Macromolecules **1998,** *31,* 501−507

Poly(arylene ether azomethine)s: Synthesis by Aldimine-Activated Nucleophilic Aromatic Substitution, Characterization, and Thin Films Morphological Study

Romain Gauderon, Christopher J. G. Plummer, and Jöns G. Hilborn*

Polymer Laboratory, Materials Department, Swiss Federal Institute of Technology, Lausanne, CH-1015 Lausanne, Switzerland

Daniel M. Knauss

Department of Chemistry and Geochemistry, Colorado School of Mines, Golden, Colorado 80401

Received June 9, 1997; Revised Manuscript Received October 14, 1997

ABSTRACT: A series of new, relatively high molecular weight poly(arylene ether azomethine)s was prepared by condensation of silylated bisphenols with bis[*N*-(4-fluorobenzylideneaniline)]s (BFBAs) in polar aprotic solvents in the presence of a catalytic amount of cesium fluoride. The polymerization reaction was the formation of an aryl ether linkage by nucleophilic aromatic substitution. Studies of model compounds demonstrated the required electron withdrawal and the ability of the aldimine to activate the fluoride in the *ipso* position towards the substitution reaction. The resulting polymers were light yellow in color, had intrinsic viscosities between 0.31 and 0.42 dL g^{-1}, and could be solution cast to form amorphous creasable thin films, with glass transition temperatures in the range of 147 to 208 °C. Several of the polymers became partially crystalline on prolonged exposure to the solvent vapor, and the resulting morphologies were investigated by transmission electron microscopy of ultra thin films. Thermogravimetric analysis studies showed little thermal decomposition under nitrogen for temperatures up to 460−492 °C.

Introduction

Aromatic polyazomethines derived from aromatic dialdehydes and diamines, often termed poly(Schiff base)s, have many attractive properties. These properties include excellent thermal stability,[1] the ability to chelate with metals,[1] semiconductivity,[2] and thermally induced crosslinking without the evolution of volatiles.[3] Over the last 10 years, there has been renewed interest in the preparation of high molecular weight poly(Schiff base)s because of their potential for applications in optoelectronics.[4]

The azomethine or aldimine bond (CH═N) is formed during the condensation of an amine with an aldehyde. The first polyazomethines were prepared by Adams *et al.* in 1923,[5] and, in the 1950s fully aromatic polyazomethines were synthesized by Marvel *et al.*;[1] the latter had relatively low molecular weights because of the poor solubility of the rigid molecules. Research was continued by Suematsu *et al.*[6] and Morgan *et al.*[7] in the 1980s. With the introduction of a flexible linkage, such as an aryl ether or an aliphatic unit, the polymers could be made soluble and melt processable.[2,7] Poly(arylene ether azomethine)s can be obtained by reacting an aromatic dialdehyde and an aromatic diamine or derivatives thereof, with the ether linkage being incorporated into one of the two monomers. This approach was used by Morgan *et al.*[7] to make flexible, fiber-forming polymers and more recently by Banerjee *et al.*[2] to make polyazomethines with semiconducting properties when doped with iodine.

An alternative approach is to preform aldimine moieties in the monomer synthesis step, and to connect them with ether linkages in the polymerization step. In 1967, Johnson *et al.*[8] obtained poly(arylene ether sulfone)s by the nucleophilic displacement of bis(aryl halide)s with bisphenoxides in polar aprotic solvents. The polymerization reaction involves the nucleophilic attack by a phenoxide on a bis(aryl fluoride) monomer, activated by an electron-withdrawing group situated in a *para* position with respect to the fluorine atom. The activating group increases the positive charge density of the fluorine-bearing carbon and accepts by resonance the negative charge associated with the phenoxide, giving an intermediate Meisenheimer-like complex, that reduces the activation energy of the reaction. Several methods have successfully been used to predict the potential reactivity of aryl fluorides towards displacement via the S_NAr route.[9−12] These methods are based on the inductive contribution of the activating group, although in reality, the leaving group also polarizes the C−F bond. Generally, the more partial positive charge there is on the carbon bearing the fluoride, the higher the reactivity.

Since the pioneering work of Johnson *et al.*,[13,14] nucleophilic aromatic substitution has been widely acknowledged as a choice method for the preparation of poly(arylene ether)s. During the last 4 years, the same strategy, using new activating groups, has been adopted for example for the preparation of poly(arylene ether ketimine)s,[15,16] poly(arylene azo ether)s,[17] poly(arylene ether phenylquinoxaline)s,[10] 1, 2, 4-triazole poly(arylene ether)s,[11] poly(arylene ether benzimidazole)s,[18] and poly(arylene ether pyrimidine)s.[19] However, to our knowledge, the use of the aldimine group has not been successful, probably for two reasons: firstly, because the aldimine group is hydrolytically labile and therefore does not survive conventional reaction conditions; and secondly, the use of too rigid

---

* To whom correspondance should be addressed.

S0024-9297(97)00815-2 CCC: $15.00

monomers in an inadequate solvent causes premature precipitation at the start of polymerization.[16] We report here on procedures for the synthesis of soluble poly(arylene ether azomethine)s using bis[*N*-(4-fluorobenzylideneaniline)] monomers (BFBAs) in which the aldimine moiety functions as an electron-withdrawing group, thus activating the BFBA compounds for nucleophilic aromatic substitution polymerization, while at the same time employing conditions compatible with hydrolytically labile groups.

Experimental Section

Materials. Unless stated otherwise, commercially available materials were used as received. *N*,*N*-Dimethylacetamide (DMAc; Aldrich) was dried over phosphorus pentoxide, distilled at ambient pressure, and stored under nitrogen over molecular sieves (3 Å). Diphenyl sulfone (DPS; Aldrich) was distilled from calcium hydride. Cesium fluoride (Fluka) was dried and stored in a vacuum oven at 140−200 °C over phosphorus pentoxide or calcium chloride. 4-Fluorobenzaldehyde (Aldrich) was dried over calcium hydride, distilled at reduced pressure, and stored under nitrogen. Toluene was dried and deoxygenated prior to use by purging with nitrogen during azeotroping. Molecular sieves (3 Å; Fluka) were heated at 200 °C for 12 h in a vacuum prior to use.

(4-*t*-Butylphenoxy)trimethylsilane (1). 4-*t*-Butylphenol (10.13 g, 67.43 mmol) and 1,1,1,3,3,3-hexamethyldisilazane (HMDS; excess, 28.5 mL, 21.8 g, 135 mmol) were introduced into a 100-mL, three-necked, round-bottomed flask equipped with a reflux condenser and a nitrogen inlet. As an aid to dissolution, 6 mL of ethyl acetate were added. The mixture was heated at reflux in a oil bath at 133 °C for 18 h. The ethyl acetate and the excess HMDS were then removed by rotary evaporation under reduced pressure. The resulting product was purified by fractional distillation under reduced pressure to give 11 g (73% yield) of **1**, which was stored under argon in a sealed flask.

***N*-(4-Fluorobenzylidene)aniline (2).** 4-Fluorobenzaldehyde (11.57 g, 93.22 mmol) and aniline (8.27 g, 88.8 mmol) were refluxed for 4 h in toluene under nitrogen with the removal of water by a Dean-Stark trap. The reaction was quantitative as determined by gas chromatography (GC). The solvent was evaporated, and the low-melting solid was distilled under reduced pressure, mp 40.5−42.5 °C. ^{1}H NMR ($CDCl_3$): δ 8.42 (s, 1H), 7.91 (dd, 2H), 7.44−7.35 (m, 2H), 7.28−7.10 (m, 5H). Anal. Calcd for $C_{13}H_{10}FN$: C, 78.37; H, 5.06; N, 7.03; found: C, 78.20; H, 5.12; N, 7.07.

Model Reaction. *N*-[4-(4′-*t*-Butylphenoxy)benzylidene]aniline (3). Freshly distilled silylated phenol **1** (2.2377 g, 10.062 mmol) was introduced using a syringe into a 50-mL, three-necked, round-bottomed flask equipped with a reflux condenser and a positive nitrogen pressure. Compound **2** (2.0045 g, 10.061 mmol) was then added, and the weighing pan was carefully washed with DMAc (22 mL) flowing directly into the reaction vessel. The volume of solvent was calculated to give a solid composition of $\sim$25%. A catalytic quantity of CsF ($\sim$70 mg) was added, and the mixture was heated in an oil bath to 160 °C. The reaction was monitored by regularly taking out aliquots for GC analysis. After cooling to ambient temperature, the solution was diluted with 25 mL of CH_2Cl_2, washed with water (3 × 20 mL), dried with $MgSO_4$, and filtered. The solvents were removed by rotary evaporation, and the remaining oil was allowed to cool overnight. The resulting solid was recrystallized (1×) from MeOH and dried in a vacuum oven (5 h, 50 °C) to yield 2.22 g (59% yield) of **3** in the form of light yellow needles, mp 95−97 °C. ^{1}H NMR ($CDCl_3$): δ 8.41 (s, 1H), 7.86 (d, 2H, $J = 8.4$ Hz), 7.43−7.35 (m, 4H), 7.25−7.18 (m, 3H), 7.08−6.98 (m, 4H), 1.61 (s, 9H). FTIR (KBr): 1636 ($C{=}N$), 1248 cm^{-1}(Ph-O-Ph). Anal. Calcd for $C_{23}H_{23}NO$: C, 83.85; H, 7.04; N, 4.25; found: C, 83.67; H, 7.05; N, 4.26.

Synthesis of Monomers. Bis{4-[*N*-(4′-fluorobenzylidene)amino]phenyl} ether (4). Bis(4-aminophenyl) ether (9.71 g, 48.5 mmol), 4-fluorobenzaldehyde (13.0 mL, 15.0 g, 121 mmol), and toluene (400 mL) were introduced into a 500-mL, three-necked, round-bottomed flask equipped with a nitrogen inlet and a Dean-Stark trap fitted with a condenser. The reaction mixture was refluxed for 17 h in an oil bath at 160 °C. The solution was first allowed to cool to ambient temperature and then quenched in ice water. The product crystallized during the cooling, giving 19.29 g of a white fluffy solid after filtration. After recrystallization from toluene, filtration, and drying at 140 °C under vacuum, 15.91 g (yield 80%) of **4** were obtained, mp 213−215 °C. ^{1}H NMR ($CDCl_3$): δ 8.45 (s, 2H), 7.91 (dd, 4H), 7.21−7.04 (m, 12H). Anal. Calcd for $C_{26}H_{18}F_2N_2O$: C, 75.72; H, 4.40; N, 6.79; found: C, 75.64; H, 4.51; N, 6.86.

Bis{4-[*N*-(4′-fluorobenzylidene)amino]phenyl}methane (5). The synthesis was carried out using the same setup as for **4**, with bis(4-aminophenyl)methane (9.66 g, 48.7 mmol), 4-fluorobenzaldehyde (excess, 15.0 mL, 17.3 g, 140 mmol), and toluene (250 mL). The mixture was refluxed in an oil bath at 140 °C for 4 h. During cooling, the product partially precipitated. After filtration, 8.02 g (yield 40%) of **5** in the form of a white fluffy solid were recovered. A further fraction of the desired product was obtained by precipitation with hexane, mp values of 125−127, 134−136, and 140−143 °C (main). ^{1}H NMR ($CDCl_3$): δ 8.42 (s, 2H), 7.89 (dd, 4H), 7.21−7.11 (m, 12H), 4.02 (s, 2H). Anal. Calcd for $C_{27}H_{20}F_2N_2$: C, 79.01; H, 4.91; N, 6.82; found: C, 78.87; H, 4.98; N, 6.87.

Bis{4-[*N*-(4′-fluorobenzylidene)amino]}benzene (6). Freshly sublimed 1,4-diaminobenzene (7.50 g, 69.4 mmol) and 4-fluorobenzaldehyde (18.10 g, 146.0 mmol) were combined in toluene (250 mL) and azeotroped for 4 h to yield 20.1 g (90% yield) of isolated yellow crystals after crystallization from the toluene reaction mixture, mp 173−175 °C. ^{1}H NMR ($CDCl_3$): δ 8.49 (s, 2H), 7.94 (dd, 4H), 7.23−7.14 (m, 8H). Anal. Calcd for $C_{20}H_{14}F_2N_2$: C, 74.99; H, 4.41; N, 8.74; found: C, 75.00; H, 4.50; N, 8.79.

2,2-Bis[4′-(trimethylsiloxy)phenyl]propane (7). 2,2-Bis(4′-hydroxyphenyl)propane (bisphenol-A; 12.25 g, 53.66 mmol) and HMDS (23.0 mL, 17.6 g, 109 mmol) were introduced into a 100-mL, three-necked, round-bottomed flask equipped with a reflux condenser and a nitrogen inlet. The mixture was heated overnight in an oil bath at 140 °C. The excess HMDS was removed at atmospheric pressure under nitrogen, and the product was purified by fractional vacuum distillation. The distilled liquid was stored under argon in a sealed flask. ^{1}H NMR ($CDCl_3$): δ 7.07 (d, 4H), 6.72 (d, 4H), 1.62 (s, 6H), 0.25 (s, 18H).

2,2-Bis[4′-(trimethylsiloxy)phenyl]hexafluoropropane (8). The method of synthesis of **8** was identical to that of **7**, with 2,2-bis(4′-hydroxyphenyl)hexafluoropropane (bisphenol-AF; 14.0 g, 41.6 mmol) as the starting material. The compound was purified by vacuum distillation and isolated as a white, low-melting solid, mp 46−51 °C. ^{1}H NMR ($CDCl_3$): δ 7.24 (d, 4H), 6.80 (d, 4H), 0.29 (s, 18H).

Polymerizations. Polymerization of 4 with 7 (9). A detailed procedure is provided: 2.7364 g (7.3431 mmol) of **7** were introduced into a 50-mL, three-necked, round-bottomed flask equipped with an overhead stirrer, a funnel, and an argon inlet. A few drops of HMDS were added, the funnel was replaced by a reflux condenser, and the mixture was maintained for 2 h at 120 °C in an oil bath and then for 2 h at 140 °C. Next, 3.0286 g (7.3431 mmol) of **4** and 18 mL (17.3 g, solids composition $\approx$ 25%) of DMAc were added to the mixture, the weighing pan and the funnel being carefully washed with the solvent, along with a catalytic amount of CsF ($\sim$70 mg). The funnel was replaced with a reflux condenser and the reaction mixture was heated to 165 °C in an oil bath. After 2.25 h, a dramatic increase in viscosity was observed. The reaction temperature was maintained for a further 2.5 h, and the viscous solution was poured into 500 mL of water. The coagulated polymer was isolated and then stirred vigorously with water in a blender, filtered and washed with hot water (2 × 24 h), and finally dried at 100 °C under vacuum over P_2O_5. ^{1}H NMR ($CDCl_3$): δ 8.43 (s, 2H), 7.86 (d, 4H, $J = 8.9$ Hz), 7.28−7.20 (m, 8H), 7.09−6.96 (m, 12H), 1.71 (s, 6H). FTIR (KBr): 1624 (C=N), 1217 cm^{-1} (Ph-O-Ph).

Polymerization of 4 with 8 (10). The polymer was synthesized from 1.7730 g (3.6891 mmol) of **8** and 1.5215 g (3.6890 mmol) of **4** in 11 mL (10.4 g) of DMAc at 165−170 °C in the presence of a catalytic amount of CsF. After 20 h, the viscous solution was poured into water and treated as for **9**. ^{1}H NMR (CDCl$_3$): δ 8.47 (s, 2H), 7.92 (d, 4H, J = 8.6 Hz), 7.40 (d, 4H, J = 8.6 Hz), 7.22−7.02 (m, 16H). FTIR (KBr): 1626 (C=N), 1249 cm^{-1} (Ph-O-Ph).

Polymerization of 5 with 7 (11). The polymer was synthesized from 1.5946 g (4.2791 mmol) of **7** and 1.7564 g (4.2790 mmol) of **5** using 13 mL of DMAc and a catalytic amount of CsF. The solution was heated at 165−175 °C for ∼48 h. Subsequent treatment was as for **9**. ^{1}H NMR (CDCl$_3$): δ 8.41 (s, 2H), 7.85 (d, 4H, J = 8.5 Hz), 7.27−6.95 (m, 20H), 4.01 (s, 2H), 1.71 (s, 6H). FTIR (KBr): 1627 (C=N), 1241 cm^{-1} (Ph-O-Ph).

Polymerization of 5 with 8 (12). The polymer was synthesized from 2.3574 g (4.9051 mmol) of **8** and 2.0135 g (4.9053 mmol) of **5** using 13 mL of DMAc and a catalytic amount of CsF at 166 °C for 43 h. Subsequent treatment was as for **9**. ^{1}H NMR (CDCl$_3$): δ 8.44 (s, 2H), 7.90 (d, 4H, J = 7.5 Hz), 7.39 (d, 4H, J = 7.5 Hz), 7.21−7.01 (m, 16H), 4.02 (s, 2H). FTIR (KBr): 1626 (C=N), 1249 cm^{-1}(Ph-O-Ph).

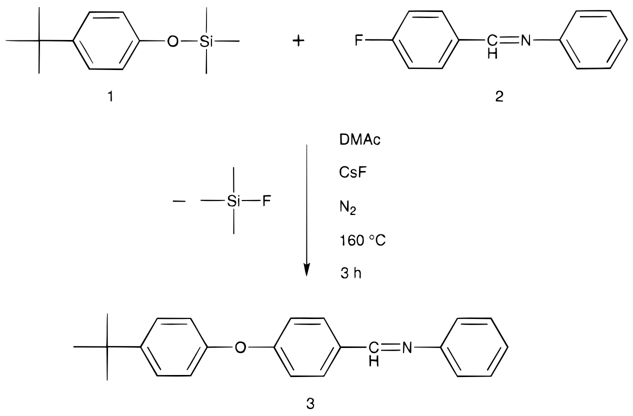
Polymerization of 6 with 7 (13). The polymer was synthesized from 2.4149 g (7.552 mmol) of **6** and 2.8144 g (7.552 mmol) of **7**, using 20 g of DPS at 230 °C as a solvent, with a catalytic amount of CsF. After 1.5 h, the viscous solution was precipitated into methanol, filtered, washed for 24 h in methanol, and refiltered. FTIR (KBr): 1625 (C=N), 1248 cm^{-1} (Ph-O-Ph). Anal. Calcd for $(C_{35}H_{28}N_2O_2)_n$: C, 82.65; H, 5.55; N, 5.51; found: C, 81.28; H, 5.58; N, 5.24.

Polymerization of 6 with 8 (14). The polymer was synthesized from 2.4925 g (7.781 mmol) of **6** and 3.7379 g (7.781 mmol) of **8** using 20 g of DPS at 230 °C as a solvent, with a catalytic amount of CsF. The solution was heated for 6 h. The same procedure was then used as for **9**. FTIR (KBr): 1623 (C=N), 1241 cm^{-1} (Ph-O-Ph). Anal. Calcd for $(C_{35}H_{22}F_6N_2O_2)_n$: C, 68.18; H, 3.60; N, 4.54. Found: C, 67.80; H, 3.71; N, 4.51.

Characterization. ^{1}H NMR spectra were recorded using the Bruker AC-P-200 instrument (200 MHz), with tetramethylsilane used as the reference. IR spectra were obtained with a Nicolet FTIR spectrophotometer. Glass transition temperatures (T_g), taken as the midpoint of the change in slope of the heat flow rate versus temperature, were measured with a Perkin-Elmer DSC-7 differential scanning calorimeter (DSC) at a heating rate of 10 K min^{-1}. Thermogravimetric analyses (TGA) of polymer samples were carried out using a Perkin-Elmer TGA-7 at a heating rate of 10 K min^{-1} in nitrogen. Intrinsic viscosity measurements (one-point determination) were made in DMAc at 25 °C at a concentration of 0.5 g dL^{-1} with a Cannon-Ubbelohde dilution viscometer. Purities of monomers were determined by GC analysis using the Perkin-Elmer Autosystem. Elemental analyses were performed at the Laboratory of Pharmaceutical Chemistry, University of Geneva, Switzerland.

For morphological investigations, films of ∼50 nm in thickness were solution cast from chloroform onto mica or glass, dried under vacuum, and transferred onto distilled water. The films were then picked up on carbon-covered transmission electron microscopy (TEM) grids and dried. All subsequent treatments were carried out *in situ*. TEM observations were made using the Phillips EM 430 ST, equipped with a low dose unit; at 300 kV. Electron diffraction patterns were calibrated using aluminium samples and the internal calibration feature of the EM 430 ST. High-resolution micrographs were obtained at magnifications of between ∼50 and 80 K, at an estimated defocus of 100 nm and a total electron dose of ∼0.1 C cm^{-2}. The images were recorded on Kodak SO-165 film that was developed for 10 min in full-strength Ilford D-19 and digitized as 512 × 768 pixel arrays for subsequent analysis.

Scheme 1. Model reaction.



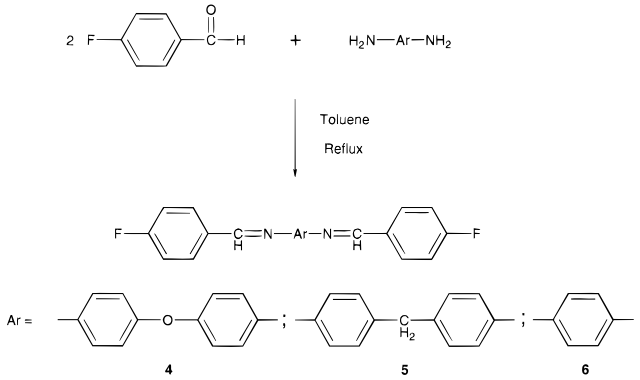
Results and Discussion

The synthetic route for the preparation of new poly(arylene ether azomethine)s was nucleophilic aromatic substitution by a phenoxide of a bis(aryl fluoride) compound activated in the *para* positions by aldimine groups. Prior to the present work, it was known that the ketimine group is able to activate a bis(aryl fluoride) for nucleophilic aromatic displacement,[15] and we thought it likely that the aldimine group would have a similar activating influence. One indication of whether the conditions for the S$_N$Ar reaction are fulfilled is the electron-withdrawing capacity of the activating group.[11] The electronic effect of the aldimine group on the 4-fluorophenyl moiety may be evaluated by ^{1}H NMR, the deshielding of protons *ortho* to the electron-withdrawing substituent being indicative of the strength of the electron-withdrawing group.[11,12] The ^{1}H NMR spectrum of **2** reveals a relatively strong attraction by the aldimine, giving a resonance of δ 7.91 ppm for the *ortho* protons. This value is comparable with those for other groups known to activate nucleophilic aromatic substitution. The sulfone group gives a resonance at δ 8.0 ppm, and the ketone group gives a resonance at δ 7.73 ppm.[20]

Model Reaction. A model reaction was therefore performed to investigate the feasibility of the aldimine-activated synthesis. Traditionally, a weak base, such as potassium carbonate is used to generate the nucleophilic phenoxide from a phenol *in situ*.[10,11,15−17] *N*-(4-Fluorobenzylidene)aniline (**2**) and 4-*t*-butylphenol were therefore reacted in DMAc at 130−165 °C in the presence of an excess of potassium carbonate. The progress of the reaction was monitored by GC. After 48 h, the analysis revealed the formation of a product identified as **3**, but it was also observed that **2** was partially hydrolyzed during the reaction. Consequently, another synthetic route had to be chosen, which avoided protic species. We envisaged that the corresponding aryl silyl ether should circumvent this problem, and a synthetic route was developed employing the silylated phenol as a precursor. Stoichiometric amounts of **1** and **2** were therefore reacted in DMAc with CsF as catalyst (Scheme 1). Analysis by GC revealed the complete conversion of the starting materials and the formation of a single product **3** within 3 h, thus demonstrating the feasability of the new polymer-forming reaction.

Analysis by ^{1}H NMR confirmed the structure of **3**. The azomethine proton resonated as a singlet at δ 8.41 ppm, the two protons *ortho* to the carbon of the C=N bond resonated as a doublet at 7.86 ppm, and the 11

Scheme 2. Synthesis of monomers



other aromatic protons were distributed among three multiplets resonating between 6.98 and 7.43 ppm. The presence of the *t*-butylphenoxy moiety was confirmed by the signal of the nine protons of the *t*-butyl group, which resonated as a singlet at 1.61 ppm. The formation of the ether linkage was confirmed by Fourier transform infrared (FTIR) spectroscopy, with a relatively strong absorption being observed at 1248 cm^{-1}.

Synthesis of Monomers. BFBA monomers were synthesized by the facile reaction of 4-fluorobenzaldehyde with three different aromatic diamines (Scheme 2). The reaction was performed under nitrogen to prevent the reagents from oxidizing. Toluene was used as the solvent, and water (a byproduct of the reaction) was removed azeotropically by distillation. The reaction was straightforward and gave good yields for monomers **4** to **6**.

The structures of the monomers were confirmed by ^{1}H NMR spectroscopy and elemental analysis. The ^{1}H NMR spectra of monomers **4**, **5**, and **6** showed singlets at δ 8.42, 8.45, and 8.49 ppm, respectively, corresponding to the two azomethine protons, a doublet at δ 7.9 ppm corresponding to the four protons *ortho* to the carbons of the C═N bonds, and a multiplet at δ 7.0–7.2 ppm corresponding to the remaining aromatic protons. The two methylene protons of **5** resonated at δ 4.02 ppm as a singlet. The NMR spectra were consistent with the presence of only one stable isomer (the *trans*–*trans* isomer) for each monomer. DSC analysis of BFBA monomers revealed relatively broad melting peaks. Moreover, monomer **5** showed two distinct subsidiary peaks, in addition to the main melting peak, which is evidence of polymorphism. Indeed, there have been many reports of the isolation of azomethine compounds in more than one crystalline form.[21]

An attempt was made to determine the purity of the monomers by thin layer chromatography. This technique did not prove very satisfactory however. The chromatogram of samples of **4** and **5** recrystallized twice from toluene (with ethyl acetate as the eluent) each showed two intense peaks, separated by an additional, fainter peak. Because the monomers were effectively pure, as borne out by their subsequent successful polymerization, the best explanation for this result would be partial hydrolysis of the BFBAs on the silica chromatographic plate (due to the acid silanol groups that cover the surface of the plate). This result is an indication of the susceptiblity of the aldimine to undergo hydrolysis in the presence of protic species.

Synthesis of Polymers. Polymerizations of BFBAs (**4** to **6**) with two different silylated bisphenols were carried out in a polar aprotic solvent in the presence of a catalytic amount of cesium fluoride (Scheme 3). The solvents used were DMAc with monomers **4** and **5** and DPS with the more rigid monomer **6**. As with the model reaction, the key to obtaining high molecular weight polymers was to perform the reaction in the complete absence of water. This requirement was achieved by working with extra-dry solvent, monomers, and catalyst, and by drying the system before the polymerization. A typical synthesis proceeded as follows: the silylated bisphenol was first introduced into the flask under inert atmosphere (N_2 or Ar), with a syringe. The weight of the syringe was carefully measured before and after injection of the silylated bisphenol to determine precisely the injected amount and to calculate the required stoichiometric quantity of the BFBA monomer. A few drops of HMDS were then added, and the solution was heated for ~2 h at 120 °C. This step was necessary to fully silylate any traces of monosilylated monomer resulting from partial hydrolysis during the transfer. The mixture was then heated for a further 2 h at 140 °C to remove any excess HMDS. The stoichiometric amount of BFBA monomer was carefully added, with the weighing pan being washed with solvent flowing directly into the flask. The amount of solvent was calculated to give ~25% solids composition. A catalytic amount of cesium fluoride (~70 mg) was added, and the mixture was heated to 165 °C. The color of the solution turned gradually from bright yellow to amber-yellow. The reaction was allowed to continue at this temperature until a substantial rise in the solution viscosity was observed, which was indicative of high molecular weight. In the case of polymer **9**, a noticeable increase in the solution viscosity was observed after 2.25 h. Heating was maintained for a further 2.5 h, after which the reaction was considered to be complete. The mixture was then poured into rapidly stirred water in a blender. The coagulated polymer was filtered and washed in hot water for 2 × 24 h. This procedure was used for the synthesis of polymers **9**, **10**, **13**, and **14**.

Scheme 3. Polymerizations

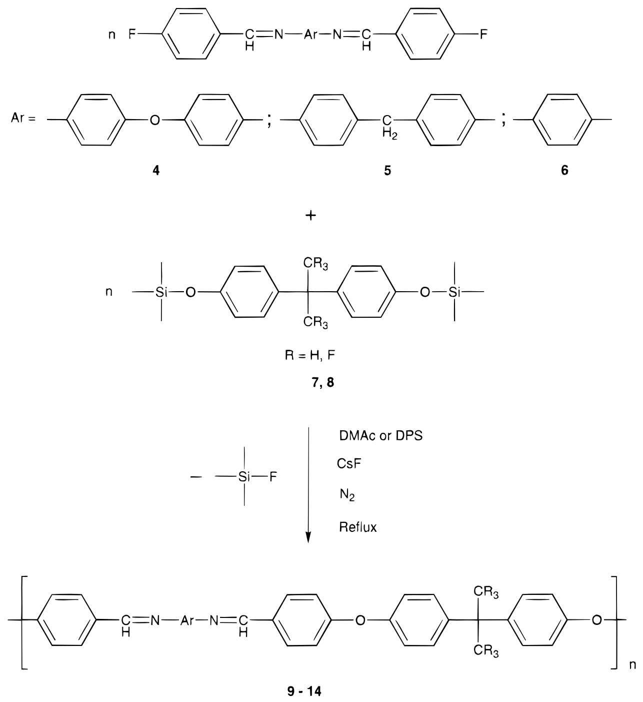


Table 1. Intrinsic Viscosity Data (η), Glass Transition Temperatures (T_g), Crystalline Melting Points (T_m), 5% Weight Loss Temperatures ($T_{d,\ 5\%}$), Char Residues, and Weight Losses on Isothermal Aging of Poly(arylene ether azomethine)s 9−14[a]

polymer	[η] at 25 °C (dL g^{-1})	T_g, (T_m), at 10 K min^{-1} (°C)	$T_{d,\ 5\%}$ (°C)	residue at 750 °C (wt%)	weight loss at 400 °C (wt% h^{-1})
9 (Ar = Ph-O-Ph; R = H)	0.42	149 (310)	487	46	14.5
10 (Ar = Ph-O-Ph; R = F)	0.41	169	492	51	12.3
11(Ar = Ph-CH2-Ph; R = H)	0.31	147	481	49.5	18.4
12 (Ar = Ph-CH2-Ph; R = F)	0.40	166	460	52	15.2
13 (Ar = Ph; R = H)	NA[b]	208 (253)	470	60	9.8
14 (Ar = Ph; R = F)	NA	NA	480	63	NA

[a] Thermal data measured under nitrogen. [b] NA, Not available.

The initial stages of the procedure were slightly different for polymers **11** and **12**. In the first step, both monomers and DMAc were introduced into the flask along with a small quantity (0.1−0.3 mL) of HMDS, and the mixture was heated at 130 °C for 2 h, and then at 160−165 °C for 2 h. This method has the advantage of drying the whole system before the addition of the catalyst.

The model reaction was rapid (<3 h), so we also expected the polymerizations to be rapid. Moreover, it is known that in the synthesis of poly(arylene ether ester)s by this method, a large increase in viscosity is observed after 2−6 h.[22] The reaction was indeed rapid for polymers **9**, **13**, and **14**, and a large increase of the viscosity of the solution was observed after ~2 h. In the case of polymers **10**−**12**, reaction times of 20, 48, and 43 h, respectively, were necessary to obtain a significant change of the viscosity. This longer time was almost certainly not due to differences in the reactivities of the monomers because the monomers have very similar structures. The rapidity of the reactions in DPS (1.5 and 6 h for polymers **13** and **14**, respectively) was thought to be due to the high reaction temperature (230 °C) allowed by this solvent. The temperature was not significantly different for the various reactions in DMAc (165−170 °C), so that the critical parameter was probably the amount of solvent in the reaction mixture. When the concentrations are calculated from the effective amounts of solvent introduced, the solids composition is 25% in the case of polymer **9** and <25% (in the 20−25% range) in the case of polymers **10**−**12**. As the synthesis of **9** was the most rapid, it appears that a solids composition of 25% is optimal in DMAc and larger dilutions significantly decrease the reaction rate.

Characterization of Polymers. Polymers **9**−**12** exhibited unlimited solubility in a variety of solvents, including dichloromethane, chloroform, DMAc, and NMP. On solution casting from DMAc, they produced clear, yellow, fingernail-creasable films. The intrinsic viscosities were measured in DMAc at 25 °C, giving values of between 0.31 and 0.42 dL g^{-1} (Table 1). These values, along with the ability to obtain creasable films, confirm the formation of relatively high molecular weight polymers because similar values are found in the literature for other poly(arylene ether)s.[10,11,15−19] Polymers **13** and **14** were only sparingly soluble in these solvents, and complete dissolution was only possible in molten DPS; therefore, viscosity data could not be obtained.

The repeat units of polymers **9**−**12** were characterized by ^{1}H NMR. The spectra confirmed the expected molecular structures. The spectrum of polymer **12** in deutereted chloroform is shown in Figure 1. The two azomethine protons resonated as a singlet at δ 8.44 ppm. The four protons *ortho* to the carbons of the C=N bonds resonated at δ 7.90 ppm as a doublet. The doublet at δ 7.39 ppm could be assigned to the four protons *ortho* to the relatively electron-withdrawing hexafluoroisopropylidene group; these peaks were not observed in the spectrum of polymer **11**, the nonfluorinated analogue of **12**. The 16 remaining aromatic protons were distributed between a multiplet at δ 7.21−7.01 ppm. The two aliphatic protons of the methylene moiety resonated at δ 4.02 ppm as a singlet.

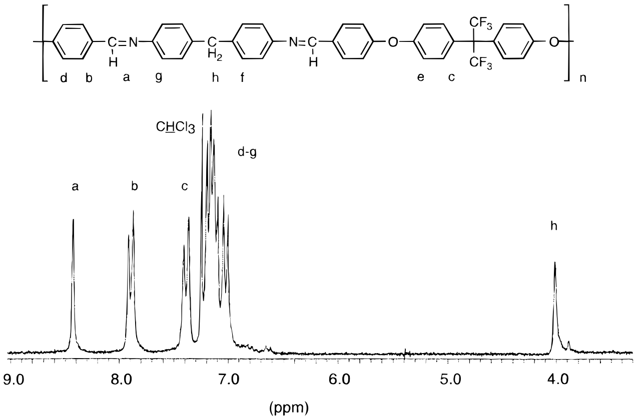


Figure 1. ^{1}H NMR (200 MHz, $CDCl_3$) spectrum of polymer **12**.

The presence of ether linkages formed during the polymer-forming reaction was established by FTIR, a strong absorption being observed in the range 1241−1249 cm^{-1}. The absorbances due to the imine bond were observed in the range 1623−1626 cm^{-1}. Polymers **13** and **14**, being only sparingly soluble in common organic solvents, had their compositions verified by elemental analysis. The values obtained were in good agreement with the calculated ones.

The T_gs of polymers **9**−**12** ranged from 147 to 169 °C (Table 1). These values were obtained after a single run up to 230 °C. Subsequent runs with the same sample showed a significant increase in T_g. For example, a T_g of 166 °C was measured for polymer **12** after a first run (10 K min^{-1}). After cooling, a second run at the same heating rate gave a value of 180 °C. This result may indicate slight crosslinking of the material,[3] a hypothesis that is supported by the fact that the sample did not redissolve completely in dichloromethane after the second run.

Interestingly, it was observed that amorphous films of polymer **9** and **13** could be recrystallized by exposure to dichloromethane vapor for a few hours. Corresponding melting endotherms were observed at 253 and 310 °C, respectively, although in neither case were suitable conditions identified for melt crystallization [this may be a result of crosslinking, but it is also significant that the difference between the crystalline melting point (T_m)

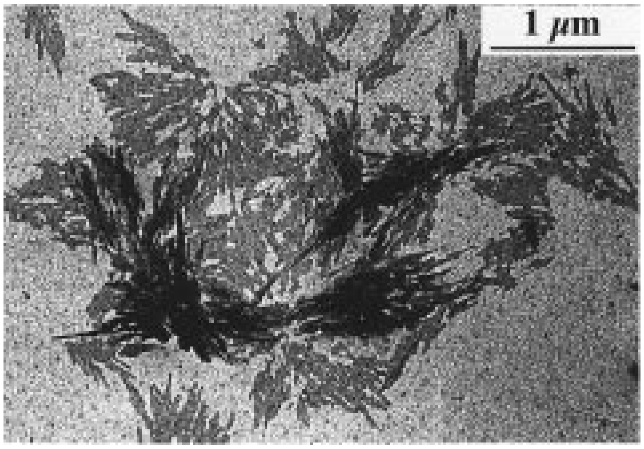


Figure 2. Morphology of a thin film of polymer **9** after overnight exposure to dichloromethane vapor.

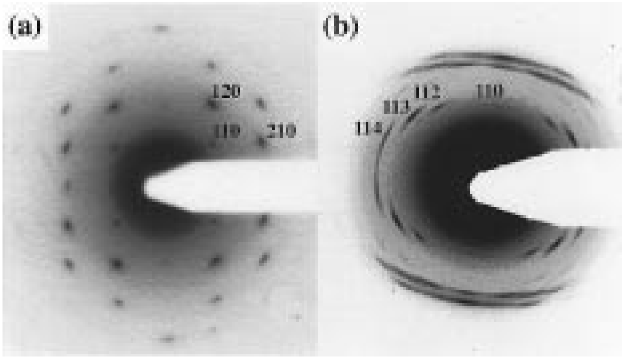


Figure 3. Electron diffraction patterns: (a) single crystal pattern from polymer 13; (b) tilted fiber pattern from polymer 9 (indexed assuming an orthorhombic unit cell).

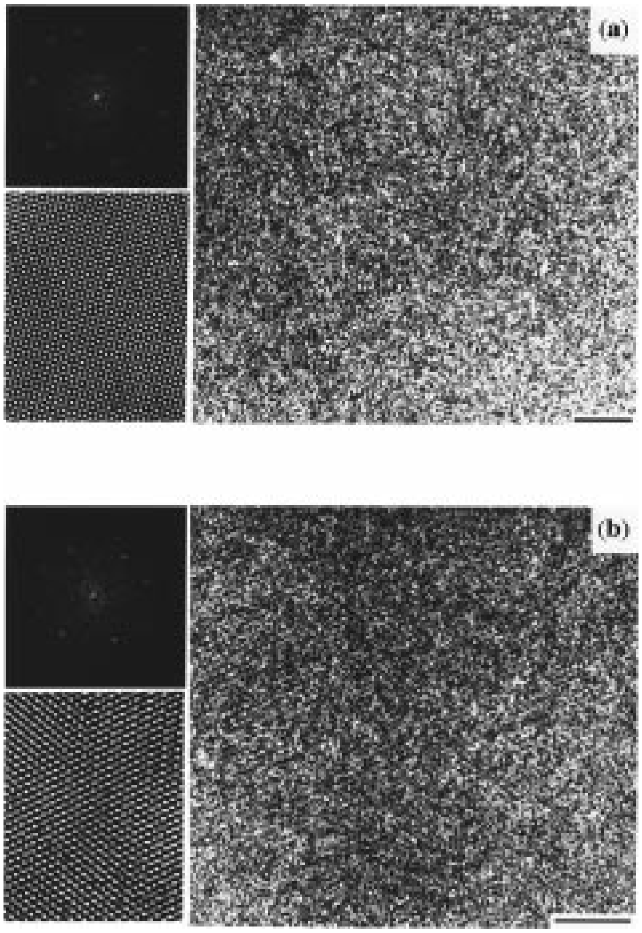


Figure 4. High-resolution TEM images from single lamellae in (a) polymer **13** and (b) polymer **9**. The insets show the image power spectrum and the result of Fourier filtering (scale bar, 5 nm).

and the T_g is relatively low, so that chain mobility in the melt may be severely restricted in temperature regimes in which the undercooling is sufficient to provide a substantial driving force for crystallization]. As-synthesized, polymer **13** did exhibit a melting endotherm in the first DSC heating run, but after cooling, a subsequent heating run showed a T_g at 208 °C and no trace of recrystallization or of a melting endotherm.

Figure 2 shows the morphology of a thin film of polymer **9** after overnight exposure to dichloromethane vapor. The film initially showed considerable dewetting of the carbon substrate, which was followed by the growth of the agglomerations of branched platelets shown. Electron diffraction patterns were indicative of a highly disordered structure locally, but use of a highly focused beam to reduce the illuminated area to $\sim$50 nm^2 suggested *c* to be approximately perpendicular to the substrate in each case, and *pgg* basal symmetry for the unit cell (Figure 3a). The corresponding lattice parameters were $a = 9.3$ Å and $b = 10.6$ Å for polymer **9**, and $a = 8.2$ Å and $b = 10.4$ Å for polymer **13**. Attempts to crystallize the samples with *c* parallel to the plane of the films with oriented substrates or by shearing the polymer at high temperature onto a mica substrate were unsuccessful, and the beam intensities required to obtain single crystal patterns made systematic tilting to look at other orientations difficult. However, tilted fiber patterns could be obtained in samples illuminated over large areas, as shown in Figure 3b (because of the limited range of tilts available in the EM 430 ST, such patterns were obtained using a Phillips EM 300 at 100 kV). Indexing of these patterns according to an orthorhombic unit cell suggested approximate fiber repeats of 31.5 and 27.5 Å for polymers **9** and **13**, respectively, which are consistent with an extended chain conformation with one polymer repeat unit per unit cell in the *c* direction in each case. Figure 4 shows high resolution micrographs of polymers **9** and **13** along with the Fourier power spectra and Fourier filtered images. These results indicate a four-chain unit cell in both cases, with pseudo hexagonal packing, corresponding to a crystal density of $\sim$1.4 g cm^{-3} (taking the dark regions to correspond to axes of individual chains; the projected charge density approximation is assumed here, which is not unreasonable for thin organic crystals).

The thermal stability of the polymers was investigated by both dynamic and isothermal TGA in nitrogen (Table 1). The polymers exhibited good thermal stability, and the 5% weight loss temperatures ranged from 460 to 492 °C (although crosslinking may occur at these temperatures). Moreover, char residues in the 50−60% range were obtained at 750 °C, which is indicative of good flame-retardant characteristics. However, in our opinion, a more significant parameter is the long-term behavior of the polymers at high temperatures. Isothermal aging experiments revealed a weight loss in the 9.8−18.4% range at 400 °C after 1 h. It is likely that improved long-term thermal stability of polyazomethines, as well as increased T_g, can be acheived by use of highly dipolar groups, such as sulfone or carbonyl, in the place of the methylene bridge. Not surprisingly, the polymers with a methylene bridge were less stable than the corresponding polymers containing an ether bridge. Also, the replacement of the methyl groups by their perfluorinated analogue improved the thermal stability. Finally, the use of a more rigid, more conjugated structure, as in polymers **13** and **14** improved the stability, but at the expense of solubility.

Conclusions

A series of new, relatively high molecular weight, poly(arylene ether azomethine)s was prepared. The polymerization reaction was the formation of an aryl ether linkage by nucleophilic displacement, the aldimine being preformed during monomer synthesis. The aldimine group has the necessary activating effect for the displacement of fluorine in the *para* position of a benzene ring by phenoxides. However, conventional polymerization conditions involving elimination of water have been shown to hydrolyze the aldimine and were considered unsuitable. Silylated bisphenol monomers were therefore reacted with bis[*N*-(4-fluorobenzylideneaniline)]s in polar aprotic solvents in the presence of a catalytic amount of cesium fluoride. Because the phenoxide was generated from silylated bisphenols, protic species were avoided, thus permitting the formation of an aryl ether linkage in the presence of a hydrolytically labile group. The polymers synthesized in this way successfully combined the high processability of poly(arylene ether)s with the high thermal stability of aromatic azomethines.

Morphological investigations were performed on thin films of polymers recrystallized by exposure to dichloromethane vapor. High-resolution micrographs along with the Fourier power spectra indicated a four-chain unit cell with pseudo hexagonal packing in both cases studied.

References and Notes

(1) Marvel, C. S.; Hill, W. S. *J. Am. Chem. Soc.* **1950**, *72*, 4891.
(2) Banerjee, S.; Gutch, P. K.; Saxena, C. *J. Polym. Sci. Part A: Polym. Chem.* **1995**, *33*, 1719.
(3) Mikroyannidis, J. A. *J. Polym. Sci. Part A: Polym. Chem.* **1989**, *27*, 3465.
(4) Lee, K. S.; Samoc, M. *Polym. Commun.* **1991**, *32*, 361.
(5) Adams, R.; Bullock, R. E.; Wilson, W. C. *J. Am. Chem. Soc.* **1923**, *45*, 521.
(6) Suematsu, K. N.; Takada, K. J. *Coll. Polym. Sci.* **1983**, *261*, 470.
(7) Morgan, P. W.; Kwolek, S. L.; Pletcher, T. C. *Macromolecules* **1987**, *20*, 729.
(8) Johnson, R. N.; Farnham, A. G.; Clendinning, R. A.; Hale, W. F.; Merriam, C. N. *J. Polym. Sci. A-1* **1967**, *5*, 2375.
(9) Lozano, A. E.; Jimeno, M. L.; de Abajo, J.; de la Campa, J. G. *Macromolecules* **1994**, *27*, 7164.
(10) Hedrick, J. L.; Twieg, R.; Matray, T.; Carter, K. *Macromolecules* **1993**, *26*, 4833.
(11) Carter, K. R.; Miller, R. D.; Hedrick, J. L. *Macromolecules* **1993**, *26*, 2209.
(12) Hedrick, J. L.; Labadie, J. W. *Macromolecules* **1990**, *23*, 1561.
(13) Labadie, J. W.; Hedrick, J. L. *Macrom. Chem., Macromol. Symp.* **1992**, *54/55*, 313.
(14) Maiti, S.; Mandai, B. *Prog. Polym. Sci.* **1986**, *12*, 111.
(15) Mohanty, D. K.; Allen, R. D.; Yeakel, C.; Gower, K.; Mani, R. S. *Makromol. Chem.* **1993**, *194*, 2779.
(16) Matsuo, S.; Nakao M. *Polym. J.* **1994**, *26*, 738.
(17) Mohanty, D. K.; Bhatnagar, A.; Mueller, J.; Osborn, D. J.; Martin, T. L.; Wirtz, J. *Polymer* **1995**, *36*, 3019.
(18) Twieg, R.; Matray, T.; Hedrick, J. L. *Macromolecules* **1996**, *29*, 7335.
(19) Herbert, C. G.; Bass, R. G.; Watson, K. A.; Connell, J. W. *Macromolecules* **1996**, *29*, 7709.
(20) Pretsch; Clerc; Seibl; Simon *Tabellen zur Strukturaufklärung organischer Verbindungen mit spektroskopischen Methoden;* Springer-Verlag: Berlin, Heidelberg, New York, 1976.
(21) McCarty, C. G. In *The Chemistry of the Carbon-Nitrogen Double Bond*; Patai, Ed.; Interscience: New York, 1970.
(22) Hilborn, J. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36(1)*, 765.

MA9708151