# A New Polyketone Synthesis Involving Nucleophilic Substitution via Carbanions Derived from Bis($\alpha$-aminonitrile)s. 1. Semicrystalline Poly(arylene ketone sulfone)s[1,2]

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ABSTRACT: Poly(arylene ether ketone)s are arguably the most important class of high-performance polymers. These polymers have excellent heat and chemical resistance which has been instrumental in their use in advanced composites. A vexing shortcoming of these polymers is their limited processability. We now report a novel nucleophilic carbon–carbon bond-forming polymerization route for the synthesis of new poly(arylene ketone sulfone)s, devoid of any ether linkages in the backbone, via soluble precursors. These polymers can be synthesized at moderate temperatures and in high yields.

## Introduction

High-performance polymers are used in applications demanding enhanced temperature sustenance where maintainence of structural integrity and resistance to chemical environment are of paramount importance. Some of the important polymers in this class are polyamides, polyimides, polybenzazoles, and poly(arylene ether ketone)s. Each of the above polymers has a common problem of processing difficulty either thermally or from solution, the reason being strong interchain forces, semicrystallinity, inherent macromolecular rigidity, or unreacted end groups.

**A. Polyketones.** A critical contribution of the ketone functionality in polymers is the crystallinity which it imbues. This leads to the very desirable property of solvent resistance. Unfortunately, the crystalline nature of polyketones leads to synthetic and processing difficulties. A key element of this research is the avoidance of this problem by means of initial production of an amorphous precursor polymer, convertible to the desired crystalline polyketone material.

The nucleophilic aromatic substitution approach to polyketones involves the use of activated aromatic halides (or in some few cases, nitroaromatics) in which the carbonyl group serves as the activating moiety.[4–6] The nucleophile is a phenolate (di)anion. The reaction thus produces poly(ether ketone)s. These materials display very good physical properties, including high modulus, toughness, and good thermal stability,[7,8] and are widely used as engineering polymers in structural and composite applications. Reviews are available.[4,8] Because of the crystallinity arising from the presence of the keto functionalities, depending of course on the nature of the rest of the backbone, high temperatures are (e.g., >325 °C) required for their synthesis. In these cases, solvents such as diphenyl sulfone are used to accommodate the temperatures.[4,5,9] Side reactions such as ether exchange and cleavage become important at high temperatures,[4,9] necessitating careful optimization.

Synthesis of a soluble precursor polymer and an *in situ* chemical reaction to yield the final polymer is one solution to the processability problem that has already received attention. In the first approach, the ethylene glycol ketal of 4,4′-dihydroxybenzophenone is reacted with 4,4′-difluorobenzophenone[10] to produce a polyketal which is amorphous. Conversion to poly(ether ketone) is achieved quantitatively by acid hydrolysis of the polyketal. The second approach involves formation of the amorphous *tert*-butylated poly(ether ketone) from *tert*-butylhydroquinone and 4,4′-difluorobenzophenone.[11] Lewis or Brønsted (preferably) acid-catalyzed cleavage of the *tert*-butyl substituent (retro Friedel–Crafts alkylation) produced high molecular weight poly(ether ketone). In a third approach the imine from 4,4′-difluorobenzophenone and aniline is reacted with a bisphenol to produce a soluble, amorphous poly(ether ether ketimine) which by acid hydrolysis is converted to the poly(ether ether ketone).[12]

Reaction of trimethylsilylated phenols with 4,4′-difluorobenzophenone in the presence of potassium fluoride (KF) in the melt avoids the use of base and the potential for reactions with solvent[13,14] but presents its own processing and purification difficulties.[4] Nucleophilic ring-opening polymerization has been reported as a means of providing low-viscosity material for reactive processing to form high-performance poly(ether ketone)s.[15]

Recently the nickel-catalyzed coupling of the diketo ether dichlorides in NMP, DMAc, or dimethylformamide (DMF) at 80 °C was reported to produce poly(ether ketone)s.[16] As might have been expected,[4] the para isomers precipitated because of their crystallinity while the amorphous meta isomers did not. The para isomers were of low molecular weight. For the meta isomers, only low to medium molecular weights were achieved. Higher temperatures gave lower molecular weights. Very recently Deeter and Moore reported Pd(II)-catalyzed cross couplings of diacid chlorides and bis(stannane)s that produce high molecular weight polyketones, although solubility problems were encountered.[17]

It has also been recognized that fewer ether oxygen atoms and more carbonyl groups in the backbone lead to higher melting points and a greater propensity to crystallize.[18] One obvious synthetic pathway toward poly(arylene ketone)s is the Friedel–Crafts acylation (electrophilic aromatic substitution). Friedel–Crafts and related chemistries present a major limitation in that the substrate must be activated for electrophilic aromatic substitution, such as by an alkyl or an ether moiety. Generally, the former are avoided because of their thermooxidative instability. Another limitation is that the site of electrophilic attack must not be affected by prior acylation. For example, use of benzene as an AA monomer is not possible because of the deactivation caused by initial

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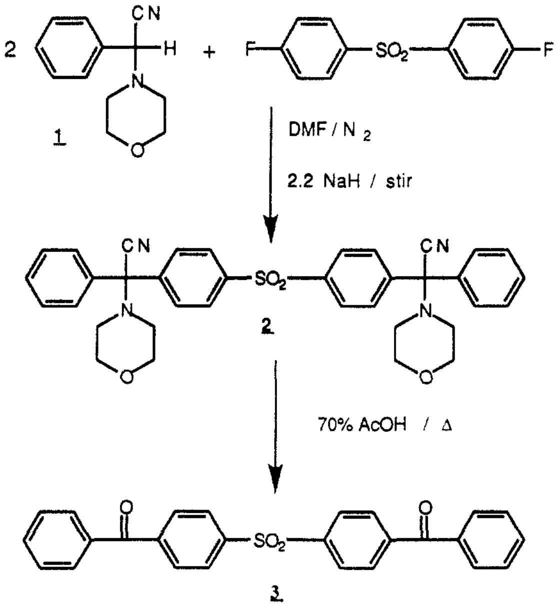
acylation. Even in the case of suitable substrates for acylation, the crystallinity of the product polymeric ketones often leads to precipitation at low molecular weights.[4] It has been found that use of a Lewis acid in greater than 2.5:1 molar proportion relative to the acid chloride group prevents premature precipitation through complexation of the polyketone's carbonyl groups.[4] Of course, the use of such quantities of Lewis acid and disposal of its byproducts represent significant obstacles to large-scale utilization of such processes.[4] Side reactions, e.g., with solvents, in the presence of such quantities of Lewis acids are also problematic. Alternatively, HF–$BF_3$[4,19,20] and $CF_3SO_3H$[4,21] are capable of producing polymers, but these are very corrosive media.

**B. Aminonitriles.** α-Aminonitriles and bis(α-aminonitrile)s were used by us[22a] as precursors to Reissert compounds[23] as part of an overall program using these intermediates in polymer synthesis.[22b] α-Aminonitriles themselves show an interesting chemistry. The conjugate bases of the α-aminonitriles are selective and powerful nucleophiles which can displace activated halides,[24] forming a C–C bond. Hydrolysis of the aminonitrile under acidic conditions regenerates the carbonyl moiety, resulting in products otherwise difficult to synthesize.

We decided to investigate this reaction and try activated aromatic halides like bis(p-fluorophenyl) sulfone for polymer synthesis. We now report and discuss a nucleophilic carbon–carbon bond-forming synthetic polymerization pathway, by the use of α-aminonitrile chemistry, to soluble poly(arylene ketone sulfone) precursors and conversion to poly(arylene ketone sulfone)s, the backbones of which are devoid of ether oxygen atoms.

## Results and Discussions

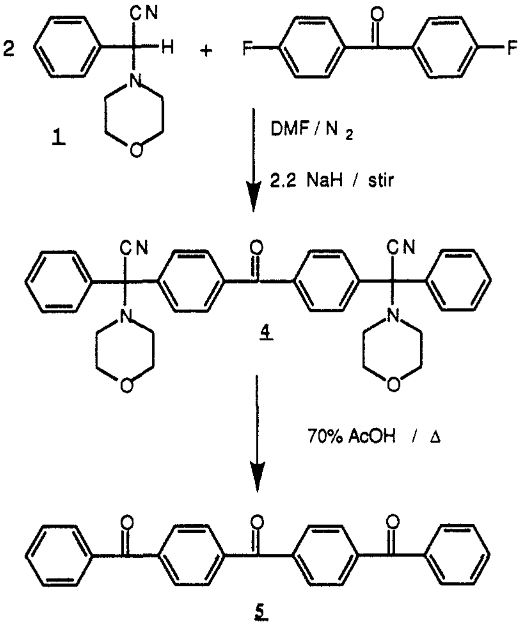
**Model Reactions.** When α-morpholinobenzyl cyanide (1)[25] was condensed with bis(p-fluorophenyl) sulfone in a 2:1 stoichiometric ratio in dry dimethylformamide, the resultant product (diastereomeric) 2 was obtained in 100% crude yield. The FTIR spectrum of the product showed no absorbance in the carbonyl region, strong peaks corresponding to $SO_2$, and characteristic peaks matching the general structural features of the molecule. The $^1H$ NMR spectrum lent strong credence to the structure 2. The product showed a broad melting range and was purified by recrystallization. The relative atomic proportions were confirmed by elemental analysis.



The aminonitrile moieties can be hydrolyzed in the presence of an acid, and the carbonyl can be regenerated, the reverse of aminonitrile formation. 3 was obtained when 2 was suspended in 70% aqueous acetic acid and refluxed for 1.5 h. The FTIR spectrum of 3 showed a sharp intense carbonyl stretching absorption at 1668 $cm^{-1}$, with a shoulder at 1654 $cm^{-1}$ corresponding to benzophenone derivatives and sulfone stretching absorptions at 1331 and 1165 $cm^{-1}$. The $^1H$ NMR spectrum is devoid of any aliphatic protons, and the pattern obtained is in agreement with the structural features of 3. Elemental analysis confirmed its composition. The literature shows only one reported synthesis (patented)[26] from diphenyl sulfide and benzoyl chloride via the Friedel–Crafts method and eventual oxidation of the sulfide to the sulfone; ours is the first synthesis via nucleophilic aromatic substitution.

Next, 4,4′-difluorobenzophenone was used as the activated aromatic dihalide, and the condensation with 1 was done in an analogous manner. The resultant product 4 (diastereomeric) was obtained in quantitative yield. It exhibited a broad melting point and was soluble in all common solvents in high proportions. The FTIR spectrum showed peaks corresponding to the nitrile stretch, carbonyl stretch, and the C–O–C of the morpholine ring. The $^1H$ NMR spectrum corresponded to the structure 4.

Upon refluxing a suspension of 4 in 70% aqueous acetic acid, the aminonitrile was hydrolyzed, yielding 5 in nearly quantitative yield. The FTIR spectrum and the $^1H$ NMR spectrum of 5 are in agreement with the structure.



The solubility of 5 was in sharp contrast to that of 4; it was highly insoluble in most of the common solvents and was purified by recrystallization from dimethylformamide. 5 was also much less soluble than 3 and higher melting (231–232 °C versus 203–204 °C). Its melting point agrees with a literature report.[26] This directly compares the effect of the carbonyl group with respect to the sulfone group. The intermolecular forces in 5 are stronger than in 3 partly due to the larger dipole moment and more planar structure, resulting in tighter packing of crystals.

Not many such selective nucleophilic aromatic substitution reactions are known. Grignard reagents and lithio carbanions both show a high propensity to attack a carbonyl moiety; this rules out the synthesis of 4 and possibly 2 via either a Grignard reagent or a lithio carbanion. The aminonitrile carbanion is a hindered *soft*

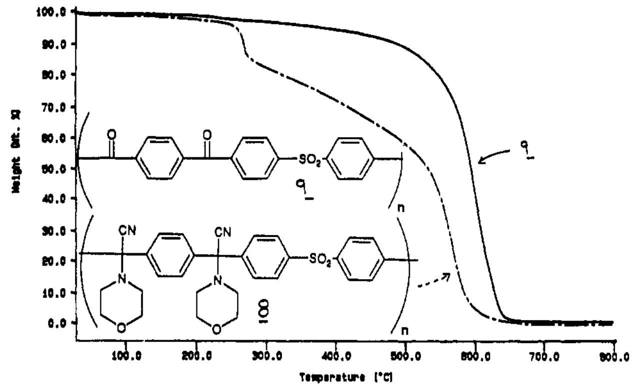
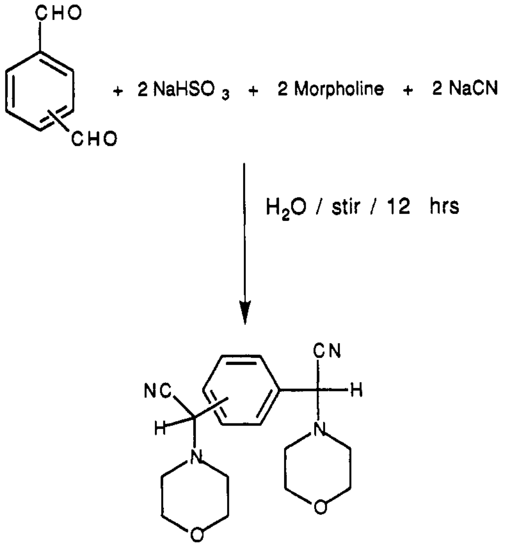


Figure 1. TGA of 8 and 9 (10 °C/min, in air).

*nucleophile* and thus shows no propensity to attack a *hard electrophile* like the carbonyl group. The result is a highly efficient and selective nucleophilic aromatic substitution.

**A-A Monomeric Bis($\alpha$-aminonitrile)s Based on Dialdehydes. Monomer Synthesis.** Next, we focused on novel A-A type monomers derived from dialdehydes. We decided to use terephthalaldehyde and isophthalaldehyde in the aqueous one-pot method of the Strecker synthesis.[27] Two new aromatic bis($\alpha$-aminonitrile)s 6 and 7 were thus prepared in quantitative yields. 6 is much less soluble than 7 and ca. 100 °C higher melting. The FTIR spectra exhibited peaks for nitrile stretch, C-O-C stretch, and aromatic bends. $^1$H NMR and elemental analyses confirm the structures.



6, p-isomer; 7, m-isomer

**Polymer Synthesis. Novel Poly(arylene ketone ketone sulfone)s.** When 6 was condensed with bis($p$-fluorophenyl) sulfone at 105 °C in dimethylformamide with sodium hydride (6 g of product scale) for ca. 3 days and eventually quenched into water, a pale yellow solid 8 was obtained in 99% yield. The $^1$H NMR spectrum of 8 showed an AA'BB' pattern and a singlet in the aromatic region and two multiplets in the aliphatic region corresponding to the morpholine ring. The symmetry and the integration ratios suggested either an oligomer or a polymer or a cyclic structure. A 10% weight loss occurred at 252 °C (in air) followed by approximately 60% retention of weight up to 500 °C and a complete loss of weight at 600 °C as detected by TGA (Figure 1). The FTIR spectrum shows peaks for carbonyl (weak, probably some hydrolysis during workup), $SO_2$, and C-O-C. An absolute molecular weight determination by GPC (NMP, 60 °C) indicated an $M_n$ of 345 and an $M_w$ of 3400. There was no evidence of identifiable end groups by either FTIR spectroscopy or $^1$H NMR spectroscopy. Certainly some side reaction occurred that seriously affected the yield of the expected poly(aminonitrile sulfone) 8.

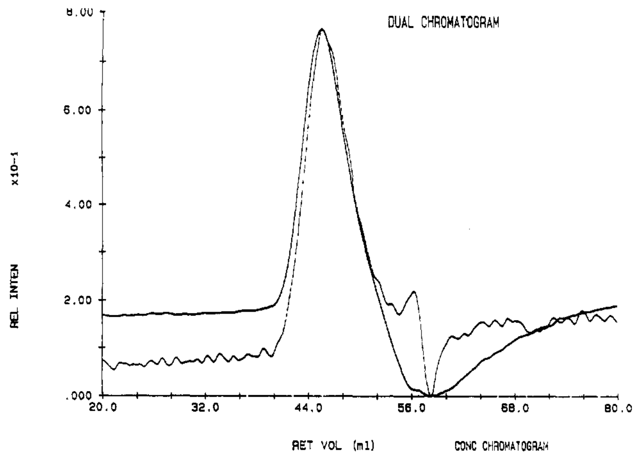
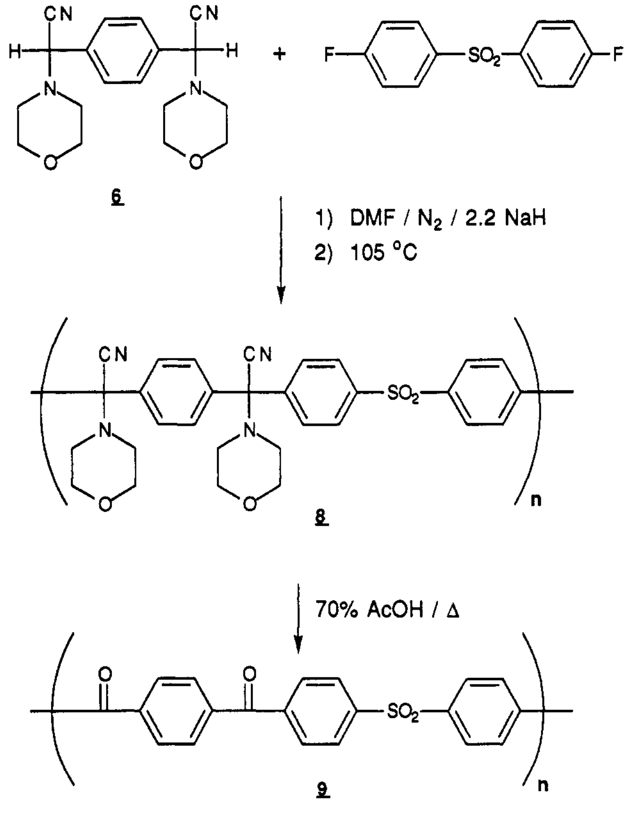


Figure 2. GPC of 8 (sample AP-3-62).

Table 1. Attempts To Optimize the Molecular Weight of 8

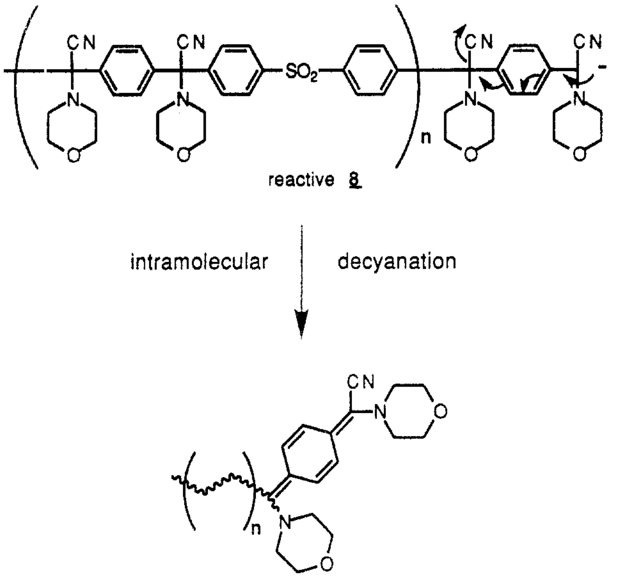
| sample | temp/time (°C/h) | scale[a] | $M_n$[b] | $M_w$[b] |
|---|---|---|---|---|
| AP-3-12 | 105/69 | 5 | 345 | 3 400 |
| AP-3-17 | ambient/168 | 1 | [$\eta$][c] = 0.1 dL/g | |
| AP-3-59 | ambient/120 | 6 | 5000 | 15 4000 |
| AP-3-62 | ambient/120 | 3 | 8600 | 17 200 |

[a] Theoretical grams of polymer 8. [b] Absolute molecular weights by GPC in NMP/0.5% LiCl at 60 °C. [c] In dimethylformamide at 23 °C.



When the reaction was carefully repeated several times, $M_n$ was increased to 8600 and $M_w$ was increased to 17 200 (sample AP-3-62, GPC; Figure 2) by carrying out the reaction at ambient temperature to avoid side reactions. The data are tabulated in Table 1.

Thus, although reasonable molecular weights are attained, it is evident that there is a side reaction which is curtailing the growth of the polymer chain particularly at higher temperatures. When bis(4-chlorophenyl) sulfone was used with **6**, the resulting polymer (99%) had a $M_n$ = 4.0 × 10$^3$ and $M_w$ = 7.7 × 10$^3$ after three precipitations from THF into ice cold methanol/water (1:1); no low molecular weight fraction was detected. Looking carefully at the structure of polymer **8**, we realize that the active chain end is an $\alpha$-cyanobenzylic carbanion and such a system could undergo an *intramolecular* elimination by ejecting the remote nitrile, which is a good leaving group, and forming quinodimethane end groups as shown in **10**. This would lead to loss of reactivity at the chain ends, causing cessation of the step-growth process and limiting the molecular weight. This is even more likely to happen at high temperatures near the end of the polymerization since the polymerization is a bimolecular reaction and the concentration of the nucleophilic and electrophilic ends is low. However, the intramolecular expulsion of the nitrile is a unimolecular reaction and independent of conversion. Thus the elimination reaction may predominate toward the end of the polymerization. Other possibilities are formation of cyclics as has been very elaborately shown recently for polycarbonates.[28] The purification procedure (three precipitations into a nonsolvent from a good solvent) should fractionate out most of the cyclics, though.



When a small portion of **8** (sample AP-3-59; Table 1) was suspended in 70% acetic acid and refluxed 1.5 h, the resulting pale brown solid **9** was insoluble in all common solvents including dimethylformamide. In contrast, **8** was soluble in common moderate polarity solvents like THF, acetone, and chloroform. The reason for the vast solubility difference lies in the absence of the polar, symmetric, and planar carbonyl moieties in **8** (vis-a-vis **9**) and also is due to the htereotacticity of the tetrahedral stereogenic centers at the carbons bearing the aminonitrile, leading to the amorphous character of **8** in contrast to the semicrystalline nature of **9**. The FTIR spectrum of **9** shows an intense carbonyl absorption and *loss of the peak* characteristic of the C–O–C stretch of the morpholine ring.

**9** exhibited a 10% weight loss at 493 °C (in air; Figure 1). This means that removal of the aminonitrile linkage by hydrolysis yielded **9** which displays a much higher stability to elevated temperatures (a gain of ca. 240 °C in the 10% weight loss temperature) than **8**.

The DSC results for the precursor poly(aminonitrile) (sample AP-3-59) did not show any transitions up to 250 °C (both first and second heats) beyond which it started degrading. When the hydrolyzed sample **9** was analyzed by DSC, it showed a $T_g$ of 199 °C, an exothermic crystallization peak at 266 °C, and an endothermic melting peak at 415 °C (first heat; Figure 3). The second heat (Figure 4), after cooling at 10 °C/min, showed a $T_g$ at 228 °C and a (smaller) endothermic melting peak at 414 °C. When the sample was quenched rapidly from 460 °C and then heated, a $T_g$ of 225 °C was detected along with a small exothermic crystallization peak at 290 °C. These results indicate that the polymer has a low rate of crystallization. The increase in $T_g$ in the second heat probably indicates the presence of residual solvent which plasticized the polymer, resulting in a low $T_g$ during the first heat. The lower value of the endothermic melting transition during the second heat, coupled with the nonexistence of a melting transition when the polymer was quenched rapidly, strongly indicates a low rate of crystallization; this is understandable because of the presence of the sulfone group. Wide-angle X-ray crystal structure analysis was indicative of the semicrystalline nature of **9** as isolated from the reaction mixture (Figure 5). That there was a melting transition was a pleasant surprise, since the commercial polysulfones are predominantly amorphous and polysulfones generally exhibit a lack of crystallinity, although a few bulk crystallizable polysulfones have been reported.[29] The melting point, 414 °C, is among the highest reported to date in the literature of poly(arylene ketone)s.[30]

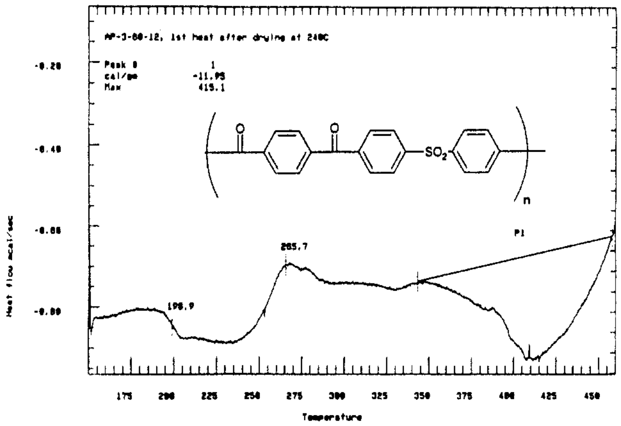


**Figure 3.** DSC of 9 (first heat, 10 °C/min heating rate).

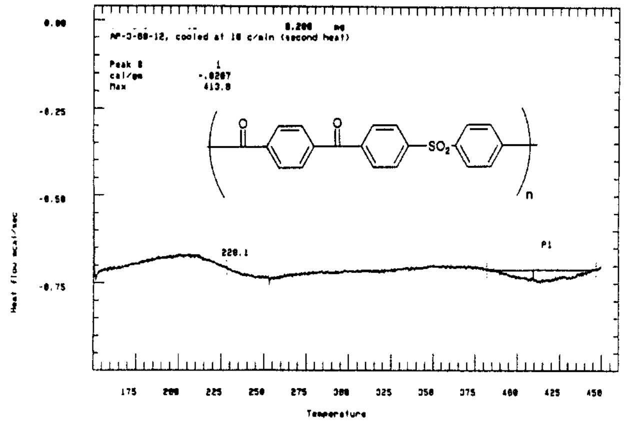


**Figure 4.** DSC of 9 (second heat, 10 °C/min heating rate).

Carlier et al.[29] have reported a correlation between $T_g$ and a variable called PRCL (percent rigid chain length) for a number of poly(arylene ether)s containing sulfone or ketone groups. The observed $T_g$ of **9** (225 °C) fits very well in the proposed linear correlation based on PRCL calculations (77%). Yet another variable proposed is the PRCL$_{ns}$ (percent rigid chain length not including the sulfone group), which ought to be above a threshold of

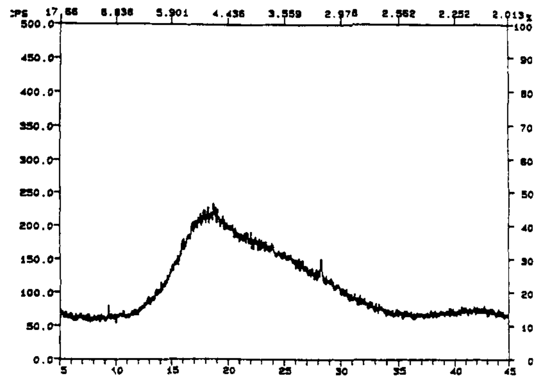
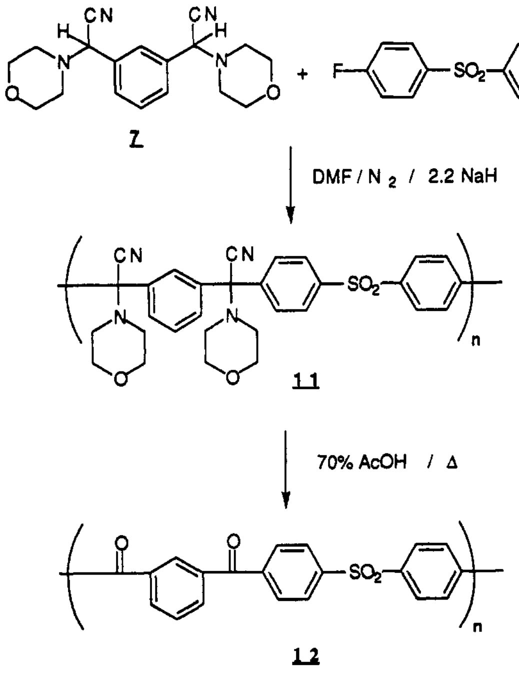


**Figure 5.** Wide-angle X-ray pattern of 9.

61% if the polysulfone is expected to be bulk crystallizable.[29] Calculation based on structural features of 9 reveals a $PRCL_{ns}$ of 59%, and it does exhibit a $T_m$ of 414 °C.

This is the first synthesis of a poly(arylene ketone ketone sulfone). Due to the carbanionic aromatic nucleophilic displacement reaction employed for the polycondensation, it was possible to eliminate the presence of oxygen-connecting atoms in the backbone.

The intramolecular decyanation can be eliminated if a meta-linked system is used as the bis(aminonitrile). When 7 was condensed with bis(*p*-fluorophenyl) sulfone in dimethylformamide under $N_2$, polymer 11 was readily obtained with an $M_n$ of $3.23 \times 10^4$ and an $M_w$ of $4.40 \times 10^4$ (absolute GPC, NMP, 60 °C; Figure 6). 11 was soluble in common moderate polarity solvents like THF, acetone, and chloroform. The $^1H$ NMR spectrum of 11 showed two multiplets in the aliphatic region corresponding to the morpholino group. The aromatic protons were assigned by the COSY spectrum (Figure 7). The structure of 11 was also confirmed by the $^{13}C$ NMR spectrum (Figure 8) and the $^1H$–$^{13}C$ HETCOR spectrum (*HET*eronuclear *COR*relation spectroscopy; Figure 9).



7

11

12

When 11 was analyzed thermogravimetrically, the 10% weight loss (in air) was detected at 298 °C and that increased by 254 °C to 552 °C when 11 was hydrolyzed to 12 (Figure 10). The DSC of 11 during the first heat showed an exothermic peak at ca. 278 °C. In its second heat, the exotherm (smaller in magnitude than the first heat) shifted to beyond ca. 370 °C. The TGA of 11 had shown incipient degradation at ca. 260 °C.

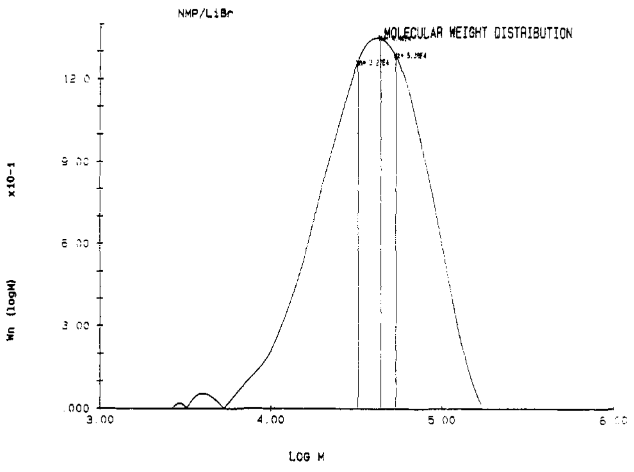


**Figure 6.** GPC of 11.

Hydrolysis of 11 was carried out in refluxing 70% acetic acid and hydrochloric acid. In contrast to 11, the hydrolysis product 12 was insoluble in common moderate polarity solvents such as THF, acetone, and chloroform; it was soluble in polar solvents such as DMF, DMSO, and NMP. The reason for the vast solubility difference lies in the absence of the polar, symmetric, and planar carbonyl moieties in 11 (vis-a-vis 12) and also is due to the heterotacticity of the tetrahedral stereogenic centers at the carbons bearing the aminonitrile in 11. Complete hydrolysis of 11 was achieved. This is supported by the absence of absorbance characteristic of the C–O–C and aliphatic C–H stretches of the morpholino moieties in the FTIR spectrum; the $^1H$ NMR spectrum shows no signal in the aliphatic region corresponding to the morpholino group. The $^{13}C$ NMR spectrum of 12 also showed the signal of a carbonyl carbon at 192.4 ppm and the removal of morpholino and cyanide groups (Figure 11). The structure of 12 was further confirmed by the COSY spectrum (Figure 12) and the $^1H$–$^{13}C$ HETCOR spectrum (Figure 13).

When 12 was analyzed calorimetrically (Figure 14), a $T_g$ of 188 °C was detected with an endothermic transition peak at 446 °C. In the second heating, a $T_g$ of 208 °C and a large endothermic transition peak at 458 °C were obtained. The melting point, 458 °C, is the highest melting point reported to date in the literature of poly(arylene ketone)s.[30]

Hence, we were able to synthesize two novel poly(arylene ketone ketone sulfone)s, a combination of functional groups hitherto not synthesized, and the polymers look quite promising from their initial thermal and GPC characterization. Since the poly(arylene aminonitrile) precursors to the poly(arylene ketone ketone sulfone)s are very soluble in conventional solvents, *it may perhaps be possible to obtain a good coating of the matrix to the fiber for composite manufacture; then a mild acid wash can hydrolyze the aminonitrile, transforming the resin into a high-performance matrix.* Similarly, fiber drawing through an acidic medium might yield polyketone fibers.

## Conclusions

Condensation of 6 and 7 with bis(*p*-fluorophenyl) sulfone resulted in novel poly(arylene ketone sulfone)s 9 and 12 which were obtained by hydrolysis of the intermediate poly(arylene aminonitrile)s 8 and 11. The synthetic method employed is mild, carried out at moderate temperatures, and produces solution processable precursors,

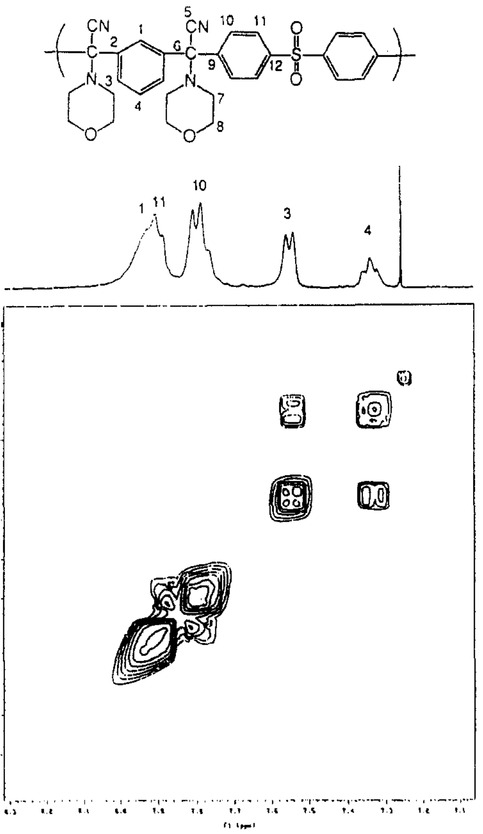


**Figure 7.** COSY spectrum of 11.

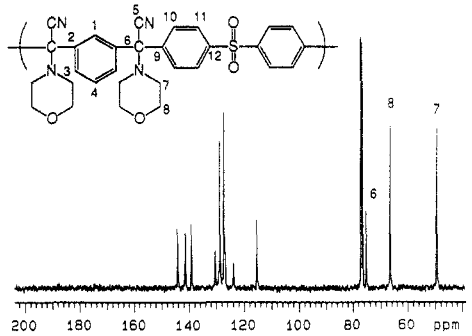


**Figure 8.** $^{13}$C NMR spectrum of 11.

bereft of metal ions, to poly(arylene ketone sulfone)s. 12 displayed the highest $T_m$ obtained to date in poly(arylene ketone)s. That 12 displayed a $T_m$ was a pleasant surprise because poly(sulfone)s are rarely semicrystalline. Polymers from the condensation of 6 and 7 with 4,4′-difluorobenzophenone have also been synthesized and characterized. This work represents the subject of the next paper in this series of publications.

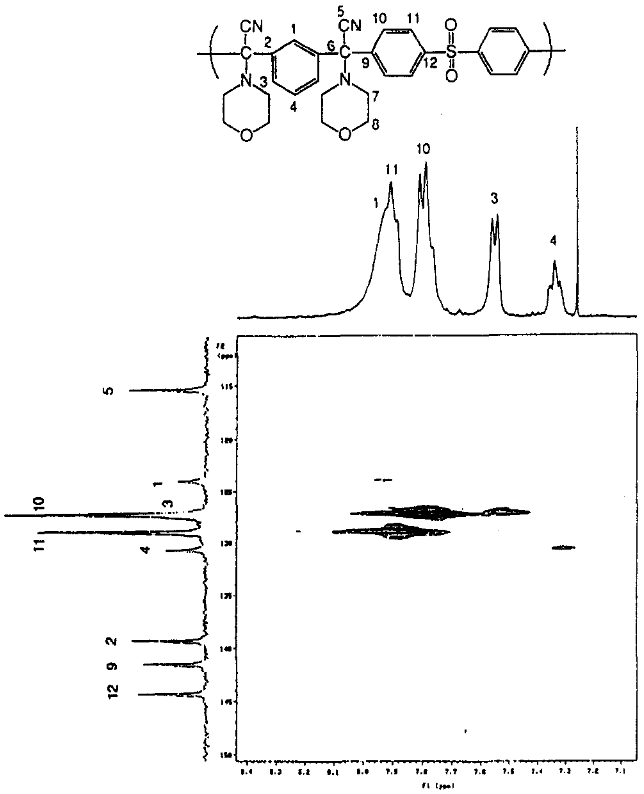


**Figure 9.** HETCOR spectrum of 11.

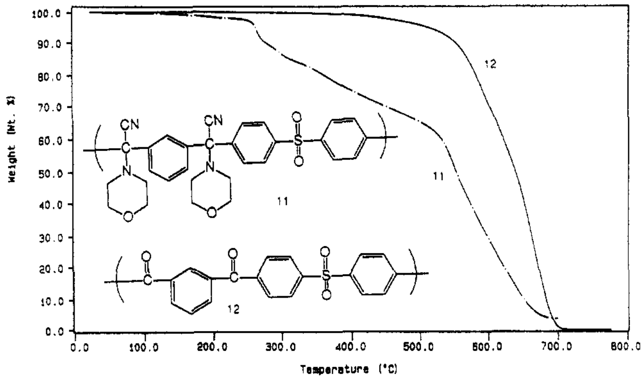


**Figure 10.** TGA of 11 and 12 (10 °C/min, in air).

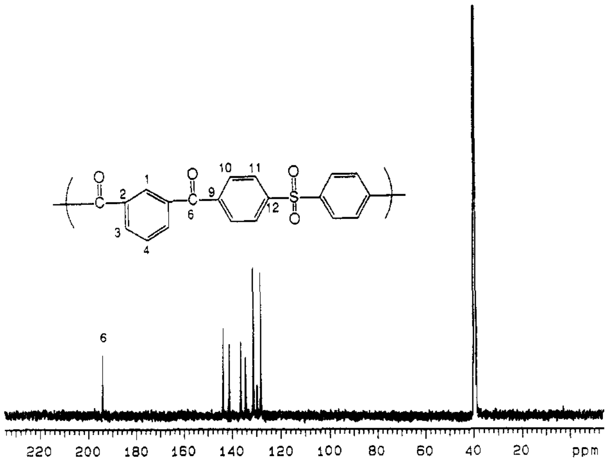


**Figure 11.** $^{13}$C NMR spectrum of 12.

## Experimental Section

Monomers were either triply recrystallized to a constant melting point range or vacuum distilled prior to use. NaI (Fisher Biotech grade, 99+%) was dried at 100 °C in vacuo. Dimethylformamide used for polymerization was purchased from Aldrich (Sure Seal) and used as such. Sodium hydride was used as a 60% dispersion in light mineral oil, as obtained from Aldrich. All yields are for crude products unless otherwise stated. Melting points were determined on a Haake Buchler melting point apparatus which was periodically calibrated. Thermogravimetric analyses (*in an air atmosphere*) and glass transition temperature determinations were carried out on a Perkin-Elmer 7700 thermal analyses system, interfaced to an IBM PS2 desktop computer and a Hewlett Packard 7550A graphics plotter, the heating rate being 10 °C/min in both cases. Proton NMR and $^{13}$C NMR spectra were recorded on Bruker 270-MHz and Varian unity 400-MHz instruments interfaced to an Aspect 2000 and a Hewlett Packard 7550A graphics plotter; tetramethylsilane was used as the internal standard. FTIR spectra were recorded on a Nicolet MX-1 on KBr pellets. Elemental analyses were performed by Atlantic Microlabs, Norcross, GA. GPC analyses were done either with a Waters 590 or a Waters 150C ALC/GPC system with Permagel $10^2$–$10^6$-Å polystyrene–divinylbenzene columns. The

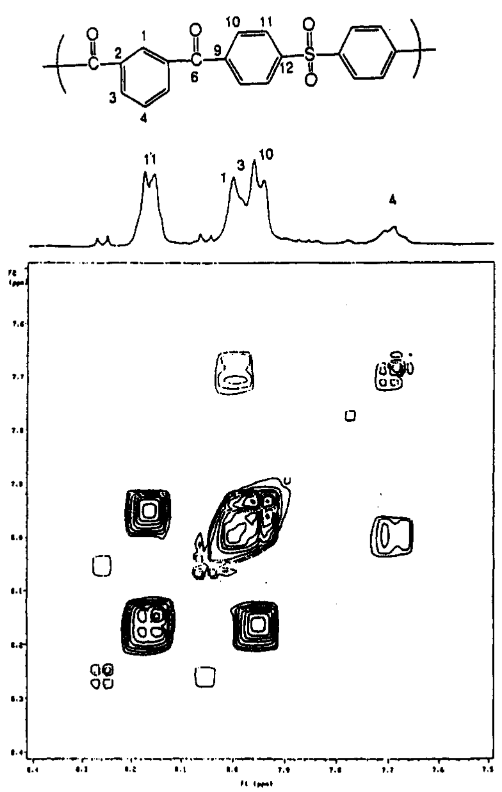


Figure 12. COSY spectrum of 12.

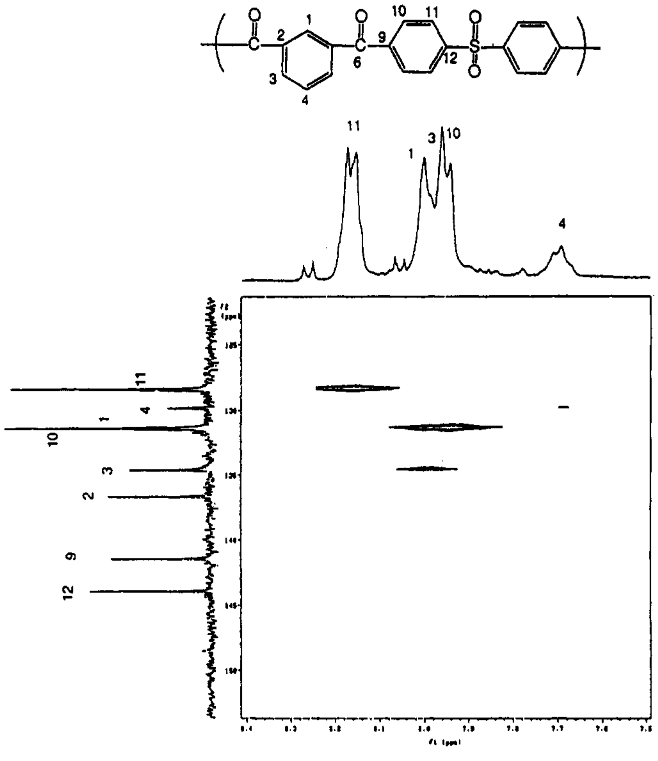


Figure 13. HETCOR spectrum of 12.

former instrument was fitted with refractive index and UV detectors and was calibrated with polystyrene standards. The latter instrument was equipped with Viscotek 100 differential viscometer, differential refractive index, and Chroatix KMX-6 low-angle laser light scattering detectors. Inherent viscosities were measured on 1.5% by weight solutions of the polymers, and intrinsic viscosities were measured on polymer solutions by the successive dilution technique beginning with a 1% by weight solution of the polymer in a Cannon–Fenske type viscometer; care was taken to have the measured "*t*" values between 1.7 and 1.1 $t_0$.

**α-*N*-Morpholinobenzyl Cyanide (1).** To a solution of $NaHSO_3$, 10.5 g (100 mmol), in 150 mL of water was added 11 mL (100 mmol) of benzaldehyde, and the mixture was stirred for 2 h until homogeneous. A total of 8.7 mL (100 mmol) of morpholine was added in one aliquot, and the stirring was continued for 2 h. Finally, 5 g (100 mmol) of NaCN was added, and the solution was stirred for 6 h, at the end of a which shiny, white solid had precipitated out. The yield was 19.8 g (98%), mp 66.8–67.8 °C. It was recrystallized from 150 mL of hexane/EtOAc (1:1) to yield shiny, white platelets, mp = 67–68 °C (lit.[25] mp 68–70 °C). FTIR (cm$^{-1}$): 2228 (nitrile), 1454 (methylene scissor), 1117 (C–O–C), 739, 703 (monosubstituted benzene). $^1$H NMR ($CDCl_3$): δ 7.55–7.35 (m, 5H), 4.82 (s, 1H), 3.78–3.65 (m, 4H), 2.59–2.56 (t, 4H, *J* = 4.7 Hz).

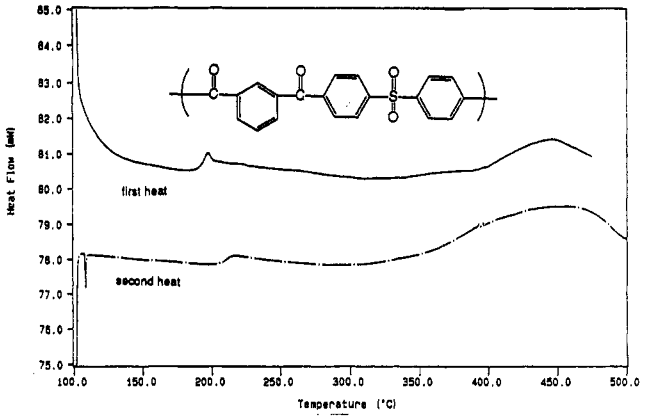


Figure 14. DSC (first and second heats) of 12 (10 °C/min).

**4,4′-Bis(α-cyano-α-*N*-morpholinobenzyl)diphenyl Sulfone (2).** To a solution of 1.63 g (8.07 mmol) of α-*N*-morpholinobenzyl cyanide (1) in 12.5 mL of dry DMF was added 1.04 g (4.04 mmol) of 4,4′-difluorodiphenyl sulfone in a dry round-bottomed flask under $N_2$. After 15 m of stirring to homogenize the solution, 366 mg (17.7 mmol) of 60% NaH was added in one aliquot and immediately the vigorous bubbling of $H_2$, a slight exotherm, and a change in color to green were observed. Within about 15 min, the color had changed to pale honey and stayed that way for the 12 h of stirring that was allowed. Upon quenching the reaction mixture into 125 mL of ice/water, a white precipitate was collected and dried, 2.51 g (100%), mp 125–165 °C (diastereomeric). The crude sample was crystallized thrice from benzene/hexane to yield white, shiny flakes, mp 145–220 °C. Elem anal. Found (calcd for $C_{36}H_{34}N_4O_4S/0.5C_6H_6$): C, 70.96 (71.21); H, 5.65 (5.67); S, 4.89 (4.87). FTIR (cm$^{-1}$): 1450 (methylene scissor), 1324, 1161 (sulfone), 1117 (C–O–C), 747 (monosubstituted benzene). $^1$H NMR ($CDCl_3$): δ 8–7.9 (m, 4H), 7.7–7.6 (m, 2H), 7.4–7.2 (m, 2H), 3.8–3.7 (m, 4H), 2.7–2.5 (m, 4H).

**4,4′-Bis(benzoyl)diphenyl Sulfone (3).** A suspension of 1 g of 4,4′-bis(α-cyano-α-*N*-morpholinobenzyl)diphenyl sulfone (2) in 25 mL of 70% AcOH was refluxed for 1 h. Within about 10 min, the solid had dissolved, and in 5 more min, white solid started separating out. The mixture was cooled and the solid collected and dried, 0.63 g (83%), mp 192–195 °C. It was recrystallized thrice from toluene/EtOH (9:1) to give shiny, colorless, fluffy crystals, mp 203.5–204 °C (lit.[26] mp 196–197 °C). FTIR (cm$^{-1}$) 1668 (CO), 1654 (C=C aromatic), 1331, 1165 (sulfone), and 704 (monosubstituted benzene). $^1$H NMR ($CDCl_3$): δ 8.11 (d, 2H, *J* = 8.2 Hz), 7.92 (d, 2H, *J* = 8.2 Hz), 7.79–7.51 (m, 5H). Elem anal. Found (calcd for $C_{26}H_{18}O_4S$): C, 73.16 (73.22); H, 4.30 (4.25); S, 7.77 (7.52).

**4,4′-Bis(α-cyano-α-*N*-morpholinobenzyl)benzophenone (4).** A procedure analogous to the synthesis of 2 from 1 was used to obtain 4 (by using 4,4′-difluorobenzophenone in place of 4,4′-difluorophenyl sulfone) from 1 in 100% crude yield, mp 80–122 °C (diastereomeric). The crude sample was purified by column chromatography (silica gel, gradient elution with 35% EtOAc/65% hexanes as the highest polarity solvent mixture), and the white shiny solid, mp 125–142 °C, was thoroughly dried (in vacuo at 110 °C for 16 h). Elem anal. Found (calcd for $C_{37}H_{34}N_4O_3/0.25CH_3CO_2C_2H_5$): C, 75.31 (75.48); H, 5.97 (6.00); N, 9.35 (9.27). FTIR (cm$^{-1}$): 2227 (weak, nitrile), 1734 (carbonyl, residual ethyl acetate), 1664 (benzophenone derivative), 1606, 1492 (phenyl), 1449 (methylene scissor), 1117 (C–O–C), 1008 (alicyclic ring vibration) and 754, 703 (monosubstituted benzene). $^1$H NMR ($CDCl_3$): $\delta$ 7.85–7.65 (m, 6H), 7.45–7.20 (m, 3H), 3.90–3.70 (m, 4H), 2.75–2.45 (m, 4H).

**4,4'-Dibenzoylbenzophenone (5).** A procedure analogous to the synthesis of 3 from 2 was used to obtain 5 from 4 in 100% crude yield. Recrystallization from ethanol/DMF afforded shiny off-white crystals, mp 231–232 °C (lit.[26] mp 226–228 °C). FTIR (cm$^{-1}$): 1648 (CO), 793 (para-disubstituted benzene) and 693 (monosubstituted benzene). $^1$H NMR (DMSO-$d_6$): $\delta$ 8.0–7.9 (m, 4H), 7.8 (m, 2H), 7.75 (d, 1H), and 7.6 (m, 2H).

***α,α'*-Dicyano-*α,α'*-bis(*N*-morpholino)-*p*-xylene (6).** To a solution of 11.05 g (100 mmol) of $NaHSO_3$ in 300 mL of $H_2O$ was added 6.85 g (50 mmol) of terephthalaldehyde, and the mixture was stirred for 2 h to give a solution. A total of 9.15 mL (100 mmol) of morpholine was syringed in at this time, and the solution was stirred for 2 h to give a solution of the bis(aminal). A solution of 5.2 g (100 mmol) of NaCN in 100 mL of $H_2O$ was then added over a period of 2 h, and the stirring was continued overnight. The pale cream solid was filtered, and the dry crude solid weighed 16 g (100%), mp 224–227 °C. It was recrystallized from DMF/EtOH twice to yield off-white, shiny crystals, mp 230–232 °C. FTIR (cm$^{-1}$): 2230 (nitrile), 1510 (aromatic C=C), 1458 (methylene scissor), 1112 (C–O–C), and 803 (para-disubstituted benzene). $^1$H NMR ($CDCl_3$): $\delta$ 7.61 (s, 2H), 4.85 (s, 1H), 3.85–3.69 (m, 4H), 2.72–2.52 (m, 4H). Elem anal. Found (calcd for $C_{18}H_{22}N_4O_2$): C, 66.50 (66.23); H, 6.75 (6.80); N, 17.23 (17.17).

***α,α'*-Dicyano-*α,α'*-bis(*N*-morpholino)-*m*-xylene (7).** A procedure analogous to the synthesis of 6 was used to obtain 7 (by using isophthalaldehyde in place of terephthalaldehyde) in 100% crude yield which was recrystallized twice from 95% EtOH to obtain a pale yellow powder, mp 118.5–135.5 °C. After thorough drying, it was placed in a fritted-disk funnel, washed with 200 mL of 95% EtOH by gravity filtration, and dried in a vacuum over at 60 °C overnight. FTIR (cm$^{-1}$): 2228 (weak, CN), 1456 (methylene scissor), 1113 (C–O–C) and 760 (meta-disubstituted phenyl). $^1$H NMR ($CDCl_3$): $\delta$ 7.67, 7.62 (s, diastereomeric protons, 1H), 7.57 (d, 2H, $J$ = 8.0 Hz), 7.48–7.43 (m, 1H), 4.85, 4.84 (s, 1H, diastereomeric acid protons), 3.90–3.70 (m, 8H), and 2.80–2.50 (m, 8H). Decoupling experiments consisted of irradiating the signal at 7.64 ppm and then at 7.59 ppm. None of the peaks changed, but a change in the coupling of the multiplet was observed when the 7.59 ppm signal was irradiated. This proved that the peaks at 7.67 and 7.62 ppm are $H_1$ and the product is diastereomeric in nature. $^{13}$C NMR ($CDCl_3$, APT): $\delta$ 133.52, 133.51 (CH), 123.47, 129.31 (CH), 128.74, 128.64 (CH), 127.67, 127.39 (C), 114.82 (CN), 66.53, 66.51 ($CH_2$), 62.07 ($CH_2$) and 49.93 (CH). Elem anal. Found (calcd for $C_{18}H_{22}N_4O_2$): C, 66.23 (66.24); H, 6.80 (6.80); N, 17.14 (17.17).

**Polymerization of Bis(4-fluorophenyl) Sulfone and *α,α'*-Dicyano-*α,α'*-bis(*N*-morpholino)-*p*-xylene (6) To Form Poly(*α*-aminonitrile) 8. (a) At ca. 105 °C.** To a solution of 3.0260 g (9.2711 mmol) of α,α'-dicyano-α,α'-bis(*N*-morpholino)-*p*-xylene (6) in 20 mL of dry DMF was added 2.3574 g (9.2719 mmol) of bis(4-fluorophenyl) sulfone at 105 °C (solution temperature) in a flame-dried flask under $N_2$. Upon the addition of 830 mg (21 mmol) of 60% NaH, a vigorous bubbling and an immediate color change to deep maroon were seen. The solution was stirred for a total of 69 h and quenched in ice cold 5% aqueous NaCl to yield 4.97 g (99%) of a pale brown solid. Purification was done by dissolving it in 1:1 DMF/acetone and precipitating in water thrice. It was dried in a vacuum oven at 50 °C overnight. TGA: 10% weight loss (in air) at 252 °C followed by a 60% weight retention up to 500 °C and complete weight loss at 600 °C. FTIR (cm$^{-1}$) 1676 (weak, CO), 1594 (aromatic C=C), 1456 (methylene scissor), 1327, 1160 (sulfone), and 1117 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$ 8.12–7.48 (m, 12H), 3.97–3.63 (br s, 8H), 2.72–2.38 (m, 8H). Absolute molecular weight determination by GPC (in NMP at 60 °C) yielded an $M_n$ of $3.45 \times 10^2$ and an $M_w$ of $3.3 \times 10^3$.

**(b) At ca. 25 °C.** To a suspension of 3.6223 g (11.098 mmol) of α,α'-dicyano-α,α'-bis(*N*-morpholino)-*p*-xylene (6) in 25 mL of dry DMF was added 2.8216 g (11.098 mmol) of bis(4-fluorophenyl) sulfone at ambient temperature in a flame-dried flask under $N_2$. The mixture was stirred for 20 min and stayed heterogeneous because of the insolubility of the bis(aminonitrile) at the reaction temperature. Upon the addition of 1.02 g of 60% NaH (23.0 mmol), a vigorous bubbling and an immediate color change to deep maroon were seen. The solution was stirred for a total of 120 h and quenched into 250 mL of ice cold 5% aqueous NaCl to yield 6.05 g (100%) of a pale yellow solid. Purification was done by dissolving it in DMF and precipitating in water once. Then it was twice precipitated from a $CHCl_3$ solution into 10-fold excess ice cold MeOH. It was dried in a vacuum oven at 50 °C overnight. TGA: 10% weight loss (in air) at 268 °C followed by a 60% weight retention up to 500 °C and complete weight loss at 640 °C. DSC analysis showed no transitions up to 250 °C, beyond which degradation started. FTIR (cm$^{-1}$): 1678 (weak, CO), 1591 (aromatic C=C), 1452 (methylene scissor), 1331, 1158 (sulfone), and 1114 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$ 8.1–7.3 (m, 12H), 4.0–3.6 (br s, 8H), 2.7–2.4 (m, 8H). An absolute molecular weight determination by GPC yielded an $M_n$ of $5.0 \times 10^3$ and an $M_w$ of $1.5 \times 10^4$.

**Poly(sulfonyl-*p*-phenylenecarbonyl-*p*-phenylenecarbonyl-*p*-phenylene) (9).** A suspension of 1.00 g of 8 was refluxed in 25 mL of 70% AcOH for 1.5 h. The resultant solid was filtered and dried thoroughly after washing exhaustively with water and MeOH, 0.65 g. TGA showed a 10% weight loss at 491 °C (i.e., *an increase of 233 °C* relative to 8). It was insoluble in any solvent that was tried, including toluene, DMF, acetone, and THF. FTIR (cm$^{-1}$): 1668 (carbonyl), 1594, 1500 (phenyl) and 1328, 1164 ($SO_2$). The first heating in DSC showed a $T_g$ of 199 °C, a crystallization exotherm at 266 °C, and an (endothermic) melting transition at 415 °C. After cooling at 10 °C/min, the second heating displayed a $T_g$ of 228 °C and a melting peak at 414 °C. When heated after quench cooling, only a $T_g$ at 225 °C was discernible. Wide-angle X-ray analysis was indicative of semicrystallinity in the polymer as isolated from the reaction mixture (Figure 5).

**Polymerization of Bis(4-fluorophenyl) Sulfone and *α,α'*-Dicyano-*α,α'*-bis(*N*-morpholino)-*m*-xylene (7) To Form Poly(*α*-aminonitrile) 11.** To a solution of 3.6608 g (11.216 mmol) of α,α'-dicyano-α,α'-bis(*N*-morpholino)-*m*-xylene (7) in 25 mL of dry DMF was added 2.8520 g (11.217 mmol) of bis(4-fluorophenyl) sulfone at ambient temperature in a flame-dried flask under $N_2$. The mixture was stirred for 20 min and became completely homogeneous at room temperature. Upon the addition of 1.04 g (24.5 mmol) of 60% NaH, a vigorous bubbling and an immediate color change to pale yellow and then yellow-green were seen. After 24 h, the color of the reaction mixture was brown. The temperature was raised to 50 °C and the stirring was continued. The color changed to a pale orange in 0.5 h and was pale honey after 24 h of stirring at 50 °C. The temperature was then raised to 72 °C and stirring was continued for 24 h, at the end of which an increase in the solution viscosity was evident. The solution was quenched in ice cold 5% aqueous NaCl to yield, after drying, 6.1 g (100%) of a pale yellow solid. Purification was done by dissolving it in DMF and precipitation into water. Then it was twice precipitated from a $CHCl_3$ solution into ice cold methanol. It was dried in a vacuum oven at 50 °C overnight. TGA: 10% weight loss (in air) at 298 °C. FTIR (cm$^{-1}$): 1678 (weak, CO), 1591 (aromatic C=C), 1452 (methylene scissor), 1331, 1158 (sulfone) and 1114 (C–O–C). $^1$H NMR ($CDCl_3$): $\delta$ 7.95 (s, 1H, H-1), 7.80 (d, 4H, H-10), 7.55 (d, 2H, H-3), 7.88 (m, 1H, H-4), 4.0–3.5 (br s, 8H, H-8), 2.7–2.2 (br s, 8H, H-7). $^{13}$C NMR ($CDCl_3$): $\delta$ 144.27 (C-12), 141.44 (C-9), 139.22 (C-2), 130.66 (C-4), 128.88 (C-11), 127.25 (C-10 and C-3), 123.96 (C-1), 115.35 (C-5), 75.29 (C-6), 66.52 (C-8), and 49.38 (C-7). DSC showed a relatively large exotherm at 278 °C, indicative of some reaction, on the first heat. On the second heat, the maximum of the exotherm had shifted beyond the range of heating (i.e., at ca. 370 °C). Absolute molecular weight determination by GPC yielded an $M_n$ of $3.23 \times 10^4$ and an $M_w$ of $4.40 \times 10^4$.

**Poly(sulfonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl-*p*-phenylene) (12).** A suspension of 0.50 g of 11 was refluxed in 20 mL of 70% AcOH and 5 mL of HCl for 2 h. The solid was filtered and dried thoroughly after washing exhaustively with water and MeOH, 0.32 g (100%). FTIR (cm$^{-1}$): 1675, 1663 (carbonyl), 1328, 1155 ($SO_2$) and 704 (meta-disubstituted benzene). $^1$H NMR (DMSO-$d_6$): $\delta$ 8.17 (d, 8H, H-11), 8.14 (s, 1H, H-1), 8.00 (d, 2H, H-3), 7.95 (d, 4H, H-10), and 7.69 (m, 1H, H-4). A pair of small doublets at 8.25 and 8.05 ppm was also detected. $^{13}$C NMR (DMSO-$d_6$): $\delta$ 194.20 (C-6), 143.92 (C-12), 141.46 (C-9), 136.65 (C-2), 134.61 (C-3), 131.37 (C-10), 131.31 (C-1), 129.78

(C-4), and 128.88 (C-11). TGA showed a 10% weight loss at 552 °C (i.e., *an increase of 254 °C* relative to **11**). DSC showed a $T_g$ of 188 °C on the first heat and a $T_m$ of 446 °C. On the second heat, a $T_g$ of 208 °C and a $T_m$ of 458 °C were obtained.

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