

Synthesis and Characterization of Aromatic Poly(ether sulfone imide)s Derived from Sulfonyl Bis(ether anhydride)s and Aromatic Diamines

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ABSTRACT: Two sulfonyl group-containing bis(ether anhydride)s, 4,4'-[sulfonylbis(1,4-phenylene)dioxy]diphthalic anhydride (**IV**) and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]diphthalic anhydride (Me-**IV**), were prepared in three steps starting from the nucleophilic nitrodisplacement reaction of the bisphenolate ions of 4,4'-sulfonyldiphenol and 4,4'-sulfonylbis(2,6-dimethylphenol) with 4-nitrophthalonitrile in *N,N*-dimethylformamide (DMF). High-molar-mass aromatic poly(ether sulfone imide)s were synthesized via a conventional two-stage procedure from the bis(ether anhydride)s and various aromatic diamines. The inherent viscosities of the intermediate poly(ether sulfone amic acid)s were in the ranges of 0.30–0.47 dL/g for those from **IV** and 0.64–1.34 dL/g for those from Me-**IV**. After thermal imidization, the resulting two series of poly(ether sulfone imide)s had inherent viscosities of 0.25–0.49 and 0.39–1.19 dL/g, respectively. Most of the polyimides showed distinct glass transitions on their differential scanning calorimetry (DSC) curves, and their glass transition temperatures (T_g) were recorded between 223–253 and 252–288°C, respectively. The results of thermogravimetry (TG) revealed that all the poly(ether sulfone imide)s showed no significant weight loss before 400°C. The methyl-substituted polymers showed higher T_g 's but lower initial decomposition temperatures and less solubility compared to the corresponding unsubstituted polymers. © 1998 John Wiley & Sons, Inc. *J Polym Sci A: Polym Chem* 36: 1649–1656, 1998

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INTRODUCTION

Aromatic polyimides as a class of polymers are known for their outstanding thermal, mechanical, and electrical properties as well as excellent chemical resistance.^{1,2} Because of these outstanding properties, they are widely used as industrial films, coatings, adhesives, and moldings at high temperature. However, aromatic polyimides are basically intractable or only processable under extreme conditions, due to strong enthalpic interac-

tions and the minimal increase in conformational entropy associated with their dissolution or melting. The most common technique for the preparation of polyimides is a two-step polymerization process which allows the use of a soluble precursor, poly(amic acid), to deposit thin films, followed by thermal dehydration to achieve the fully imidized structure. There are, however, certain problems connected with the instability of poly(amic acid) solutions, such as completeness of imidization, elimination of released water, and formation of microvoids in the final bulk materials. To overcome these limitations, structural modifications of the polymer backbone, such as the introduction of bulky lateral units,^{3,4} flexible

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side chains,⁵ noncoplanar biphenylene moieties,⁶ and kinked comonomers,⁷ have been utilized to modify the polymer properties, either by lowering the interchain interactions or reducing the stiffness of the polymer chain.

Introduction of flexible linkages such as ether and isopropylidene in the polyimide backbone leads to a decreased glass transition and an enhanced moldability. An important example is Ultem resin developed by General Electric Co.,⁸ which exhibits reasonable thermal stability and good mechanical properties together with good moldability. Its structure, including as it does aliphatic units, contributes to solvent and high-temperature sensitivity. The insertion of sulfone groups into the macromolecular chain generally results in an improved solubility, together with interesting properties such as increased T_g and high thermo-oxidative stability. Hence, the goal of better thermal stability together with good processability may be achieved in preparing polyimides bearing both sulfone and flexibilizing links such as ether.

The present study deals with the synthesis and basic characterization of the poly(ether imide)s based on the sulfonyl bis(ether anhydride)s (Scheme 1, compounds **IV** and Me-**IV**) and aromatic diamines. Although some of the polymers have been reported in the literature^{9,10} by the researchers of General Electric Co., the properties of these polymers are still not well realized. The effect of methyl substitution on the benzene rings on polymer properties are also evaluated.

EXPERIMENTAL

Materials

4,4'-Sulfonyldiphenol (**I**) (Sigma), 4,4'-sulfonylbis(2,6-dimethylphenol) (Me-**I**) (Aldrich), 4-nitrophthalonitrile (TCI), *N,N*-dimethylformamide (DMF) (Fluka), potassium carbonate (K_2CO_3) (Fluka), and acetic anhydride (Janssen) were used as received. *p*-Phenylenediamine (**V_a**) (Wako) was purified by sublimation; *m*-phenylenediamine (**V_b**) (Janssen) was vacuum-distilled prior to use. Benzidine (**V_c**) was purified by recrystallization from a benzene and ethanol mixture. 4,4'-Oxydianiline (**V_d**) (TCI), (4,4'-diaminophenyl)methane (**V_f**) (TCI), 3,4'-diaminodiphenyl ether (**V_e**) (Mitsui Petrochemical Ind.), and 1,4-bis(4-aminophenoxy)benzene (**V_g**) (TCI) were used without previous purification. According to a literature proce-

dure,¹¹⁻¹⁴ 4,4'-bis(4-aminophenoxy)biphenyl (**V_h**) (mp 198–199°C), 4,4'-[sulfonylbis(1,4-phenylene)dioxy]dianiline (**V_i**) (mp 185–187°C), and 4,4'-[sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]dianiline (**V_j**) (mp 186–188°C) were prepared by the nucleophilic substitution reaction of the corresponding bisphenol precursors, i.e. 4,4'-biphenol, 4,4'-sulfonyldiphenol, and 4,4'-sulfonylbis(2,6-dimethylphenol), with *p*-chloronitrobenzene in the presence of the potassium carbonate, followed by hydrazine catalytic reduction of the intermediate dinitro compounds. *N,N*-Dimethylacetamide (DMAc) was purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves.

Monomer Synthesis

4,4'-[Sulfonylbis(1,4-phenylene)dioxy]diphthalodinitrile (**II**) and 4,4'-[Sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]diphthalodinitrile (Me-**II**)

In a 300-mL flask, 15.32 g (0.05 mol) of 4,4'-sulfonylbis(2,6-dimethylphenol) and 13.82 g (0.1 mol) of K_2CO_3 were suspended in a mixture of 100 mL of DMF and 70 mL of toluene and heated with stirring at a reflux temperature using a Dean-Stark trap to remove the water azeotropically. After complete removal of water, the residual toluene was distilled off. Then, the temperature of reaction solution was cooled to about 60°C, and 17.31 g (0.1 mol) of 4-nitrophthalonitrile was added with heating continued at 60°C for 20 h. Then, the reaction mixture was poured into 700 mL of water, and the precipitated white solid was collected and washed thoroughly with methanol and water. The crude product was purified by recrystallization from acetonitrile to afford pure Me-**II** as colorless needles. The yield of the purified product was 22.5 g (80%); mp 251–253°C. The IR spectrum (KBr) exhibited absorptions at 2230 (C≡N), 1310, 1139 (—SO₂—), and 1249 cm⁻¹ (C—O—C).

Anal. Calcd for C₃₂H₂₂N₄O₄S (558.61): C, 68.61%; H, 3.97%; N, 10.03%. Found: C, 68.06%; H, 3.98%; N, 10.10%.

4,4'-[Sulfonylbis(1,4-phenylene)dioxy]diphthalodinitrile (**II**) was synthesized in an analogous procedure from 4,4'-sulfonyldiphenol and 4-nitrophthalonitrile. The crude product was recrystallized from acetonitrile to yield light yellow crystals: yield 78%; mp 229–230°C (lit.¹⁵ 229–230°C). IR (KBr): 2232 (C≡N), 1312, 1152 (—SO₂—), and 1251 cm⁻¹ (C—O—C).

Anal. Calcd for $C_{28}H_{14}N_4O_4S$ (502.51): C, 66.93%; H, 2.81%; N, 11.15%. Found: C, 66.22%; H, 2.81%; N, 11.02%.

4,4'-[Sulfonylbis(1,4-phenylene)dioxy]diphthalic Acid (III) and 4,4'-[Sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]diphthalic Acid (Me-III)

The bis(ether dinitrile) Me-II (20.0 g; 0.036 mol) was added to a mixture of potassium hydroxide (40 g; 0.71 mol), ethanol (100 mL), and water (100 mL). The mixture was stirred and boiled under reflux. The suspension turned into a clear solution after about 2 h. Reflux was continued for about 24 h until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any possible insoluble impurities. The hot filtrate was allowed to cool and acidified by concentrated HCl to pH = 2–3. The white precipitated product was filtered out, washed with water, and dried under vacuum, to give a quantitative yield of bis(ether diacid) Me-III. IR (KBr): 3600–2500 (O—H), 1716 (C=O), 1300, 1135 (—SO₂—), and 1218 cm⁻¹ (C—O—C).

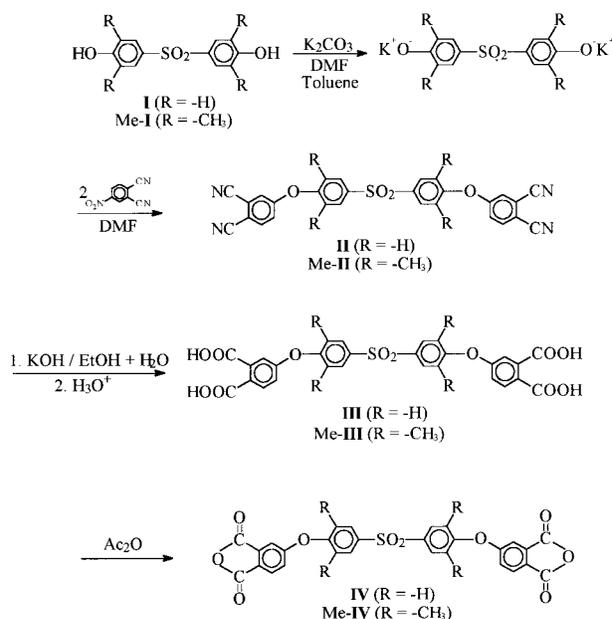
Using a similar synthetic procedure, the bis(ether dinitrile) II was converted to the corresponding 4,4'-[sulfonylbis(1,4-phenylene)dioxy]diphthalic acid (III) in a quantitative yield. IR (KBr): 3600–2500 (O—H), 1710 (C=O), 1310, 1148 (—SO₂—), and 1236 cm⁻¹ (C—O—C).

4,4'-[Sulfonylbis(1,4-phenylene)dioxy]diphthalic Anhydride (IV) and 4,4'-[Sulfonylbis(2,6-dimethyl-1,4-phenylene)dioxy]diphthalic Anhydride (Me-IV)

In a 500-mL flask, 22 g of bis(ether diacid) Me-III was dispersed in a mixture of 150 mL of acetic acid and 300 mL of acetic anhydride. The suspension solution was heated to reflux until turning into a clear solution. The resulting hot, clear solution was filtered to remove any insoluble impurities. On cooling, the colorless fine needles phased out of the solution, which was collected by filtration, washed with dry toluene, and dried *in vacuo*, to give 18.7 g (87%) of bis(ether anhydride) Me-IV; mp 287–289°C (lit.¹⁰ 288–290°C). IR (KBr): 1850, 1776 (C=O), 1310, 1136 (—SO₂—), and 1215 cm⁻¹ (C—O—C).

Anal. Calcd for $C_{32}H_{22}O_{10}S$ (598.58): C, 62.21%; H, 3.70%. Found: C, 63.20%; H, 3.67%.

4,4'-[Sulfonylbis(1,4-phenylene)dioxy]diphthalic anhydride (IV) was prepared from bis(ether diacid) III in a similar method: yield 86%; mp 242–243°C (DSC 248°C) (lit.¹⁶ 251–252°C).



Scheme 1.

IR (KBr): 1848, 1776 (C=O), 1284, 1149 (—SO₂—), and 1232 cm⁻¹ (C—O—C).

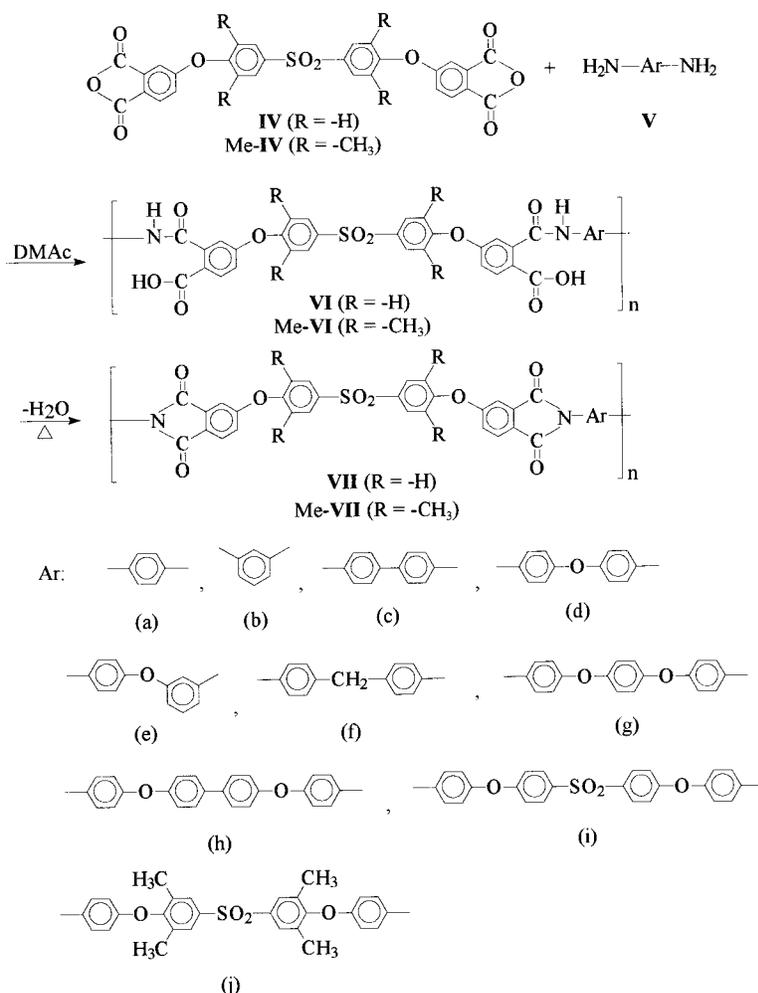
Anal. Calcd for $C_{28}H_{14}O_{10}S$ (542.48): C, 61.99%; H, 2.60%. Found: C, 60.83%; H, 2.86%.

Synthesis of Poly(ether sulfone imide)s

A typical polymerization procedure is as follows. 4,4'-Oxydianiline (**V_d**) (0.2696 g; 1.35 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.7304 g (1.35 mmol) of 4,4'-[sulfonylbis(1,4-

phenylene)dioxy]diphthalic anhydride (**IV**) was added in one portion. The mixture was stirred at room temperature for about 3 h. The inherent viscosity of the resulting poly(ether sulfone amic acid) (**VI_d**) in DMAc was 0.44 dL/g, measured at a concentration of 0.5 g/dL at 30°C. The polymer solution obtained was poured into a $\phi = 9$ cm glass culture dish, which was placed in a 90°C oven overnight to remove the solvent. The semi-dried poly(ether sulfone amic acid) film was further dried and transformed into poly(ether sulfone imide) by sequential heating at 150°C for 20 min, 175°C for 20 min, 200°C for 20 min, 225°C for 20 min, and 250°C for 30 min. By being soaked in hot water, a flexible poly(ether sulfone imide) film of **VII_d** self-stripped off the glass surface.

IR of **VI_d** (film): 2500–3600 (N—H and O—H str.), 1719 (C=O), 1407 (C—N), 1320–1289



Scheme 2.

[asym. S(=O)₂ str.], 1150–1107 [sym. S(=O)₂ str.], and 1240 cm⁻¹ (C—O—C). IR of **VII_d** (film): 1779 (asym C=O str.), 1726 (sym. C=O str.), 1381 (C—N), 1323–1289 [asym. S(=O)₂ str.], 1152–1109 [sym. S(=O)₂ str.], 1242 cm⁻¹ (C—O—C), 1095 and 746 cm⁻¹ (imide ring deformation).

Other poly(ether sulfone imide)s were synthesized by an analogous procedure.

Characterization

IR spectra were recorded on a Jasco IR-700 infrared spectrometer. Elemental analyses were run in a Perkin-Elmer model 2400 C, H, N analyzer. A Sinku Riko DSC-7000 differential scanning calorimeter equipped with a Sinku Riko TA-7000 analyzer was used to determine the thermal transitions. The heating rate was 20°C/min. The glass

transition temperature (T_g s) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling from 450°C. The inherent viscosities were measured with an Ubbelohde viscometer at 30°C. Thermogravimetry (TG) was conducted with a Rigaku Thermoflex TG 8110 coupled to Rigaku TAS-100 thermal analysis station. Experiments were carried out on 10 ± 1 mg samples heated in flowing nitrogen or air (50 cm³/min) at a heating rate of 20°C/min. An Instron testing machine model HT-9102 (Hung Ta Instrument Co., Ltd., Taiwan) with a load cell of 100 kg was used to study the stress-strain behavior of the samples. A gauge of 2 cm and a crosshead speed of 5 cm/min were used for this study. Measurements were performed at room temperature with film specimens (6 cm long, 0.5 wide, and about 0.1 mm thick), and an average of at least five individual

determinations was used. Wide-angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu K α radiation (40 kV, 15 mA).

RESULTS AND DISCUSSION

Monomer Synthesis

According to the reported procedures,^{17–22} the bis(ether anhydride)s containing the sulfone group, **IV** and Me-**IV**, were prepared by a three-stage route from readily available reagents (Scheme 1). The yield of each step was high, usually above 75%. The structure of the bis(ether anhydride)s was confirmed by elemental analysis and infrared spectroscopy. The IR spectra of the bis(ether anhydride)s show characteristic cyclic anhydride absorbances near 1850 and 1780 cm⁻¹ suggesting the asymmetric and symmetric stretching vibration of C=O.

Polymer Synthesis

Serial polyimides Me-**VII**_{a–j} and **VII**_{a–j} having ether and sulfone groups on the polymer backbone were prepared by the two-stage process outlined in Scheme 2, described above in detail for the poly(ether sulfone imide) **VII**_d derived from bis(ether anhydride) **VI** and 4,4'-oxydianiline (**V**_d). Polymer preparation involved adding the bis(ether anhydride) to a diamine in dry DMAc solution to form the poly(ether amic acid), pouring the poly(ether amic acid) solution onto a glass substrate, slowly evaporizing the solvent, and then thermally dehydrating to form the poly(ether sulfone imide). Thus, all the polymers were obtained in the form of films. The results of the polymer syntheses are summarized in Table I. The inherent viscosities of poly(amic acid)s **VI**_{a–j} and the corresponding polyimides **VII**_{a–j} stayed in the range of 0.30–0.47 and 0.25–0.49 dL/g, respectively. The low viscosity of those polymers does not necessarily indicate a low molecular weight, because they have flexible ether and sulfone linkages along the polymer backbone. For example, poly(amic acid) **VI**_f could be coated and transformed into a flexible and tough polyimide film, even though it has a relatively low inherent viscosity of 0.3 dL/g. The thin films of the polyimides (**VII**_{a–c}) derived from rigid *p*-phenylenediamine, *m*-phenylenediamine, and benzidine cracked

Table I. Preparation of Poly(ether sulfone imide)s

Poly(ether sulfone amic acid)s		Poly(ether sulfone imide)		
Code	η_{inh}^a (dL/g)	Code	λ_{inh} (dL/g)	Film Quality
VI _a	0.40	VII _a	0.40 ^b	Brittle
VI _b	0.34	VII _b	0.25 ^a	Brittle
VI _c	0.47	VII _c	0.42 ^b	Brittle
VI _d	0.44	VII _d	0.49 ^a	Flexible
VI _e	0.36	VII _e	0.40 ^a	Flexible
VI _f	0.30	VII _f	0.39 ^a	Flexible
VI _g	0.36	VII _g	0.44 ^a	Flexible
VI _h	0.41	VII _h	0.46 ^a	Flexible
VI _i	0.40	VII _i	0.31 ^a	Flexible
VI _j	0.45	VII _j	0.40 ^a	Flexible
Me- VI _a	1.00	Me- VII _a	0.38 ^b	Brittle
Me- VI _b	0.64	Me- VII _b	0.40 ^b	Brittle
Me- VI _c	1.22	Me- VII _c	0.52 ^b	Brittle
Me- VI _d	1.16	Me- VII _d	0.67 ^b	Brittle
Me- VI _e	0.72	Me- VII _e	0.40 ^b	Brittle
Me- VI _f	0.83	Me- VII _f	0.48 ^b	Brittle
Me- VI _g	1.19	Me- VII _g	1.08 ^b	Flexible
Me- VI _h	1.34	Me- VII _h	1.19 ^b	Flexible
Me- VI _i	0.82	Me- VII _i	0.51 ^b	Brittle
Me- VI _j	0.96	Me- VII _j	0.43 ^b	Brittle

^a Measured at a concentration of 0.5 g/dL in DMAc at 30°C.

^b Measured at a concentration of 0.5 g/dL in concentrated H₂SO₄ at 30°C.

upon creasing, which may be due to the structural rigidity of their polymer chains. The other polyimides of this series (**VII**_{d–j}) afforded good-quality and creasable films.

The introduction of methyl substituents on the benzene ring increases the segmental rigidity of the macromolecular backbone, thus resulting in increased solution viscosity of the polymer. As shown in Table I, poly(amic acid)s Me-**VI**_{a–j} exhibited higher inherent viscosities (0.64–1.34 dL/g) compared to their unsubstituted analogues. However, it is worth noting that almost all the casting films of the Me-**VII** series polyimides, except for Me-**VII**_g and Me-**VII**_h, are noncreasable. This may be attributable to the presence of methyl substituents which hinder rotational freedom and, consequently, increase chain rigidity.

IR spectroscopy allows monitoring of the imide ring formation during cure. When the poly(amic acid) was converted into the polyimide, the characteristic absorption bands of amide and carboxyl groups in the regions of 2700–3500 and 1500–1720 cm⁻¹ disappeared, and those of the imide

Table II. Solubility of Poly(ether sulfone imide)s^a

Polymer Code	Solvent ^b					
	DMI	NMP	DMAc	DMSO	DMF	<i>m</i> -Cresol
VII_a	—	+	—	—	—	—
VII_b	+	+	+	+	+	+
VII_c	—	—	—	—	—	—
VII_d	+	+	+	+	+	+
VII_e	+	+	+	+	+	+
VII_f	+	+	+	+	+	+
VII_g	+	+	+h	+h	+h	+h
VII_h	+	+	+	+h	+h	+h
VII_i	+	+	+	+	+	+h
VII_j	+	+	+	+	+	+
Me- VII_a	—	—	—	—	—	—
Me- VII_b	—	+h	—	—	—	+h
Me- VII_c	—	—	—	—	—	—
Me- VII_d	+	+	+h	—	—	+h
Me- VII_e	+h	+h	+h	—	+h	+h
Me- VII_f	+h	+h	—	—	—	+h
Me- VII_g	—	—	—	—	—	—
Me- VII_h	+h	+h	+h	—	—	+h
Me- VII_i	+	+	+	+h	+	+
Me- VII_j	+h	+h	—	—	—	+h

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

^b DMI, 1,3-dimethyl-2-imidazolidone; NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide; DMF, *N,N*-dimethylformamide.

ring were observed near 1780 (asym. C=O str.), 1725 (sym. C=O str.), 1380 (C—N), 1095 and 750 cm⁻¹ (imide ring formation). Other characteristic absorptions include C—O—C stretching near 1240 cm⁻¹ and —SO₂— stretching near 1300 and 1150 cm⁻¹.

Properties of Poly(ether sulfone imide)s

Solubility of the poly(ether sulfone imide)s prepared in this study was determined for the film samples in excess solvents, and the results are listed in Table II. With the exception of polymers **VII_a** and **VII_c**, all the poly(ether sulfone imide)s of the **VII** series were soluble in all the solvents tested that included 1,3-dimethyl-2-imidazolidone (DMI), NMP, DMAc, DMSO, DMF, and *m*-cresol. The improved solubility of these polymers as compared to that of common polyimides can be explained by the presence of the sulfone group and other flexible linkages such as ether in the polymer main chain in addition to the increased distance between the imide rings. The poor solubility for **VII_a** and **VII_c** can be attributed to the existence of the rigid planar 1,4-bis(phthalimid-

o)phenylene or 4,4'-bis(phthalimido)biphenylene segments in their polymer backbones, leading to a better packing of polymer chains. Methyl substitution reduced the polymer solubility significantly. All methyl-substituted polyimides, except for Me-**VII_i**, were considerably less soluble in a number of solvents. In most cases, they were just soluble in hot DMI, NMP, DMAc, or *m*-cresol. Clearly, high structural rigidity hindered their solubility markedly.

The crystallinity of the prepared poly(ether sulfone imide)s was evaluated by wide-angle X-ray diffraction experiments. All the polymers did not show any strong reflection peaks over the 2 θ range of 5–40°, indicating an amorphous nature. The flexible polyimide films were subjected to a tensile test. The tensile strength and elongation-to-break of these films were in the ranges of 56–115 MPa and 4–14%, respectively. They behave as strong and hard materials.

Thermal properties of all the poly(ether sulfone imide)s were evaluated by thermogravimetry (TG) and differential scanning calorimetry (DSC). The values of glass transition temperature (T_g), 10% weight loss temperature (T_{10}) in

Table III. Thermal Properties of Poly(ether sulfone imide)s

Polymer Code	T_g^a (°C)	T_{10}^b (°C)		Residue ^c wt %
		In N ₂	In Air	
VII _a		505	530	36.4
VII _b	240	497	519	37.3
VII _c		537	548	49.3
VII _d	250	535	544	57.1
VII _e	230	514	528	47.5
VII _f	240	496	506	55.1
VII _g	223	517	527	40.3
VII _h	235	529	538	53.2
VII _i	245	517	525	47.8
VII _j	253	436	439	43.3
Me-VII _a		429	429	49.6
Me-VII _b	270	412	421	33.7
Me-VII _c		440	437	46.6
Me-VII _d	288	438	459	38.2
Me-VII _e	252	439	439	39.2
Me-VII _f	275	435	447	51.6
Me-VII _g	272	448	478	43.6
Me-VII _h	278	453	467	46.6
Me-VII _i	278	443	449	44.9
Me-VII _j		409	416	37.8

^a From the second DSC heating traces with a heating rate of 20°C/min in nitrogen.

^b Decomposition temperatures at which 10% weight losses were recorded by TG.

^c At 800°C in nitrogen.

nitrogen or air, and residual wt % at 800°C in nitrogen of all polymers are summarized in Table III. Except for the polyimide VII_j which contains methyl substituents in the diamine moiety, all the VII series polymer exhibited T_{10} values near or above 500°C. It is quite reasonable that the methyl-substituted polyimides began to decompose at lower temperatures compared with the unsubstituted ones. The T_{10} 's of the Me-VII series polyimides were recorded between 409–453°C in nitrogen and 416–478°C in air.

Thermal transitions were investigated by DSC in the temperature range from 50 to 450°C. Due to the chain stiffness, transitions were not observed for polymers VII_a, VII_c, Me-VII_a, Me-VII_c, and Me-VII_j at the rate of 20°C/min. A distinct glass transition was observed for the other polyimides. Glass transition temperatures (T_g 's), defined as the temperature at the midpoint of the baseline shift, of the two series poly(ether sulfone imide)s VII_{a-j} and Me-VII_{a-j} were recorded in the ranges of 223–253 and 252–288°C, respectively. As expected, the methyl-substituted poly-

mers exhibited higher T_g than the corresponding unsubstituted ones due to the increased backbone rigidity. The T_g 's reported here for Me-III_b and Me-III_f are lower than those reported in a patent literature,¹⁰ i.e., for Me-III_b 270 versus 302°C from ref. 10 and for Me-III_f 275 versus 289°C from ref. 10. The difference in T_g may be attributed to different imidization methods and molecular weights of the polyimides.

CONCLUSIONS

Two series of aromatic poly(ether sulfone imide)s having moderate to high molecular weights have been synthesized via a conventional two-stage polymerization technique from aromatic diamines with the bis(ether anhydride)s based on 4,4'-sulfonyldiphenol and 4,4'-sulfonylbis(2,6-dimethylphenol). The aromatic poly(ether sulfone imide)s synthesized from the methyl-substituted monomers had higher T_g 's and increased chain rigidity but lower initial decomposition temperatures and less solubility compared to the corresponding polymers derived from the unsubstituted monomers.

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REFERENCES AND NOTES

1. D. Wilson, H. D. Stenzenberger, and P. M. Hergenrother, Eds., *Polyimides*, Blackie, Glasgow and London, 1990.
2. M. K. Ghosh and K. L. Mittal, Eds., *Polyimides: Fundamental and Applications*, Marcel Dekker, New York, 1996.
3. C.-P. Yang and W.-T. Chen, *Macromolecules*, **26**, 4865 (1993).
4. C.-P. Yang and J.-H. Lin, *J. Polym. Sci., Part A: Polym. Chem.*, **32**, 423 (1994).
5. J. R. Sasthav and F. W. Harris, *Polymer*, **36**, 4911 (1996).
6. F. W. Harris, S.-H. Lin, F.-M. Li, and S. Z.-D. Cheng, *Polymer*, **37**, 5049 (1996).
7. S. Tamai, A. Yamaguchi, and M. Ohta, *Polymer*, **37**, 3683 (1996).
8. J. G. Wirth in *High Performance Polymers: Their Origin and Development*, R. B. Seymour and G. S. Kirshenbaum, Eds., Elsevier, Amsterdam, 1986.
9. T. Takekoshi, J. E. Kochanowski, J. S. Manello,

- and M. J. Webber, *J. Polym. Sci., Polym. Symp.*, **74**, 93 (1986).
10. E. N. Peters (General Electric Co.), Jpn Kokai Tokyo Koho JP 59-141573 (1984), U.S. Pat. 4,523,006 (1985), U.S. Pat. 4,543,416 (1985).
 11. S.-H. Hsiao, C.-P. Yang, and C.-K. Lin, *J. Polym. Res.*, **2**, 1 (1995); *Chem. Abstr.*, **123**, 287811g (1995).
 12. C.-P. Yang and J.-J. Cherng, *J. Polym. Sci., Part A: Polym. Chem.*, **33**, 2209 (1995).
 13. C.-P. Yang and W.-T. Chen, *Makromol. Chem.*, **194**, 1595 (1993).
 14. S.-H. Hsiao, C.-P. Yang, and J.-C. Fan, *Macromol. Chem. Phys.*, **196**, 3041 (1995).
 15. D. R. Heath and J. G. Wirth (General Electric Co.), U.S. Pat. 3,787,475 (1974).
 16. T. Takekoshi, J. E. Kochanowski, J. S. Manello, and M. J. Webber, *J. Polym. Sci., Polym. Chem. Ed.*, **23**, 1759 (1985).
 17. G. C. Eastmond, J. Paprotny, and I. Webster, *Polymer*, **34**, 2865 (1993).
 18. G. C. Eastmond and J. Paprotny, *Polymer*, **35**, 5148 (1994).
 19. G. C. Eastmond and J. Paprotny, *Macromolecules*, **28**, 2140 (1995).
 20. G. C. Eastmond, J. Paprotny, and R. S. Irwin, *Macromolecules*, **29**, 1328 (1996).
 21. G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, **6**, 1455 (1996).
 22. G. C. Eastmond and J. Paprotny, *J. Mater. Chem.*, **6**, 1459 (1996).