Chapter 4

Synthesis of wholly Aromatic Polyketones without Ether Linkages by Soluble Precursors Derived from Bis(α-aminonitrile)s

3.1 Introduction

As discussed in Chapter 1, PAEKs are an important class of high performance thermoplastic polymers.[1] One of the important properties of PAEKs is the crystallinity contributed, at least in part, by the keto functionality in the polymer backbone. In contrast to amorphous engineering plastics such as poly(ether sulfone)s, PAEKs are usually crystalline and resistant to chemical solvents. However, it is the crystallinity and the resulting insolubility combined with high melting points, which lead to synthetic and processing difficulties.

PAEKs are usually synthesized by the nucleophilic aromatic substitution of activated dihalides and bisphenolates, or by the electrophilic aromatic substitution (Friedel-Crafts acylation) of arylene ethers. The major problem with these two synthetic routes is the insolubility of the polymeric product that requires the use of harsh reaction conditions in order to obtain high molecular weight. To address the solubility problem, several approaches by soluble precoursor polymers have been reported.[2,3,4,5,6] A polymerization reaction based on

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[1] Staniland, P. A. Poly(ether ketone)s. In *Comprehensive Polymer Science*; Allen, G.; Bevington, J. C., Eds.; Pergamon Press: New York, **1989**; Vol. 5, pp 484-497.

[2] Mohanty, D. K.; Lin, T. S.; Ward, T. C.; McGrath, J. E. *Int. SAMPE Symp. Exp.* **1986**, 31, 945.

[3] Risse, W.; Sogah, D. Y. *Macromolecules* **1990**, 23, 4029.

[4] Kelsey, D. R.; Robeson, L. M.; Clendinning, R. A. *Macromolecules* **1987**, 20, 1204.

the cross coupling of bisstannanes and diacid chlorides was reported to produce high molecular weight aromatic polyketones without ether linkages; however, alkyl substituents in the aromatic rings had to be used to address the solubility problem and obtain high molecular weight polymers.[7]

This chapter describes the synthesis of high molecular weight wholly aromatic polyketones and poly(ketone sulfone)s without ether linkages or alkyl sustituents in the aromatic rings.

4.2 Results and Discussion

4.2.1 Synthesis and Characterizations of Poly(ketone ketone sulfone) (4.3)

A. Bis(α-aminonitrile)s from Dialdehydes

α-Aminonitriles can be easily synthesized from aldehydes and secondary amines in high yields by the Strecker reaction.[8,9] The cabanions of α-aminonitriles are selective and powerful nucleophiles which can displace activated halides to form carbon-carbon bonds.[8] Hydrolysis of aminonitriles under acidic conditions reforms the carbonyl group. Bis(α–aminonitrile)s **4.1a** and **4.1b** were synthesized by the aqueous one-pot method of the Strecker synthesis in high yields (Scheme 4.1). The proton NMR spectrum (Figure 4.1) of compound

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[5] Mohanty, D. K.; Lowery, R. C.; Lyle, G. D.; McGrath, J. E. *Int. SAMPE Symp. Exp.* **1987**, 32, 408.

[6] Phillips, R. W.; Sheares, V. V.; Samulski, E. T.; DeSimone, J. M. *Macromolecules* **1994**, 27, 2354.

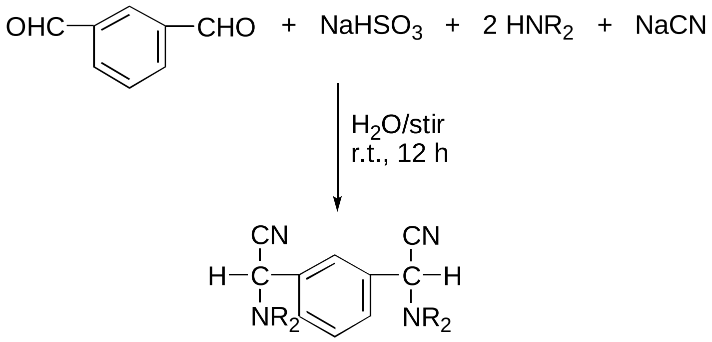
[7] Deeter, G. A.; Moore, J. S. *Macromolecules* **1993**, 26, 2535.

[8] McEvoy, F. J.; Albright, J. D. *J. Org. Chem.* **1979**, 44, 4597.

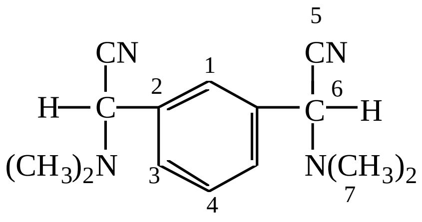
[9] Pandya, A.; Yang, J.; Gibson, H. W. *Macromolecules* **1994**, 27, 1367.

4.1b showed a methyl singlet at 2.35 ppm and the methine proton signal at 4.83 ppm in the aliphatic region and three signals in the aromatic region. The IR spectrum and elemental analysis were consistent with the structure. The ^{13}C NMR spectrum of compound **4.1a** showed two signals for every carbon due to its diastereomeric nature. However, the ^{13}C NMR spectrum of purified compound **4.1b** showed only one signal for each carbon, probably as a result of fractionation during purification by recrystallization. Each carbon was assigned according to the APT (Attached Proton Test,) and ^{1}H-^{13}C HETCOR (HETeronuclear CORrelation, Figure 4.2) spectra.

Scheme 4.1



4.1a: R_2=-$CH_2CH_2OCH_2CH_2$-
4.1b: R = CH_3



4.1b

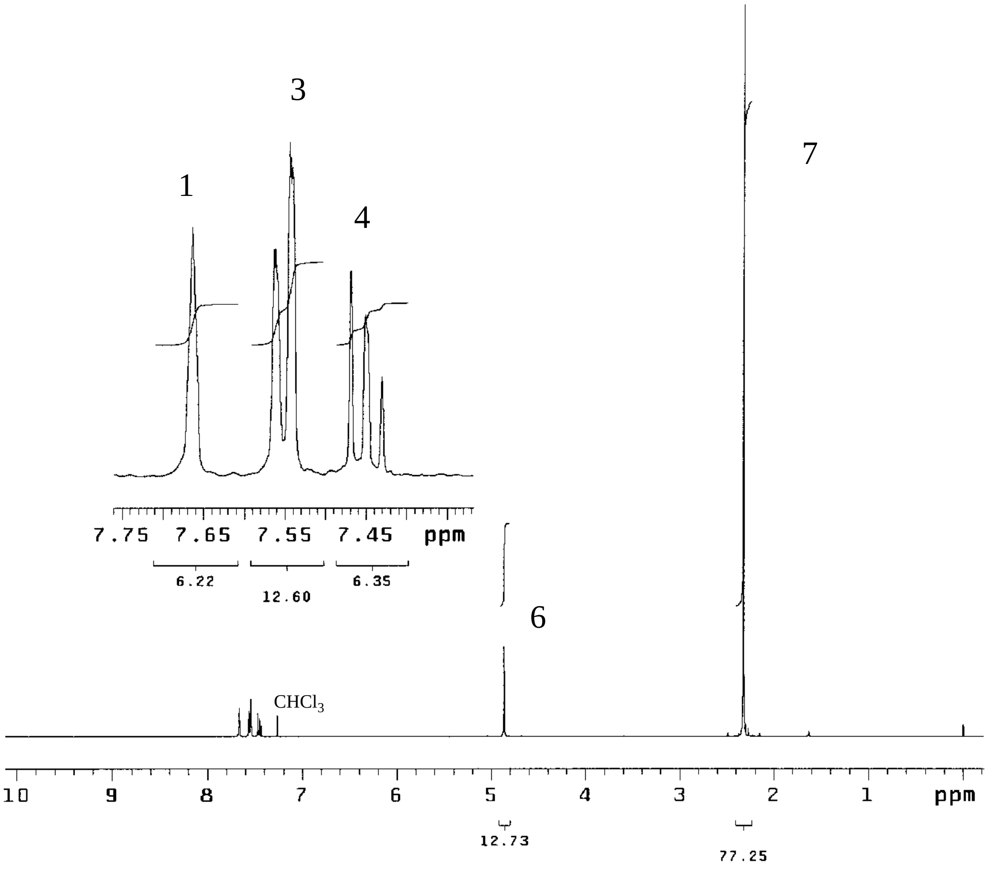


Figure 4.1 400MHz ^{1}H NMR Spectrum of Compound **4.1b** in CDCl$_3$.

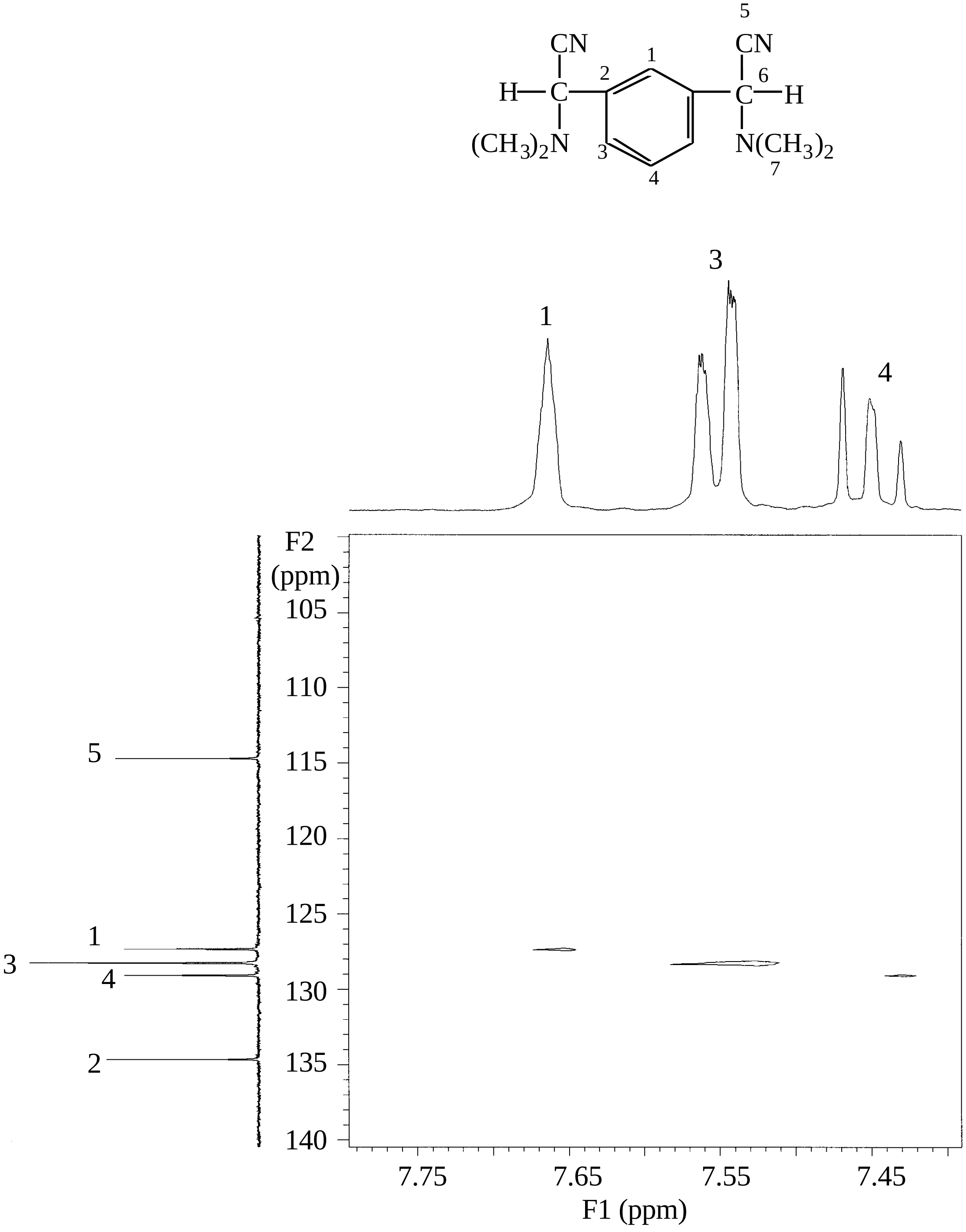
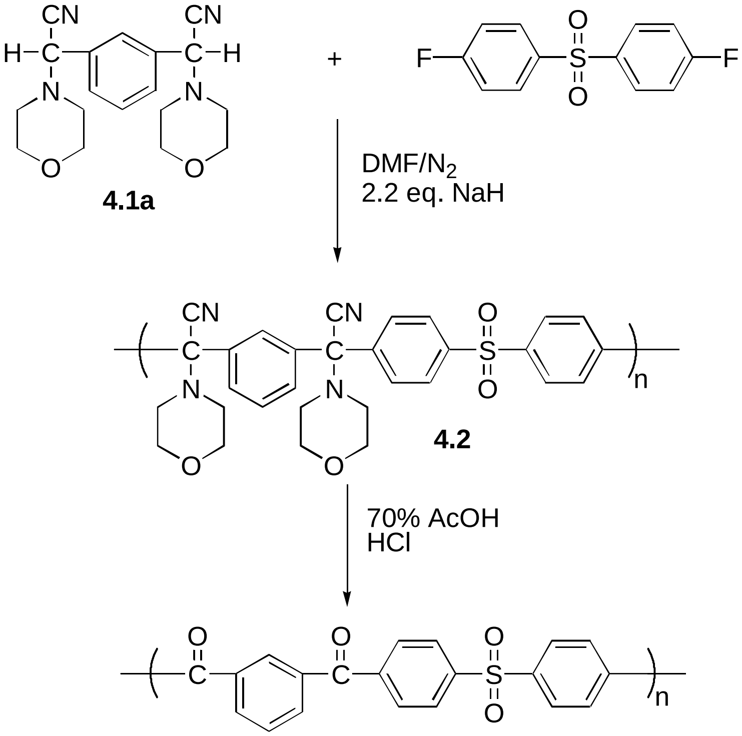


Figure 4.2 400 MHz ^{1}H-^{13}C HETCOR spectrum of compound **4.1b** in CDCl$_3$.

B. Synthesis of Poly(ketone ketone sulfone) (4.3)

As discussed in Chapter 2, Pandya[9] used bis(α–aminonitrile) **2.5** to polymerize with bis(*p*-fluorophenyl) sulfone in DMF using NaH as base. High molecular weight polymer could not be obtained due to a side reaction. The intramolecular decyanation can be eliminated if bis(α–aminonitrile) **4.1a** with a *meta* linkage is used. When **4.1a** was condensed with bis(*p*-fluorophenyl) sulfone in dimethylformamide (DMF) under N_2, polymer **4.2** was readily obtained with a M_n of 32.3 kg/mol and M_W of 44.0 kg/mol (absolute GPC, NMP, 60 °C).[9] **4.2** was soluble in common moderate polarity solvents like THF, acetone and chloroform.[9]

Scheme 4.2

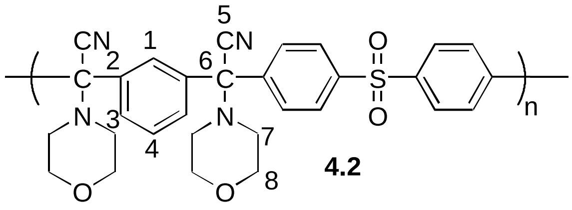


Hydrolysis of polyaminonitrile **4.2** to poly(ketone ketone sulfone) (**4.3**) was carried out in refluxing 30% aqueous acetic acid. Only partial hydrolysis was achieved. The ^{1}H

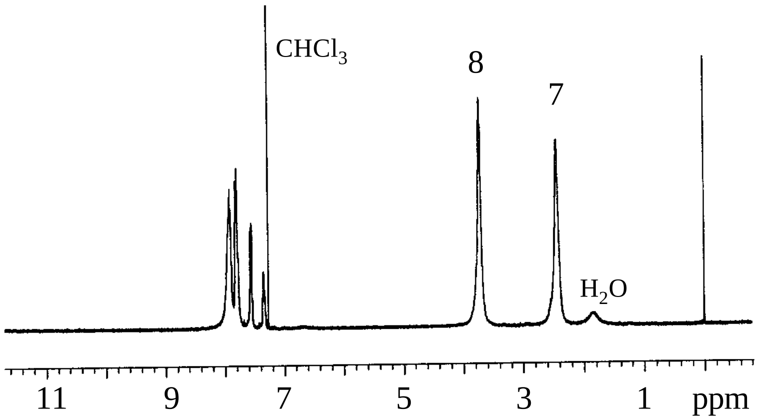
NMR spectrum of polymer **4.3** showed residual peaks in the aliphatic region corresponding to the morpholino groups.[9]

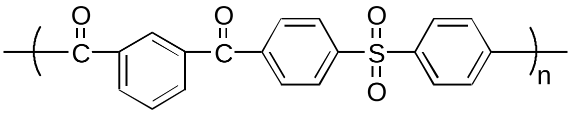
Following the same procedure, in the present study polymer **4.2** was prepared from **4.1a** and bis(*p*-fluorophenyl) sulfone in DMF using 2.2 equivalents of NaH as base. The ^{1}H NMR spectrum (Figure 4.3) and IR spectrum (Figure 4.4) are consistent with the structure of the polymer. The ^{1}H NMR spectrum of **4.2** showed two multiplets in the aliphatic region corresponding to the morpholino group. The aromatic protons were assigned by the COSY spectrum (Figure 4.5). The structure of **4.2** was also confirmed by the ^{13}C NMR spectrum (Figure 4.6) and the ^{1}H-^{13}C HETCOR spectrum (Figure 4.7). GPC analysis (absolute, NMP, 60 °C) indicated an M_n of 22.2 kg/mol and an M_w of 42.6 kg/mol.

Aminonitrile **4.1a** was also condensed with bis(4-chlorophenyl) sulfone at room temperature in DMF with sodium hydride as base. When the solution was quenched into water and methanol, a pale yellow solid **4.2** was obtained in 99% yield. The ^{1}H NMR and IR spectra are the same as those of **4.2** from bis(4-fluorophenyl) sulfone. The GPC (absolute, NMP, 60 °C) analysis indicated an M_n of 12.9 kg/mol and an M_w of 20.3 kg/mol were obtained.



4.2





4.3

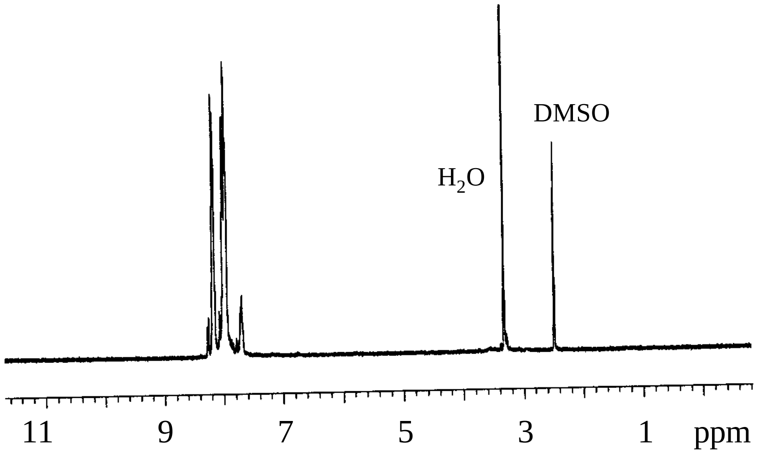


Figure 4.3 400 MHz ^{1}H NMR spectra of **4.2** in $CDCl_3$ and **4.3** in DMSO-d_6.

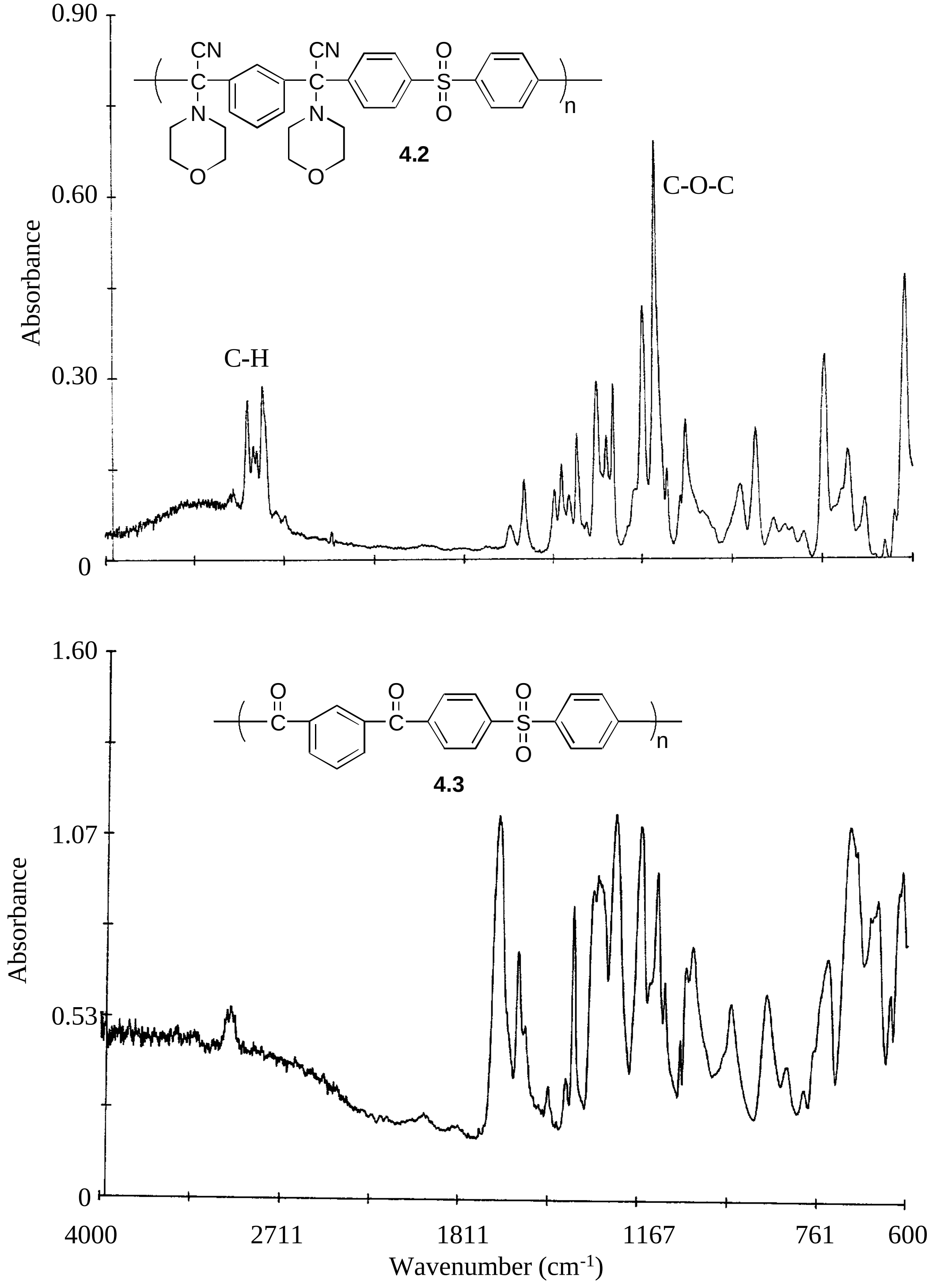


Figure 4.4 FTIR spectra of polymers **4.2** and **4.3** (KBr).

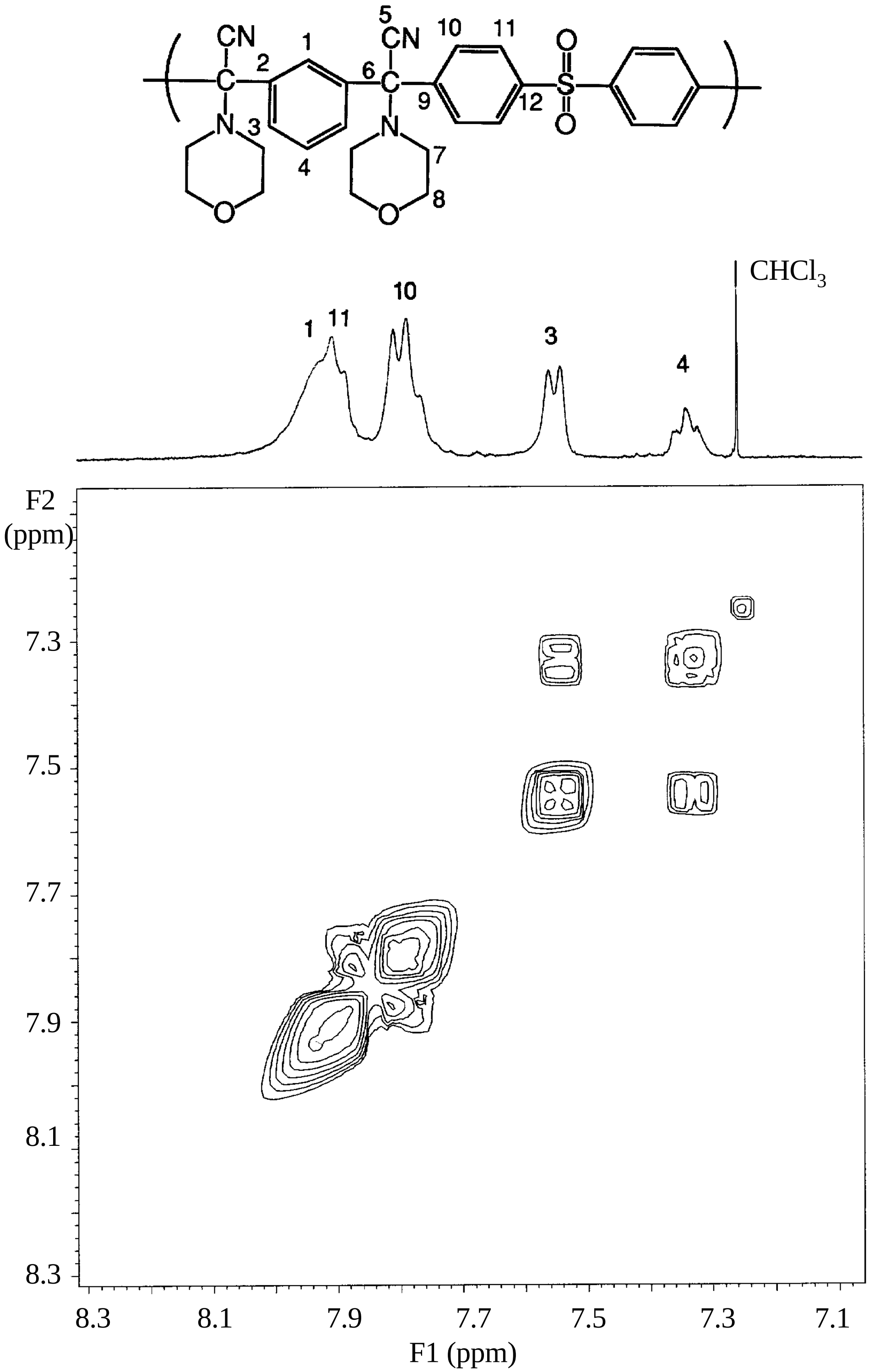


Figure 4.5 400 MHz ^{1}H-^{1}H COSY spectrum of polymer **4.2** in $CDCl_3$.

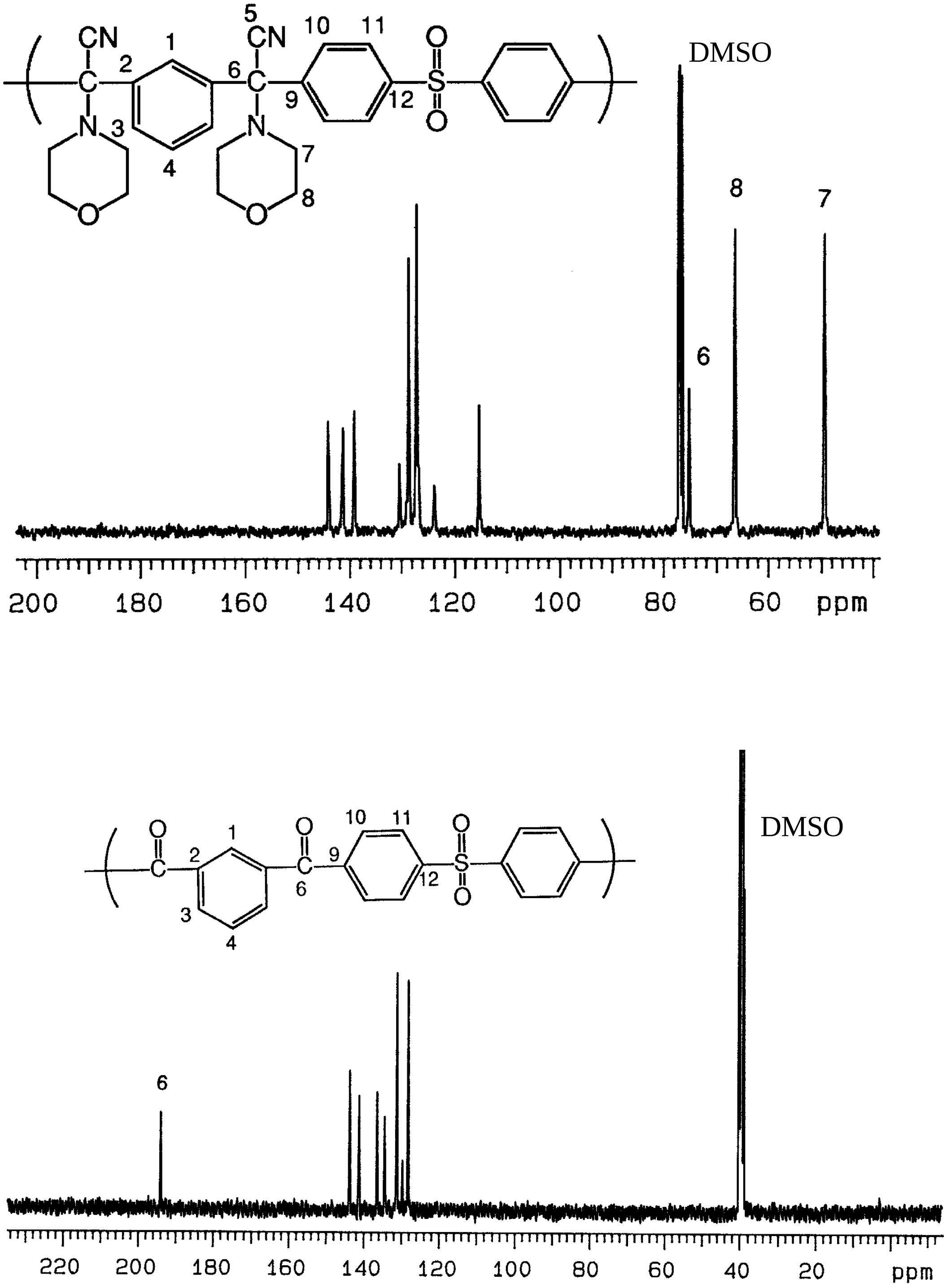


Figure 4.6 100 MHz ^{13}C NMR spectra of **4.2** in CDCl$_3$ and **4.3** in DMSO-d$_6$.

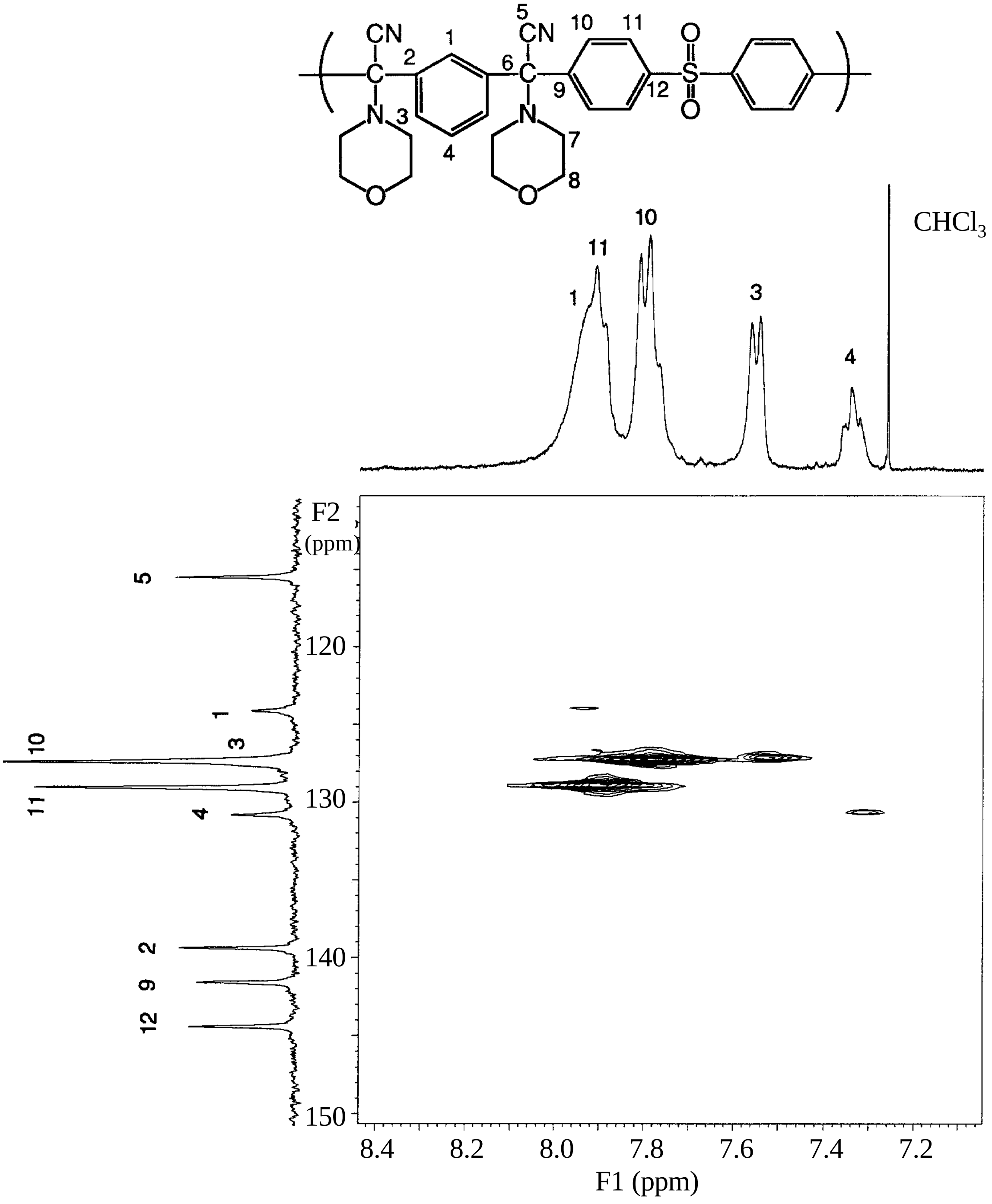
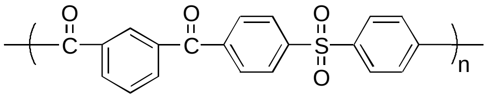


Figure 4.7 ^{1}H-^{13}C 2D-HETCOR spectrum of polymer **4.2** in CDCl$_3$.

Hydrolysis of **4.2** was carried out in refluxing 70% aqueous acetic acid and hydrochloric acid mixture. In contrast to **4.2**, the hydrolysis product **4.3** was insoluble in common moderate polarity solvents such as THF, acetone and chloroform; it was slightly soluble in polar solvents such as DMF, DMSO, NMP, etc. The reason for the vast solubility difference lies in the absence of the polar, symmetric and planar carbonyl moiety in **4.2** and also due to the heterotacticity of the tetrahedral stereogenic centers at the carbons bearing the aminonitrile moietiesin **4.2**. Complete hydrolysis was achieved. This is supported by the absence of absorbances characteristic of the C-O-C and aliphatic C-H stretches of the morpholino moieties in the FTIR spectrum (Figure 4.4); and the ^{1}H NMR spectrum (Figure 4.3) shows no signals in the aliphatic region corresponding to the morphino group. The ^{13}C NMR spectrum of **4.3** also showed the signal of carbonyl carbon at 192.4 ppm and the removal of morpholino and cyanide groups (Figure 4.6). The structure of **4.3** was further confirmed by the COSY spectrum and the ^{1}H-^{13}C HETCOR spectrum.

Complete hydrolysis of polymer **4.2** to **4.3** was also achieved in concentrated sulfuric acid at 80 °C. The ^{1}H NMR spectrum of the hydrolysis product shows no signals in the aliphatic region corresponding to the morpholino groups.

When **4.2** was analyzed thermogravimetrically at 10 °C/min heating rate, the 5% weight loss in air was detected at 265 °C and that increased by 244 ° to 509 °C when **4.2** was hydrolyzed to **4.3**. It is generally accepted that poly(ether sulfone)s do not crystallize from the melt due to the asymmetric structure of the sulfone groups, while PAEKs crystallize readily on cooling from the melt due to the planar, symmetric and polar carbonyl moieties. This poly(ketone ketone sulfone) contains two carbonyl groups and one sulfone group in each repeat unit. When **4.3** was analyzed calorimetrically (Figure 4.8), 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 broad endothermic transition peak at 458 °C were obtained. This is a good "crystallization window" with such a large temperature difference between T_g and T_m.



4.3

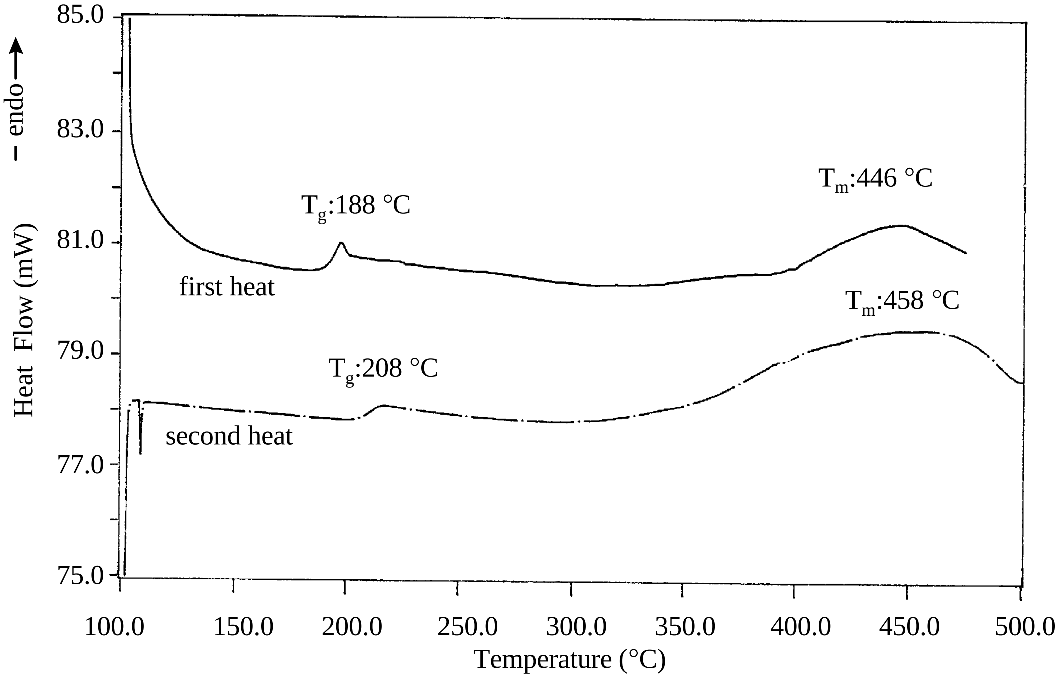


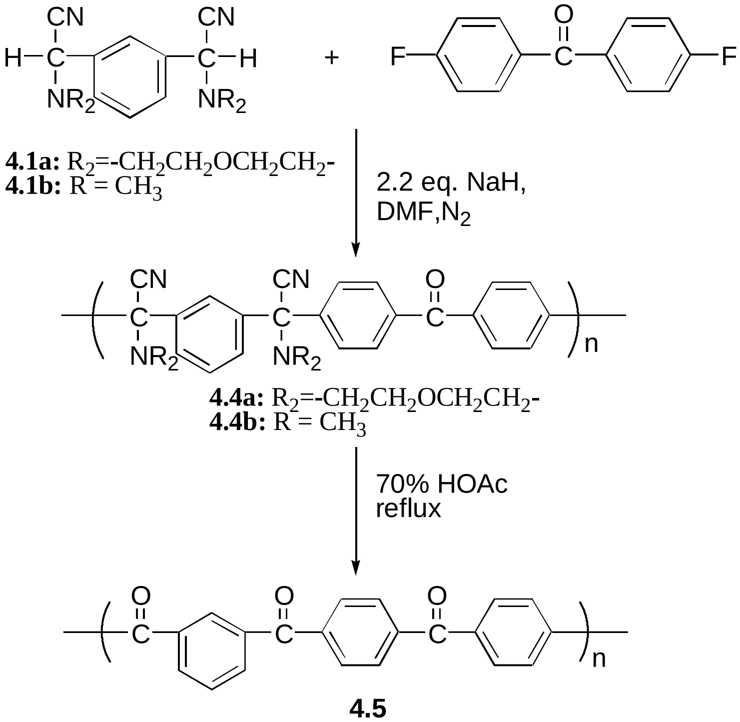
Figure 4.8 DSC traces of polymer **4.3** (10 °C/min).

4.2.2 Synthesis and Characterization of Wholly Aromatic Polyketone without Ether Linkages

A. Polyaminonitrile Synthesis

Bis(α–aminonitrile) **4.1a** was polymerized via its anion with 4,4'-difluorobenzophenone in DMF using sodium hydride as base at room temperature (Scheme 4.3). The resultant polymer **4.4a** was soluble in common organic solvents such as THF, chloroform, acetone, etc. GPC analysis indicated a bimodal distribution (absolute GPC, NMP, 60 °C, Figure 4.9). The low molecular weight fraction is possibly due to cyclic species favored by the *meta* linkage of the isophthalaminonitrile. The number average molecular weight, M_n, and the weight average molecular weight, M_w, estimated for the polymer not including the low molecular fraction were 43.2 kg/mol and 89.8 kg/mol, respectively. The calculations including the low molecular fraction indicated an M_n of 16.7 kg/mol and an M_w of 59.1 kg/mol, with a polydispersity of 3.54. Most of the low molecular weight fraction was removed by Soxhlet extraction with ethanol. GPC analysis of this polymer after extraction indicated an M_n of 27.0 kg/mol and an M_w of 63.1 kg/mol, with a polydispersity of 2.34 (Figure 4.9). According to the elemental analysis results of this polymer, the average number of repeat units ($\bar{n}$) is approximately 50, which corresponds to a number average molecular weight of 25.2 kg/mol, in good agreement with the GPC results.

Scheme 4.3


CN
CN
H
C
C
H
NR2
NR2
+
F
O
C
F
4.1a: R2=-CH2CH2OCH2CH2-
4.1b: R = CH3
2.2 eq. NaH,
DMF,N2
CN
CN
C
C
O
C
NR2
NR2
n
4.4a: R2=-CH2CH2OCH2CH2-
4.4b: R = CH3
70% HOAc
reflux
O
O
O
C
C
C
n
4.5

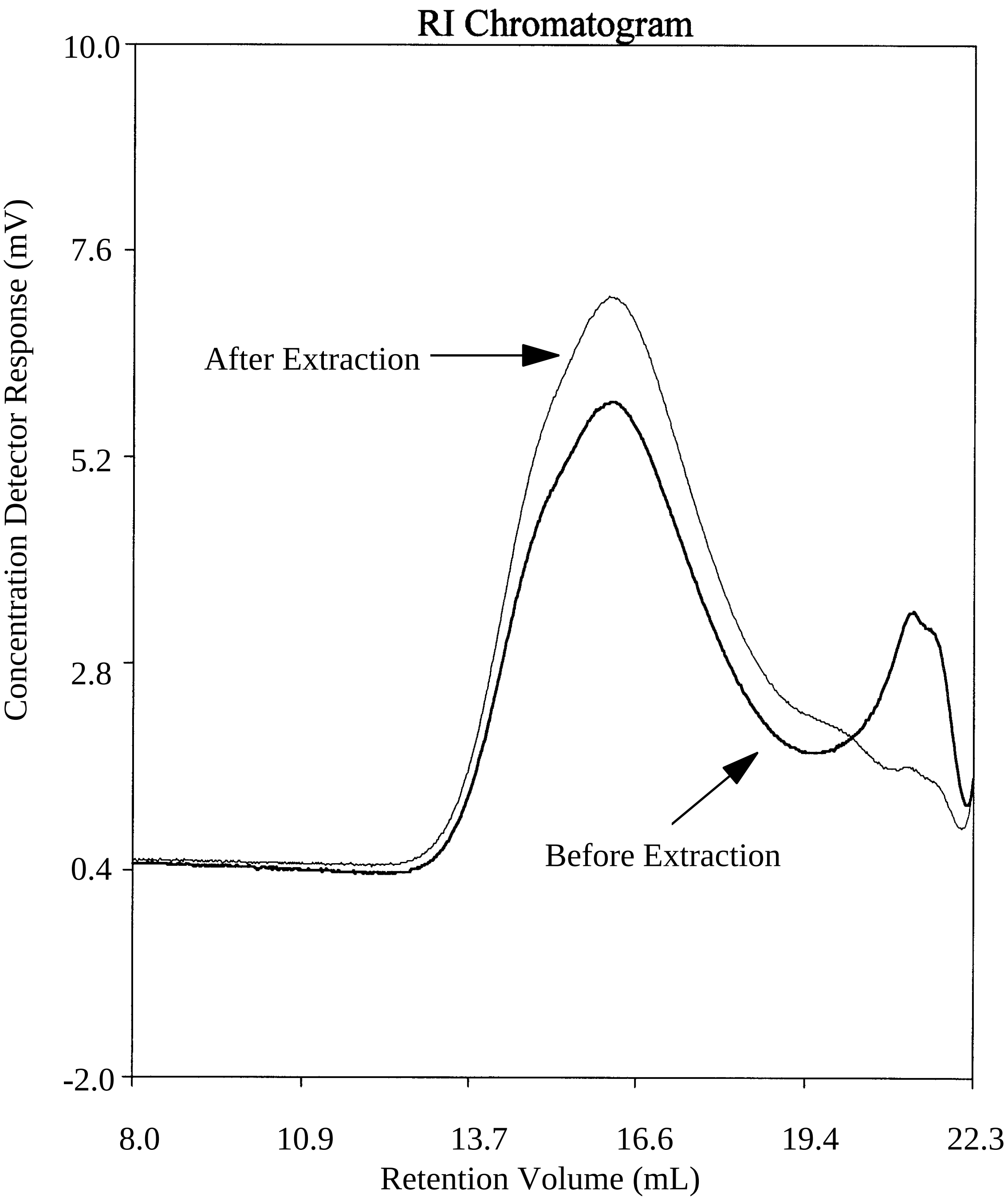


Figure 4.9 GPC traces (NMP, 60 °C, 1 mL/min, RI detector) of polymer **4.4a**.

The IR spectrum of polyaminonitrile **4.4a** showed aliphatic C-H stretches at 2963 and 2851 cm^{-1}, a strong carbonyl absorbance at 1668 cm^{-1} and the C-O-C stretches of the morpholino groups at 1118 cm^{-1} (Figure 4.10). The ^1H NMR spectrum (Figure 4.11) of **4.4a** showed only two broad signals in the aliphatic region at about 2.5 and 3.8 ppm corresponding to the methylene protons of the morpholino units. No methine proton signal (4.8 ppm) was detected. The protons in the aromatic region were assigned by the 2D-COSY spectrum. The ^{13}C NMR (APT) spectrum showed a carbonyl signal at 194.32 ppm, nitrile carbon signal at 115.84 ppm and three signals in the aliphatic region corresponding to the morpholino and quaternary carbons. The rest of the carbon atoms in the aromatic region were assigned according to the ^1H-^{13}C HETCOR spectrum (Figure 4.12). The doubling of C-1 is consistent with the presence of both *meso* and *racemic* structures.

Bisaminonitrile **4.1b** was polymerized with 4,4’-difluorobenzophenone at lower temperature (0-10°C) and higher concentration (Scheme 4.3). Compared with polymer **4.4a**, polymer **4.4b** had a smaller low molecular weight fraction and the low molecular weight fraction was easier to remove by Soxhlet extraction using ethanol as solvent. According to GPC (absolute, NMP, 60 °C), an M_n of 16.1 kg/mol and an M_w of 32.9 kg/mol were obtained after extraction. The elemental analysis results of this polymer agree well with the structure and the molecular weight data. Polymerization of **4.1b** with 4,4’-difluorobenzophenone using a 1:0.995 mole ratio, respectively, under the same conditions gave similar results; GPC analysis gave an M_n of 15.8 kg/mol and an M_w of 28.0 kg/mol after extraction.

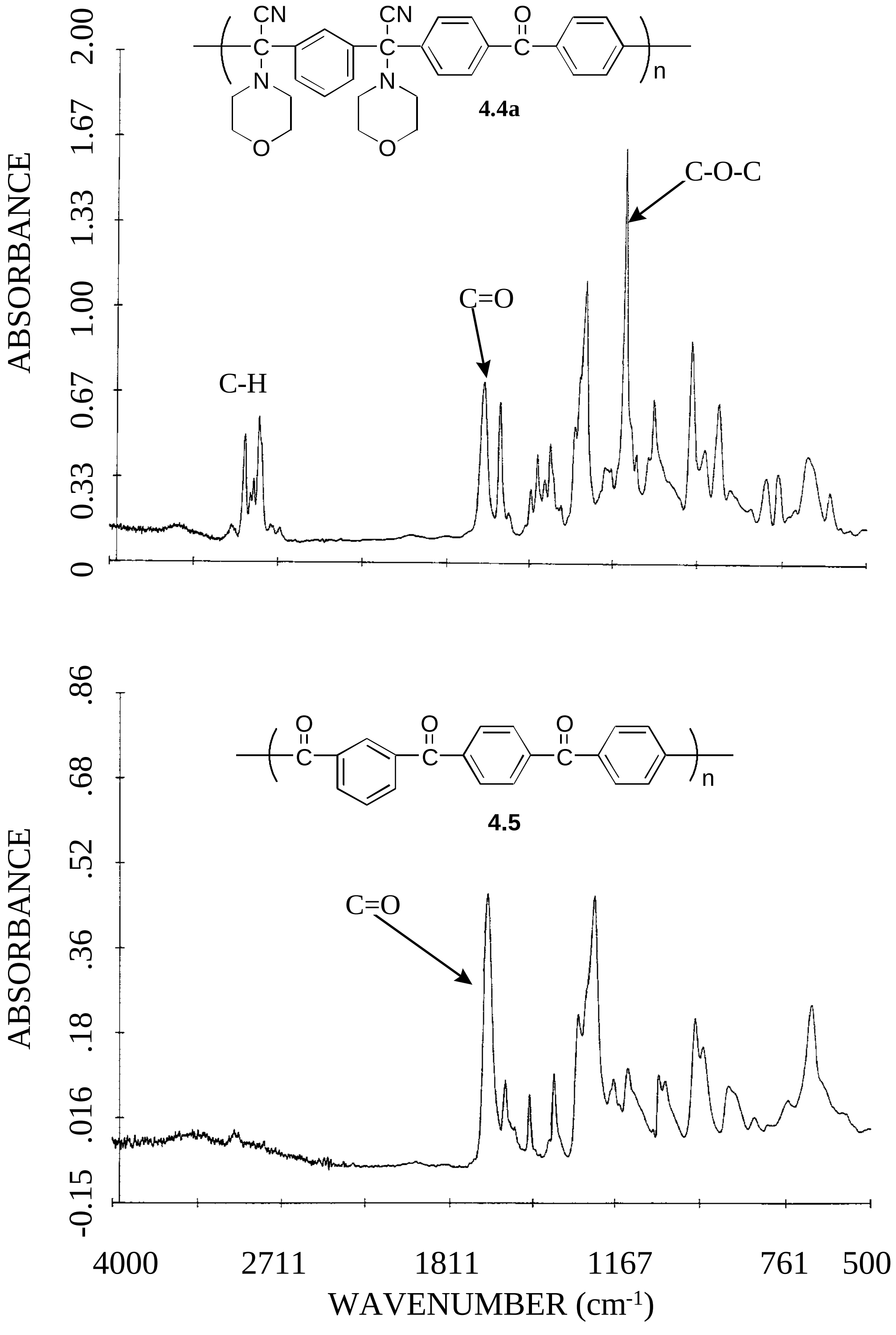


Figure 4.10 FTIR spectra of polymers **4.4a** and **4.5** (KBr).

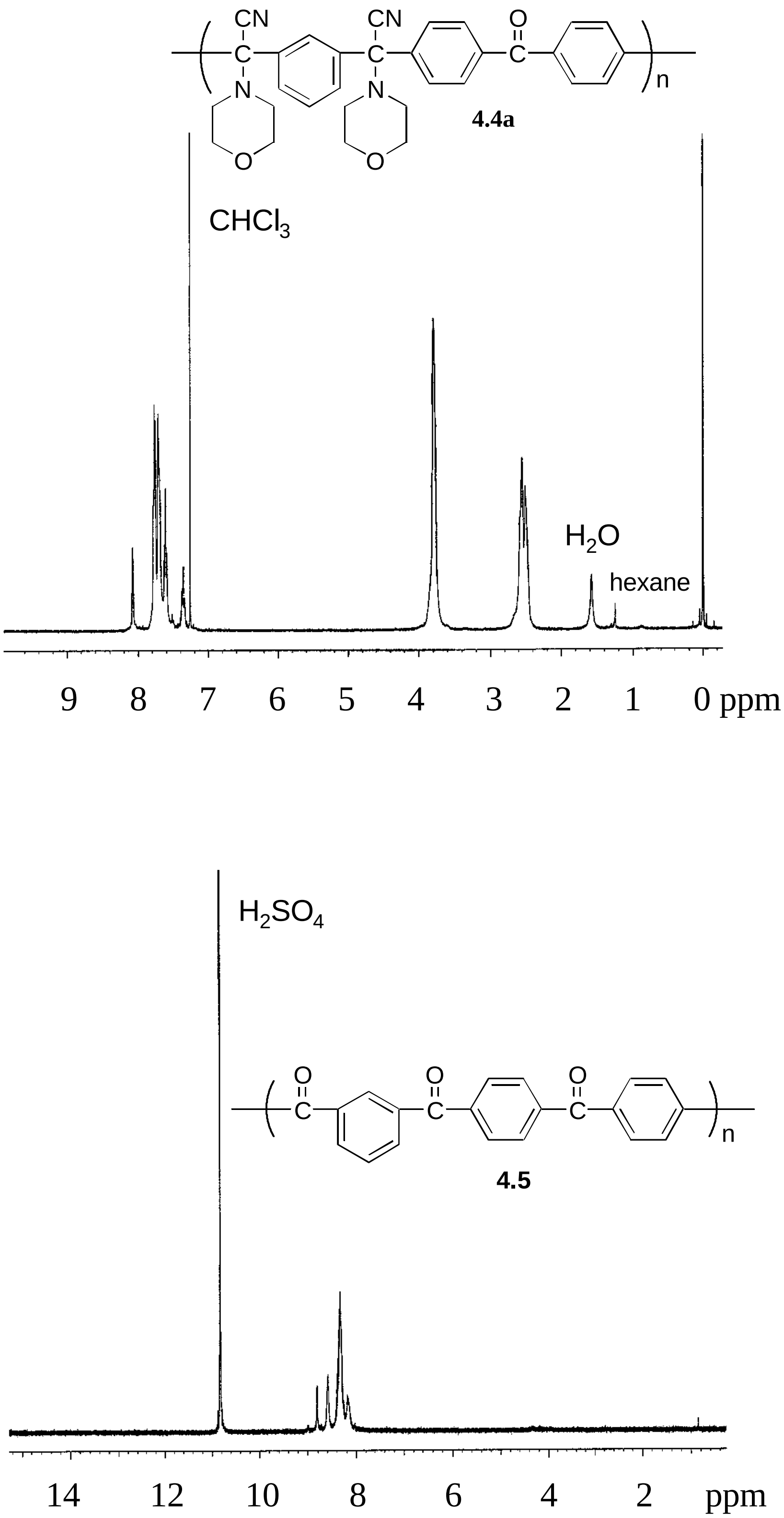
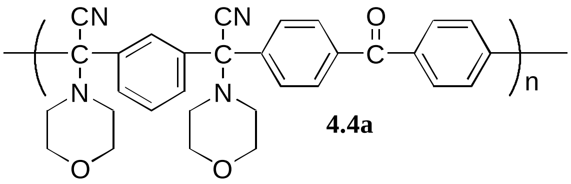


Figure 4.11 400 MHz ^{1}H NMR spectra of **4.4a** in $CDCl_3$ and **4.5** in D_2SO_4.



4.4a

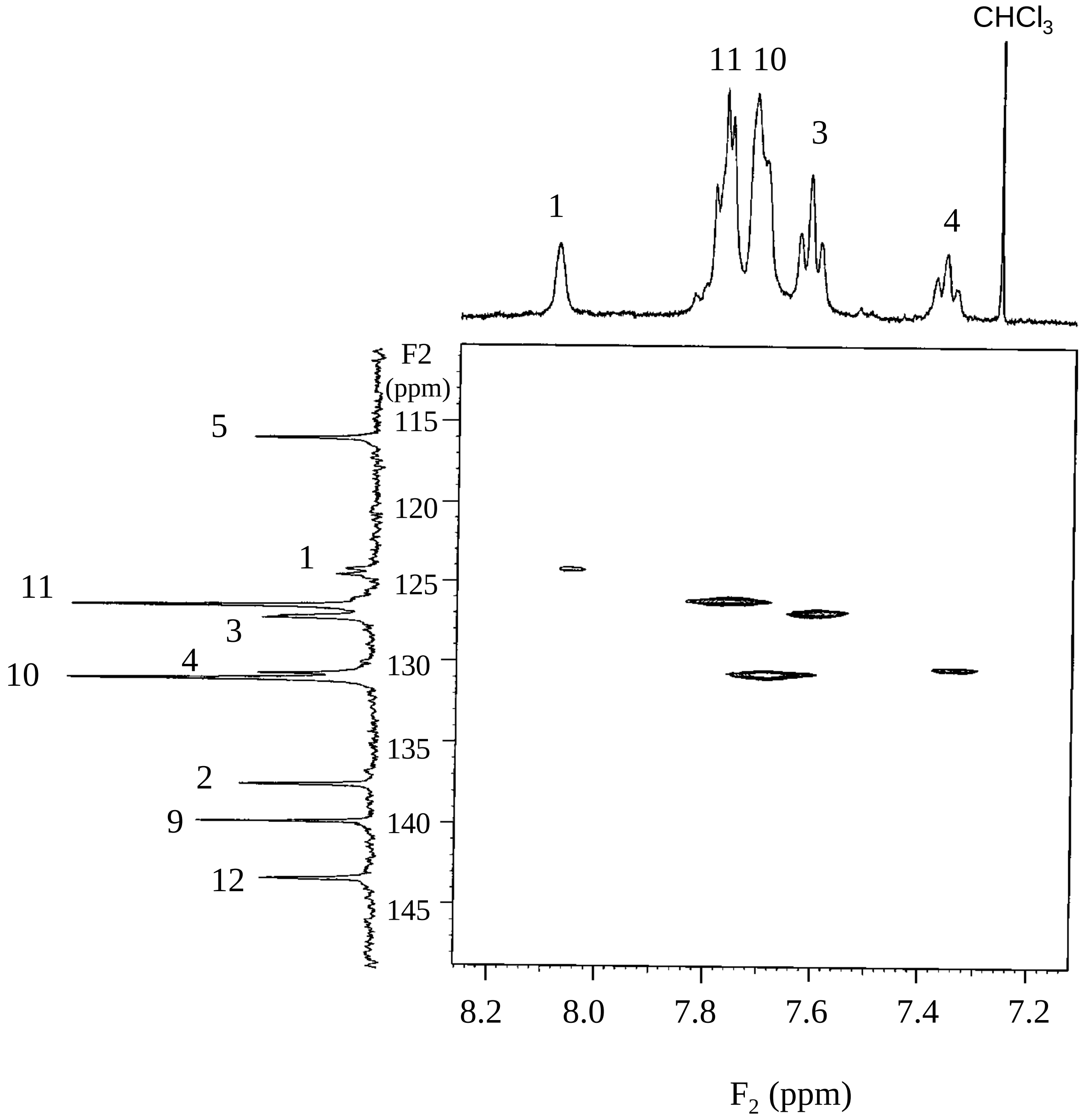


Figure 4.12 ^{1}H-^{13}C 2D-HETCOR spectrum of polymer **4.4a** in $CDCl_3$.

Bisaminonitrile **4.1a** was polymerized with 4,4’-dichlorobenzophenone using NaH as base. The procedural details are the same as those of polymer obtained from **4.1a** and 4,4'-difluorobenzophenone. The GPC in $CHCl_3$ (PS standards) showed M_n = 11.4 kg/mol and M_w = 20.4 kg/mol.

B. Hydrolysis: A Wholly Aromatic Polyketone without Ether Linkages

Hydrolysis of polymer **4.4a** with 70% aqueous acetic acid and concentrated HCl afforded wholly aromatic polyketone **4.5** (Scheme 4.3). In contrast to precursor polymer **4.4a**, this polyketone was not soluble in common organic solvents such as THF, chloroform, DMSO, DMAc, NMP, etc. It was only soluble in very strong acids, such as concentrated sulfuric acid. The main reason for the dramatic difference in solubility between polymers **4.4** and **4.5** is due to amorphous nature of **4.4** caused in part by the atacticity arising from the chiral centers at the carbon atoms of the aminonitrile units and the disorder of **4.4** versus the more rigid, polar, planar carbonyl moieties in **4.5**, which promote crystallinity.

The hydrolysis of aminonitrile units to carbonyl units was complete as shown by the proton NMR and IR spectra. The IR spectrum of polymer **4.5** showed very strong carbonyl absorbance at 1662 cm^{-1} and the absence of aliphatic C-H stretches and C-O-C modes due to the removal of the morpholino groups (Figure 4.10). The proton NMR spectrum of polymer **4.5** in concentrated D_2SO_4 showed no signals in the aliphatic region that also indicated the removal of the morpholino groups (Figure 4.11). All the proton signals were shifted downfield due to the protonation of the carbonyl groups under the strongly acidic conditions. The COSY spectrum is consistent with the structure of polymer **4.5**. Hydrolysis of polymer

4.4b also gave polyketone **4.5**. The ^{1}H NMR spectrum of the product was the same as that from polymer **4.4a**.

Thermogravimetric analysis of polyaminonitrile **4.4a** in air shows a 5% weight loss at 263 °C. Polyketone **4.5** shows a 5% weight loss at 501 °C (Figure 4.13). The DSC trace of polymer **4.5** showed no T_g either in the first heating or the second heating. No melting transition was observed up to 500 °C. However, the wide angle X-ray diffraction pattern of polymer **4.5** shows sharp peaks due to the crystallinity of the polymer (Figure 4.14). The melting point must be > 500 °C.

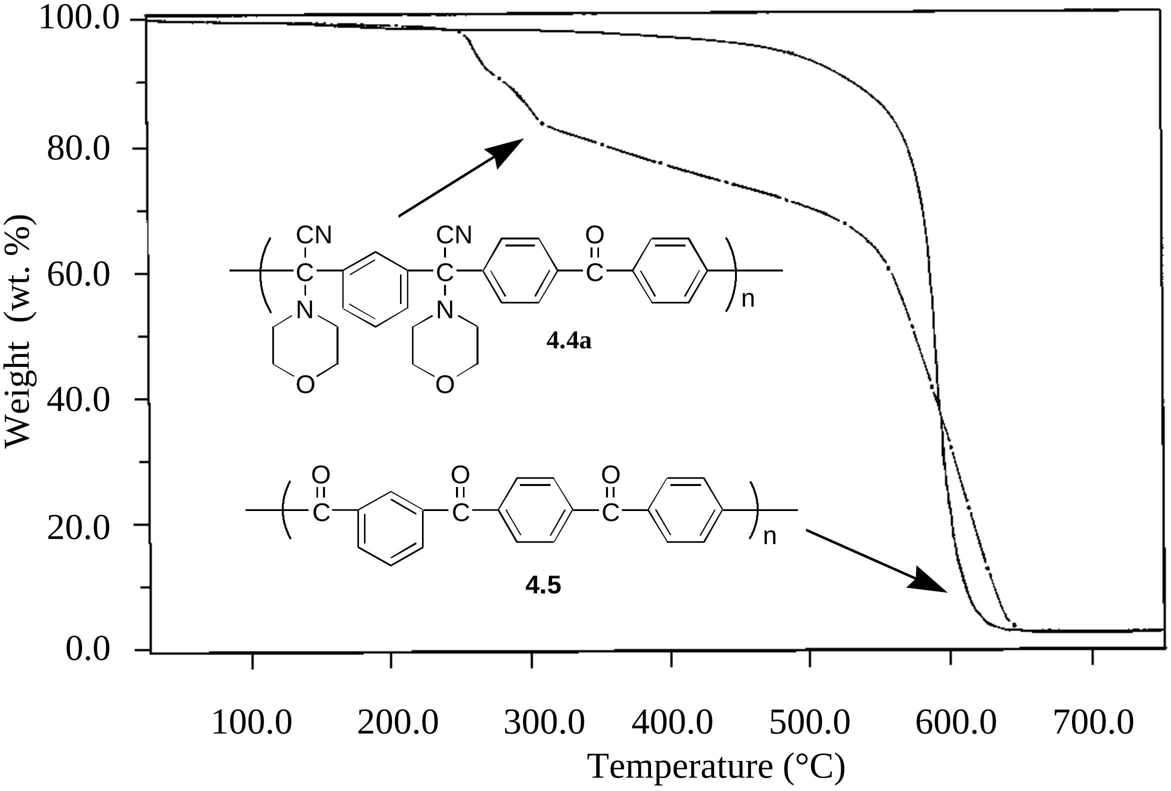


Figure 4.13 Thermogravimetric curves of polymers **4.4a** and **4.5** in air at 10 °C/min.

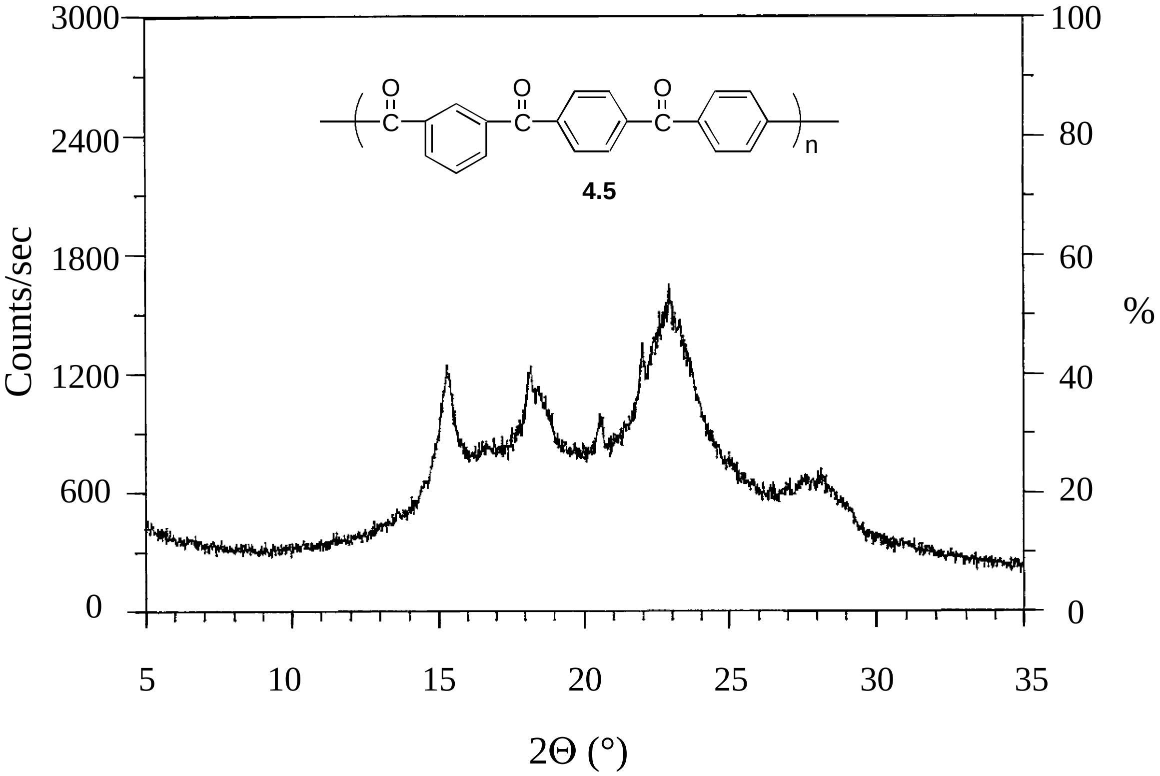


Figure 4.14 Wide angle X-ray diffraction pattern of polymer **4.5**.

4.3 Synthesis of Other Aromatic Polyketones

Polyaminonitriles **4.7a-c** were synthesized in high molecular weight by the condensation of bisaminonitrile **4.1a** with activated aromatic dihalides in DMF using sodium hydride as base at room temperature, as shown in Scheme 4.4. The polyaminonitriles **4.7a-c** contain two chiral centers per repeat unit. They are generally amorphous and soluble in many common organic solvents, such as THF, acetone, DMSO, DMAc, etc. These polymers were also 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 4.1.

Scheme 4.4

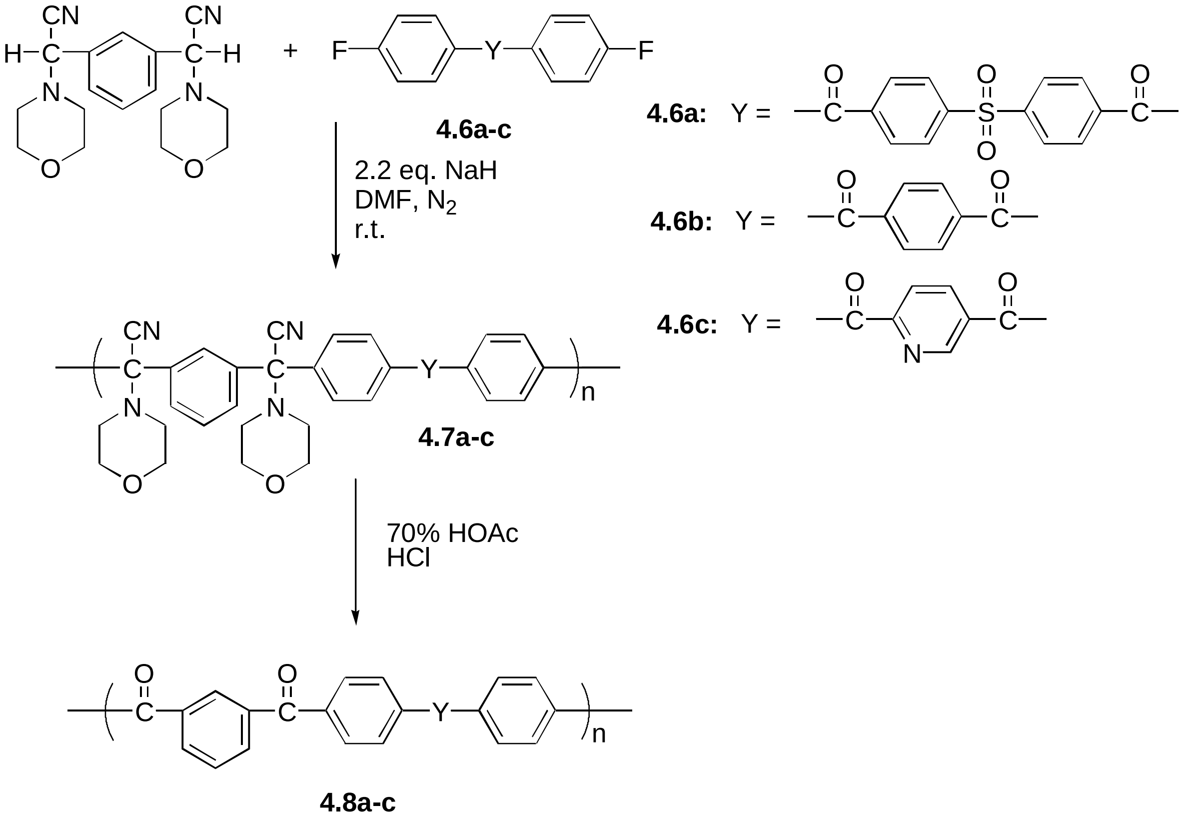


Table 4.1 GPC data of polyaminonitriles (NMP, 60 °C, 1 mL/min)

Polymer	M_n (kg/mol)	M_w (kg/mol)	M_w/M_n
4.2	32.3	44.0	1.36
4.4a	27.0	63.1	2.3
4.7a	17.0	57.1	3.35
4.7b	22.7	31.4	1.38
4.7c	11.6	19.5	1.68

Hydrolysis of these polyaminonitriles in refluxing aqueous acetic acid and hydrochloric acid solution gave corresponding polyketones **4.8a-c**. In contrast to the polyaminonitriles **4.7a-c**, the hydrolysis products **4.8a-c** are insoluble in most common organic solvents such as THF, $CHCl_3$, DMF, NMP, etc. They are only soluble in very a strong acid 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. According to the TGA analysis, these polyketones also display high thermal stability. The TGA and DSC data are summarized in Table 4.2.

Table 4.2 The thermal properties (TGA and DSC) of aromatic polyketones

Polymer	T_g (°C)	T_m (°C)	5% Weight loss in Air (°C)[c]
4.3	208[a]	458[a]	509
4.5	--	>500	501
4.8a	198[b]	>500	495
4.8b	195[b]	>500	514
4.8c	177[a]	386[a]	493

a) Second heating at 10 °C/min

b) First heating at 10 °C/min

c) Heating rate: 10 °C/min

4.4 Conclusions

We have presented a polymerization reaction to synthesize wholly aromatic polyketones and poly(ketone sulfone)s based on condensation of bisaminonitriles and activated dihalides. Soluble, high molecular weight polyaminonitriles were successfully synthesized by condensation of the anions of bisaminonitriles **4.1a** and **4.1b** with activated aryl dihalides under mild reaction conditions. Hydrolysis of the polyaminonitriles yielded the corresponding polyketones, which display excellent thermal stability and chemical resistance. This polymerization method has successfully addressed the solubility problem associated with conventional polyketone syntheses. Moreover, wholly aromatic polyketones without ether linkages or alkyl substituents, e.g., **4.5**, **4.8a-c,** can be synthesized by this approach under mild reaction conditions.

4.4 Experimental

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 hours prior to use. Sodium hydride (60% dispersion in light mineral oil) and anhydrous DMF were purchased from Aldrich and used as received. Melting points were determined using a Haake-Buchler apparatus and are corrected. The proton NMR spectra were obtained on a Varian Unity 400 spectrometer operating at 399.95 MHz and reported in δ units. Tetramethylsilane was used as the internal standard. All ^{1}H COSY (COrrelated SpectroscopY) 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. Zerofilling, 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 (76.9) as solvent and internal standard. FTIR spectra were recorded on a Nicolet MX-1 with KBr pellets. GPC analyses were done with a Waters 150C ALC/GPC system with permagel 10^{2}-10^{6} Angstrom polystyrene-divinylbenzene columns. This instrument was equipped with a Viscotek 100 differential viscometer and differential refractive index detectors. The viscometric data by the universal calibration yielded absolute molecular weights. Thermogravimetric analyses were carried out on a Perkin-Elmer 7700 thermal analysis system at a heating rate of 10 °C/min. Differential scanning calorimetric analyses were performed on a Perkin-Elmer DSC-4 at a scan rate of 10 °C/min in a nitrogen atmosphere. Wide angle X-ray diffraction was carried out on a XDS-200 diffractometer using a PAD V diffraction system.

α,α'-Dicyano-α,α'-bis(*N*-morpholino)-*m*-xylene (4.1a)

To a solution of 10.41 g (100 mmol) of $NaHSO_3$ in 250 mL of H_2O was added 6.84 g (50 mmol) of isophthalaldehyde (98%) and the mixture was stirred for 2 hours until homogenous. Morpholine (8.71 g, 100 mmol) was then added all at once and the solution was stirred for 2 hours. NaCN (4.90 g, 100 mmol) was then added in one aliquot and the flask was transferred to a steam bath where it was heated for 8 hours with occasional stirring. The pale yellow solid was suction filtered and washed with H_2O several times. The dry crude product weighted 16.16 g (99%). It was recrystallized from 95% EtOH twice to give a white powder, mp 143.0-144.6 °C. ^{1}H NMR ($CDCl_3$) δ 7.62, 7.67 (s, diastereomeric protons, 1 H), 7.57 (d, 2 H, J = 8.0 Hz), 7.48-7.43 (m, 1 H), 4.85, 4.84 (s, 1H, diastereomeric methine protons), 3.90-3.70 (m, 8 H). ^{13}C NMR ($CDCl_3$) δ 133.52, 133.51 (CH), 129.37,129.31 (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). FTIR (KBr) 2861, 2831 (C-H stretch), 2228 (CN), 1457 (phenyl), 1116 (C-O-C), 760 (*m*-substitued phenyl) cm^{-1}.

α,α'-Dicyano-α,α'-bis(dimethylamino)-m-xylene (4.1b)

To a 1 L three-necked round bottom flask equipped with a mechanical stirrer were added 25.97 g (193.6 mmol) of isophthalaldehyde, 40.30 g (387.2 mmol) of sodium bisufite and 600 ml of distilled water. The mixture was stirred until it became homogeneous. Then 43.65 g (387.2 mmol) of 40% dimethylamine in water was added to the flask and the stirring was continued until it became homogenous. A solution of 18.98 g (387.2 mmol) of NaCN in water (100 mL) was added dropwise by a dropping funnel. A light yellow gummy material was formed; it solidified after ca. two days. The solid was suction filtered, washed with water and air dried to give 42.23 g (98%) of crude product, with a melting point of 63.0-91.0 °C (diastereomers). Purification was done by dissolving it in 200 mL of methylene chloride and the solution was passed through a short silica gel column. Upon removing the methylene chloride on a rotary evaporator, the oil was washed with a small amount of hexane to give white crystals which were recrystallized from hexane/ethyl acetate three times to give long white needles, mp 96.4-97.1 °C (27.87 g, 66%). FTIR (KBr) 3100-2800 (C-H stretches), 2235 (nitrile), cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 7.66 (s, 1 H, H-1), 7.55 (m, diastereomeric protons, 2 H, H-3), 7.45 (m, 1 H, H-4), 4.86 (s, 2 H, H-6), 2.32 (s, 12 H, H-7). ^{13}C NMR ($CDCl_3$) δ 134.67 (C-2), 129.10 (C-1), 128.27 (C-3), 127.34 (C-4), 114.72 (C-5), 62.78 (C-6), and 41.70 (C-7). Elemental analysis calcd. (found) for $C_{14}H_{18}N_4$: C, 69.39 (69.42); H, 7.48 (7.46); N, 23.12 (23.10).

Polymerization of Bis(*p*-fluorophenyl) Sulfone and Compound 4.1a to Form Polyaminonitrile (4.2)

Compound **4.1a** (3.6608 g, 11.216 mmol) was dissolved along with 2.8520 g (11.217 mmol) of bis(*p*-fluorophenyl) sulfone at room temperature in a flame dried flask in 25 mL of dry DMF under N_2. The mixture was stirred for 20 minutes and became homogenous. Upon addition of 1.04 g (24.5 mmol) of 60% NaH, vigorous bubbling and an immediate color change to yellowish green and then brown were seen. The temperature was raised to 50 °C and the stirring was continued for 24 hours. Then the temperature was raised to 72 °C and the stirring was continued for another 24 hours, at the end of which an increase in the solution viscosity was evident. The solution was quenched into ice cold 5% aqueous NaCl to yield 6.10 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 $CHCl_3$ solution into ice cold MeOH. It was dried in a vacuum oven at 60 °C for 24 hours. ^{1}H NMR ($CDCl_3$) δ 7.95 (s, 1 H, H-1), 7.80 (d, 4 H, H-10), 7.55 (d, 2 H, H-3), 7.88 (m, 1 H, H-4), 4.0-3.5 (br, s, 8 H, H-8) and 2.7-2.2 (br, s, H-7). ^{13}C NMR ($CDCl_3$) δ 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). FTIR (KBr) 2962, 2853 (C-H stretch),1594 (phenyl), 1458 (methylene scissors), 1326, 1160 (sulfone), and 1116 (C-O-C), cm^{-1}.

Poly(sulfonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl-*p*-phenylene) (4.3)

In a 100 mL round bottom flask, 0.50 g of polymer **4.2** (ground) was suspended in 20 mL of 70 % aqueous acetic acid and 5 mL of concentrated HCl. The mixture was heated at reflux for 3 h and then quenched into 500 mL of distilled water. The white powder was suction filtered and washed with water and then methanol. It was dried in a vacuum oven at 140 °C for 30 h. ^{1}H NMR (DMSO-d_6) δ 8.17 (d, 8 H, H-11), 8.14 (s, 1 H, H-1), 8.00 (d, 2 H, H-3), 7.95 (d, 4 H, H-10), 7.69 (m, 1 H, H-4). A pair of small doublets at 8.25 and 8.05 ppm was also detected. ^{13}C NMR (DMSO) δ 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). FTIR (KBr) 1668 (carbonyl), 1596 (phenyl), 1325, 1159 (sulfone), 705 (*m*-phenyl), cm^{-1}.

Poly(sulfonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl-*p*-phenylene) (4.3)

Hydrolysis in Concentrated H_2SO_4

1.00 g of polymer **4.2** was added to 25 mL of concentrated H_2SO_4 and 0.5 mL of H_2O in a 50 mL round-bottom flask equipped with magnetic stirrer and condenser. A color change to brown was observed. The temperature was raised to 80 °C and the stirring was continued for 1 hour until all solid was dissolved. Then the solution was quenched into ice cold water and the pale yellow solid was suction filtered and washed with H_2O and MeOH. It was dried in a vacuum oven at 60 °C for 36 hours, 0.65 g (100%). The ^{1}H NMR spectrum and FTIR spectrum are the same as those of polymer **4.3** hydrolyzed in 70% acetic acid and hydrochloric acid.

Polymerization of Compound 4.1a with Bis(*p*-chlorophenyl) Sulfone (4.2)

Into a flame dried 50 mL round bottom flask equipped with mechanical stir under N_2, 0.88 g (22 mmol) of 60% NaH and 25 mL of dry DMF was added. Then 3.2640 g (10.000 mmol) of compound **4.1a** and 2.8717 g (10.000 mmol) of bis(4-chlorophenyl) sulfone were added to the flask. A vigorous bubbling and an immediate color change to yellowish green and then brown were observed. After 4 hours stirring at room temperature, it became a homogeneous solution. The stirring was continued for 10 days until the color of the solution faded to light yellow. A white precipitate (NaCl) was observed. The solution was quenched into ice cold 1:1/MeOH:H_2O. The pale yellow solid was suction filtered and washed with H_2O and MeOH, 5.12 g (99%). Purification was done by three times precipitation from THF into ice cold 1:1/MeOH:H_2O. It was dried in a vacuum oven at 60 °C for 36 h. All other data including NMR, FTIR and TGA are the same as that for polymer **4.2** from bis(*p*-chlorophenyl) sulfone.

Polymerization of Compound 4.1a with 4,4'-Difluorobenzophenone to form Polymer 4.4a

To a flame dried 100 mL round bottom flask were added 2.4480 g (7.5000 mmol) of compound **4.1a**, 1.6365 g (7.5000 mmol) of 4,4'-difluorobenzophenone and 25 mL of anhydrous DMF under nitrogen. NaH (0.75 g, 19 mmol, 60% in light mineral oil) was added to the flask. Vigorous bubbling and an immediate color change to yellowish green and then dark brown were observed. The mixture was stirred at room temperature under nitrogen for 14 days until the color of the solution faded to light yellow. The solution was then quenched into 600 mL of cold water. The pale yellow precipitate was filtered, washed with methanol and air-dried, 3.95 g (99%). Purification was done by precipitation form DMF into water using a high-speed blender and then from THF into hexane twice to remove light mineral oil from the NaH. FTIR (KBr) 2963, 2851 (C-H stretches), 1668 (carbonyl), 1064 (phenyl), 1118 (C-O-C), 1270, cm^{-1}. ^1H NMR ($CDCl_3$) δ 8.07 (br. s, 1 H, H-1), 7.76 (br. m, 4 H, H-11), 7.68 (br. m, 4 H, H-10), 7.58 (m, 2 H, H-3), 7.35 (m, 1 H, H-4), 3.70-3.93 (br, m, 8 H, H-8) and 2.42-2.74 (br, m, H-7). ^{13}C NMR ($CDCl_3$) δ 194.32 (C-13), 143.19 (C-12), 139.69 (C-9), 137.39 (C-2), 130.90 (C-10), 130.55 (C-4), 127.13 (C-3), 127.01 (C-10), 125.37, 124.40 (C-1), 115.85 (C-5), 75.64 (C-6), 66.80 (C-8) and 49.57 (C-7). Elemental analysis calcd. (found) for $[F(C_{31}H_{28}N_4O_3)_{50}H]$: C, 73.73 (72.94); H, 5.59 (5.64); N, 11.09 (11.04), F, 0.08 (0.09).

Polymerization of Compound 4.1b with 4,4'-Difluorobenzophenone to form Polymer 4.4b

The procedural details were the same as polymer **4.4a** with following modification: the temperature was controlled between 0-10 °C using a ice bath. The reaction time was 6 days. The yield was 97 %. Most of the low molecular weight species were removed by Soxhlet extraction with ethanol for three days. FTIR (KBr) 2996, 2958, 2894, 2875, 2791 (C-H stretches), 1666 (carbonyl), 1062 (phenyl), 1404, 1275, 1038, 930, 708, cm^{-1}. ^{1}H NMR ($CDCl_3$) δ 8.14, 8.10 (br. s, 1 H, H-1), 7.78 (br. m, 4 H, H-11), 7.71 (br. m, 4 H, H-10), 7.57 (m,, 2 H, H-3), 7.30 (m, 1 H, H-4), and 2.31 (s, 12 H, CH_3). ^{13}C NMR ($CDCl_3$) δ 194.57 (C=O), 144.39 (C-12), 140.71 (C-9), 137.15 (C-2), 130.69 (C-10), 129.63 (C-4), 126.73, 126.58 (C-3), 126.09 (C-10), 123.82, 123.47 (C-1), 115.83 (C-5), 41.38 (CH_3). Elemental analysis calcd. (found) for $[F(C_{27}H_{24}N_4O)_{35}H]$: C, 77.01 (76.97); H, 5.75 (5.72); N, 13.31 (12.94), F, 0.13 (0.16).

Polymerization of Compound 4.1b with 4,4'-Difluorobenzophenone to form Polymer 4.4b using 99.5 mol% of 4,4'-Difluorobenzophenone

The procedural details are the same as above. Compound **4.1b** (2.4232 g, 10.000 mmol), 2.1711 g (9.9500 mmol) of 4,4’-difluorobenzophenone and 15 mL of anhydrous DMF were used. The yield was 4.15 g (99%). Most of the low molecular weight species were removed by Soxhlet extraction with ethanol for three days. The NMR and IR apectra were almost the same as above.

Poly(phenylenecarbonyl-*p*-phenylenecarbonyl-*m*-phenylenecarbonyl) (4.5)

In a 100 mL round bottom flask, 0.50 g of polymer **4.4a** (ground) was suspended in 20 mL of 70 % aqueous acetic acid and 5 mL of concentrated HCl. The mixture was heated at reflux for 3 h and then quenched into 500 mL of distilled water. The white powder was suction filtered and washed with water and then methanol. It was dried in a vacuum oven at 140 °C for 30 h. The product weighed 0.31 g (100%). Polymer **4.5** was insoluble in $CHCl_3$, THF, acetone, ethyl acetate, DMF, DMSO, DMAc, NMP, etc. It was only soluble in very strong acids such as concentrated sulfuric acid. FTIR (KBr) 1662 (carbonyl), 1596 (phenyl), 1309, 1245, 930, cm^{-1}. ^1H NMR (D_2SO_4) δ 10.90 (s, H_2SO_4, reference), 8.90 (br. s, 1 H), 8.67 (br. m, 2 H), 8.38 (br. m, 8 H) and 8.23 (br. m, 1 H). Elemental analysis calcd. (found) for $[F(C_{21}H_{12}O_3)_{50}H]$: C, 80.66 (79.84); H, 3.87 (4.04); F, 0.12 (0.20).

Synthesis of Polyaminonitrile 4.7a

Compound **4.1a** (3.2640 g, 10.000 mmol) was dissolved along with 4.6247 g (10.000 mmol) of compound **4.6a** at room temperature in a flame dried flask in 30 mL of dry DMF under N_2. The mixture was stirred for 20 minutes and became homogenous. Upon addition of 0.88 g (22.00 mmol) of 60% NaH, vigorous bubbling and an immediate color change to yellowish green and then dark brown were seen. After 20 h of stirring, the temperature was raised to 65 °C and the stirring was continued for 24 hours, at the end of which the color of the solution had faded to light brown and a gel-like solid appeared in the flask. The solution was allowed to cool to room temperature and then quenched into ice cold 5% aqueous NaCl solution to yield 7.88 g (100%) of a light yellow solid. Purification was done by precipitation three times from THF into water. It was dried in a vacuum oven at 65 °C for 24 hours. ^{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 (d, 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}. It was dissolved in THF and precipitated into hexane to remove the mineral oil. It was allowed to air dried for 48 h. The ^{1}H NMR spectrum showed the removal of the mineral oil.

Synthesis of Poly(ketone sulfone) 4.8a

In a 100 mL round bottom flask, 1.00.g of polymer **4.7a** was suspended in 30 mL of AcOH, 10 mL of H_2O and 10 mL of concentrated HCl. The mixture was heated at reflux for 20 h. The mixture was then quenched into 500 mL of H_2O. The light yellow powder was filtered and washed with water and methanol. It was boiled in methanol 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. The sample weighed 0.87 g (100%). Polymer **4.8a** is insoluble in most common organic solvents such as $CHCl_3$, THF, DMF, 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 (d, br, 4 H), 8.52-8.64 (d, br, 2 H), 8.75 (s, br, 1 H). FTIR (KBr) 1665 (C=O), 1595, 1500 (phenyl), 1326, 1161 (sulfone), 1248, 928, cm^{-1}.

Synthesis of Polyaminonitrile 4.7b

The procedural details are similar to those of **4.7a**. 3.2640 g (10.000 mmol) of **4.1a** were dissolved along with 3.2231 g (10.000 mmol) of **4.6b** at room temperature in a flame dried flask in 30 mL of dry DMF under N_2. NaH (0.88 g, 22 mmol, 60% in mineral oil) was added. The temperature was raised to 65 °C and the stirring was continued for 2 days. The solution was allowed to cool to room temperature and then quenched into ice cold water. The white precipitate was filtered and washed with water and methanol. **4.7b** 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), 7.18 (m, 0.3 H, end group), 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).

Synthesis of Polyketone 4.8b

The procedural details are the same as that of **4.8a**. 2.00 g of **4.7b** were used. The yield is 1.35 g (99%). **4.8b** is insoluble in most common organic solvents such as $CHCl_3$, THF, DMF, 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), 7.52 (m, 0.38 H, F end group), 8.08-8,16 (m, br, 1 H), 8.19-8.39 (m, br, 8 H), 8.56 (d, 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}.

Synthesis of Polyaminonitrile 4.7c

4.1a (3.2640 g, 10.000 mmol) was dissolved along with **4.6c** (3.2330 g, 10.000 mmol) at room temperature in a flame-dried flask in 30 mL of dry DMF under N_2. The mixture was stirred for 20 minutes and became homogenous. Upon addition of 0.88 g (22 mmol) of 60% NaH, a vigorous bubbling and an immediate color change to yellowish green and then dark brown were seen. After 7 days of stirring, the color of the solution remained dark brown. The temperature was raised to 65 °C and the stirring was continued for 2 days. The solution was allowed to cool to room temperature and then quenched into ice cold water. The yellow precipitate was filtered and washed with water and methanol. Polyaminonitrile **4.7c** is soluble in most common organic solvents such as $CHCl_3$, THF and acetone. ^1H NMR ($CDCl_3$) δ 2.40-2.60 (m, br., CH_2, 8 H), 3.53-3.83 (m, br., CH_2, 8 H), 7.18 (m, 0.3 H, end group), 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).

Synthesis of Polyketone 4.8c

In a 100 mL round bottom flask, 2.00.g of **4.7c** was suspended in 30 mL of 70% AcOH and 5 mL of concentrated HCl. The mixture was heated to reflux for 20 h. The mixture was then quenched into 500 mL of H_2O. The light yellow powder was filtered and washed with water and methanol. It was boiled in methanol for 10 h. It was dried at 110 °C in a vacuum oven for 24 h and then in a drying pistol at 202 °C (NMP) for 24 h. The sample weighed 1.34 g (98%). Polymer **4.8c** is insoluble in most common organic solvents such as $CHCl_3$, THF, DMF, 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 (d, 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).