A Polyketone Synthesis Involving Nucleophilic Substitution via Carbanions Derived from Bis(α-aminonitrile)s. 5.[1−4] A New, Well-Controlled Route to "Long" Bisphenol and Activated Aromatic Dihalide Monomers

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ABSTRACT: Very efficient syntheses of "long" bisphenol and activated dihalide monomers containing keto groups were developed on the basis of α-aminonitrile chemistry. Known and novel activated dihalide monomers were obtained in quantitative yields and without isomeric impurities. This method is suitable for any activated dihalide by reaction with 2 equiv of the anion of *p*-fluorobenzalaminonitrile (**8**), followed by hydrolysis to produce a monomer with two more *p*-fluorobenzoyl units. Similarly, use of the anion of *p*-methoxybenzalaminonitrile (**15**) by reaction with activated dihalides provides a general route to bisphenols. Less expensive dichloro monomers, e.g., 4,4′-dichlorobenzophenone, can be used to synthesize these "long" bisphenol and activated dihalide monomers.

Introduction

Aromatic polymers containing thermally stable, fully oxidized linkages, such as sulfone, carbonyl, and ether groups, are accessible by nucleophilic routes.[5] Different polymer structures can be synthesized from monomers bearing different sequences of the linkages between adjacent aromatic rings. The inherent properties of these polymers, such as crystallinity and thermomechanical properties, depend on the structures of the polymer backbones. One of the critical contributions of the ketone functionality in polymers is the crystallinity which it imbues. This leads to the very desirable property of solvent resistance.[5] It is generally accepted that poly(ether sulfone)s are usually amorphous polymers and subject to attack (swelling or dissolution) by common solvents. However, one of the desirable properties of polymers containing sulfone groups is a high glass transition temperature. Poly(ketone ketone sulfone) synthesized from aminonitrile precursors has a T_g at 208 °C and a T_m at 458 °C.[1] It would be interesting to study analogous polymers containing sulfone, ketone, and ether groups in regular sequences.For nucleophilic routes, activated difluoro monomers are the main raw materials for the synthesis of high molecular weight poly(arylene ether ketone)s (PAEKs). They are not readily available in industry. They are usually synthesized by Friedel−Crafts processes using fluorobenzene or *p*-fluorobenzoyl chloride.[6,7] Staniland and co-workers[8] synthesized activated aromatic dihalide monomers **2a**−**b** by Friedel−Crafts acylation of fluorobenzene with arylene diacid chlorides **1a**−**b** in about 75% overall yield (Scheme 1). The corresponding diphenol monomers **3a**−**b** were obtained by hydrolysis of difluoro monomers **2a**−**b** with potassium hydroxide in DMSO in 60−70% yields.

Wolfe and co-workers[9,10] developed an efficient synthesis for activated arylene dihalides and diphenols utilizing nucleophilic aromatic substitution reactions of acyl anion equivalent **4** with activated dihalides **5a**−**d** (Scheme 2). Condensation of excess α-lithio-4-fluorophenylacetonitrile (**4**), prepared from the nitrile and *n*-BuLi, with the appropriate activated arylene dihalides in THF gave intermediate bisnitriles **6a**−**d**, followed by phase transfer catalyzed oxidative decyanation in toluene using triethylbenzylammonium chloride (TEBAC) as catalyst which afforded monomers **7a**−**d**. The overall yields of this two step reaction were >80% for all difluoro monomers.

α-Aminonitriles derived from secondary amines readily form carbanions that are potent nucleophiles;[11] hydrolysis of the alkylated or arylated products produces ketones.[11] Thus, aminonitrile anions serve as acyl anion equivalents. In the previous papers,[1−4] we reported an 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 describe very efficient syntheses of bisphenol and activated aromatic dihalide monomers using α-aminonitrile chemistry.

Results and Discussion

Difluorotriketone and Difluorodiketone Sulfone Monomers 2a−**b.** *p*-Fluorobenzalaminonitrile (**8**) was synthesized from *p*-fluorobenzaldehyde in 93% yield.[11] Attempts to polymerize this AB type monomer in DMF using NaH as base failed, and only starting material **8** was recovered; the nonactivated fluoro group is not susceptible to nucleophilic displacement under these conditions. This aminonitrile can thus be utilized to synthesize activated aryl dihalide monomers for synthesis of PAEKs. Condensation of 2 equiv of **8** with bis(*p*-chlorophenyl) sulfone in DMF with sodium hydride yielded new bis(fluoroaminonitrile) sulfone **9a** in quantitative yield (Scheme 3). After the reaction was completed, as indicated by the loss of the dark brown color of the carbanion, the reaction mixture was precipitated into distilled water. The ^{1}H NMR spectrum (Figure 1a)

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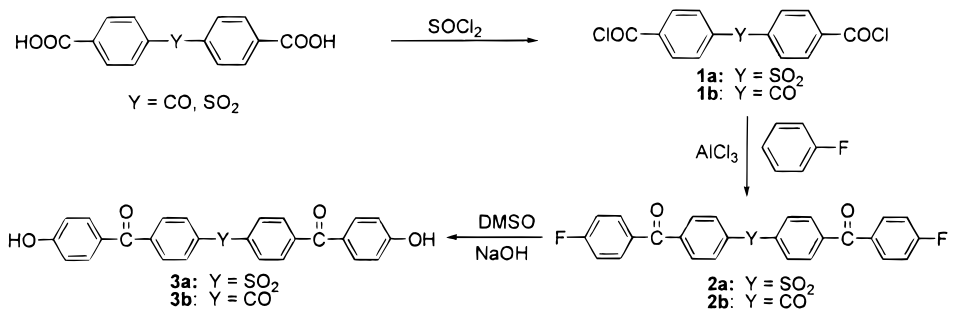
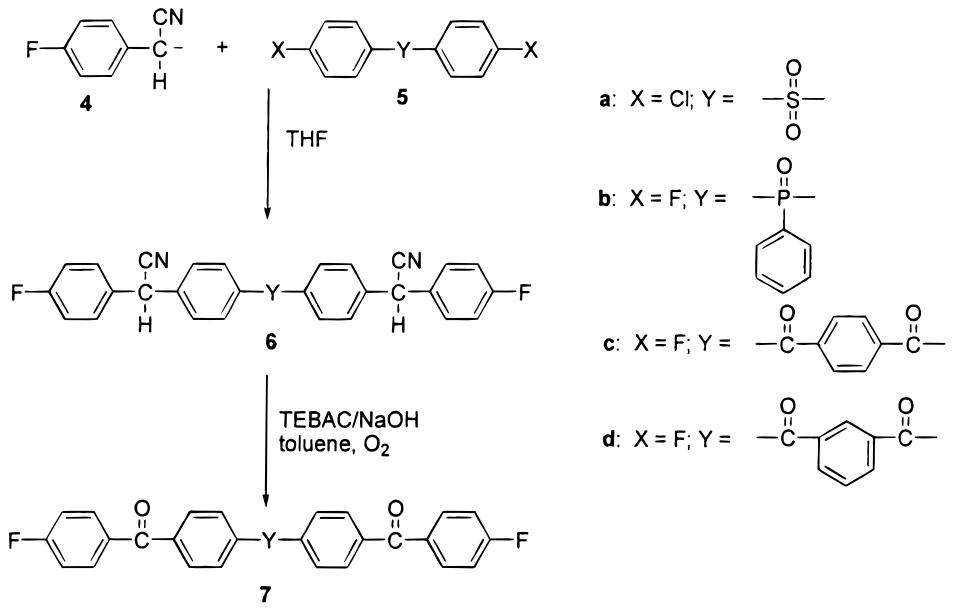
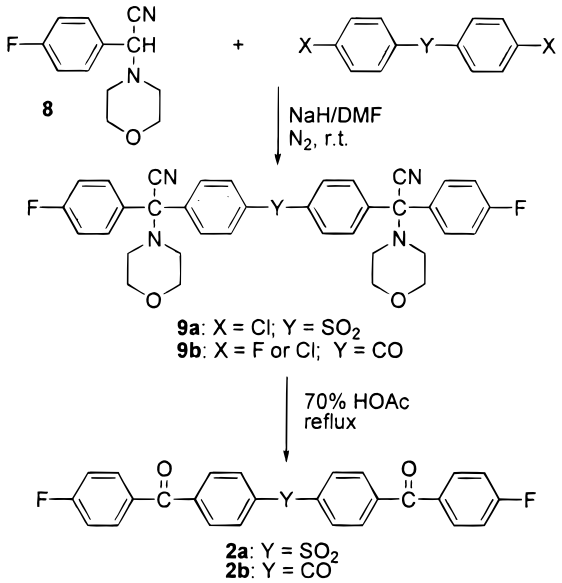
Scheme 1



Scheme 2



Scheme 3



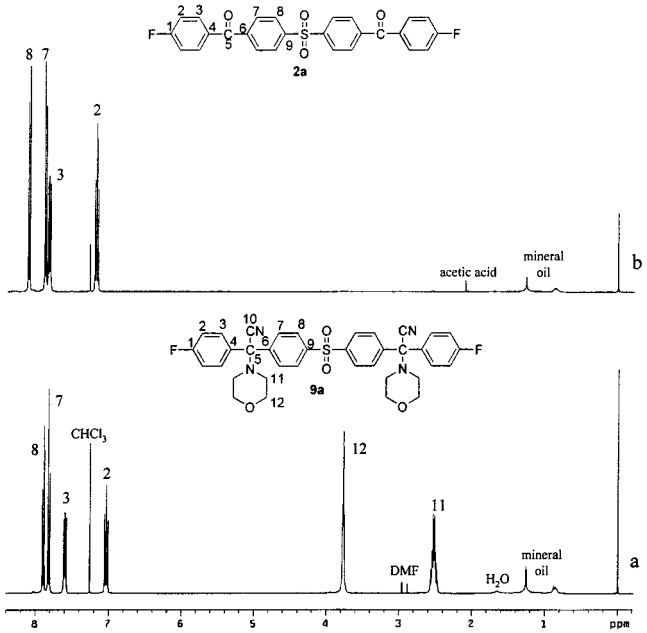


Figure 1. The 400 MHz ^{1}H NMR spectra of (a) **9a** and (b) **2a** in $CDCl_3$.

of the crude product shows no signal of either starting material, which indicates complete conversion. It also shows two signals in the aliphatic region corresponding to the morpholino groups and four signals in the aromatic region. The COSY spectrum in the aromatic region shows two pairs of doublets at 7.81 and 7.89 ppm coupled to each other and a doublet of doublets at 7.03 ppm coupled with a multiplet at 7.58 ppm due to fluorine coupling. The ^{13}C NMR spectrum (Figure 2a) of **9a** shows three signals in the aliphatic region corresponding to the aminonitrile groups and other signals consistent with the assigned structure. The IR spectrum reveals a sulfone absorbance at 1326, 1163

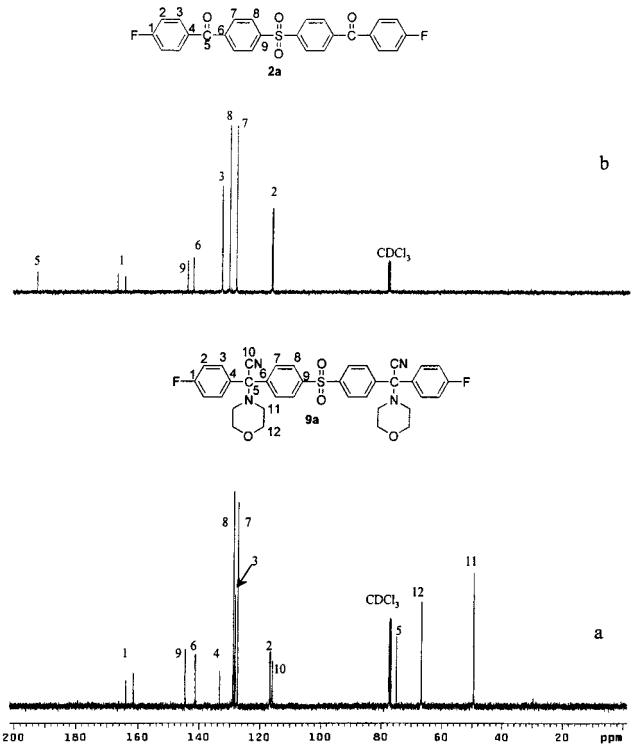


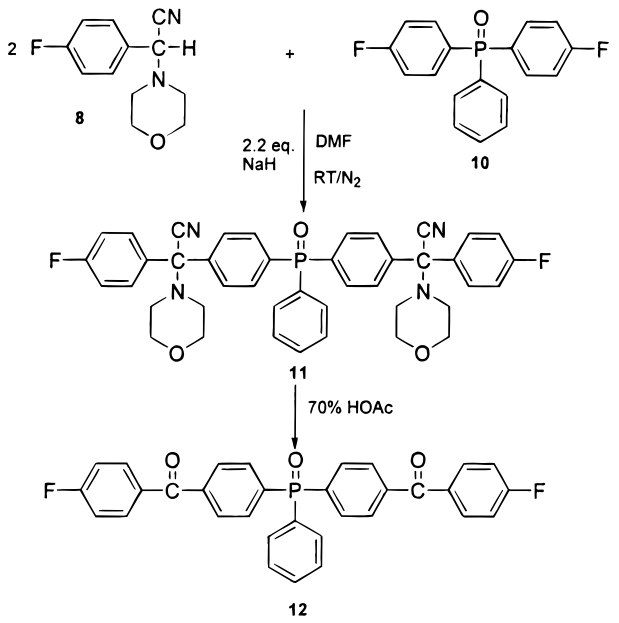
Figure 2. The 100 MHz ^{13}C NMR spectra of (a) **9a** and (b) **2a** in $CDCl_3$.

cm^{-1}, a nitrile stretch at 2228 cm^{-1}, and a strong C−O−C band at 1116 cm^{-1}.

This aminonitrile **9a** was hydrolyzed in 70% acetic acid to produce activated difluorodiketone sulfone monomer **2a** in quantitative yield. The IR spectrum of **2a** shows a strong carbonyl absorbance at 1660 cm^{-1} and the complete disappearance of the C−O−C peak at about 1116 cm^{-1} and aliphatic C−H stretches from 2800 to 3000 cm^{-1}, which is evidence of complete hydrolysis. The ^1H NMR spectrum (Figure 1b) of the crude hydrolysis product shows no signal in the aliphatic region corresponding to the morpholino groups, which indicates the complete hydrolysis of aminonitrile groups to ketone groups. The ^{13}C NMR spectrum (Figure 2b) of **2a** shows no signal in the aliphatic region which confirms the complete hydrolysis. Compound **2a** has a melting point of 183−184 °C, slightly higher than a previously reported value.[8] It is soluble in many common organic solvents, such as $CHCl_3$, THF, DMF, etc. Compound **2a** was polymerized with isophthalaminonitrile in DMF using NaH as base, followed by acid hydrolysis to yield a novel poly(ketone sulfone).[4]

The new compound **9b** was obtained from *p*-fluorobenzalaminonitrile (**8**) and 4,4′-difluorobenzophenone in quantitative yield. The NMR and IR spectra agree well with the structure. Hydrolysis of **9b** yielded difluorotriketone monomer **2b** in quantitative yield. Compound **2b** has a melting point somewhat higher than the reported value.[8] One possible reason for the higher melting points observed here relative to previous reports is that monomers **2a**−**b** previously synthesized by Friedel−Crafts acylation may contain ortho acylation products, which are difficult to separate from para acylation products. The major advantage of this aminonitrile approach is that monomers synthesized are very pure and do not need complicated purification procedures. For polymers synthesized by step growth polymerization, one of the critical requirements to obtain high molecular weight is the purity of monomers. The overall yields of this two-step reaction for compounds **2a** and **2b** are essentially 100%. The overall crude yields for compounds **2a** and **2b** synthesized by Friedel−Crafts acylation (Scheme 1) were only 55−75%.[8] And these crude products needed further purification by column chromatography or recrystallization several times to obtain pure monomers. Compounds **2a** and **2b** are also good precursors for synthesis of rigid arylene marcrocycles.[12,13]

Scheme 4



To test whether this aminonitrile route to activated dihalides is accessible to dichloro monomers, the experiment was repeated in the same reaction conditions using less expensive 4,4′-dichlorobenzophenone. The ^1H NMR spectrum of the crude product **9b** showed a residual methine proton signal at 4.80 ppm and signals in the aromatic region corresponding to unreacted 4,4′-dichlorobenzophenone. The percent conversion of dichlorobenzophenone was determined as 89% from the integration of the appropriate ^1H NMR peaks. The crude product was used for hydrolysis in 70% aqueous HOAc without further purification. The ^1H NMR spectrum of the crude product **2b** in DMSO-d_6 at 100 °C showed that it was mixture of compound **2b** and dichlorobenzophenone. The dichlorobenzophenone was easily removed by recrystallization from DMF to give pure **2b** in 85% isolated yield. The ^1H NMR spectrum and the melting point were the same as those of compound **2b** synthesized from 4,4′-difluorobenzophenone.

Difluoro Monomer Containing Triphenylphosphine Oxide Moiety (12). Compound **11** was synthesized from aminonitrile **8**[11,14] and activated difluoride compound **10**[15−16] under the same conditions in 100% yield. Hydrolysis of compound **11** in 70% aqueous HOAc solution yielded the corresponding difluoro monomer **12** in 98% isolated yield. The structures of compounds **11** and **12** were confirmed by elemental analysis, ^1H NMR, COSY, and ^{13}C NMR spectra.

Difluorotetraketone Sulfone Monomer (14). Difluorodiketone sulfone (**2a**) was synthesized from aminonitrile **8** and bis(*p*-chlorophenyl) sulfone. Further extension of this activated dihalide was done using the same chemistry. Condensation of 2 equiv of **8** with **2a**

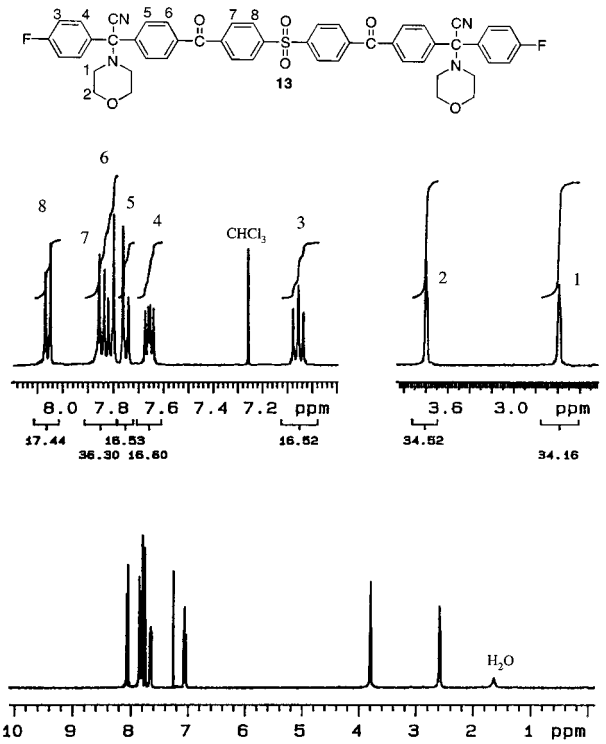
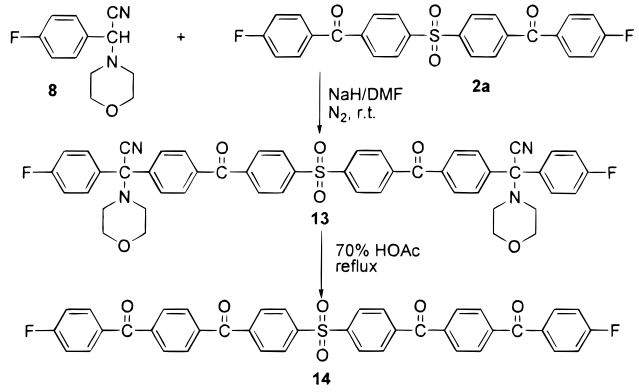


Figure 3. The 400 MHz ^{1}H NMR spectrum of compound **13** in $CDCl_3$.

Scheme 5



in DMF using NaH as base gave the bisaminonitrile intermediate **13** in 99% yield (Scheme 5). The ^{1}H NMR spectrum (Figure 3) in $CDCl_3$ showed two signals in the aliphatic region due to the methylene protons of the morpholino groups. Peaks in the aromatic region agree well with the structure of **13**. Hydrolysis of **13** in 70% acetic acid yielded new activated dihalide monomer **14** in 96% yield. The ^{1}H NMR spectrum of **14** in DMSO showed no signal in the aliphatic region, which indicated that hydrolysis was complete. The assignment of the aromatic protons was done according to the COSY spectrum (Figure 4). Compound **14** was slightly soluble in the moderately polar solvents such as DMSO and DMAc. It was recrystallized from DMAc. This activated dihalide monomer can be polymerized with bisaminonitriles or bisphenols to give the corresponding new poly(ketone sulfone)s with specific functional group sequences.

Aryl Diketophenol Monomers. *p*-Methoxybenzalaminonitrile (**15**)[11] was synthesized from *p*-anisaldehyde in 97% yield. Condensation of 2 equiv of **15** with bis(*p*-chlorophenyl) sulfone or 4,4′difluorobenzophenone

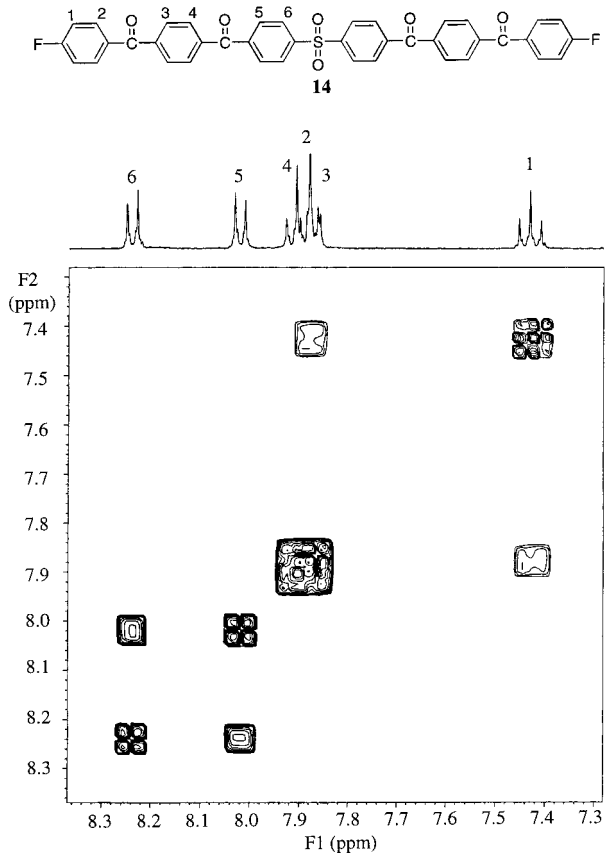
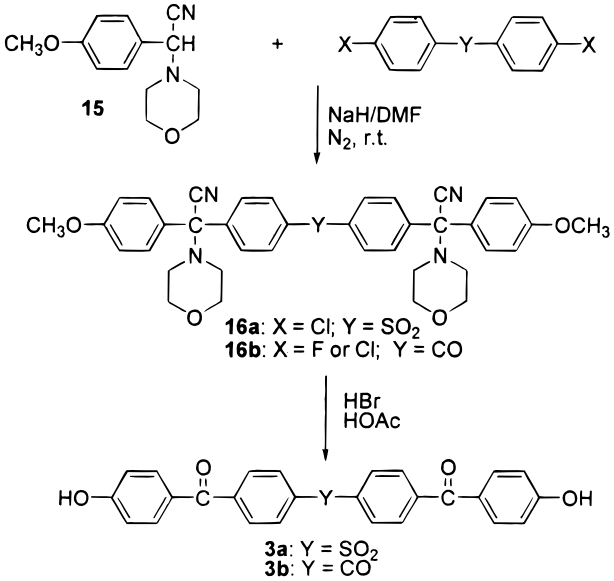


Figure 4. The 400 MHz COSY spectrum of compound **14** in DMSO-d_6.

Scheme 6



in DMF using NaH as base gave protected keto phenol compounds **16a**−**b** in 99% yield (Scheme 6). The IR and NMR spectra of **16a**−**b** agree with the structures shown. Condensation of less reactive 4,4′-dichlorobenzophenone with compound **15** afforded **16b** in 98% yield. The melting point and NMR spectra were the same as those of **16b** synthesized from 4,4′-difluorobenzophenone. Hydrolysis and cleavage of the ether group in HBr and acetic acid yielded the known ketophenol monomers **3a**−**b** in 96% yield. The structures were confirmed by FTIR and NMR spectra. The overall yields of this two-step synthesis for **3a**−**b** were >95%, much higher than

reported yields (45−53%) by the acylation route of Scheme 1.[8] This two-step reaction offers a new route to high purity "long" bisphenol monomers bearing keto groups in very high yields, avoiding the use of expensive bisfluoro monomers.

Similarly, a series of other new monomers could be prepared using this aminonitrile chemistry, including keto phenols and their sulfone analogues. These keto monomers could be used to synthesize a wide variety of new poly(ether ketone)s or their copolymers. These new keto compounds can also be used as precursors for synthesis of rigid arylene macrocycles with low viscosity, which can be polymerized by ring opening to produce high-performance polymers.[12,13]

Conclusions

A very efficient, general synthesis for activated dihalide monomers containing keto groups was developed on the basis of α-aminonitrile chemistry. The aminonitrile intermediates and activated dihalide monomers were obtained in quantitative yields and high purity. Further chain extension was also demonstrated. This method is suitable for any activated dihalide by reaction with 2 equiv of *p*-fluorobenzalaminonitrile (**8**) and NaH, followed by hydrolysis to produce a new monomer with two more *p*-fluorobenzoyl units. Similarly, diphenol monomers can also be synthesized in high yield using *p*-methoxybenzalaminonitrile (**15**). Less reactive and much less expensive dichloro monomers can be used to synthesize these "long" bisphenol and activated dihalide monomers.

Experimental Section

Materials and Instrumentation. 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 ^{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−^{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) as solvent and internal standard. FTIR spectra were recorded on a Nicolet MX-1 with KBr pellets.

α-(*N*-Morpholino)-*p*-fluorobenzyl Cyanide (8).[11] $NaHSO_3$ (15.61 g, 150 mmol) was dissolved in 250 mL of water; 15.84 mL (150 mmol) of 4-fluorobenzaldehyde was added to the flask, and the mixture was stirred for 2 h until homogeneous. Morpholine (13.07 mL, 150 mmol) was added all at once, and the stirring was continued for 2 h. Then 7.35 g (150 mmol) of NaCN was added to the solution, and the solution was stirred for 6 h, at the end of which a shiny white solid had precipitated out. The stirring was continued for another 10 h. The solid was filtered and dried to yield 30.63 g (93%) of **8**; mp 61.7−63.2 °C. It was recrystallized from 19:1/hexanes: EtOAc to give shiny white needles; mp 62.8−63.8 °C (lit.[14] 60−63 °C). ^{1}H NMR ($CDCl_3$): δ 2.57−2.59 (m, 4 H), 3.71−3.77 (m, 4 H), 4.79 (s, 1 H), 7.09−7.13 (m, 2 H), 7.50−7.54 (m, 2 H). FTIR (KBr): 2862, 2826 (C−H stretch), 2226 (CN), 1606, 1508 (phenyl), 1456 (methylene scissor), 1116 (C−O−C), cm^{-1}.

Bis{*p*-[*p*′-fluoro-α-cyano-α-(*N*-morpholino)benzyl]phenyl} Sulfone (9a). Compound **8** (4.41 g, 20 mmol) was dissolved in 30 mL of dry DMF along with 2.87 g (10 mmol) of bis(*p*-chlorophenyl) sulfone in a flame-dried round-bottom flask under N_2. NaH (0.88 g, 22 mmol, 60% in mineral oil) was added all at once, and immediately the vigorous bubbling of H_2 and a color change to greenish and then brown were observed. The stirring was continued for 3 days until the color of the solution faded to light yellow. The solution was then quenched into ice cold water; a white precipitate was collected and dried to yield 6.55 g (100%) of **9a**, mp 231 °C (decomposition). The crude product was extracted with MeOH and dried. ^{1}H NMR ($CDCl_3$): δ 2.46−2.55 (m, 8 H), 3.75−3.77 (m, 8 H), 7.03 (m, 4 H), 7.56−7.61 (m, 4 H), 7.81(d, J = 8.8 Hz, 4 H), 7.89 (d, J = 8.8 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 163.94, 161.45 (C-1), 144.59 (C-9), 141.28 (C-6), 133.29, 133.25 (C-4), 128.80 (C-8), 128.26, 128.17 (C-3), 127.35 (C-7), 116.62, 116.40 (C-2), 115.75 (C-10), 75.01 (C-5), 66.71 (C-12), 49.41 (C-11). FTIR (KBr): 2963, 2894 (C−H stretch), 2228 (CN), 1601, 1506 (phenyl), 1456 (methylene scissor), 1326, 1163 (sulfone), 1116 (C−O−C), cm^{-1}. Elemental analysis calcd. (found) for $C_{36}H_{32}N_4O_4F_2S$: C, 66.03 (65.89); H, 4.93 (5.01); N, 8.56 (8.35).

Bis[*p*-(*p*′-fluorobenzoyl)phenyl] Sulfone (2a). Compound **9a** (2.00 g, 4.32 mmol) was suspended in 25 mL of 70% AcOH, and the mixture was refluxed. Within about 10 min, the solid had dissolved, and in about 10 more min, a white precipitate was observed. The mixture was quenched into 200 mL of cold H_2O, and the solid was filtered, washed with H_2O, and dried (1.41 g, 100%). It was recrystallized from benzene to give white needles; mp 183−184 °C (lit.:[6] 177−178 °C). ^{1}H NMR ($CDCl_3$): δ 7.18 (t, J = 8.6 Hz, 4 H), 7.82 (m, 4 H), 7.88 (d, J = 8.4 Hz, 4 H), 8.10 (d, J = 8.4 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 193.28 (C-5), 167.16, 164.62 (C-1), 144.15 (C-9), 142.17 (C-6), 132.74, 132.64 (C-3), 130.27 (C-8), 127.94 (C-7), 115.93, 115.71 (C-2); FTIR (KBr) 1660, 1656 (C═O), 1598, 1506 (phenyl), 1330, 1163 (sulfone), cm^{-1}.

4,4′-Bis[*p*-fluoro-α-cyano-α-(*N*-morpholino)benzyl]benzophenone (9b). Procedural details were the same as for the synthesis of compound **9a**. Compound **8** (4.40 g, 20 mmol), 4,4′-difluorobenzophenone (2.18 g, 10 mmol), and NaH (0.88 g, 22 mmol, 60% in mineral oil) were stirred in 30 mL of dry DMF at room temperature for 3 days. The yield was 5.68 g (100%); mp 98−139 °C (diastereomers). ^{1}H NMR ($CDCl_3$): δ 2.57−2.61 (m, 8 H), 3.78−3.82 (m, 8 H), 7.06 (t, J = 8.4 Hz, 4 H), 7.64−7.68 (m, 4 H), 7.73 (d J = 8.6 Hz, 4 H), 7.78 (d, J = 8.6 Hz, 4 H). ^{13}C NMR ($CDCl_3$): δ 194.55 (C═O), 163.86, 161.38 (CF), 143.35 (C), 137.24 (C), 133.87, 133.83 (C), 130.80 (CH), 128.26, 128.18 (CH), 126.32 (CH), 116.45, 116.23 (CH), 116.05 (CN), 75.16 (C), 66.80 (CH_2), 49.43 (CH_2). FTIR (KBr): 2967, 2854 (C−H stretch), 2226 (CN), 1661 (C═O), 1603,1506 (phenyl), 1116 (C−O−C), cm^{-1}. Elemental analysis calcd. (found) for $C_{37}H_{32}N_4O_3F_2$: C, 71.82 (71.63); H, 5.22 (5.31); N, 9.06 (8.91).

4,4′-Bis[*p*-fluoro-α-cyano-α-(*N*-morpholino)benzyl]benzophenone (9b) from 4,4′-Dichlorobenzophenone. Procedural details were the same as for the synthesis of compound **9a**. Compound **8** (2.203 g, 10.0 mmol), 4,4′-dichlorobenzophenone (1.256 g, 5.000 mmol), and NaH (0.440 g, 11.0 mmol, 60% in mineral oil) were stirred in 20 mL of dry DMF at room temperature for 24 h. The crude product was used for hydrolysis without further purification.

4,4′-Bis(*p*-fluorobenzoyl)benzophenone (2b). Procedural details were the same as for the synthesis of compound **2a**. The crude yield was 100%. Recrystallization from DMF afforded white crystals; mp 293−295 °C (lit.:[8] 282−283 °C). ^{1}H NMR (DMSO-d_6, 100 °C): δ 7.37 (t, J = 8.4 Hz, 4 H), 7.87 (d, J = 8.4 Hz, 4 H), 7.88 (m, 4 H), 7.93 (d, J = 8.4 Hz, 4 H). FTIR (KBr): 1646 (C═O), 1592, 1504 (phenyl), cm^{-1}. It is insoluble in most common organic solvents at room temperature.

4,4′-Bis(*p*-fluorobenzoyl)benzophenone (2b) from 4,4′-Dichlorobenzophenone. Procedural details were the same as for the synthesis above. The crude product was recrystallized from DMF to give white shiny flakes; 1.15 g (85%), mp 294−296 °C. The NMR and IR data were the same as those of **2b** synthesized from 4,4′-difluorobenzophenone.

Bis{*p*-[*p*′-fluoro-α-cyano-α-(*N*-morpholino)benzyl]-phenyl}phenylphosphine Oxide (11). Procedural details were the same as for the synthesis of compound **9a**. Compound **8** (4.405 g, 20.00 mmol), compound **10** (3.143 g, 10.00 mmol), and NaH (0.880 g, 22.0 mmol, 60% in mineral oil) were stirred in 30 mL of dry DMF at room temperature for 24 h. The yield was 7.14 g (100%); mp 158−194 °C (diastereomers). ^{1}H NMR ($CDCl_3$): δ 2.55 (m, 8 H), 3.77 (m, 8 H), 7.04 (m, 4 H), 7.46 (m, 2 H), 7.52−7.66 (m, 11 H), 7.77 (m, 4 H). ^{13}C NMR (APT, $CDCl_3$): δ 163.88, 161.39 (C), 142.97 (C), 133.67, 133.64 (C), 133.31, 133.28 (C), 132.95, 132.85 (CH), 132.28, 132.25 (C), 131.96, 131.86 (CH), 128.82, 128.70 (CH), 128.30, 128.22 (CH), 126.60, 126.48 (CH), 116.45, 116.23 (CH), 115.98 (CN), 75.16 (C), 66.75 (CH_2), 49.41 (CH_2). The sample for elemental analysis was precipitated from EtOAc into hexane to remove light mineral oil and then further purified by silica gel column chromatography eluting with 1:1/hexane:EtOAc and gradually increasing to 100% EtOAc. Upon removing the solvents, the sample was dried in a drying pistol at 65 °C (MeOH) for 36 h. According to the integrals of the ^{1}H NMR spectrum, the molar ratio of **11**:EtOAc was 3:1. Elemental analysis calcd. (found) for $C_{42}H_{37}N_4O_3F_2P/(CH_3COOCH_2CH_3)_{1/3}$: C, 69.95 (69. 57); H, 5.37 (5.33); N, 7.53 (7.59).

Bis[*p*-(*p*′-fluorobenzoyl)phenyl]phenylphosphine Oxide (12). Procedural details were the same as for the synthesis of compound **2a**. The yield was 98%; mp 196−198 °C. ^{1}H NMR (DMSO-d_6): δ 7.18 (t, J = 8.6 Hz, 4 H), 7.55 (m, 2 H), 7.63 (m, 1 H), 7.73 (m, 2 H), 7.82−7.88 (m, 12 H). ^{13}C NMR (APT, $CDCl_3$): δ 194.34 (CO), 167.04, 164.50 (C), 140.83 (C), 136.65, 135.63 (C), 132.92 (C), 132.88, 132.79 (CH), 132.72, 132.69 (CH), 132.21, 132.11 (CH), 132.11, 132.01 (CH), 131.50 (CH), 130.45 (CH), 129.65, 129.53 (CH), 128.99, 128.86 (CH), 115.91, 115.69 (CH). The sample for elemental analysis was purified by recrystallization three times from CH_2Cl_2/EtOAc and then dried in a drying pistol at 65 °C (MeOH) for 36 h. The ^{1}H NMR spectrum indicated it contained one molecule of CH_2Cl_2 for every seven molecules of **12**. Elemental analysis calcd. (found) for $C_{32}H_{21}O_3F_2P\cdot(CH_2Cl_2)_{1/7}$: C, 72.21 (72.08); H, 4.01 (4.08).

Bis{*p*-[*p*′-fluoro-α-cyano-α-(*N*-morpholino)benzyl]benzoylphenyl} Sulfone (13). Procedural details were the same as for the synthesis of compound **9a**. Compound **2a** (2.31 g, 5.00 mmol), compound **8** (2.20 g, 10.0 mmol), and NaH (0.44 g, 11 mmol, 60% in mineral oil) were stirred in 30 mL of dry DMF at room temperature for 2 days. The yield was 4.08 g (99%); mp 162−200 °C (diastereomers). The crude product was washed with MeOH and dried. ^{1}H NMR ($CDCl_3$): δ 2.59 (m, CH_2, 4 H), 3.79 (m, CH_2, 4 H), 7.06 (m, 2 H), 7.65 (m, 2 H), 7.75 (d, J = 8.4 Hz, 2 H), 7.81 (d, J = 8.4 Hz, 2 H), 7.85 (d, J = 8.4 Hz, 2 H), 8.06 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 163.94, 161.45 (C), 144.59 (C), 141.28 (C), 133.29, 133.25 (C), 128.80 (CH), 128.26 (CH), 128.17 (CH), 127.35 (CH), 116.62, 116.40 (CH), 115.75 (CN), 75.01 (C), 66.71 (CH_2), 49.41 (CH_2). Elemental analysis calcd. (found) for $C_{50}H_{40}N_4O_6F_2S$: C, 69.58 (69.67); H, 4.68 (4.53); N, 6.50 (6.78).

Bis[*p*-(*p*′-fluorobenzoyl)benzoylphenyl] Sulfone (14). Procedural details were the same as for the synthesis of compound **2a**. The yield was 96%; mp 281.2−282.8 °C. Compound **14** is slightly soluble in moderately polar solvents such as DMAC, DMF, DMSO, etc. ^{1}H NMR (DMSO-d_6): δ 7.42 (m, 2 H), 7.85−7.92 (m, 6 H), 8.02 (d, J = 8.4 Hz, 2 H), 8.24 (d, J = 8.4 Hz, 2 H). ^{13}C NMR ($CDCl_3$): δ 194.55 (C=O), 163.86, 161.38 (CF), 143.35 (C), 137.24 (C), 133.87, 133.83 (C), 130.80 (CH), 128.26, 128.18 (CH), 126.32 (CH), 116.45, 116.23 (CH), 116.05 (CN), 75.16 (C), 66.80 (CH_2), 49.43 (CH_2). Elemental analysis calcd. (found) for $C_{40}H_{24}O_6F_{2S}$: C, 71.63 (71.76); H, 3.61 (3.59).

α-(*N*-Morpholino)-*p*-methoxybenzyl Cyanide (15). The procedural details were the same as those for compound **8**.[1] The yield was 97%; mp 76.1−78.5 °C. It was recrystallized from hexanes to give white shiny needles; mp 78.4−79.8 °C (lit.[11] 77−79 °C). ^{1}H NMR ($CDCl_3$): δ 2.55−2.58 (m, 4 H), 3.69−3.73 (m, 4 H), 4.75 (s, 1 H), 6.92 (d, J = 8.6 Hz, 2 H), 7.43 (d, J = 8.6 Hz, 2 H). FTIR (KBr): 2970,2933, 2823 (C−H stretch), 1616 (phenyl), 1118 (C−O−C), cm^{-1}.

Bis{*p*-[*p*′-methoxy-α-cyano-α-(*N*-morpholino)benzyl]-phenyl} Sulfone (16a). Procedural details were the same as the synthesis of compound **9a**. Compound **15** (4.97 g, 20 mmol), bis(*p*-chlorophenyl) sulfone (2.87 g, 10 mmol), and NaH (0.88 g, 22 mmol, 60% in mineral oil) were stirred in 30 mL of dry DMF under N_2 at room temperature for 3 days. Yield was 6.76 g (100%); mp 98−139 °C (diastereomers). ^{1}H NMR ($CDCl_3$): δ 2.36−2.50 (m, 4 H), 2.52−2.70 (m, 4 H), 3.75−3.77 (m, 14 H), 6.83 (d, J = 9.0 Hz, 4 H), 7.49 (d, J = 9.0 Hz, 4 H), 7.81 (d, J = 8.6 Hz, 4 H), 7.87 (d, J = 8.6 Hz, 4 H). ^{13}C NMR (APT, $CDCl_3$): δ 159.94 (C), 145.14 (C), 141.04 (C), 129.24 (C), 128.68 (CH), 127.60 (CH), 127.27 (CH), 116.05 (CN), 114.67 (CH), 75.27 (C), 66.79 (CH_2), 55.37, 55.34 (CH_3), 49.36 (CH_2). FTIR (KBr): 2962, 2853 (C−H stretch), 2226 (CN), 1606, 1510 (phenyl), 1326, 1160 (sulfone), 1116 (C−O−C), cm^{-1}. Elemental analysis calcd. (found) for $C_{38}H_{38}N_4O_6S$: C, 67.23 (67.35); H, 5.65 (5.75); N, 8.26 (8.36).

4,4′-Bis[*p*-methoxy-α-cyano-α-(*N*-morpholino)benzyl]-benzophenone (16b). Procedural details were the same as the synthesis of compound **9a**. Compound **15** (9.29 g, 40.0 mmol), 4,4′difluorobenzophenone (4.36 g, 20.0 mmol), and NaH (0.88 g, 22 mmol, 60% in mineral oil) were stirred in 30 mL of dry DMF under N_2 at room temperature for 3 days. Yield was 12.72 g (99%); mp 111−155 °C (diastereomers). ^{1}H NMR ($CDCl_3$): δ 2.36−2.50 (m, 4 H), 2.54−2.62 (m, 8 H), 3.76−3.82 (m, 14 H), 6.86 (d, J = 9.2 Hz, 4 H), 7.56 (d, J = 9.2 Hz, 4 H), 7.72 (d, J = 8.6 Hz, 4 H), 7.78 (d, J = 8.6 Hz, 4 H). ^{13}C NMR (APT, $CDCl_3$): δ 194.74 (C=O), 159.80 (C), 143.88 (C), 137.08 (C), 130.71 (CH), 129.84 (C), 127.64 (CH), 126.26 (CH), 116.35 (CN), 114.56 (CH), 75.20 (C), 66.88 (CH_2), 55.36 (CH_3), 49.40 (CH_2). FTIR (KBr): 2962, 2921, 2838, 2825 (C−H stretch), 2227 (CN), 1663 (C=O), 1606, 1509 (phenyl), 1116 (C−O−C), cm^{-1}. Elemental analysis calcd. (found) for $C_{38}H_{38}N_4O_6S$: C, 72.86 (72.84); H, 5.96 (6.00); N, 8.72 (8.46).

4,4′-Bis[*p*-methoxy-α-cyano-α-(*N*-morpholino)benzyl]-benzophenone (16b) from 4,4′-Dichlorobenzophenone. Procedural details were the same as the synthesis of compound **9a**. Compound **15** (2.323 g, 10.00 mmol), 4,4′dichlorobenzophenone (1.256 g, 5.000 mmol), and NaH (0.440 g, 11.0 mmol, 60% in mineral oil) were stirred in 20 mL of dry DMF under N_2 at room temperature for 24 h. Yield was 3.14 g (98%). The melting point, NMR, and IR data were the same as those of **16b** synthesized from 4,4-difluorobenzophenone.

Bis[*p*-(*p*′-hydroxybenzoyl)phenyl] Sulfone (3a). The dimethoxy ether **16a** (3.39 g, 5.00 mmol) was dissolved in 36 mL of HBr (0.200 mol, 45 w/v% in acetic acid) and 10 mL of distilled H_2O. The mixture was heated at reflux for 24 h. Upon heating, the mixture became reddish brown. The mixture was quenched into 500 mL of distilled H_2O. A light pink solid was filtered and dried under vacuum at 100 °C for 36 h, 2.27 g (99%). It was recrystallized from 40% aqueous HOAc, 2.20 g (96%); mp 229.1−230.8 °C (lit.[8] 224−225 °C). ^{1}H NMR (DMSO-d_6): δ 6.89 (d, J = 8.6 Hz, 2 H), 7.65 (d, J = 8.6 Hz, 2 H), 7.87 (d, J = 8.6 Hz, 2 H), 8.18 (d, J = 8.6 Hz, 2 H), 10.09 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 195.43 (C=O), 161.37 (C), 153.29 (C), 141.34 (C), 129.46 (CH), 128.87 (C), 127.12 (CH), 125.05 (CH), 116.75 (CN). FTIR (KBr): 1659 (C=O), 1600 (phenyl), 1334, 1161 (sulfone), cm^{-1}.

4,4′-Bis(*p*-hydroxybenzoyl)benzophenone (3b). Procedural details were the same as for the hydrolysis of compound **3a**. Compound **16b** (3.21 g, 5.00 mmol) and 36 mL of HBr in acetic acid were used. The yield was 2.14 g (97%); mp 252.3−253.5 °C (lit.[8] 248−249 °C). ^{1}H NMR (DMSO-d_6): δ 6.91 (d, J = 8.7 Hz, 2 H), 7.85 (d, J = 8.7 Hz, 2 H), 7.91 (d, J = 8.6 Hz, 2 H), 8.18 (d, J = 8.6 Hz, 2 H), 10.03 (s, 2 H). ^{13}C NMR ($CDCl_3$): δ 195.43 (C=O), 161.37 (C), 153.29 (C), 141.34 (C), 129.46 (CH), 128.87 (C), 127.12 (CH), 125.05 (CH), 116.75 (CN). FTIR (KBr): 3235 (OH, broad), 1649 (C=O), 1598 (phenyl), cm^{-1}.

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