Synthesis and Characterization of New Fluorene-Based Poly(ether imide)s

SHENG-HUEI HSIAO, CHIN-TANG LI

Department of Chemical Engineering, Tatung Institute of Technology, 40 Chungshan North Road, Sec. 3, Taipei, Taiwan, Republic of China

ABSTRACT: A novel bis(ether anhydride) monomer, 9,9-bis[4-(3,4-dicarboxyphenoxy)-phenyl]fluorene dianhydride (**4**), was synthesized from the nitrodisplacement of 4-nitrophthalonitrile by the bisphenoxide ion of 9,9-bis(4-hydroxyphenyl)fluorene (**1**), followed by alkaline hydrolysis of the intermediate tetranitrile and dehydration of the resulting tetracarboxylic acid. A series of poly(ether imide)s bearing the fluorenylidene group were prepared from the bis(ether anhydride) **4** with various aromatic diamines **5a–i** via a conventional two-stage process that included ring-opening polyaddition to form the poly(amic acid)s **6a–i** followed by thermal cyclodehydration to the polyimides **7a–i**. The intermediate poly(amic acid)s had inherent viscosities in the range of 0.39–1.57 dL/g and afforded flexible and tough films by solution-casting. Except for those derived from p-phenylenediamine, m-phenylenediamine, and benzidine, all other poly-(amic acid) films could be thermally transformed into flexible and tough polyimide films. The glass transition temperatures (T_g) of these poly(ether imide)s were recorded between 238–306°C with the help of differential scanning calorimetry (DSC), and the softening temperatures (T_s) determined by thermomechanical analysis (TMA) stayed in the range of 231–301°C. Decomposition temperatures for 10% weight loss all occurred above 540°C in an air or a nitrogen atmosphere. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 1403–1412, 1999
Keywords: 9,9-bis(4-hydroxyphenyl)fluorene; 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride; poly(ether imide)s

INTRODUCTION

Aromatic polyimides are condensation polymers that are normally synthesized from aromatic tetracarboxylic dianhydrides and aromatic diamines. Because the heterocyclic imide units give the polymer chain rigidity and impart high interchain interactions, they are considered high-performance polymer materials which show excellent mechanical and electrical properties, thermal stability, and chemical resistance.[1,2] However, the combination of these properties make them diffi-cult to process in the melt or with the solvents due to their high glass transition temperature (T_g) and insolubility. Most conventional processing techniques involve the fabrication of poly(amic acid) precursors followed by thermal or chemical imidization. But the process still has some disadvantages connected with the limited storage stability of the intermediate poly(amic acid)s and with the evolution of water during the cycloimidization. Therefore, there has been considerable research carried out aimed at the development of aromatic polyimides that are processable in the imide form.

One approach to increase the solubility and processability of polyimides is the introduction of flexible linking units into the polymer chain.[3] The

linkages not only create angular bonds in the polymer chain, but also permit the rotation of aromatic units. However, the loss of thermal stability and significant decrease in tensile strength on heating are almost always a consequence of the reduced chain stiffness. Introduction of flexibilizing groups as well as bulky groups into the polymer backbone may result in soluble polyimides while maintaining a high T_g.[4–9]

An impressive series of high T_g soluble polymers, referred as cardo polymer, was pioneered in the early 1960s and reviewed by Korshak, Vinogradova, and Vygodskii.[10] Such polymers contain at least one element in the repeating unit that includes a cyclic side group which imparts a combination of enhanced thermal stability, high T_g, and excellent solubility. It has been demonstrated that incorporation of both ether and a cyclic side cardo group, such as a fluorene, a phthalide, or a phthalimidine group, into the macromolecular backbone resulted in aromatic polyimides with good thermal stability, high T_g, and excellent solubility in organic solvents.[11–14]

One of the main potential applications of polyimides is as membranes for gas separation. Several general rules for the design of improved gas-separating membrane materials have been identified.[15–18] Increased polymer fractional free volume generally increases gas permeability, while inhibition of polymer chain flexibility generally increases permselectivity. It has long been recognized that bulky groups inhibiting tight packing of the polymer chains should lead to membrane materials with enhanced selectivity without loss of permeability. In this sense, the packing-disruptive cardo groups are ideal. For example, the incorporation of 9,9-fluorenylidene connector group can increase the segmental rigidity of the macromolecular backbone, thus resulting in increased gas permeability and selectivity.[19,20]

The current study focuses on the synthesis and characterization of a series of cardo poly(ether imide)s derived from 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride and aromatic diamines. It is hoped that these fluorenylidene-containing poly(ether imide)s will have enhanced processability and superior membrane properties.

EXPERIMENTAL

Materials

9-Fluorenone (Fluka), phenol (Wako), zinc chloride (ZnCl$_2$; Wako), 4-nitrophthalonitrile (TCI), N,N-dimethylformamide (DMF; Fluka), potassium carbonate (K$_2$CO$_3$; Fluka), and acetic anhydride (Janssen) were used as received. p-Phenylenediamine (5a) was purified by sublimation. m-Phenylenediamine (5b) (Janssen) was vacuum-distilled prior to use. Benzidine (5c) (TCI) was purified by recrystallization from a benzene/ethanol mixture. 4,4′-Methylenedianiline (5d) (TCI), 4,4′-oxydianiline (5e) (TCI), and 1,4-bis(p-aminophenoxy)benzene (5f) (TCI) were used without further purification. According to a reported method,[21,22] 4,4′-bis(4-aminophenoxy)biphenyl (5g), 2,2-bis[4-(4-aminophenoxy)-phenyl]propane (5h), and α,α′-bis[4-(4-aminophenoxy)phenyl]-1,4-diisopropylbenzene (5i) were prepared by the nucleophilic substitution reaction of p-chloronitrobenzene with the corresponding bisphenol precursors, i.e. 4,4′-biphenol (Fluka), 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) (Wako), and α,α′-bis(4-hydroxyphenyl)-1,4-diisopropylbenzene, in DMF in the presence of 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.

Synthesis of 9,9-Bis(4-hydroxyphenyl)fluorene (1)

In a 500-mL flask, 28.7 g (0.159 mol) of 9-fluorenone and 5 g of ZnCl$_2$ were dissolved in 60.0 g (0.637 mol) of molten phenol. The mixture was heated at about 60°C on an oil bath and then dry hydrogen chloride was bubbled in for about 1 h. The reaction system became very dark and was quite viscous but in about 4 h it suddenly solidified. The resulting solid was redissolved with 100 mL of hot isopropanol, and the mixture was diluted with 700 mL of water to give a lump of viscous, pale yellow product. Washing by hot water, the viscous mass solidified gradually. The pale yellow solid was collected, washed, and dried. The yield of the crude product was 55.1 g (99.1%). The crude product was purified by recrystallization from toluene to give white granular crystals with a yield of 26.6 g. The filtrate was concentrated to about 1/3 its original volume, and another 11.7 g of the product was collected. Thus, a total yield was about 69% theoretically. The melting point of bisphenol 1 was 220–222°C (lit.[23] 224°C). IR (KBr): 3480 cm^{-1} (O-H). ^{1}H-NMR (DMSO-d_6): δ = 9.34 (s, -OH, 2H), 7.87 (d, H$_a$, 2H), 7.27–7.38 (m, H$_b$, 6H), 6.93 (d, H$_c$, 4H), 6.65 ppm (d, H$_d$, 4H). ^{13}C-NMR (DMSO-d_6): δ = 156.01

(C^{11}), 151.70 (C^1), 139.35 (C^6), 136.04 (C^8), 128.71 (C^9), 127.65 (C^3), 127.28 (C^4), 125.95 (C^2), 120.32 (C^5), 114.96 (C^{10}), 63.63 ppm (C^7).

ANAL. Calcd for $C_{25}H_{18}O_2$ (350.42): C, 85.69; H, 5.18. Found: C, 85.72; H, 5.19.
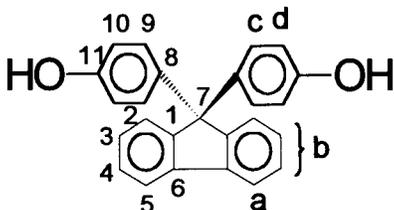
Synthesis of 9,9-Bis[4-(3,4-dicyanophenoxy)phenyl]fluorene (2)

In a 300-mL flask equipped with a Dean-Stark trap, 20.0 g (0.057 mol) of biphenol **1** was dissolved in a mixture of toluene (30 mL) and DMF (150 mL). Anhydrous potassium carbonate (15.8 g; 0.1141 mol) was added and the reaction mixture was heated until the solvent began to reflux at approximately 140°C. Water was continuously removed via the Dean—Stark trap. The reflux temperature was maintained for 4–5 h until the accumulation of water was no longer evident in the Dean—Stark trap. Then the residual toluene was distilled off from the system. The reaction medium was allowed to cool to about 60°C, then 19.9 g (0.1141 mol) of 4-nitrophthalonitrile was added and the reaction was carried out at 60°C for about 24 h. The resulting solution was added slowly into 500 mL of water to precipitate a light yellow solid, which was collected by filtration and dried. The yield of the crude product was 34.2 g (99%). The crude product was recrystallized from dimethyl sulfoxide/methanol (1 : 1 by volume) to afford 21.6 g (63%) of pure tetranitrile **2**; m.p.: 260–262°C. IR (KBr): 2,232 cm^{-1} (C≡N str.), 1,591–1,421 cm^{-1} (arom. C=C str.), 1,251 cm^{-1} (C—O—C str.).

ANAL. Calcd. for $C_{41}H_{22}N_4O_2$ (602.65): C, 81.71%; H, 3.68%; N, 9.30%. Found: C, 81.23%; H, 3.70%; N, 8.93%.

Synthesis of 9,9-Bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene Dianhydride (4)

In a 500-mL flask were added tetranitrile **2** (21 g, 0.0348 mol), potassium hydroxide (39.2 g, 0.7 mol), and 1 : 1 volume mixture of water-ethanol (150 mL/150 mL). The suspension was refluxed

for about 10 h to form a clear solution. The resulting hot clear solution was filtered to remove any insoluble impurities. After cooling, the filtrate was acidified by concentrated hydrogen chloride to pH = 2–3. The precipitated product was collected, washed thoroughly with water until neutral, and dried to give a quantitative yield of 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene (**3**). IR (KBr): 2,500–3,500 cm^{-1} (O—H str.), 1,700 cm^{-1} (C=O str.), and 1,274, 1,232 cm^{-1} (C—O—C str.).

In a 250-mL flask, 25.3 g of bis(ether diacid) **3** was suspended in 170 mL of acetic anhydride. The suspension was boiled under reflux until turning into a clear solution. The obtained hot, clear solution was filtered to remove any insoluble impurities. On cooling, pale brown needles crystallized from the filtrate and next day the product was collected, washed with dry toluene, and dried *in vacuo* to give 10.05 g (45%, based on tetranitrile **2**) of bis(ether anhydride) **4**; m.p. 239–241°C. IR (KBr): 1,851, 1,778 cm^{-1} (C=O str.), 1,620–1,447 cm^{-1} (arom. C=C str.), 1,280, 1,227 cm^{-1} (C—O—C str.).

Crystal data: $C_{41}H_{22}O_8$, pale-brown crystal, $0.30 \times 0.30 \times 0.35$ mm, monoclinic $C\,2/c$ with $a = 30.745(4)$, $b = 7.1295(12)$, $c = 31.324(3)$ Å, $\beta = 117.535(9)°$, $V = 6088.4(14)$ Å^3, $Z = 8$, $d_c = 1.402$ g/cm^3, $T = 25°C$, λ (Cu Kα) = 1.5418 Å, $\mu = 7.529$ cm^{-1}, $R_w = 0.036$ for 3,595 observed reflections

ANAL. Calcd. for $C_{41}H_{22}O_8$ (642.62): C, 76.63%; H, 3.45%. Found: C, 76.55%; H, 3.38%.

Synthesis of Poly(ether imide)s

A typical polymerization procedure is as follows. 4,4′-Methylenedianiline (**5d**) (0.2358 g, 1.189 mmol) was dissolved in 9.5 mL of dried DMAc in a 50-mL flask. After the diamine was dissolved completely, 0.7642 g (1.189 mmol) of bis(ether anhydride) **4** was added in one portion. The mixture was stirred at room temperture for 2 h. The inherent viscosity of the resulting poly(ether amic acid) **6d** was 0.63 dL/g, measured in DMAc at a concentration of 0.5 g/dL at 30°C. The polymer solution obtained was poured into a $\varphi = 9$ cm glass culture dish, which was placed in a 80°C oven overnight to remove the solvent. The semi-dried poly(ether amic acid) film was further dried and transformed into poly(ether imide) by sequential heating at 150°C for 20 min, 180°C for 20 min, 220°C for 20 min, 250°C for 20 min, 270°C for 20 min. By being soaked in hot water, a flex-

ible poly(ether imide) film of **7d** self-stripped off from the glass surface.

IR of **6d** (film): 3,000–3,500 cm^{-1} (O-H, N-H str.), 1,697 cm^{-1} (C=O, carboxylic acid), 1,600 cm^{-1} (C=O, amide), 1,224 cm^{-1} (C—O str.).

IR of **7d** (film): 1,778 cm^{-1} (asym. C=O), 1,726 cm^{-1} (sym. C=O) 1,506, 1,602 cm^{-1} (arom. C=C), 1,376 cm^{-1} (C—N), 1,239 cm^{-1} (C—O), 1,172 and 746 cm^{-1} (imide ring deformation).

Characterization

IR spectra were recorded on a Jasco FT/IR-7000 Fourier-transform spectrometer. ^{1}H- and ^{13}C-NMR spectra were measured on a Jeol EX-400 NMR spectrometer with perdeuterodimethyl sulfoxide (DMSO-d_6) as an external reference, working at 400 and 100 MHz, respectively. Elemental analyses were run in a Perkin-Elmer model 2400 C, H, N analyzer. The X-ray crystallographic data were collected on a CAD-4 diffractometer. The inherent viscosities were measured with an Ubbelohde viscometer thermostated at 30°C. 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. Glass transition temperatures (T_g) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quick cooling. Thermomechanical analysis (TMA) was conducted with a Rigaku TMA 8140 coupled to a Rigaku TAS-100 thermal analysis station using a loaded penetration probe at a scan rate of 10°C/min. The TMA experiments were conducted in duplicate. Softeninng temperatures (T_s) were taken as the intersection of the extrapolation of the baseline with the extrapolation of inflection from the second TMA traces. Thermogravimetry (TG) was conducted with a DuPont 951 Thermogravimetric Analyzer coupled to a DuPont 2000 Thermal Analyst. Experiments were carried out on 9–11 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of 20°C/min. 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$_\alpha$ radiation (40 kV, 15 mA). The scanning rate was 2°/min over a range of $2\theta = 5$–40.° An Instron universal tester model HT-9102 (Hung Ta Instrument Co., Taiwan) with a load cell 10 kg was used to study the stress-strain behavior of the polymer films (6 cm long, 0.5 cm wide, and about 0.1 mm thick). A cross-
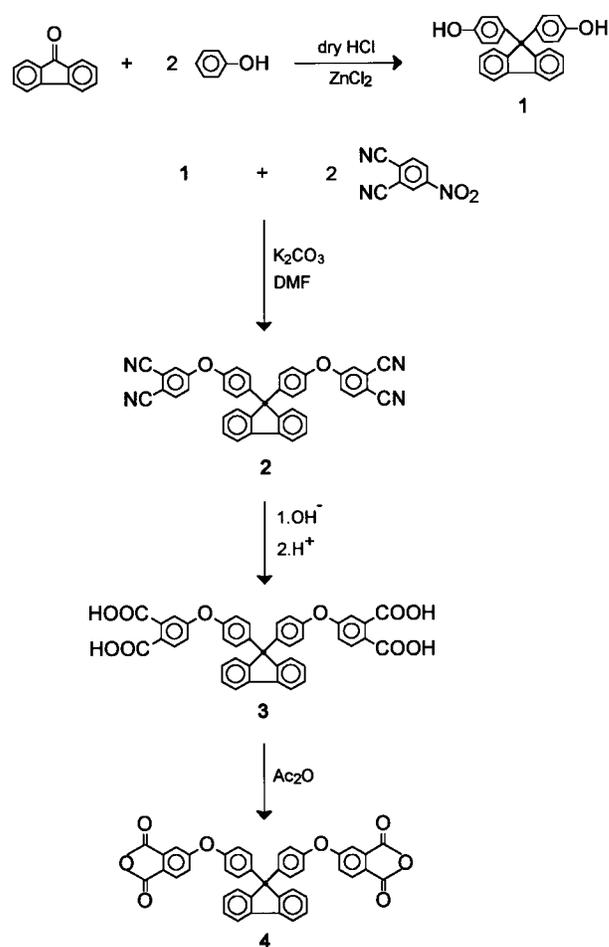

Scheme 1. Synthesis of 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride.

head gauge of 2 cm and a strain rate of 5 cm/min were used. An average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

The most common bisphenol synthesis is the condensation of a ketone with excess phenol in the presence of an acidic condensing agent.[23] Fluorenone was highly reactive in this reaction, giving high yields in a few hours. As shown in Scheme 1, 9,9-bis(4-hydroxyphenyl)fluorene (**1**) has four phenyl rings connected to one carbon atom and is highly stable thermally and chemically. The structure of diol **1** was confirmed by IR, ^{1}H- and ^{13}C-NMR spectroscopy, and elemental
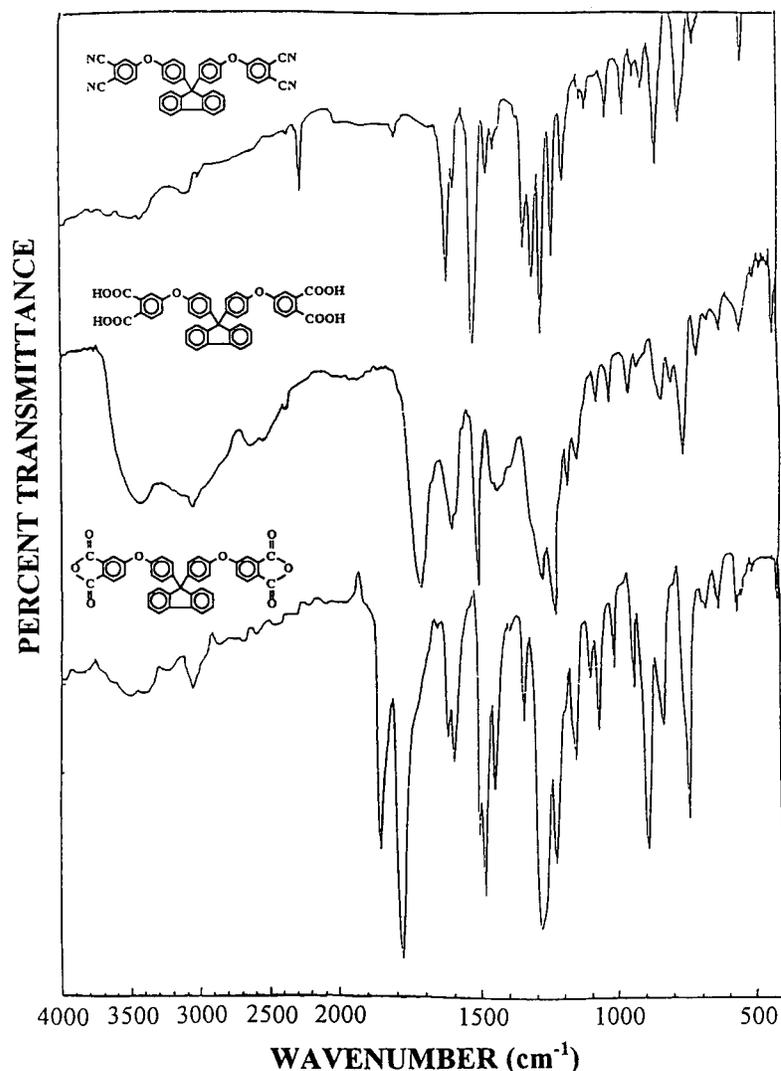
Figure 1.   Infrared spectra of 9,9-bis[4-(3,4-dicyanophenoxy)phenyl]fluorene (**2**), 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene (**3**), and 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride (**4**).

analysis, and the results were in good agreement with the proposed structure.

9,9-Bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride (**4**) was prepared by the well-developed method.[24–26] As shown in Scheme 1, the synthesis started from the nitrodisplacement reaction of 4-nitrophthalodinitrile with diol **1** in DMF in the presence of potassium carbonate to yield 9,9-bis[4-(3,4-dicyanophenoxy)phenyl]fluorene (**2**). The bis(ether dinitrile) **2** was subsequently hydrolyzed in an alkaline solution and acidified to yield 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene (**3**) which was then dehydrated to bis(ether anhydride) **4**. The structures of the intermediate bis(ether dinitrile) **2** and tet-

racarboxylic acid **3** and the final bis(ether anhydride) **4** were confirmed by elemental analysis and IR spectroscopy. Their IR spectra are reproduced in Figure 1. In Figure 1, the sharp absorption of $C\equiv N$ group near the 2,232 cm^{-1} disappeared after the cyano groups was hydrolyzed to the carboxyl group, and the characteristic absorptions of carboxyl groups appeared around 2,500–3,500 cm^{-1} and 1,700 cm^{-1}. When tetracarboxylic acid **3** was dehydrated to bis(ether anhydride) **4**, the absorptions due to carboxyl groups disappeared and the characteristic $C\!=\!O$ stretching absorptions of the cyclic anhydride unit appear around 1,851 and 1,778 cm^{-1}. The structure **4** was also elucidated by X-ray crystallographic

Table I. Crystal Data and Conditions for Crystallographic Data Collection and Structure Refinement

Formula	$C_{41}H_{22}O_8$
Formula Weight	642.61
Space Group	Monoclinic C 2/c
a (Å)	30.745 (4)
b (Å)	7.1295 (12)
c (Å)	31.324 (3)
β (deg.)	117.535 (9)
V (Å^3)	6088.4 (14)
Z	8
$D_{calc.}$ (g/cm^3)	1.402
λ (Å)	1.5418
F (000)	2665
Unit Cell Detn: #; (2θ Range)	25; (34.00–47.74 deg.)
Scan Type	$\theta/2\theta$
Scan Width (deg.)	$2(0.65 + 0.15 \tan(\theta))$
Scan Speed (deg./min)	1.83–8.24
(2θ) max.	120.0
h k l Ranges	(−34; 30) (0; 7) (0; 35)
μ (cm^{-1})	7.529
Crystal Size (mm)	0.30 * 0.30 * 0.35
Temperature (K)	298
No. of Measd. Reflns.	4525
No. of Obsd Reflns. (I > 2.0sig(I))	3595
No. of Unique Reflns.	4433
R_f^a; R_w^b	0.037; 0.036
G_0F^c	1.14
Refinement Program	NRCVAX
No of Atoms	71
No. of Refined Params.	443 (3595 out of 4433 Reflns.)
Minimize Function	$\Sigma[w(F_0 - F_c)^2]$
(Δ/σ)max.	0.0013
Residual in Final D-map (e/Å^3)	$-0.160 \to 0.160$

^{a} $R_f = \Sigma(F_0 - F_c)/\Sigma(F_0)$.
^{b} $R_w = \Sigma w^{1/2} (F_0 - F_c)/\Sigma w^{1/2} F_0$.
^{c} $G_0F = [\Sigma w(F_0 - F_c)^2/(\text{No. of relfns} - \text{No. of paramas.})]$; 3 standard reflections (4,−2,−10; 4,2,−10; 14,0,−4) monitored every 3600 seconds, intensity variation < 9%.

analysis. Single crystals of bis(ether anhyride) **4** were obtained from dilute acetic anhydride solution by slow evaporation of the solvent. X-ray crystal data for **4** are given in Table I, and refinement results in the structure shown in Figure 2. The structure of **4** looks like a chelate configuration and exhibits symmetrical and bulky molecular characteristics. The fluorenylidene plane is nearly orthogonal to the phenylene rings. Selected bond distances and bond angles are summarized in Tables II and III, respectively. The structure coincides with the proposed one.

Synthesis of Poly(ether imide)s

The fluorene-based poly(ether imide)s **7a–i** were prepared by two step method in which the first step was formation of the poly(ether amic acid) (Scheme 2). Poly(ether amic acid)s **6a–i** prepared from bis(ether anhydride) **4** with various diamines exhibited inherent viscosities ranged from 0.39 to 1.57 dL/g (Table IV) and could afford free-standing films by solution casting, which are indicative of high molecular weights. The imidization step was carried out by thermal dehydration of poly(ether amic acid)s by sequential heating to 270°C. Probably due to the rigid nature of polymer chains, the films of poly(ether imide)s **7a** and **7c** derived from rigid diamines such as *p*-phenylenediamine and benzidine were embrittled during thermal cure. The cured film of polymer **7b** from *m*-phenylenediamine cracked upon creasing, possibly due to lower molecular weight. The other poly(ether imide) films are flexible and tough.

Properties of Poly(ether imide)s

The solubilities of poly(ether imide)s were tested in some organic solvents such as *N*-methyl-2-pyrrolidone (NMP), DMAc, DMF, DMSO, *m*-cresol, and tetrahydrofuran. Except for poly(ether imide)s **7h** and **7i** derived from aromatic diamines such as **5h** and **5i** which swelled in dipolar aprotic solvents such as NMP and DMAc, all the polymers could not be dissolved in all the solvents tested. These results indicate that the incorporation of bulky fluorenylidene unit along the poly-
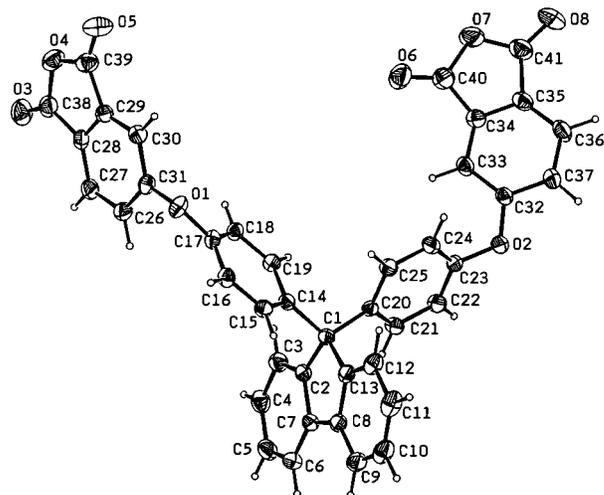
Figure 2. X-ray crystal structure of bis(ether anhydride) **4**.

Table II.   Selected Bond Distance for Bis(ether anhydride) **4**

Atoms[a]	Distance[b] (Å)	Atoms[a]	Distance[b] (Å)
O1-C17	1.395(3)	C14-C15	1.391(3)
O1-C31	1.378(3)	C14-C19	1.390(3)
O2-C23	1.402(3)	C15-C16	1.391(3)
O2-C32	1.364(3)	C16-C17	1.369(3)
O3-C38	1.192(4)	C17-C18	1.385(3)
O4-C38	1.399(4)	C18-C19	1.381(3)
O4-C39	1.193(4)	C20-C21	1.385(3)
O5-C39	1.196(4)	C20-C25	1.386(3)
O6-C40	1.393(3)	C21-C22	1.384(3)
O7-C40	1.407(4)	C22-C23	1.366(3)
O8-C41	1.188(4)	C23-C24	1.374(3)
C1-C2	1.537(3)	C24-C25	1.383(3)
C1-C13	1.534(3)	C26-C27	1.377(4)
C1-C14	1.536(3)	C26-C31	1.384(3)
C1-C20	1.536(3)	C27-C28	1.374(4)
C2-C3	1.379(4)	C28-C29	1.374(4)
C2-C7	1.396(3)	C28-C38	1.460(4)
C3-C4	1.391(4)	C29-C30	1.372(4)
C4-C5	1.372(4)	C29-C39	1.473(4)
C5-C6	1.379(5)	C30-C31	1.382(3)
C6-C7	1.384(4)	C32-C33	1.386(4)
C7-C8	1.466(4)	C32-C37	1.386(3)
C8-C9	1.388(3)	C33-C34	1.378(3)
C8-C13	1.394(3)	C34-C35	1.369(4)
C9-C10	1.388(5)	C34-C40	1.466(4)
C10-C11	1.373(5)	C35-C36	1.381(4)
C11-C12	1.387(4)	C35-C41	1.462(4)
C12-C13	1.384(4)	C36-C37	1.381(4)

[a] The atom labeling used here is the same as in Figure 2.
[b] Estimated standard deviations in the least significant figure are given in parentheses.

mer chain failed to enhance the solubility of these poly(ether imide)s. This may be due to the presence of rigid 9,9-diphenylfluorene core, in which the rotational freedom of phenylene units was inhibited by the bulky fluorenylidene unit.

The crystallinity of the poly(ether imide)s was evaluated by wide-angle X-ray diffraction measurement. X-ray diffractograms of some represesentative poly(ether imide)s are illustrated in Figure 3. As expected, all the polymers displayed amorphous diffraction patterns due to the bulkiness of kinked 9,9-fluorenylidene structure. The steric repulsion of the bulky 9,9-fluorenyliene unit twist the rings dramatically out of plane. The resulting twisted conformation inhibits chain packing and crystallinity. With the exception of more rigid **7a**, **7b**, and **7c**, the other polymers could be fabricated into flexible and tough films,

showing tensile strengths in the range 76–107 MPa and elongation at break of 5–10 % (Table V).

The thermal properties of the poly(ether imide)s were evaluated by means of differential

Table III.   Selected Bond Angles for Bis(ether anhydride) **4**

Atoms[a]	Angle[b] (deg)	Atoms[a]	Angle[b] (deg)
C17-O1-C31	118.37(17)	C20-C21-C22	121.16(21)
C23-O2-C32	120.44(18)	C21-C22-C23	119.70(20)
C38-O4-C39	109.18(21)	O2-C23-C22	118.01(20)
C40-O7-C41	108.96(22)	O2-C23-C24	120.99(21)
C2-C1-C13	100.84(17)	C22-C23-C24	120.75(21)
C2-C1-C14	108.85(18)	C23-C24-C25	119.14(21)
C2-C1-C20	112.74(17)	C20-C25-C24	121.49(20)
C13-C1-C14	114.91(18)	C27-C26-C31	120.60(22)
C13-C1-C20	107.15(18)	C26-C27-C28	117.62(23)
C14-C1-C20	111.93(17)	C27-C28-C29	121.17(23)
C1-C2-C3	129.18(20)	C27-C28-C38	130.59(25)
C1-C2-C7	110.68(20)	C29-C28-C38	108.24(23)
C3-C2-C7	120.14(22)	C28-C29-C30	122.30(22)
C2-C3-C4	118.92(23)	C28-C29-C39	107.77(23)
C3-C4-C5	120.6(3)	C30-C29-C39	129.93(24)
C4-C5-C6	121.06(24)	C29-C30-C31	116.28(22)
C5-C6-C7	118.77(23)	O1-C31-C26	120.88(21)
C2-C7-C6	120.50(24)	O1-C31-C30	117.03(21)
C2-C7-C8	108.74(20)	C26-C31-C30	122.02(23)
C6-C7-C8	130.76(22)	O2-C32-C33	123.28(21)
C7-C8-C9	130.63(24)	O2-C32-C37	115.02(22)
C7-C8-C13	108.91(20)	C33-C32-C37	121.66(22)
C9-C8-C13	120.4(3)	C32-C33-C34	115.95(22)
C8-C9-C10	118.7(3)	C33-C34-C35	122.85(24)
C9-C10-C11	120.83(25)	C33-C34-C40	129.5(3)
C10-C11-C12	120.8(3)	C35-C34-C40	107.69(22)
C11-C12-C13	118.97(25)	C34-C35-C36	121.18(23)
C1-C13-C8	110.76(21)	C34-C35-C41	108.5(3)
C1-C13-C12	128.83(21)	C36-C35-C41	130.3(3)
C8-C13-C12	120.25(22)	C35-C36-C37	116.99(24)
C1-C14-C15	123.04(19)	C32-C37-C36	121.34(25)
C1-C14-C19	119.11(19)	O3-C38-O4	120.3(3)
C15-C14-C19	117.76(20)	O3-C38-C28	132.2(3)
C14-C15-C16	121.29(21)	O4-C38-C28	107.56(25)
C15-C16-C17	119.30(20)	O4-C39-O5	121.2(3)
O1-C17-C16	116.91(19)	O4-C39-C29	107.25(25)
O1-C17-C18	121.90(20)	O5-C39-C29	131.5(3)
C16-C17-C18	120.94(21)	O6-C40-O7	120.9(3)
C17-C18-C19	119.11(20)	O6-C40-C34	131.3(3)
C14-C19-C18	121.60(20)	O7-C40-C34	107.8(3)
C1-C20-C21	121.16(19)	O7-C41-O8	120.0(3)
C1-C20-C25	120.84(19)	O7-C41-C35	107.05(24)
C21-C20-C25	117.75(20)	O8-C41-C35	133.0(3)

[a] The atom labeling used here is the same as in Figure 2.
[b] Estimated standard deviations in the least significant figure are given in parentheses.
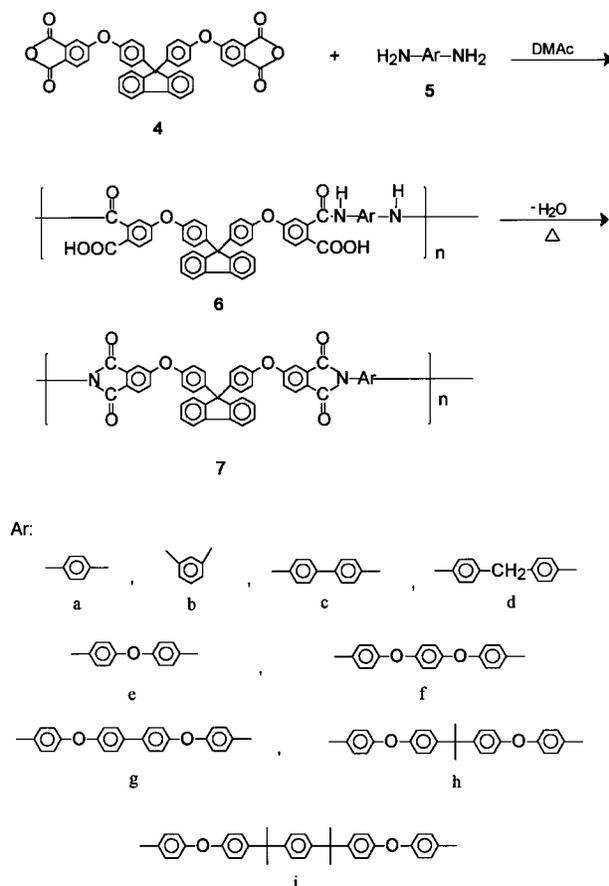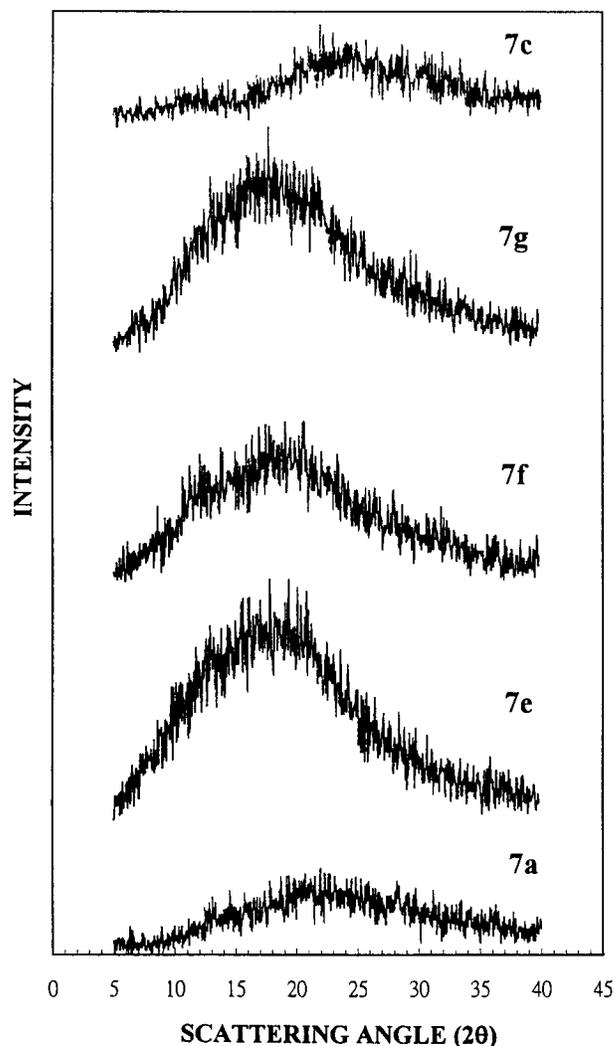
Scheme 2. Syntheses of poly(ether imide)s based on 9,9-bis[4-(3,4-dicarboxyphenoxy)phenyl]fluorene dianhydride.

scanning calorimetry (DSC), thermomechanical analysis (TMA), and thermogravimetric analysis (TG). Some thermal behavior data of all the poly-

Figure 3. Wide-angle x-ray diffractograms of poly-(ether imide)s.

Table IV. Inherent Viscosities of Poly(ether amic acid)s and Film Quality of Poly(ether imide)s

Poly(ether amic acid)s		Poly(ether imide)s	
Code	η_{inh} [a] (dL/g)	Code	Film Quality
6a	0.53	**7a**	Highly Brittle
6b	0.39	**7b**	Slightly Brittle
6c	0.62	**7c**	Slightly Brittle
6d	0.63	**7d**	Flexible
6e	0.56	**7e**	Flexible
6f	0.68	**7f**	Flexible
6g	1.57	**7g**	Flexible
6h	0.63	**7h**	Flexible
6I	0.79	**7i**	Flexible

[a] Measured on 0.5 g/dL in DMAc at 30°C.

(ether imide)s are presented in Table V. The polymer's T_gs were determined from the DSC thermograms of samples that had been heated to 350°C and rapidly quenched prior to the run. The T_g values of these polymers varied in the range of 238–306°C. The softening temperatures (T_s, which may be considered as apparent T_g) of polymers were determined by TMA method using a loaded penetration probe. The results are also summarized in Table V. These poly(ether imide)s showed T_s at the range of 231–301°C, which are comparable to the T_g values observed by DSC. The dependence of T_g or T_s on the structure of diamine moiety among the poly(ether imide)s **7a–i** is in agreement with the expectation. Introduction of less symmetric *m*-phenylene unit or

Table V. Tensile and Thermal Properties of Poly(ether imide) Films

Polymer Code	Tensile Properties		T_g [b] (°C)	T_s [c] (°C)	Decomposition[d] Temperature (°C)		Char Yield[e] (%)
	Strength at Break (MPa)	Elongation at Break (%)			In N_2	In Air	
7a	—[a]	—	292	285	576	578	63.5
7b	—	—	275	272	557	572	61.6
7c	—	—	306	301	587	580	68.2
7d	82	6	275	277	566	574	65.7
7e	107	7	274	277	576	577	64.3
7f	102	8	261	255	580	573	62.7
7g	102	10	268	251	583	575	66.6
7h	107	7	249	241	542	543	62.5
7i	76	5	238	231	555	548	54.7

[a] The film was too brittle to test.
[b] Base line shifts in the second heating DSC traces, with a heating rate of 20°C/min.
[c] Softening temperatures measured by the TMA (penetration method) with a load of 5 g at a heating rate of 10°C/min.
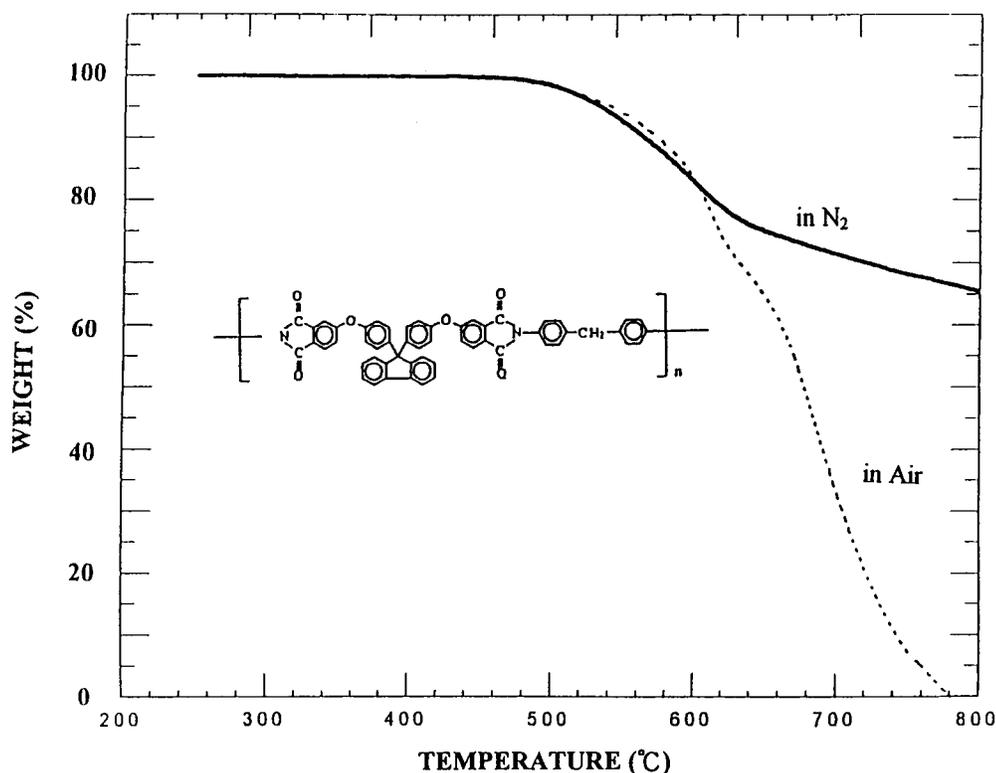[d] Temperature at which 10% weight loss was recorded by TG at a heating rate of 20°C/min.
[e] Residual weight % when heated to 800°C in nitrogen.

flexible ether or isopropylidene linkages into the macromolecular backbone generally results in decreasing T_g or T_s. For example, poly(ether imide)s **7h** and **7i** which were derived from multiring flexible diamines revealed a relatively lower T_g or T_s.

The thermal stability of the poly(ether imide)s was ascertained by TG. Figure 4 presents typical

Figure 4. TG curves for poly(ether imide) **7d** with a heating rate of 20°C/min.

TG curves of polymer **7d** in nitrogen and air. The decomposition temperature at which 10% weight loss was recorded in both nitrogen and air as well as the anaerobic char yield at 800°C for all poly-(ether imide)s are also listed in Table V. Dynamic TG data indicated that all the polymers possess excellent thermal stability, with no significant weight loss up to temperatures of approximately 500°C in air or nitrogen, and their 10% weight loss temperatures ranged from 542–587°C in nitrogen and 543–580°C in air. It should be noted that the amount of carbonized residue of the poly-(ether imide)s at 800°C in nitrogen atmosphere was very high and reached up to 68.2%.

CONCLUSIONS

9,9-Bis[4-(3,4-dicrboxyphenoxy)phenyl]fluorene dianhydride was synthesized from readily available compounds in four main steps and used for preparing a new series of fluorene-based poly-(ether imide)s. All the poly(ether imide)s showed poor solubility in organic solvents, although they are amorphous in nature. However, most of these polymers exhibited good film formability, high thermal stability, and moderate to high T_gs or T_ss. In addition, these poly(ether imide)s may have high permeability/selectivity due to the presence of the bulky fluorene unit, which may prove useful in membrane applications.

REFERENCES AND NOTES

1. Polyimides; Wilson, D., Stenzenberger, H. D., and Hergenrother, P. M., Eds.; Chapman and Hall: New York, 1990.
2. Polyimides: Fundamentals and Applications; Ghosh, M. K., Mittal, K. L., Eds.; Marcel Dekker: New York, 1996.
3. Tamai, S.; Yamaguchi, A.; Ohta, M. Polymer 1996, 37, 3683.
4. Yang, C.-P.; Chen, W.-T. Macromolecules 1993, 26, 4865.
5. Maier, G.; Wolf, M. Macromol Chem Phys 1996, 197, 781.
6. Eastmond, G. C.; Paprotny, J. J Mater Chem 1997, 7, 589.
7. Hsiao, S.-H.; Yang, C.-Y. J Polym Sci Part A Polym Chem 1997, 35, 2801; 1998, 36, 216.
8. Chern, Y.-T.; Shiue, H.-C. Macromolecules 1997, 30, 4646.
9. Chern, Y.-T.; Shiue, H.-C. Macromolecules 1997, 30, 5766.
10. Korshak, V. V.; Vinogradova, S. V.; Vygodskii, Y. S. J Macromol Sci Rev Macromol Chem Part C 1974, 11, 45.
11. Yang, C.-P.; Lin, J.-H. J Polym Sci Part A Polym Chem 1993, 31, 2153.
12. Yang, C.-P.; Lin, J.-H. J Polym Sci Part A Polym Chem 1994, 32, 369.
13. Yang, C.-P.; Lin, J.-H. J Polym Sci Part A Polym Chem 1994, 32, 423.
14. Yang, C.-P.; Lin, J.-H. Polymer 1995, 36, 2607.
15. McHattie, J. S.; Koros, W. J.; Paul, D. R. Polymer 1991, 32, 840.
16. McHattie, J. S.; Koros, W. J.; Paul, D. R. Polymer 1991, 32, 2618.
17. McHattie, J. S.; Koros, W. J.; Paul, D. R. Polymer 1992, 33, 1701.
18. Pixton, M. R.; Paul, D. R. Polymer 1995, 36, 3165.
19. Langsam, M.; Burgoyne, W. F. J Polym Sci Part A Polym Chem 1993, 31, 909.
20. Aguilar-Vega, M.; Paul, D. R. J Polym Sci Part B Polym Phys 1993, 31, 1599.
21. Hsiao, S.-H.; Yang, C.-P.; Lin, C.-K. J Polym Res 1995, 2, 1; Chem Abstr 1995, 123, 287811g.
22. Hsiao, S.-H.; Yang, C.-P.; Fan, J.-C. Macromol Chem Phys 1995, 196, 3041.
23. Morgan, P. W. Macromolecules 1970, 3, 536.
24. Eastmond, G. C.; Paprotny, J.; Wester, I. Polymer 1993, 34, 2865.
25. Eastmand, G. C.; Page, P. C. B.; Paprotny, J.; Richards, R. E.; Shaunak, R. Polymer 1994, 35, 4215.
26. Hsiao, S.-H.; Yang, C.-P.; Chu, K.-Y. Macromolecules 1997, 30, 165.