Synthesis and Properties of Poly(arylene ether imine)s

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ABSTRACT: Poly(arylene ether)s containing imine units were prepared by the aromatic nucleophilic displacement reaction of potassium salt of bisphenols with bis(fluorophenyl) compound activated by imine in *N*-methyl-2-pyrrolidone at elevated temperature. Polymers having inherent viscosities of 0.3–0.6 dL g⁻¹ were obtained after polymerization for 4–7 h. The polymers had glass transition temperatures from 141 to 198°C and decomposition temperatures (5% weight loss under air atmosphere) from 445 to 544°C depending on the bisphenols used. Isothermal TGA measurements (400°C under air or nitrogen atmosphere) revealed that the 4,4'-biphenol-based poly(arylene ether imine) belonged to the superior class of heat resistant polymers. The cast films of these polymers exhibited tensile strength, moduli, and elongations at 23°C of 70–100 MPa, 2.5–3.6 GPa, and 6–17%, respectively.

KEY WORDS High Performance Aromatic Polyethers / Aromatic Nucleophilic Substitution Polymerization / Imine-Containing Aromatic Polyether / Thermal Behavior / Tensile Properties /

Many kinds of poly(arylene ether)s have been prepared via nucleophilic aromatic substitution polymerization.^{1–3} Sulfone-containing poly(arylene ether)s such as UdelTM (Amoco) or ketone functional polymers such as PEEKTM (ICI) have gained significant commercial importance. They exhibit excellent hydrolytic and thermal stability over a wide temperature range and have good mechanical properties.^{4,5}

The electron withdrawing groups on aromatic dihalides or dinitro compounds play significant roles in the synthesis of poly(arylene ether)s *via* nucleophilic aromatic substitution reaction, which activate halogen atoms or nitro groups, so that such electron withdrawing groups as sulfone, ketone, imide, amide, nitrile, and many heterocyclic units have been applied to the preparation of poly(arylene ethers).^{6–8} Mohanty and his co-workers demonstrated the imine group to be powerful electron withdrawing ability for ether synthesis.⁹

Imine containing polymers such as polyazomethines were studied extensively in the 1950s and 1960s.^{9–16} Several polymers proved to be fibers having excellent mechanical strength.¹⁷ The low solubility and inadequate thermal stability of these polyazomethines seem responsible for the hydrogen attached to the tertiary carbon of imine. The substitution of the hydrogen for phenyl or methyl group is thus thought to increase in solubility and thermal stability. The reaction of a ketone with an amine is slower than that of an aldehyde, so the polymerization reaction of a ketone and an amine is difficult.

This paper describes the synthesis of linear poly(arylene ether)s by reactions of difluorophenyl compounds containing phenyl or methyl attached imine with bisphenols, and the thermal and mechanical properties of the polymers as well.

EXPERIMENTAL

Characterization

Inherent viscosities (I.V.) were measured in an Ostwald viscometer at 60°C at a concentration of 0.20 g of polymer in 100 ml of *N*-methyl-2-pyrrolidone.

The glass transition temperature (T_g) was measured on a Seiko DSC 220 at a heating rate of 20°C min⁻¹ up to 400°C, cooling at about 200°C min⁻¹, and then reheating at 20°C min⁻¹. T_g was taken at the midpoint of change in the slope of the base line. Thermogravimetry (TG) was performed on a Seiko TG/DTA 220 at a heating rate of 10°C min⁻¹ in air, and isothermal scans were made at 400°C over a 10 h period in air or nitrogen. IR spectra were obtained on a JASCO IR810 spectrophotometer.

Mechanical property measurements were made on a Shimadzu Autograph IS-5000 at a strain rate of 2 mm min⁻¹ using casting films from a chloroform solution.

Materials

N-Methyl-2-pyrrolidone (NMP) was vacuum distilled over phosphorus pentoxide. Toluene was used as received. 4,4'-Dihydroxytetraphenylmethane (TP) was prepared according to the method of Erich²⁰ by condensation of dichloro-diphenylmethane with phenol. 2,7-Naphthalenediol (ND) was recrystallized from methanol. 4-Fluorobenzophenone, 4-fluorobenzaldehyde, 1,4-phenylenediamine, 4,4'-diaminodiphenyl ether, hydroquinone (HQ), 4,4'-biphenol (BP), and 2,2-bis(4-hydroxyphenyl)propane (BA) were used as received without further purification. Molecular sieves (4A) were used as received.

Synthesis

Synthesis of N,N'-Bis[(4-fluorophenyl)phenylmethylene]-1,4-benzenediamine (I). A three-necked round bottom flask equipped with an argon inlet and outlet, condenser, and mechanical stirrer was charged with *p*-fluoro-

benzophenone (60.06 g, 0.3 mol), *p*-phenylenediamine (16.22 g, 0.15 mol), 85 g of molecular sieves, and 200 ml of toluene. The reaction mixture was heated 120°C with stirring for 22 h. The molecular sieves were removed by filtration while hot. On cooling, the resulting precipitate was collected. Recrystallization from toluene gave yellow needles (mp 191–192°C). The yield was 38.2 g (57.3%). The infrared (IR) spectrum (KBr) exhibited an absorption at 1622 cm⁻¹ (C=N).

Anal. Calcd for C₃₂H₂₂F₂N₂: C, 81.33%; H, 4.69%; N, 5.93%. Found: C, 80.8%; H, 4.9%; N, 5.7%.

Synthesis of N,N'-Bis[(4-fluorophenyl)phenylmethylene]-4,4'-diaminodiphenyl ether (II). A mixture of 60.0 g (0.3 mol) of 4-fluorobenzophenone, 30.03 g (0.15 mol) of 4,4'-diaminodiphenyl ether, 150 ml of toluene, and 85 g of molecular sieves was heated at 120°C for 24 h. The molecular sieves were removed by filtration. Toluene was removed by rotary evaporation under reduced pressure to afford the crude product, which was recrystallized from ethanol (pale yellow needles; mp 153°C). The yield was 50.0 g (63.1%). The IR spectrum (KBr) showed absorptions at 1601 cm⁻¹ (C=N) and 1244 cm⁻¹ (C–O–C).

Anal. Calcd for C₃₈H₂₆F₂N₂O₁: C, 80.83%; H, 4.64%; N, 4.96%. Found: C, 80.3%; H, 4.9%; N, 4.5%.

Synthesis of N,N'-Bis[(4-fluorophenyl)methylmethylene]-1,4-benzenediamine (III). To a 500 ml round bottomed flask, 4-fluoroacetophenone (41.44 g, 0.3 mol) and *p*-phenylenediamine (16.22 g, 0.15 mol) were added along with 200 ml of toluene and 85 g of molecular sieves. The reaction mixture was gently refluxed for a period of 24 h. The molecular sieves were removed by filtration during hot. On cooling, the precipitate was collected. Recrystallization from toluene gave yellow needles (mp 237–238°C). The yield was 28.7 g (54.9%). The IR spectrum (KBr) exhibited an absorption at 1624 cm⁻¹ (C=N).

Anal. Calcd for C₂₂H₁₈F₂N₂: C, 75.84%;

H, 5.21%; N, 8.04%. Found: C, 75.6%; H, 5.4%; N, 7.8%.

Synthesis of *N,N'*-Bis[(4-fluorophenyl)methylmethylene]-4,4'-diaminodiphenyl ether (IV). 4-Fluoroacetophenone (41.44 g, 0.3 mol) was reacted with 30.03 g (0.15 mol) of 4,4'-diaminodiphenyl ether in 150 ml of refluxing toluene for 24 h in the presence of 85 g molecular sieves. The product was recrystallized from toluene (yellow needles; mp 166–167°C), and the yield was 47.6 g (78.5%). The IR spectrum (KBr) exhibited absorptions at 1627 cm⁻¹ (C=N) and 1246 cm⁻¹ (C–O–C).

Anal. Calcd for C₂₈H₂₂F₂N₂O₁: C, 76.35%; H, 5.03%; N, 6.36%. Found: C, 75.9%; H, 5.3%; N, 6.1%.

Synthesis of *N,N'*-Bis[(4-fluorophenyl)methylmethylene]-1,4-benzenediamine (V). Into a 300 ml three-neck round-bottom flask were placed 4-fluorobenzaldehyde (37.23 g, 0.3 mol), 1,4-phenylenediamine (16.22 g, 0.15 mol), 150 ml of toluene, and 85 g of molecular sieves. The reaction mixture was refluxed with stirring for 10 h. On cooling, the resulting precipitate was collected by filtration and recrystallized from toluene (yellow plates; mp 179°C). The yield was 45.5 g (76.4%). The IR spectrum (KBr) showed an absorption at 1637 cm⁻¹ (C=N).

Anal. Calcd for C₂₀H₁₄F₂N₂: C, 74.99%; H, 4.40%; N, 8.74%. Found: C, 74.9%; H, 4.7%; N, 8.6%.

Synthesis of *N,N'*-Bis[(4-fluorophenyl)methylmethylene]-4,4'-diaminodiphenyl ether (VI). 4-Fluorobenzaldehyde (54.28 g, 0.437 mol) was reacted with 43.75 g (0.218 mol) of 4,4'-diaminodiphenylether in 150 ml of refluxing toluene for 10 h in the presence of 85 g molecular sieves. The product was recrystallized from toluene (yellow plates; mp 218°C), and the yield was 55.7 g (67.3%). The IR spectrum (KBr) showed absorptions at 1626 cm⁻¹ (C=N) and at 1246 cm⁻¹ (C–O–C).

Anal. Calcd for C₂₆H₁₈F₂N₂O₁: C, 74.98%; H, 5.32%; N, 6.73%. Found: C, 74.8%; H, 5.6%; N, 6.5%.

Polymerization

A typical example of polymerization is as follows. The reaction vessel used was a 100 ml 4-necked, round-bottom flask fitted with an overhead stirrer, an argon gas inlet, a thermometer, and a Dean-Stark trap fitted with a condenser. The following monomers were charged into the flask: imine compound **I** 10.50 g (22 mmol); 4,4'-biphenol 4.096 g (22 mmol); potassium carbonate 3.65 g (26 mmol); *N*-methyl-2-pyrrolidone 50 ml; toluene 15 ml. The entire reaction mixture was heated to reflux and water was removed by azeotropic distillation with toluene. The temperature was kept at 185–190°C for 5 h. On cooling, methanol was added to the reaction mixture and the white mass formed was ground to powder in a blender. The polymer collected was washed successively with water and methanol, and dried in a vacuum oven at 130°C overnight. The yield was quantitative. The IR spectrum (KBr) showed a characteristic absorption at 1245 cm⁻¹ (aryl ether).

Anal. Calcd for (C₄₄H₃₀N₂O₂)_n: C, 85.41%; H, 4.89%; N, 4.52%. Found: C, 84.9%; H, 4.6%; N, 4.3%.

RESULTS AND DISCUSSION

Monomer Synthesis

Imine compounds **I**–**VI** can be easily synthesized by the condensation of ketones or aldehydes with diamines as shown in Scheme 1 according to a modification of the method of Roovers *et al.*²¹ All of starting materials are commercially available. Most of the compounds readily crystallize except compound **II**. Yields of the purified imine compounds were 55–78%. Yields could be improved by optimizing the reaction conditions. Compounds **II**, **IV**, and **VI** containing diphenyl ether unit appeared more soluble in common organic solvents than **I**, **III**, and **V**. Aldehyde-derived imine compounds **V** and **VI** were less soluble than the ketone-derived compounds. The imine compounds were yellow crystalline

Poly(arylene ether imine)s

Scheme 1.

Scheme 2.

solids.

Polymer Synthesis

The poly(arylene ether imine)s were prepared by reactions of bis(fluorophenyl) imine compounds I—VI with various bisphenols in NMP in the presence of potassium carbonate (Scheme 2). Polymers having inherent viscosities of 0.4–0.6 dl g⁻¹ were obtained in 5–7 h using BP, HQ, and ND as monomers (Table I). The symbols for the polymers are abbreviations of imine compounds and bisphenols used in the polymer synthesis. The IR spectra showed a characteristic ether band at around

1240 cm⁻¹, indicating arylene ether formation. Polymers derived from BP and HQ such as IIIBP, IIHQ, IVBP, IVHQ, VBP, VHQB, VIBP, and VIHQ precipitated at the start of polymerization. Polymers prepared from V and VI precipitated even when TP was used as a bisphenol component. The low solubility of the imine containing polymers is similar to that of imine polymers previously reported.

Solubilities of the resulting polymers are shown in Table II. Most of the polymers except VTP and VITP showed good solubility in various organic solvents. Common solvents for these polymers are dimethylacetamide,

Table I. Synthesis and characterization of poly(arylene ether imine)s^a

Polymer	Reaction time h	Polymer		
		I.V. dl g ⁻¹	<i>T</i> _g °C	<i>T</i> _d °C
IBP	6	0.63	195	544
IHQ	5	0.47	176	507
IBA	5	0.40	161	487
IND	7	0.46	171	512
ITP	5	0.42	198	486
IIBP	5	0.54	174	530
IIHQ	5	0.46	162	485
IIBA	5	0.35	155	485
IIND	5	0.56	165	513
IITP	5	0.38	177	497
IIIBA	4	0.31	161	488
IIITP	5	0.39	178	463
IVBA	5	0.44	141	446
IVTP	5	0.40	150	469
VTP	5	b	230	457
VITP	5	b	211	445

^a Polymer IIBP, IIHQ, IVBP, IVHQ, VBP, VHQ, VIBP, VIHQ were precipitated at the start of polymerization.

^b Insoluble parts were detected.

tetrahydrofuran, and chloroform. Films of the polymers of good quality could be obtained by casting from chloroform solutions. Polymers VTP and VITP containing hydrogen attached to the tertiary carbon of the imine were insoluble in most solvents. It is apparent that the substitution of the hydrogen for phenyl or methyl group on the polymer backbone increases polymers solubility.

Thermal Properties

*T*_g and *T*_d (decomposition temperature; 5% weight loss in air) of the various poly(arylene ether imine)s are listed in Table I. *T*_g of these polymers were above 140°C, which were slightly higher than the poly(ether ketone)s containing the same bisphenol components.¹ Substantial rise in *T*_g is probably caused by the rigid nature of imine group. A comparison of *T*_g of the polymers derived from imine compounds I and III with those of polymers from II and IV showed the ether linkage of the imine component to increase flexibility.

Figures 1 and 2 show TG curves of the polymers. The poly(arylene ether imine)s dem-

Table II. Solubility of poly(arylene ether imine)s^a

Polymer	Solvent ^b					
	DMAc	DMF	THF	Toluene	MEK	Chloroform
IBP	++	—	++	—	—	++
IHQ	++	+	++	+	—	++
IBA	++	+	++	+	—	++
IND	++	+	++	—	—	++
ITP	++	+	++	+	—	++
IIBP	++	—	++	+	—	++
IIHQ	++	+	++	+	—	++
IIBA	++	+	++	++	—	++
IIND	++	—	++	+	—	++
IITP	++	+	++	+	—	++
IIIBA	++	+	++	+	—	++
IIITP	++	+	++	—	—	++
IVBA	++	+	++	+	—	++
IVTP	++	+	++	+	—	++
VTP	—	—	—	—	—	—
VITP	—	—	—	—	—	—

^a ++, soluble at room temperature; +, soluble on heating; —, insoluble.

^b DMAc, dimethylacetamide; DMF, dimethylformamide; THF, tetrahydrofuran; MEK, methyl ethyl ketone.

Figure 1. TG thermograms for poly(arylene ether imine)s **IBP**, **IHQ**, **IBA**, and **IND**.

Figure 2. TG thermograms for poly(arylene ether imine)s **IIBP**, **IIHQ**, **IIBA**, and **IIND**.

onstrated excellent thermal stability with polymer decomposition temperature in excess of 460°C except polymers from **V** and **VI**. Isothermal TG (400°C under air or nitrogen atmosphere) was used to evaluate polymer thermal stability (Table III). Bisphenol components in the polymers significantly influenced thermal stability. Polymers based on **BP**, **HQ**, and **ND** exhibited higher decomposition temperatures than other polymers. The isothermal data demonstrated that the polymer derived from **BP** was the most thermally stable. Influence of the atmosphere for isothermal

Table III. Thermal stability of poly(arylene ether imine)s

Polymer	Weight loss isothermal aging (wt% h ⁻¹) ^a	
	In air	In N ₂
IBP	0.88	0.72
IHQ	0.86	0.83
IND	0.92	1.08
IIBP	0.96	0.93
IIHQ	1.86	1.81
IIND	1.45	1.45

^a Measured at 400°C.

Table IV. Tensile properties of films of poly(arylene ether imine)s

Polymer	Tensile strength	Elongation at break	Tensile modulus
	MPa	%	GPa
IBP	88	15	3.2
IHQ	79	11	2.8
IND	93	9	3.6
IIBP	71	13	2.8
IIHQ	75	17	2.5
IIND	83	6	3.0

measurements on thermal stability is little, so decomposition seems to take place by mechanisms other than oxidative decomposition.

Mechanical Properties

All measurements for mechanical properties were carried out using cast films. Table IV shows the mechanical properties of the poly(arylene ether imine)s at room temperature. The polymers based on imine compound **I** exhibited somewhat better tensile properties than those of **II**. This seems due to ether linkages of imine compound **II**.

CONCLUSIONS

Several poly(arylene ether imine)s were prepared by the nucleophilic aromatic substitution polymerization of potassium salt of

bisphenols with bis(fluorophenyl) compounds activated by imine in NMP at 185–190°C. The polymerization provides a general method for the preparation of arylene ether-based polyimines. Polymers were characterized by good solubility and high glass transition temperatures above 140°C with high thermal stability.

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