New Organo-Soluble Aromatic Polyimides Based on 3,3′,5,5′-Tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane Dianhydride and Aromatic Diamines

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ABSTRACT: New aromatic tetracarboxylic dianhydride, having isopropylidene and bromo-substituted arylene ether structure 3,3′,5,5′-tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride, was synthesized by the reaction of 4-nitrophthalonitrile with 3,3′,5,5′-tetrabromobisphenol A, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile) and subsequent dehydration of the resulting bis(ether diacid). The novel aromatic polyetherimides having inherent viscosities up to 1.04 dL g^{-1} were obtained by either a one-step or a conventional two-step polymerization process starting from the bis(ether anhydride) and various aromatic diamines. All the polyimides showed typical amorphous diffraction patterns. Most of the polyimides were readily soluble in common organic solvents such as *N,N*-dimethylacetamide (DMAc), *N*-methyl-2-pyrrolidone (NMP), pyridine, and even in less polar solvents like chloroform and tetrahydrofuran (THF). These aromatic polyimides had glass transition temperatures in the range of 256–303°C, depending on the nature of the diamine moiety. Thermogravimetric analysis (TGA) showed that all polymers were stable, with 10% weight loss recorded above 470°C in nitrogen. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 1673–1680, 1999

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INTRODUCTION

Aromatic polyimides are widely used in the semiconductor and electronic packaging industry because of their outstanding thermal stability, good insulation properties with low dielectric constant, good adhesion to commonly substrates, and superior chemical stability.[1,2] However, their applications were limited in many fields because aromatic polyimides are normally insoluble and intractable after conversion from the polyamic acid to the polyimide form. Most conventional processing techniques involve the fabrication of polyamic acid precursors followed by thermal or chemical imidization. Problems can arise because the polyamic acids are thermally and hydrolytically unstable. The water evolved from imidization can also form voids in bulk materials. Thus, a great deal of effort was exemplified by attempts to improve the processing characteristics of the relatively intractable polyimides.[3,4] One of the successful approaches to increase solubility and processability of polyimides with

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minimal detrimental effect on their high thermal stability is the introduction of bulky phenyl pendant groups along the polymer backbone. Some organo-soluble aromatic polyimides were demonstrated by using aromatic diamines having phenyl substituents,[5–11] as well as phenylated aromatic tetracarboxylic dianhydrides.[12–14] The other effective approach to organo-soluble high-temperature polymer is the incorporation of arylene ether or other flexibilizing linkages to increase the overall chain flexibility.[15–19]

The present study is concerned with the synthesis and characterization of a series of polyimides based on the 3,3′,5,5′-tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**1**), bearing both flexible ether and isopropylidene bridge between the phenylene units and tetrabromo substituents on the phenylene unit. The incorporation of these flexible linkages into the polymer backbone is expected to reduce the crystallinity and enhance the solubility and melt moldability of the polyimides. In addition, the tetrabromo substituents on the phenylene unit would make the polymer more bulky in nature, indicating that the bromo-substituted polymers should be able to further lower the interchain interactions or prevent the polymer chains from packing and would also effectively enhance the solubility of polyimides. Furthermore, by virtue of restricted rotation about the bond joining the aromatic ring system, the 3,3′,5,5′-tetrabromobisphenol A–based polymers should have higher glass transition temperatures (T_g's) than bisphenol A–based polymers without substituent analogs. The dianhydride monomer (**1**) was used to prepare soluble polyimides by either a one-step or a two-step polymerization method with various aromatic diamines. The properties of these polyimides, such as solubility and thermal behavior, were then discussed.

EXPERIMENTAL

Materials

Reagent-grade aromatic diamines such as *m*-phenylenediamine (**2b**) (TCI) and bis(4-aminophenyl)methane (**2c**) (TCI) were purified by distillation under reduced pressure. *p*-Phenylenediamine (**2a**) (TCI) and bis(4-aminophenyl)ether (**2d**) (TCI) were purified by sublimation. Bis(4-Aminophenyl)sulfone (**2e**) was recrystallized from ethanol. 4,4′-bis(4-Aminophenoxy)biphenyl (**2h**) (mp 198–199°C) was prepared by a reported method[20] that involved the nucleophilic substitution reaction of 4,4′-biphenol with *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction of the intermediate dinitro compound using hydrazine as the reduction agent and palladium as the catalyst. The other diamines such as 1,4-bis(4-aminophenoxy)benzene (**2g**) (TCI) and 4,4′-(hexafluoroisopropylidene)dianiline (**2f**) (Aldrich) were used without purification. Isoquinoline was purchased from TCI and used as received. Reagent-grade potassium carbonate was dried under vacuum at 150°C before use. *N*-methyl-2-pyrrolidinone (NMP), dimethyl sulfoxide (DMSO), and *m*-cresol were purified by distillation under reduced pressure over calcium hydride.

Monomer Synthesis

3,3′,5,5′-Tetrabromo-2,2-bis[4-(3,4-dicyanophenoxy)-phenyl]propane (BRCN)

BRCN was synthesized by the nucleophilic substitution reaction of 3,3′5,5′-tetrabromobisphenol A with 4-nitrophthalolnitrile. In a three-neck flask, equipped with a nitrogen inlet, a Dean–Stark trap, and a condenser, were placed 22.0 g (40.4 mmol) of 3,3′5,5′-tetrabromobisphenol A and 11.15 g (80.8 mmol) of dried potassium carbonate with 100 mL DMSO and 100 mL toluene. The mixture was heated with stirring at 140°C for 6 h under nitrogen to facilitate dehydration. After complete removal of water, the residual toluene was distilled off. Then, the reaction mixture was cooled to about 60°C and 14.31 g (81.0 mmol) of 4-nitrophthalonitrile was added. The reaction was carried out with stirring at 80°C for 24 h. After cooling, the reaction mixture was precipitated into 1 L of cold water. The crude product was filtered and purified by recrystallization from acetonitrile to afford 18.23 g (56% yield) of pale yellow powders, mp 268–269°C (by DSC). The IR spectrum (KBr) exhibited absorption bands at 2229 cm^{-1} (C≡N str.), 1597–1456 cm^{-1} (aromatic C═C str.), and 1252 cm^{-1} (C—O—C str.). ^{13}C-NMR (100 MHz, DMSO-d6): δ 29.97, 42.91, 109.02, 115.37, 115.85, 117.06, 117.17, 120.45, 120.97, 131.97, 136.64, 144.89, 150.67, 159.27.

ANAL. calcd for $C_{31}Br_4H_{16}N_4O_2$: C, 46.73%; H, 2.03%; N, 7.03%. Found: C, 46.59%; H, 2.03%; N, 7.07%.

3,3′,5,5′-Tetrabromo-2,2-bis[4-(3,4-dicarboxy-phenoxy)phenyl]propane (BRCA)

BRCA was synthesized by the alkaline hydrolysis of tetranitrile compound BRCN. A mixture of

22.5 g (400 mmol) of potassium hydroxide and 15.9 g (20 mmol) of BRCN in 100 mL of ethanol and 100 mL distillate water was stirred at reflux until no further ammonia was generated. The time spent to reach this stage was about 4 days. The resulting hot, clear solution thus formed was filtered to remove any insoluble impurities. The hot filtrate was allowed to cool and the pH value was adjusted by dilute hydrochloric acid to near three. The precipitate formed was collected by filtration, washed repeatedly with water, and dried under vacuum. The yield was 16.39 g (94%) of white powder. The IR spectrum (KBr) showed absorption bands at 2500–3500 (O—H str.), 1710 cm^{-1} (C═O str.), 1604–1387 cm^{-1} (aromatic C═C str.), and 1274, 1244 cm^{-1} (C—O—C str.). ^{13}C-NMR (100 MHz, DMSO-d6): δ 30.10, 43.11, 114.46, 116.85, 117.94, 126.43, 132.12, 132.30, 136.91, 145.98, 150.63, 158.09, 167.92, 168.88. The product was used for the subsequent cyclodehydration without further purification.

3,3′,5,5′-Tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (1)

A mixture of BRCA 15.69 g (18 mmol), acetic acid (90 mL), and acetic anhydride (30 mL) was stirred at reflux for 5 h. The resulting hot, clear solution was filtered to remove any insoluble impurities. On cooling, the crystallized solid was collected by filtration, washed with dried toluene, and dried under vacuum. The yield was 12.71 g (71%), mp 267–268°C (DSC). The IR spectrum (KBr) exhibited absorption bands at 1852 cm^{-1} (asymetrical C═O str.), 1779 cm^{-1} (symetrical C═O str.), 1616–1449 cm^{-1} (aromatic C═C str.), and 1286, 1262 cm^{-1} (C—O—C str.). ^{13}C-NMR (100 MHz, DMSO-d6): (29.92, 42.98, 111.00, 117.32, 122.83, 125.61, 128.20, 132.09, 134.54, 145.32, 150.71, 162.01, 162.46, 162.67).

ANAL. calcd for $C_{31}Br_4H_{16}N_4O_8$: C, 44.50%; H, 1.93%. Found: C, 44.40%; H, 1.98%.

Polymer Synthesis

Polyimide 3d from 1 and 2d by One-Step Method

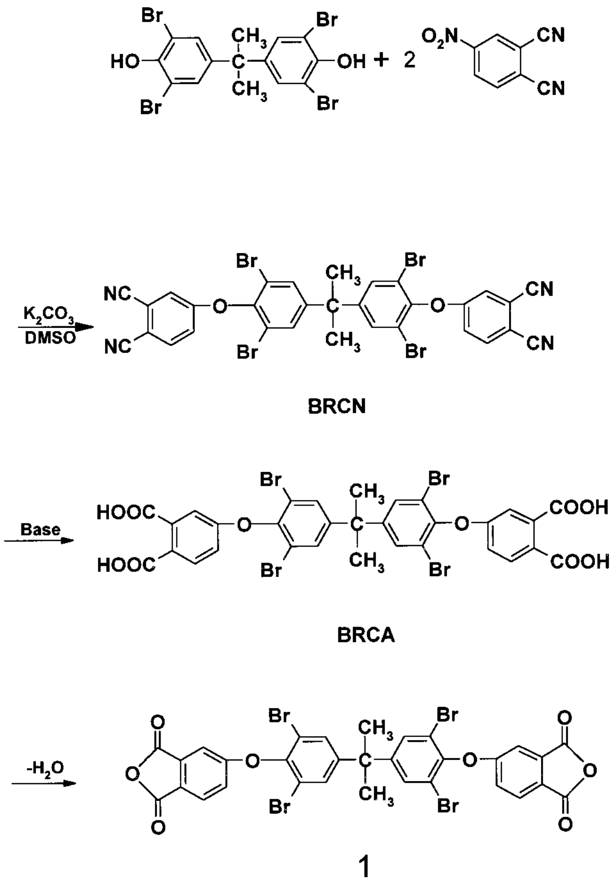
A typical procedure is as follows. The stoichiometric mixture of the diamine **2d** (0.300 g, 1.5 mmol), the dianhydride **1** (1.254 g, 1.5 mmol), and a few drops of isoquinoline in *m*-cresol (10 mL) were stirred at ambient temperature under nitrogen. After the solution was stirred for 4 h, it was heated to reflux (ca. 200°C) and maintained at that temperature for 15 h. During this time, the water of imidization was allowed to distill from the reaction mixture along with *m*-cresol. The *m*-cresol was continually replaced so as to keep the total volume of the solution constant. After the solution was allowed to cool to ambient temperature, the viscous solution then was poured slowly into 300 mL of methanol with stirring. The polymer that precipitated was collected by filtration, washed thoroughly with hot methanol, and dried under reduced pressure at 150°C for 15 h. The polyimide **3d** was obtained having inherent viscosity of 0.66 dL g^{-1} measured at a concentration of 0.5 g dL^{-1} in chloroform at 10°C. The polyimide film was obtained by casting from the NMP solution onto a glass plate and dried at 200°C for 15 h under vacuum. The IR spectrum of **3d** (film) exhibited characteristic imide absorption bands at 1779 (asymetrical C═O), 1722 (symetrical C═O), 1377 (C—N), and 742 cm^{-1} (imide ring deformation). The other polyimides were prepared by analogous procedure.

Polyimide 3d from 1 and 2d by Two-Step Method

A typical procedure is as follows. To a solution of diamine **2d** (0.300 g, 1.5 mmol) in 6 mL of NMP was added the dianhydride **1** (1.254 g, 1.5 mmol) at once at 0–5°C under nitrogen. The solution was stirred at that temperature for 1 h and then at room temperature for 5 h. The polyamic acid film was obtained by casting from the reaction solution onto a 9-cm glass culture dish and dried in a 90°C oven overnight to remove the solvent. The IR spectrum of the semidried poly(ether amic acid) film exhibited characteristic absorption bands at 2850–3500 (N—H and O—H str.), 1722 (C═O acid), 1665 cm^{-1} (C═O amide). The semidried poly(ether amic acid) film was further dried and converted to polyetherimide (**3d**) by successive heating at 150°C for 1 h, 200°C for 1 h, and then 250°C for 1 h. The flexible yellowish polyimide **3d** film was obtained with inherent viscosity of 0.58 dL g^{-1} measured at a concentration of 0.5 g dL^{-1} in chloroform at 10°C. The IR spectrum of **3d** (film) exhibited characteristic imide absorption bands at 1779 (asymetry C═O), 1722 (symetry C═O), 1377 (C—N), and 742 cm^{-1} (imide ring deformation). The other polyimides were prepared by analogous procedure.

Measurements

IR spectra were recorded on a Shimadzu FTIR-8000 Fourier transform spectrophotometer. Elemental analyses were run in a Perkin–Elmer Model 2400 C, H, N analyzer. ^{13}C-NMR spectra were recorded on a Bruker AMX-400 Fourier transform NMR spectrometer. The inherent viscosities were measured with an Ubbelohde viscometer thermostatted at 10°C. Weight-averaged molecular weight (M_w) and number-averaged molecular weight (M_n) were obtained by means of gel permeation chromatography (GPC) on the basis of polystyrene calibration on a Waters 410 apparatus (eluant: tetrahydrofuran). Qualitative solubility was determined using 10 mg of polymer in 2 ml of solvent. DSC and thermogravimetry (TG) were performed with TA instruments DSC-2910 modulated DSC and TA instruments TGA-2050, respectively. T_g's were read at the middle of the change in the heat capacity and were taken from the second heating scan after rapid cooling. Wide-angle X-ray diffraction patterns were obtained at room temperature on a Rigakudenki RU-200 apparatus with nickel-filtered CuK α radiation. Tensile properties were determined from stress–strain curves with a Toyo Baldwin Instron UTM-III-500 with a load cell of 10 kg at a drawing speed of 5 cm min^{-1}. Measurements were performed at room temperature with film specimens (6-cm long, 0.5-cm wide, and 0.1-mm thick), and an average of at least five individual determinations was reported.



Scheme 1.

RESULTS AND DISCUSSION

Monomer Synthesis

Takekoshi et al. already reported the synthesis of aromatic ether-containing tetranitriles by the nitrosubstitution reaction of 4-nitrophthalonitrile with several bisphenols and of the corresponding tetracarboxylic dianhydrides as well.[21] This route was applied in the present study to the synthesis of aromatic tetracarboxylic dianhydride, 3,3′,5,5′-tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**1**), as shown in Scheme 1.

The aromatic tetranitrile compound (BRCN) containing ether linkage and tetrabromo substituents on the phenylene unit was synthesized readily starting from 4-nitrophthalonitrile and 3,3′,5,5′-tetrabromobisphenol A in a yield of 56%, according to a slight modification of the procedure of Takekoshi et al.,[21] by using potassium carbonate as a base in DMSO–toluene mixture. The tetranitrile compound was then hydrolyzed with aqueous potassium hydroxide, giving the corresponding tetracarboxylic acid BRCA, which in turn was converted to the aromatic ether and bromo-containing tetracarboxylic dianhydride **1** in a yield of 71% by the chemical cyclodehydration with acetic anhydride.

The chemical structures of all of the newly synthesized compounds were confirmed by means of elemental analysis, IR spectroscopic techniques, and the characteristic peaks in the ^{13}C-NMR spectra. Concerning the synthesis of tetracarboxylic acid (BRCA), the disappearance of a characteristic nitrile stretching band at around 2229 cm^{-1} on the IR spectra revealed completion of the hydrolysis of the tetracyano compound (BRCN), and the most characteristic bands of bis(ether diacid) (BRCA) are observed near 1710 cm^{-1} (C═O stretching) and in the range of 2500–3500 cm^{-1} (O—H stretching). The cyclodehydration of BRCA to the corresponding tetracarboxylic dianhydride (**1**) was also supported from the observation on the IR spectrum that strong absorption bands due to carboxylic function shifted from 1710 cm^{-1} (free acid) to 1779 and 1852 cm^{-1}

Table I. Synthesis of Polyimides by Two-Step Method

Polymer Code	η_{inh}[a] (dL g^{-1})	M_n[b] ($\times 10^{-4}$)	M_w ($\times 10^{-4}$)	M_w/M_n	Elemental Analysis[c] (%) C	H	N
3a	0.58	—	—	—	48.52 (48.93)	2.32 (2.22)	3.01 (3.08)
3b	0.43	15.47	20.75	1.34	48.85 (48.93)	2.20 (2.22)	3.12 (3.08)
3c	0.47	10.64	17.62	1.66	52.73 (52.94)	2.66 (2.62)	2.89 (2.81)
3d	0.58	19.17	25.03	1.31	51.57 (51.63)	2.41 (2.42)	2.73 (2.80)
3e	0.14	1.79	3.22	1.79	49.42 (49.27)	2.30 (2.31)	2.71 (2.67)
3f	0.42	21.04	28.61	1.36	48.46 (48.71)	2.23 (2.13)	2.38 (2.47)
3g	0.60	22.46	29.46	1.31	53.66 (53.88)	2.71 (2.58)	2.60 (2.56)
3h	0.86	26.14	30.99	1.19	56.26 (56.54)	2.83 (2.76)	2.37 (2.40)

[a] Measured at a concentration of 0.5 g dL^{-1} in chloroform at 10°C.
[b] Determined by GPC on the basis of polystyrene calibration.
[c] The values in parentheses are the calculated values.

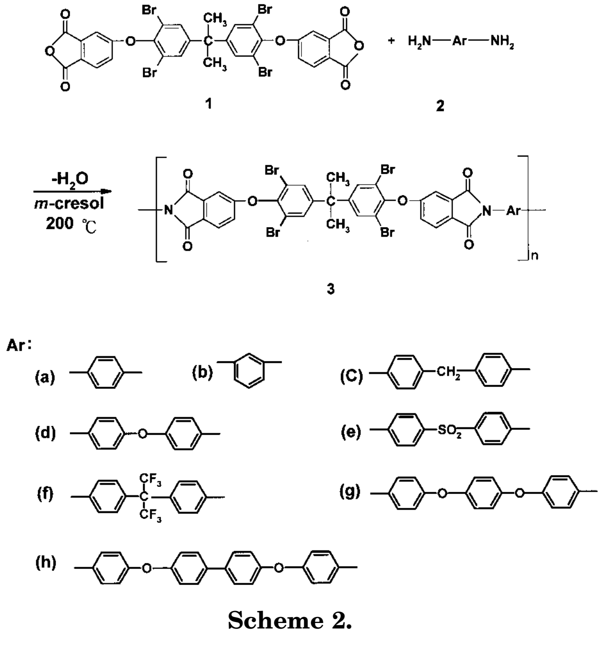
(anhydride). According to the basis of the shielding effect of carbon, the position of chemical shifts for carbon were readily assigned from the ^{13}C-NMR spectra. The ^{13}C-NMR spectra of BRCN, BRCA, and **1** exhibited exactly 14 peaks due to symmetry and were consistent with the calculated values. The elemental analysis values of all of the compounds were also in good agreement with the calculated values for the proposed structures.

Polymer Synthesis

The one-step procedure starting from aromatic diamines and tetracarboxylic dianhydrides in the presence of isoquinoline as a catalyst, as well as conventional two-step process, involving a ring-opening addition and subsequent thermal cyclodehydration, are convenient methods for the preparation of polyimides.[13] New polyimides **3a–3h** were synthesized by the two-step method starting from aromatic tetracarboxylic dianhydride **1** with aromatic diamines **2a–2h.** Table I summarizes the results of the synthesis of the new polyimides. Polyimides **3a–3h** thus obtained had inherent viscosities of 0.14–0.86 dL g^{-1}. Polymer **3e** had lower viscosity than others, which could be attributed to the low nucleophilic nature of aromatic diamine **2e** having electron-withdrawing group. The GPC curves of polyimides indicated that the M_w values were 32,200–309,900 relative to standard polystyrene, and the M_w/M_n values, a measure of molecular weight distribution, were 1.2–1.8.

Polyimides **3b–3h** could also be obtained readily by the one-step method of aromatic tetracarboxylic dianhydride **1** with aromatic diamines **2b–2h** in the presence of a catalytic amount of isoquinoline at 200°C (Scheme 2).

Except for the polymer **3a** derived from *p*-phenylenediamine (**2a**), which was partially soluble in *m*-cresol, all other polyimides remained fully soluble during the course of polymerization. Table II summarizes the results of the synthesis of the new polyimides. Polyimides having inherent viscosities of 0.34–1.04 dL g^{-1} could be isolated upon precipitation into methanol, suggesting the formation of the polymers by one-step method afforded higher inherent viscosities compared with the conventional two-step method. These viscos-



Scheme 2.

Table II. Synthesis of Polyimides by One-Step Method

Polymer Code	η_{inh}[a] (dL g^{-1})	M_n[b] ($\times10^{-4}$)	M_w[b] ($\times10^{-4}$)	M_w/M_n[b]
3a	—	—	—	—
3b	0.53	20.03	25.33	1.26
3c	0.52	11.66	17.66	1.52
3d	0.66	24.49	30.06	1.23
3e	0.34	9.43	13.47	1.43
3f	0.43	21.65	26.12	1.21
3g	0.88	23.86	30.52	1.28
3h	1.04	28.62	33.90	1.18

[a] Measured at a concentration of 0.5 g dL^{-1} in chloroform.
[b] Determined by GPC on basis of polystyrene calibration.

ity values corresponded to the M_w values of 134,700–339,000, and the ratio of M_w/M_n was 1.2–1.5. The M_w/M_n values were also smaller than those from the two-step method. The elemental analysis values of these polyimides were in good agreement with the calculated values for the proposed structures (Table I). Transparent and flexible films of the polyimides could be obtained by casting from the resulting polymer solutions. The IR spectra of the polymers exhibited characteristic imide absorptions at near 1780 (asymetric C═O), 1720 (symetric C═O), 1370 (C—N str.), and 740 cm^{-1} (imide ring deformation). The strong absorption around 1240 cm^{-1} was assigned to the aryl–ether stretching.

Polymer Characterization

The solubility of the polyimides was studied qualitatively, and the results are shown in Table III. All the polyimides dissolved readily in aprotic solvents such as NMP, DMAc, and even in less polar chloroform solvent. Polyimide **3a** with symmetric *p*-phenylene structure also showed fairly good solubility. This may be due to the amorphous nature of these polymers, as evidenced by X-ray diffractograms discussed later. The solubility behavior of the new polyimides derived from the dianhydride (**1**) and aromatic diamines was compared with those of the corresponding polyimides[22] derived from the 2,2′-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride without bromo-substituent; it was found that the solubility of the new polyimides was significantly enhanced by the introduction of bulky tetrabromo-substituted phenylene unit into the polymer backbone.

The crystallinity of the prepared polyether imides was measured by wide-angle X-ray diffraction scans. These diagrams revealed that all of the tetrabromo-substituted phenylene containing polyimides, even that obtained from *p*-phenylenediamine

Table III. Solubility of Polyimides[a]

	Polymer			
Solvent	**3a**	**3b, 3c, 3e, 3f**	**3g**	**3d, 3h**
N-methyl-2-pyrrolidone	++	++	++	++
Dimethylacetamide	+	++	++	+
Dimethylformamide	±	++	++	+
Pyridine	±	++	+	+
m-Cresol	±	+	+	+
Chloroform	++	++	++	+
Tetrahydrofuran	−	++	++	++
Methanol	−	−	−	−

[a] Solubility: ++, soluble at room temperature; +, soluble on heating at 60°C; ±, partially soluble on heating at 60°C; −, insoluble on heating at 60°C.

Table IV. Mechanical Properties of Polyimide Films[a]

Polymer Code	Tensile Strength (MPa)	Elongation at Break (%)	Tensile Modulus (GPa)
3a	92	8	2.5
3b	85	8	2.3
3c	82	9	2.2
3d	90	12	2.4
3e	72	6	1.9
3f	80	10	2.3
3g	95	12	2.3
3h	97	9	2.5

[a] Polyimide films were obtained by casting from their NMP solutions.

(**2a**), were completely amorphous. This is reasonable because the presence of bulky tetrabromo-substituted phenylene unit and both flexible ether and isopropylidene groups induce looser chain packing and revealed a large decrease in crystallinity. Thus, the amorphous nature of these polymers was reflected in their good solubility.

All polyimides could be processed into good quality with yellowish to brownish films and were subjected to tensile test. The tensile properties of these flexible films are given in Table IV. The tensile strength, elongation at break, and tensile modulus of these polymer film were 72–97 MPa, 6–12%, and 1.9–2.5 GPa, respectively.

The thermal behavior of the polymers was evaluated by DSC and TG. Figure 1 depicts typical DSC and TG curves of polymer **3a**, and the thermal behavior data of the polymers are summarized in Table V. Because the influence of residual water or solvent and history of thermal annealing was sometimes observed in the first heating scan of DSC, quenching from the elevated temperature to room temperature yields more amorphous samples so that in most cases the T_g's could be easily measured in the second heating traces of DSC. The T_g's of amorphous polyimides **3** were observed in the range of 256–303°C, depending on the structure of diamine component and decreased with decreasing rigidity of the polymer backbone. In addition, the above-mentioned tetrabromo-substituted phenylene containing polyimides **3** also had higher T_g's by about 50°C than the corresponding polymers[22] without bromo-substituent. This phenomenon can be attributed to the restricted rotation about the bond joining the aromatic ring systems. The temperatures of 10% weight loss in nitrogen and air atmosphere were determined from original thermograms and showed that the 10% weight loss temperatures of these polymers were recorded in the range of 450–480°C in air and 470–515°C in nitrogen atmospheres. The amount of carbonized residue (char yield) of these polymers in nitrogen atmosphere was in the range of 42–50% weight even at 800°C, showing high intrinsic fire-retardant characteristics.

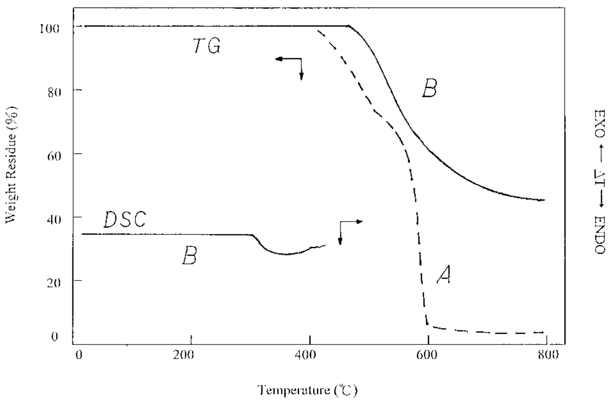


Figure 1. DSC and TG curves for polyimide **3a:** (A) in air and (B) in nitrogen. DSC and TG heating rate = 10°C/min.

Table V. Thermal Behavior Polyimide

Polymer Code	T_g[a] (°C)	Decomposition Temperature (°C)[b] In Air	Decomposition Temperature (°C)[b] In Nitrogen	Char Yield[c] at 800°C (%) in N_2
3a	303	475	500	44
3b	273	450	490	44
3c	263	460	470	46
3d	256	460	500	45
3e	265	450	470	42
3f	267	460	515	44
3g	262	480	500	46
3h	268	480	505	50

[a] From the second heating of DSC measurements conducted with a heating rate of 10°C min^{-1} in nitrogen.

[b] Temperature at 10% weight loss was recorded by TGA at a heating rate 10°C min^{-1}.

[c] Char yield was recorded by TGA at 800°C.

CONCLUSIONS

New polyimide-forming tetracarboxylic dianhydride having isopropylidene linkages and tetrabromo-substituted arylene ether structure, 3,3′,5,5′-tetrabromo-2,2-bis[4-(3,4-dicarboxyphenoxy)phenyl]propane dianhydride (**1**), was successfully synthesized in three steps starting from 4-nitrophthalonitrile and 3,3′,5,5′-tetrabromobisphenol A. The dianhydride monomer (**1**) was subjected to either one-step or conventional two-step polycondensation with various aromatic diamines, giving a series of high molecular weight polyimides. The introduction of the bulky tetrabromo-substituted phenylene unit into the polymer backbone highly improved solubility of the polyimides in organic solvents. The aromatic polyimides had glass transition temperatures of 256–303°C and 10% weight losses above 450°C in air, indicating high thermal stability. Thus, the novel organo-soluble polyimide is considered as a new and processable polymeric material.

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