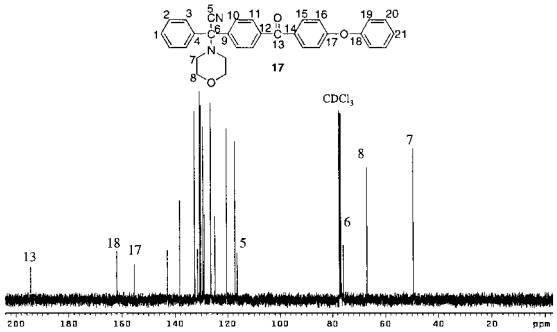


Figure 8. The 100 MHz ^{13}C NMR spectrum of compound **17** in $CDCl_3$.

compounds **16** and **17**. Any phenol formed would have been removed by the basic aqueous phase. The ^{1}H NMR spectrum of this crude product showed two different signals for the methylene protons adjacent to the oxygen of the mopholino unit. The integral of the methine proton of the aminonitrile unit was about $^1/_8$ of the integrals of the methylene protons adjacent to nitrogen (NCH_2), which indicates that about half of the methine protons of the aminonitrile were consumed. To prove that compounds **16** and **17** were formed, flash column chromatography was performed to isolate the products using hexane/ethyl acetate as eluent. According to the ^{1}H NMR spectra and the melting points, the first two fractions isolated were the starting materials **14** and **15**. The third fraction isolated was compound **17** (12%). The structure of compound **17** was confirmed by elemental analysis, ^{1}H NMR (Figure 7), ^{13}C NMR (Figure 8), and COSY (Figure 9) spectra. The fourth fraction isolated was compound **16** (15%), previously reported.[1] The ^{1}H NMR and ^{13}C NMR spectra agree well with the literature.[1] This experiment confirmed that, under these reaction conditions (the same conditions as the polymerization conditions), the carbanion of the aminonitrile attacked the activated ether linkages to form more stable phenoxide anions, which cannot further react with activated halides; this causes the cessation of the polymerization.

2.3b. Competing Reactions of Carbanions with Activated Halide and Ether Linkages. Model compound **18** (Scheme 9) is a good example to test the competing reactions of the activated halide and activated ether linkages with the anions of the aminonitriles. If the rates of these two different reactions are comparable, compound **16** and compound **19** will form as well as the normally expected product **17**. Benzalaminonitrile **14** was reacted with compound **18** (1:1

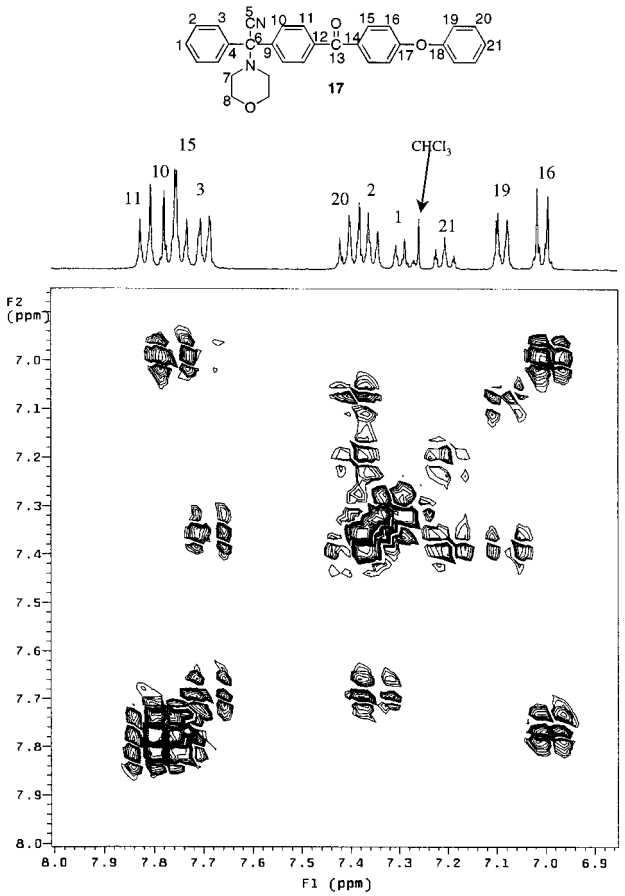
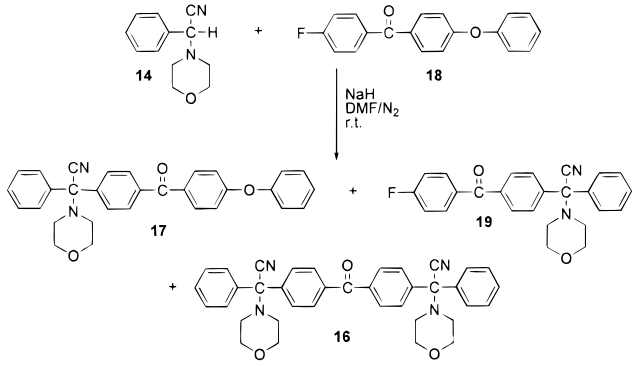


Figure 9. The 400 MHz COSY spectrum of compound **17** in $CDCl_3$.

Scheme 9



mole ratio) in DMF at room temperature using 1.1 equiv of NaH as base (Scheme 9). After 24 h, the solution was precipitated into water, and the product was isolated. The TLC of this crude product in 3:1 hexane:EtOAc showed only one spot. The ^{1}H NMR spectrum of the product agreed well with the structure of compound **17**. Most of the aminonitrile reacted with the activated fluoro group. This experiment confirmed that the reaction between the carbanion of the aminonitrile and the activated halide is much faster than the reaction between the carbanion of the aminonitrile with activated ether linkages. However, for condensation polymerizations, even small amounts of side reaction can result in low molecular weight polymers. As fluoro groups are consumed, the relative rates become such that the large numbers of ether linkages undergo reaction with the carbanions. This reduces the molec-

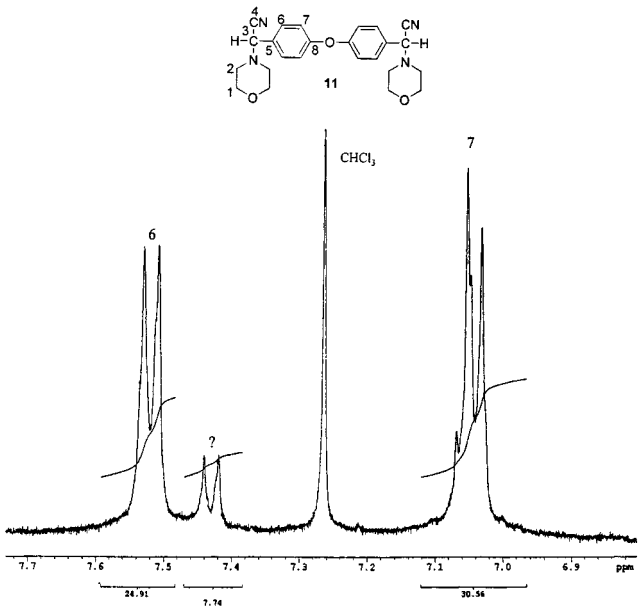


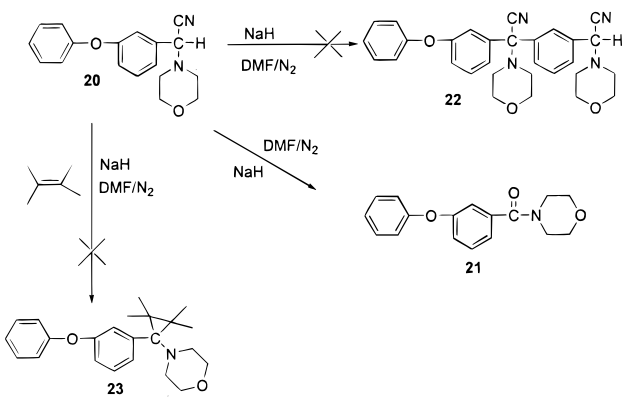
Figure 10. The 400 MHz ^{1}H NMR spectrum of the crude product (**11** + 2.2 equiv of NaH in anhydrous DMF for 24 h) in $CDCl_3$.

ular weight in two ways: (1) consumption of one of the monomers and disruption of the stoichiometry and (2) cleavage of already existing polymer molecules.

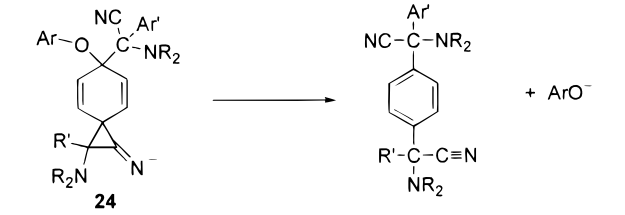
2.3c. Stability of an Aminonitrile (11) Anion with an Ether Linkage. To test the stability of aminonitriles containing ether linkages upon conversion to carbanions, bis(aminonitrile) **11** was treated in DMF with 2.2 equiv of NaH at room temperature. The mixture was stirred for 24 h and then precipitated into water. If the ether linkages are stable under these conditions, only bis(aminonitrile) **11** should be recovered. The ^{1}H NMR spectrum (Figure 10) of the precipitate showed a doublet at 7.43 ppm that represented about 30% of the two doublets (H_6, H_7) of the starting aminonitrile (Figure 2). The COSY spectrum showed that this doublet, which was coupled with the doublet at 7.06 ppm, appeared at almost the same position as the anomalous doublet of poly(aminonitrile) **12** (Figure 5). The low molecular weight of poly(aminonitrile) **12** could therefore be due to the instability of both the aminonitrile **11** and polyether **12** in the presence of NaH.

2.3d. Stability of an Aminonitrile Anion with a meta Ether Linkage (20). A simpler compound, **20**, was synthesized for model studies to test the idea that a meta ether group in the aromatic aminonitrile was not as prone toward attack by the carbanion. Compound **20** was treated with 1.1 equiv of NaH in DMF under N_2 for 3 days and then quenched into water (Scheme 10). The resultant product contained the majority of starting material **20** and a small amount of side product **21**, which was isolated by flash column chromatography. The structure of this side product **21** was confirmed by ^{1}H, ^{13}C, COSY, ^{1}H−^{13}C HETCOR NMR, FTIR, and high-resolution FAB mass spectroscopies. Further conformation of this structure was done by synthesis of **21** from 3-phenoxybenzoyl chloride and morpholine. One possible mechanism for formation of **21** is by decyanative oxidation of the carbanion of the amoninitrile **20** to form the corresponding amide **21**.[22] Even though the reaction was run under N_2, the decyanative oxidation side reaction could still occur without carefully degassing of the

Scheme 10



Scheme 11



solvent. For polymerizations of bis(α-aminonitrile)s with activated dihalides, carefully degassing of the solvent and the reaction flask should eliminate this side reaction and lead to improvement of molecular weight. The other possible mechanism is by the formation of a carbene species; this possibility was eliminated by a carbene trapping experiment with 2,3-dimethylbutene (Scheme 10). Only starting material **20** and a small amount of **21** were detected by TLC and ^{1}H NMR spectroscopy. No formation of carbene trapping product **23** was observed. Thus, unlike **11**, the meta linked compound **20** is not subject to nucleophilic attack; no **22** was detected. This rules out an inductive activation mechanism. Hence, in **11** the aminonitrile activates the ether moiety to nucleophilic attack perhaps via an intermediate such as **24** (Scheme 11), which cannot form with the meta analogues. Therefore, we expect that meta linked analogues of **6** and **11** would not be subject to this side reaction. Unfortunately, the required meta-substituted aldehyde starting materials (analogues of **5** and **10**) are not readily available.

Conclusions

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

For the synthesis of poly(aminonitrile)s **12** and **13** containing ether linkages in the backbone, only low to

medium molecular weights were achieved. The model studies proved that the carbanions of the aminonitriles react with activated ether linkages to form more stable phenoxide anions, which cannot further react with the activated fluoro sites under the polymerization conditions; this causes the cessation of the polymerization. However, the reaction between the activated fluoro sites and the carbanions of the aminonitriles is much faster than the reaction of the ether linkages with the anions of the aminonitriles. As the molecular weight of the poly(aminonitrile)s increases, the concentration of the activated fluoro chain ends decreases, and the side reactions between carbanionic polymer chain ends and the ether linkages become significant.

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. NaH (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 ^{1}H 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 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 (δ = 76.9 ppm) 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.

Poly(aminonitrile) 3a. See ref 1 for procedural details of the synthesis of **3a**. Compound **1** (3.2640 g, 10.000 mmol), compound **2a** (4.6247 g, 10.000 mmol), anhydrous DMF (30 mL), and NaH (60% in light mineral oil, 0.88 g, 22 mmol) were used. The crude yield was 7.88 g (100%). It was dissolved in THF and precipitated into hexane to remove the mineral oil and dried in a vacuum oven at 65 °C for 24 h. ^{1}H NMR (DMSO-d_6): δ 2.20−2.50 (m, br, CH_2, 8 H), 3.53−3.83 (m, br, CH_2, 8 H), 7.42−7.48 (m, 1 H), 7.54−7.60 (m, 2 H), 7.68−7.90 (m, 12 H), 7.97 (s, 0.5 H), 8.08 (s, 0.5 H), 8.02−8.18 (m, br, 4 H). FTIR (KBr): 2964, 2852, 2833 (C−H stretch), 1669 (C═O), 1601 (phenyl), 1329,1163 (SO_2), and 1117 (C−O−C), cm^{-1}.

Poly(ketone sulfone) 4a. See ref 1 for procedural details. The product was boiled in MeOH for 10 h. It was dried at 90 °C in a vacuum oven for 24 h and then in a drying pistol at 202 °C (NMP) for 24 h; 98% yield. Polymer **4a** is insoluble in most common organic solvents such as $CHCl_3$, THF, DMF, DMSO, etc. However, it is slightly soluble in hot NMP and soluble in concentrated H_2SO_4. ^{1}H NMR (D_2SO_4): δ 8.07−8.15 (m, br, 1 H), 8.20−8,28 (m, br, 12 H), 8.32−8.41 (m, br, 4 H), 8.52−8.64 (m, br, 2 H), 8.75 (s, br, 1 H). FTIR (KBr): 1665 (C═O), 1595, 1500 (phenyl), 1326, 1161 (sulfone), 1248, 928, cm^{-1}.

Poly(aminonitrile) 3b. See ref 1 for procedural details. Compound **1** (3.2640 g, 10.000 mmol), compound **2b** (3.2231 g, 10.000 mmol), anhydrous DMF (30 mL), and NaH (60% in light mineral oil, 0.88 g, 22 mmol) were used. The yield was 6.42 g (98%). Polymer **3b** is soluble in most common organic solvents such as $CHCl_3$, THF, DMSO, acetone, etc. ^{1}H NMR ($CDCl_3$): δ 2.40−2.60 (m, br, CH_2, 8 H), 3.53−3.83 (m, br, CH_2, 8 H), 7.34−7.40 (m, 1 H), 7.58−7.61 (m, 2 H), 7.78−7.87 (m, 4 H), 8.08−8.26 (m, 5 H), 8.87 (s, 1 H). ^{13}C NMR (APT, $CDCl_3$): δ 194.4 (C═O), 143.2 (C), 143.1 (C), 140.0 (C), 139.5 (C), 137.1 (C), 130.8 (CH), 130.3 (CH), 129.6 (CH), 126.9 (CH), 126.1 (CH), 124.0 (CH), 115.6 (CN), 75.4 (C), 66.6 (CH_2), and 49.3 (CH_2).

Polyketone 4b. The procedural details are the same as for **4a**. A 2.00 g sample of **3b** was used. The yield was 1.35 g (99%). **4b** is insoluble in most common organic solvents such as $CHCl_3$, THF, DMF, DMSO, etc. However, it is soluble in concentrated H_2SO_4. ^{1}H NMR (D_2SO_4): δ 3.46 (s, CH_3, 0.2 H), 8.08−8,16 (m, br, 1 H), 8.19−8.39 (m, br, 8 H), 8.56 (m, br, 2 H), 8.78 (s, br, 1 H), 8.94 (m, 0.38 H). FTIR (KBr): 1659 (C═O), 1600, 1500 (phenyl), 1303, 1250, 925, cm^{-1}.

Poly(aminonitrile) 3c. See ref 1 for procedural details. Compound **1** (3.2640 g, 10.000 mmol), compound **2c** (3.2330 g, 10.000 mmol), anhydrous DMF (30 mL), and NaH (60% in light mineral oil, 0.88 g, 22 mmol) were used. The yield was 6.41 g (97%). Poly(aminonitrile) **3c** is soluble in most common organic solvents such as $CHCl_3$, THF, and acetone. ^{1}H NMR ($CDCl_3$): δ 2.40−2.60 (m, br, CH_2, 8 H), 3.53−3.83 (m, br, CH_2, 8 H), 7.34−7.40 (m, 1 H), 7.58−7.61 (m, 2 H), 7.78−7.87 (m, 4 H), 8.08−8.26 (m, 5 H), 8.87(s, 1 H). ^{13}C NMR (APT, $CDCl_3$): δ 192.7 (C═O), 191.3 (C═O), 156.6 (C), 149.2 (CH), 143.9 (C), 143.3 (C), 139.5 (CH), 138.2 (C), 136.5 (C), 135.9 (C), 134.4 (C), 132.0 (CH), 130.9 (CH), 130.4 (CH), 126.9 (CH), 126.4 (CH), 125.9 (CH), 124.2 (CH), 124.0 (CH), 115.7 (CN), 75.5 (C), 66.6 (CH_2), and 49.4 (CH_2).

Polyketone 4c. The procedural details are the same as for **4b**. A 2.00 g sample of **3c** was used. The yield was 1.34 g (98%). Polymer **4c** is insoluble in most common organic solvents such as $CHCl_3$, THF, DMF, DMSO, etc. It is soluble in concentrated H_2SO_4. ^{1}H NMR (D_2SO_4): δ 8.14−8.18 (m, br, 1 H), 8.20−8,28 (m, br, 12 H), 8.32−8.41 (m, br, 4 H), 8.52−8.64 (m, br, 2 H), 8.75 (s, br, 1 H), 9.26−9.40 (m, 2 H), 9.56 (s, 1 H).

4,4′-Bis(*p*-formylphenoxy)biphenyl (5a). In a flame-dried 250 mL round-bottom flask equipped with a Dean-Stark trap and N_2 inlet, 4,4′-biphenol (3.724 g, 20.00 mmol) was dissolved in 35 mL of DMAc and 10 mL of toluene. K_2CO_3 (2.76 g, 20.0 mmol) was then added. The mixture was then refluxed at 140 °C for 4 h to remove water. *p*-Fluorobenzaldehyde (5.46 g, 44.0 mmol) was then added. The temperature was then raised to 160 °C by removing toluene, and reflux was continued at this temperature for 12 h. The mixture was quenched into 800 mL of H_2O; 7.78 g (99%) of pale yellow crystals was collected by suction filtration, mp 168−171 °C (lit.[20] 150−151 °C; in slow heating, it was oxidized to the carboxylic acid). ^{1}H NMR ($CDCl_3$): δ 7.12 (d, J = 8.8 Hz, 2 H), 7.17(d, J = 8.8 Hz, 2 H), 7.62 (d, J = 8.8 Hz, 2 H), 7.88 (d, J = 8.8 Hz, 2 H), 9.94 (s, 1 H). FTIR (KBr): 1694 (carbonyl), 1597 (phenyl), 1263 (C−O−C), 1496, 1152, 837, 822, cm^{-1}.

***p*-Bis(*p*′-formylphenoxy)benzene (5b).** Procedural details were the same as those for **5a**. The yield was 96%. It was dissolved in hot CH_2Cl_2 and treated with decolorizing charcoal to remove the colored impurities. The melting point was 162.8−164.5 °C (lit.[20] 157−158 °C). ^{1}H NMR (DMSO-d_6): δ 7.17 (d, J = 8.8 Hz, 2 H), 7.25 (s, 1 H), 7.93 (d, J = 8.8 Hz, 2 H), 9.93 (s, 1 H); FTIR (KBr) 1695, 1684 (carbonyl), 1600, 1579 (phenyl), 1230 (C−O−C), 1491, 1155, 874, cm^{-1}.

4,4′-Bis{*p*-[α-cyano-α-(*N*-morpholino)methyl]phenoxy}-biphenyl (6a). "Anhydrous" CH_2Cl_2 was dried over P_2O_5 for 12 h and then distilled. To a 100 mL round-bottom flask equipped with N_2 inlet and a stirring bar were added the dialdehyde **5a** (3.94 g, 10.0 mmol) and 30 mL of CH_2Cl_2. Trimethylsilyl cyanide (TMSCN, 2.98 g, 30.0 mmol) and morpholine (2.61 g, 30.3 mmol) were added to the flask. The solution was refluxed for 24 h. It was allowed to cool to room temperature (RT) and then washed with H_2O (3 × 15 mL). The CH_2Cl_2 was removed on a rotary evaporator to give a gummy oil. It was redissolved in 20 mL of CH_2Cl_2 and 2.61 g of morpholine. The solution was refluxed for 12 h. Upon

removing CH_2Cl_2, a light brown oil was obtained. It was washed with hexane to give light brown crystals, which were washed with hot EtOH to give a light pink solid, 4.46 g (76%), mp 192.0−195.7 °C. This product was then passed through a short silica gel column using CH_2Cl_2 as solvent and then recrystallized from CH_2Cl_2 and EtOAc twice to give white crystals, 2.99 g (51%); mp 193.5−194.7 °C. ^{1}H NMR ($CDCl_3$): δ 7.59 (m, 2 H), 7.51 (m, 2 H), 7.10 (m, 2 H), 7.07 (m, 2 H), 4.79 (s, 1 H), 3.73−3.75 (m, OCH_2, 4 H), 2.58−2.61 (m, NCH_2, 4 H). ^{13}C NMR ($CDCl_3$): δ 158.06 (C), 155.87 (C), 136.15 (C), 129.55 (CH), 128.35 (CH), 127.04 (C), 119.64 (CH), 118.64 (CH), 115.20 (CN), 66.64 (OCH_2), 61.84 (CH), 49.91 (NCH_2). FTIR (KBr): 2800−3000 (C−H stretches), 2220 (nitrile), 1597 (phenyl), 1244 (C−O−C), 1163 (C−O−C), 865, cm^{-1}. Elemental analysis: calcd (found) for $C_{36}H_{34}N_4O_4$: C, 73.69 (73.70); H, 5.84 (5.92); N, 9.55 (9.51).

***p*-Bis{*p*′-[α-cyano-α-(*N*-morpholino)methyl]phenoxy}-benzene (6b).** The procedural details were the same as those of diaminonitrile **6a**. Dialdehyde **5b** (8.35 g, 26.24 mmol), CH_2Cl_2 (60 mL), TMSCN (7.82 g, 78.7 mmol), and morpholine (6.85 g, 78.7 mmol) were used. The yield was 11.4 g (85%); mp 176.1−178.3 °C. ^{1}H NMR ($CDCl_3$): δ 7.49 (m, 2 H), 7.03 (s, 4 H), 7.01 (m, 2 H), 4.80 (s, 1 H), 3.67−3.79 (m, OCH_2, 4 H), 2.54−2.66 (m, NCH_2, 4 H). ^{13}C NMR ($CDCl_3$): δ 158.49 (C), 152.36 (C), 129.61 (CH), 126.75 (C), 121.04 (CH), 118.15 (CH), 115.20 (CN), 66.63 (OCH_2), 61.81 (CH), 49.91 (NCH_2). FTIR (KBr): 2800−3000 (C−H stretches), 2223 (nitrile), 1601 (phenyl), 1248 (C−O−C), 1164 (C−O−C), 868, cm^{-1}. Elemental analysis: calcd (found) for $C_{30}H_{30}N_4O_4$: C, 70.56 (70.73); H, 5.93 (5.87); N, 10.98 (10.89).

4,4′-Oxybis(methyl benzoate) (8). To a 1 L round-bottom flask were added compound **7** (51.65 g, 0.2000 mol) and MeOH (650 mL). Concentrated H_2SO_4 (20 mL) was slowly added to the reaction flask with stirring. The mixture was heated at reflux for 24 h. The white shiny flakes were filtered and washed with distilled H_2O and MeOH, 54.39 g (95%); mp 158.5−160.0 °C (lit.[23] 154−155 °C). ^{1}H NMR ($CDCl_3$): δ 8.05 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.8 Hz, 2 H), 4.92 (s, 3 H). ^{13}C NMR ($CDCl_3$): δ 166.40 (C═O), 160.17 (C═O), 131.86 (CH), 125.75 (C), 118.65 (CH), 52.13 (CH_3).

4,4′-Oxybis(benzyl alcohol) (9). To a 1 L three-neck flask were added compound **8** (42.94 g, 150.0 mmol) and dry THF (500 mL). A solution of LAH in THF (100 mL, 225.0 mmol) was added dropwise to the reaction flask. The stirring was continued for 24 h. EtOAc (150 mL) was then added to the flask, and the mixture was precipitated into H_2O. HCl was added with stirring until the solution was slightly acidic. The solution was then transferred to a separatory funnel, and the organic layer was separated. The aqueous layer was washed with EtOAc (2 × 50 mL). The solvent was removed by rotary evaporation to give the product **9**, 28.7 g (83%); mp 137−139.5 °C (lit.[24] 135.5−136 °C). ^{1}H NMR (DMSO-d_6): δ 7.34 (d, J = 8.6 Hz, 2 H), 6.93 (d, J = 8.6 Hz, 2 H), 5.17 (s, OH, 1 H), 2.01 (S, CH_2, 2 H).

4,4′-Oxybisbenzaldehyde (10). To a 500 mL round-bottom flask were added compound **9** (23.23 g, 100.0 mmol), CH_2Cl_2 (300 mL), and pyridinium chlorochromate (49.58 g, 230.0 mmol). The mixture was stirred under nitrogen for 2.5 h. The brown solid was filtered, and the filtrate was passed through a short silica gel column. The solvent was removed by rotary evaporation to give the product **10**, which was washed with hexane. The yield was 19.68 g (87%); mp 60.1−62.0 °C (lit.[25] 55−57 °C). ^{1}H NMR (DMSO-d_6): δ 10.0 (s, 1 H, aldehyde), 7.95 (d, J = 8.2 Hz, 2 H), 7.11 (d, J = 8.2 Hz, 2 H).

Bis{*p*-[α-cyano-α-(*N*-morpholino)methyl]phenyl} Ether (11). The procedural details were the same as those for bis(aminonitrile) **6a**. Dialdehyde **10** (11.31 g, 50.00 mmol), CH_2Cl_2 (75 mL), TMSCN (14.90 g, 150.0 mmol), and morpholine (13.05 g, 150 mmol) were used. The yield was 22.30 g (97%); mp 180.1−181.5 °C. ^{1}H NMR ($CDCl_3$): δ 7.52 (d, J = 8.2 Hz, 2 H), 7.04 (d, J = 8.2 Hz, 2 H), 4.81 (s, 1 H), 3.64−3.81 (m, OCH_2, 4 H), 2.53−2.65 (m, NCH_2, 4 H). ^{13}C NMR ($CDCl_3$): δ 157.34 (C), 129.67 (CH), 127.67 (CH), 119.14 (CH), 115.19 (CN), 66.67 (CH), 61.84 (OCH_2), 49.97 (NCH_2). FTIR (KBr): 2800−3000 (C−H stretches), 2222 (nitrile), 1598 (phenyl), 1245 (C−O−C), 1166 (C−O−C), 867, cm^{-1}. Elemental analysis: calcd. (found) for $C_{24}H_{26}N_4O_3$: C, 68.88 (69.10); H, 6.26 (6.26); N, 13.39 (13.38).

Poly(aminonitrile) 12 from Bis(α-aminonitrile) 11. Into a 100 mL flame-dried flask equipped with an N_2 inlet and a magnetic stirrer were added anhydrous DMF (15 mL) and NaH (0.293 g, 7.33 mmol, 60% in mineral oil). The mixture was stirred for 10 min. Bis(α-aminonitrile) **11** (1.3950 g, 3.3333 mmol) and difluorobenzophenone (0.7273 g, 3.333 mmol) were then added to the flask. Vigorous bubbling and an immediate color change to dark brown were observed. After 24 h, a small aliquot was withdrawn from the flask and precipitated into H_2O. After 48 h, another small aliquot was withdrawn from the flask and precipitated into H_2O. The stirring was continued at RT for 120 h. The color of the solution remained dark brown. The mixture was then precipitated into 300 mL of distilled H_2O, and the white precipitate was filtered and washed with MeOH. ^{1}H NMR ($CDCl_3$): δ 2.52−2.71 (m, NCH_2, 4 H), 3.64−3.83 (m, OCH_2, 4 H), 6.94 (d, J = 8.8 Hz, 2 H), 6.98−7.20 (m, 0.45 H), 7.41 (d, J = 8.4 Hz, 0.28 H), 7.63 (d, J = 8.8 Hz, 2 H), 7.74 (d, J = 8.4 Hz, 2 H), 7.80 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 194.73 (C═O), 156.87 (C), 143.54 (C), 137.22 (C), 133.16 (C), 130.80 (CH), 129.34 (C), 128.04 (CH), 126.37 (CH), 119.52 (CH), 116.12 (CN), 66.83 (C), 49.43 (OCH_2), 31.57 (NCH_2). FTIR (KBr): 2800−3000 (C−H stretches), 1660 (carbonyl), 1605 (phenyl), 1250 (C−O−C) 1169 (C−O−C), cm^{-1}.

Poly(aminonitrile) 13 from Bis(α-aminonitrile) 6a. The procedural details were the same as those for poly(aminonitrile) **12**. Anhydrous DMF (15 mL), NaH (0.2106 g, 5.260 mmol, 60% in mineral oil), bis(α-aminonitrile) **6a** (1.4040 g, 2.393 mmol), and 4,4′-difluorobenzophenone (0.5222 g, 2.3931 mmol) were used. After 36 h, a small aliquot was withdrawn from the flask and precipitated into H_2O. The white precipitate was filtered and washed with MeOH. The stirring was continued at RT for 120 h. The mixture was then precipitated into 300 mL of distilled H_2O, and the white precipitate was filtered and washed with MeOH. ^{1}H NMR ($CDCl_3$): δ 2.54−2.68 (m, NCH_2, 4 H), 3.67−3.88 (m, OCH_2, 4 H), 7.00 (d, J = 8.0 Hz, 2 H), 7.05 (d, J = 8.0 Hz, 2 H), 7.42 (d, J = 8.8 Hz, 0.42 H), 7.52 (d, 2 H), 7.63 (d, J = 8.0 Hz, 2 h), 7.76 (d, J = 8.0 Hz, 2 H), 7.82 (d, J = 8.0 Hz, 2 H). FTIR (KBr): 2800−3000 (C−H stretches), 1656 (carbonyl), 1597 (phenyl), 1230 (C−O−C) 1169 (C−O−C), cm^{-1}.

4,4′-Diphenoxybenzophenone (15). To a 100 mL three-neck round-bottom flask, equipped with magnetic stirrer, a Dean-Stark trap, and an N_2 inlet were added phenol (2.964 g, 31.50 mmol), K_2CO_3 (4.353 g, 31.50 mmol), DMAc (50 mL), and toluene (15 mL). The mixture was heated at reflux for 2 h to remove the side product H_2O. 4,4′-Difluorobenzophenone (3.273 g, 15.00 mmol) was then added to the reaction flask, and the mixture was refluxed at 135 °C for 4 h. The temperature was then raised to 150 °C by removing toluene from the Dean-Stark trap. The mixture was refluxed for another 12 h and then allowed to cool to RT. The solid residue was removed by suction filtration, and the filtrate was precipitated into 400 mL of H_2O. The white precipitate was filtered and washed with H_2O. The yield was 5.39 g (98%). It was recrystallized from EtOH to give white shiny flakes; mp 146.0−147.1 °C (lit.[26] 146−147 °C). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, J = 8.8 Hz, 4 H), 7.40 (m, 4 H), 7.21 (m, 2 H), 7.10 (m, 4 H), 7.03 (d, J = 8.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 194.20 (C═O), 161.37 (C), 155.80 (C), 132.21 (CH), 124.51 (CH), 120.09 (CH), 117.13 (CH).

Reaction of Aminonitrile 14 and Diphenoxybenzophenone (15) in the Presence of Base. Into a 100 mL flame-dried flask equipped with an N_2 inlet and a magnetic stirrer were added anhydrous DMF (25 mL) and NaH (0.44 g, 11 mmol, 60% in mineral oil). The mixture was stirred for 10 min. Compound **14** (2.023 g, 10.00 mmol) and compound **15** (1.823 g, 5.000 mmol) were then added to the flask. Vigorous bubbling and an immediate color change to dark brown were observed. After 24 h, the solution was precipitated into H_2O, and the white solid precipitate was filtered and dried. The TLC of this precipitate in 3:1 hexane:EtOAc showed four spots. Two of them were the starting materials **14** and **15**. Flash column chromatography (silica gel) using 3:1 hexane:EtOAc as eluent

gave four fractions. The first fraction was compound **15**, and the second fraction was compound **14**. The ^{1}H NMR spectra and mp of these two compounds were the same as those of the starting materials. The third fraction was identified as compound **17**, 0.29 g, (12%): mp 112.6−114.2 °C. ^{1}H NMR ($CDCl_3$): δ 7.82 (m, 4 H), 7.77 (m, 4 H), 7.74 (m, 4 H), 7.70 (m, 2 H), 7.40 (m, 2 H), 7.36 (m, 2 H), 7.29 (m, 1 H), 7.21 (m, 1 H), 7.09 (m, 2 H), 7.00 (m, 4 H), 3.77−3.85 (m, OCH_2, 4 H), 2.56−2.66 (m, NCH_2, 4 H). ^{13}C NMR ($CDCl_3$): δ 194.48 (C═O), 161.95 (C), 155.36 (C), 142.90 (C), 138.11 (C), 132.47 (CH), 131.31 (C), 130.52 (CH), 130.11 (CH), 129.28 (CH), 128.83 (C), 126.38 (CH), 126.31 (CH), 124.74 (CH), 120.27 (CH), 117.13 (CH), 116.30 (CN), 75.81 (C), 66.90 (OCH_2), 49.43 (NCH_2). FTIR (KBr): 2800−3000 (C−H stretches), 2228 (nitrile), 1663 (carbonyl), 1604 (phenyl), 1116 (C−O−C), 756, cm^{-1}. Elemental analysis: calcd (found) for $C_{31}H_{26}N_2O_3$: C, 78.46 (78.63); H, 5.22 (5.37); N, 5.90 (5.69). The fourth fraction was identified as compound **16**, 0.44 g (15%): mp 89.1−124.2 °C (lit.[1] 88−122 °C, diastereomeric). ^{1}H NMR ($CDCl_3$): δ 7.81 (m, 4 H), 7.73 (m, 4 H), 7.68 (m, 4 H), 7.36 (m, 4 H), 7.29 (m, 2 H), 3.80 (t, J = 8.2 Hz, OCH_2, 8 H), 2.53−2.67 (m, NCH_2, 8 H). ^{13}C NMR ($CDCl_3$): δ 194.72 (C═O), 143.53 (C), 137.98 (C), 137.18 (C), 130.72 (CH), 129.31 (CH), 128.89 (CH), 126.41 (CH), 126.35 (CH), 116.20 (CN), 75.79 (C), 66.87 (OCH_2), 49.43 (NCH_2).

Competing Reaction between Activated Halides and Ether Linkages, 14 + 18. The procedural details were the same as those for compound **14** with **15**. Compound **14** (1.0113 g, 5.000 mmol), compound **18** (1.4616 g, 5.000 mmol), and NaH (0.220 g, 5.50 mmol, 60% in mineral oil) were used. The crude yield was 2.34 g (97%): mp 62.0−114 °C. The TLC of the product in 3:1 hexane:EtOAc showed only one spot. ^{1}H NMR ($CDCl_3$) and ^{13}C NMR spectra were the same as compound **17** obtained from compound **14** and compound **15**.

Stability of Aminonitrile 11 in DMF and NaH. The procedural details are the same as above. Compound **11** (0.500 g, 1.20 mmol) and NaH (0.105 g, 2.63 mmol, 60% in mineral oil) were used. The mixture was stirred at RT for 24 h and then precipitated into H_2O. ^{1}H NMR ($CDCl_3$): δ 2.52−2.74 (m, NCH_2, 3.7 H), 3.63−3.85 (m, OCH_2, 5.2 H), 4.81 (s, CH, 1 H), 7.02−7.08 (m, 1.86 H), 7.43 (d, 0.48 H), 7.49−7.55 (d, 1.56 H).

α-(*N*-Morpholino)-3-phenoxybenzyl Cyanide (20). To a flame-dried 100 mL round-bottom were added 3-phenoxybenzaldehyde (9.91 g, 50.0 mmol), morpholine (4.79 g, 55.0 mmol), and 60 mL of dry THF and trimethylsilyl cyanide (TMSCN, 10.0 mL, 75.0 mmol). The solution was refluxed under N_2 for 24 h. After removal of THF by rotary evaporation, the mixture was dissolved in 150 mL of CH_2Cl_2 and extracted with two portions of water (2 × 50 mL). The organic layer was dried with anhydrous Na_2SO_4, and solvent was removed by rotary evaporation to give a light yellow oil, 13.93 g (95%). It was recrystallized from EtOH three times to give white crystals, 11.92 g (81%); mp 78.3−80.0 °C. ^{1}H NMR ($CDCl_3$): δ 7.36 (m, 2 H), 7.35 (m, 1 H), 7.28 (m, 1 H), 7.22 (m, 1 H), 7.14 (m, 1 H), 7.01 (m, 2 H), 7.00 (m, 1 H), 4.79 (s, CH, 1 H), 3.72 (m, OCH_2, 4 H), 2.59 (m, NCH_2, 4 H). ^{13}C NMR (DEPT, $CDCl_3$): δ 157.92 (C), 156.64 (C), 134.52 (C), 130.15 (CH), 129.93 (CH), 123.80 (CH), 122.53 (CH), 119.13 (CH), 119.10 (CH), 118.30 (CH), 119.99 (CN), 66.64 (OCH_2), 62.10 (CH), 49.99 (NCH_2). FTIR (KBr): 2800−3000 (C−H stretches), 2224 (nitrile), 1610,1580 (phenyl), 1117 (C−O−C), 878, cm^{-1}. Elemental analysis: calcd (found) for $C_{31}H_{26}N_2O_3$: C, 73.45 (73.34); H, 6.16 (6.16); N, 9.57 (9.47). LRMS (ESI+) *m/e* 294 $[M]^+$, 268 $[M - CN]^+$, 209 $[M - morpholine]^+$, 181 $[M - CN - morpholine]^+$, 86 $[morpholino]^+$. HRMS (FAB) exact mass calcd for $[M + 1]^+$ $C_{18}H_{18}N_2O_2$: 295.1447; found: 295.1445.

Stability of Aminonitrile 20 in DMF and NaH. The procedural details are the same as above. Compound **20** (2.94 g, 10.0 mmol), NaH (0.440 g, 11.0 mmol, 60% in mineral oil), and anhydrous DMF (20 mL) were stirred at room temperature under N_2 for 72 h and then precipitated into water. The orange oil was extracted with $CHCl_3$ (3 × 50 mL). The organic layer was dried with anhydrous Na_2SO_4, and the solvent was removed by rotary evaporation to give a light yellow oil. TLC (silica gel): 1:1/hexane:EtOAc, R_f = 0.65 (**20**), R_f = 0.27. Separation was done by flush column chromatography (silica gel), eluting with 1:1/hexane:EtOAc. The first fraction collected was compound **20**, 2.211 g; the second fraction collected was compound **21**, a colorless oil, 0.265 g (9%). ^{1}H NMR ($CDCl_3$): δ 7.38 (m, 1 H), 7.36 (m, 2 H), 7.13 (m, 1 H), 7.12 (m, 1 H), 7.05 (m, 1 H), 7.04 (m, 1 H), 7.03 (m, 2 H), 3.75 (m, br, OCH_2 + NCH_2, 4 H), 3.61 (m, br, OCH_2, 2 H), 3.44 (m, NCH_2, 2 H). ^{13}C NMR (DEPT, $CDCl_3$): δ 169.58 (C═O), 157.67 (C), 156.31 (C), 136.92 (C), 130.06 (CH), 129.90 (CH), 123.91 (CH), 121.45 (CH), 119.71 (CH), 119.36 (CH), 116.89 (CH), 66.80 (OCH_2), 48.11 (NCH_2), 42.48 (NCH_2); FTIR (KBr) 3064, 2965, 2921, 2854 (C−H stretches), 1639 (amide carbonyl), 1114 (C−O−C), cm^{-1}. LRMS (ESI+): *m/e* 283 $[M]^+$, 197 $[M - morpholino]^+$, 169 $[C_6H_5OC_6H_4]^+$, 86 $[morpholino]^+$. HRMS (FAB) exact mass calcd for $[M + 1]^+$ $C_{17}H_{17}NO_3$: 248.1287; found: 248.1289.

***N*-Morpholino-3-phenoxybenzamide (21).** To a flame-dried 100 mL round-bottom were added 3-phenoxybenzoic acid (4.28 g, 20.0 mmol), dry THF (30 mL), and thionyl chloride (4.38 mL, 60.0 mmol). The solution was refluxed under N_2 for 12 h. After removal of THF and excess $SOCl_2$ by rotary evaporation, the mixture was dissolved in 30 mL of dry THF. A solution of morpholine (1.74 g, 20.0 mmol) and pyridine (1.62 mL, 20.0 mmol) in 30 mL of dry THF was added dropwise to the flask. The mixture was stirred at RT under N_2 for 12 h. The white precipitate was filtered. From the filtrate THF was removed by rotary evaporation to give a light yellow oil, which was dissolved in 50 mL of EtOAc and washed with $NaHCO_3$ solution (2 × 50 mL) and H_2O (2 × 100), and dried with anhydrous Na_2SO_4. Solvent was removed by rotary evaporation to give a clear oil, 5.38 g (95%). The ^{1}H NMR and ^{13}C NMR and FTIR data were the same as those of compound **21** isolated from the above reaction by column chromatography.

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