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Synthesis and Characterization of New Highly Organosoluble Poly(ether imide)s Bearing a Noncoplanar 2,2′-Dimethyl-4,4′-biphenyl Unit and Kink Diphenylmethylene Linkage

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Two new bis(ether anhydride)s, 2,2′-dimethyl-4,4′-bis[4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (**4A**) and bis[4-(3,4-dicarboxy phenoxy)phenyl]diphenylmethane dianhydride (**4B**), were prepared in three steps starting from nitrodisplacement of 4-nitrophthalonitrile with 2,2′-dimethylbiphenyl-4,4′-diol and bis(4-hydroxyphenyl)diphenylmethane, respectively, followed by alkaline hydrolysis of the intermediate bis(ether dinitrile)s and subsequent dehydration of the resulting bis(ether diacid)s. A series of new highly organosoluble poly(ether imide)s were prepared from the bis(ether anhydride)s and various diamines by conventional two-stage synthesis. The resulting poly(ether imide)s had inherent viscosities in the range of 0.55−0.81 dL·g^{-1}. GPC measurement revealed that the polymers exhibited number-average molecular weight and weight-average molecular weight up to 45 000 and 82 000, respectively. All the polymers showed typical amorphous diffraction patterns. Almost all the poly(ether imide)s showed excellent solubility and readily dissolved in various solvents such as *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide (DMAc), *N*,*N*-dimethylformamide, pyridine, cyclohexanone, tetrahydrofuran, and chloroform. These polymers had glass transition temperatures in the range of 224−256 °C. Thermogravimetric analysis showed that all polymers were stable, with 10% weight loss recorded above 489 °C in nitrogen. The isothermal gravimetric analysis results demonstrated that these poly(ether imide)s showed weight losses of 7.0−10.5% after isothermal aging at 350 °C in static air for 20 h. These tough and flexible polymer films could be easily obtained by solution cast from the DMAc solution. These polymer films had tensile strength of 84−116 MPa and tensile modulus of 1.9−2.7 GPa.

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 common substrates, and superior chemical stability.[1,2] However, their applications were limited in many fields because the early polyimides were insoluble and intractable. Therefore, considerable research has been undertaken to identify new ways to circumvent these restrictions.

The introduction of flexible group and/or bulky units in the polymer backbone has been a general approach in changing the chemical structure of polyimides.[3−11] Poly(ether imide)s were developed as a result of research interests in aromatic nucleophilic displacement chemistry combined with a perceived marketplace need for high-performance polymers that could be readily fabricated by standard plastics extrusion and injection molding processes. An important example is Ultem 1000, developed and commercialized by General Electric Co.,[12] which exhibits reasonable thermal stability and good mechanical properties together with good moldability.

The present study is concerned with the synthesis and characterization of a series of new highly soluble poly-

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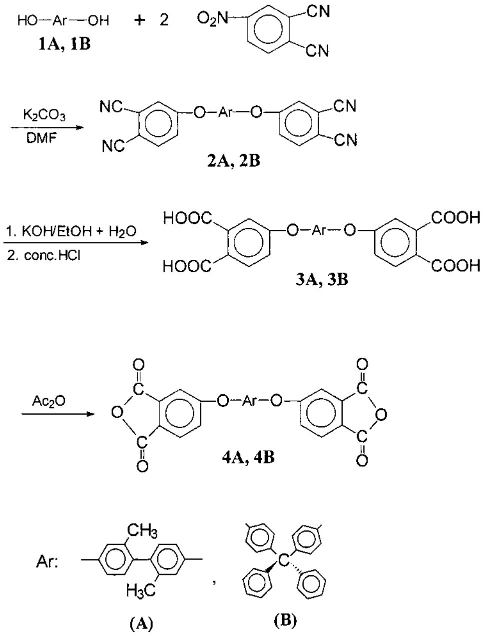
(ether imide)s based on 2,2′-dimethyl-4,4′-bis[4-(3,4-dicarboxyphenoxy)]biphenyl dianhydride (**4A**) bearing noncoplanar 2,2′-dimethyl-4,4′-biphenylene unit, and bis[4-(3,4-dicarboxy phenoxy)phenyl]diphenylmethane dianhydride (**4B**) containing a kink diphenylmethylene linkage. The incorporation of 2,2′-disubstituted biphenylene in a para-linked polymer chain reduced the interactions of polymer chains. The phenyl rings are forced by the 2,2′-disubstitution into a noncoplanar conformation, decreasing the intermolecular forces between the polymer chains. The crystallization tendency is markedly lowered and the solubilities are significantly enhanced.[13−18] On the other hand, another effective approach to obtain organosoluble polyimides is the incorporation of substituted methylene linkages, such as isopropylidene,[19−22] hexafluoroisopropylidene,[23−27] and diphenylmethylene[28] units, which provide kinks between the rigid phenyl rings in the backbone and lead to enhanced solubility of the polymer. The improved solubility of the polymers is ascribable to the presence of the kink unit in the polymer backbone, which lowered the chain rigidity. It was observed that the polymers with a diphenylmethylene unit showed better thermal stability than those containing isopropylidene and hexafluoroisopropylidene.[28] Therefore, the incorporation of noncoplanar 2,2′-dimethyl-4,4′-biphenylene and kink diphenylmethylene unit in the poly(ether imide) backbone is expected to provide organosoluble poly(ether imide)s with good thermal stability. The effect of different units on the polymer properties such as solubility and thermal and mechanical properties will also be discussed herein.

Experimental Section

Materials. The starting diols, 2,2′-dimethyl-4,4′-dihydroxybiphenyl (**1A**) and bis(4-hydroxyphenyl)diphenylmethane (**1B**), were synthesized from 2,2′-dimethyl-4,4′-diaminobiphenyl dihydrochloride[14−16] and 4,4′-dichlorodiphenylmethane, respectively.[24,25] *N*,*N*-Dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMAc), and pyridine were purified by distillation under reduced pressure before use. Acetic anhydride was purified by vacuum distillation.

Scheme 1. Synthesis of the New Bis(ether anhydride)s (4A and 4B)



Synthesis of Monomers. See Scheme 1.

*2,2′-Dimethyl-4,4′-bis[4-(3,4-dicyanophenoxy)]biphenyl (**2A**).* In a 100-mL round-bottomed flask, 7.39 g (34.5 mmol) of 2,2′-dimethyl-4,4′-dihydroxybiphenyl (**1A**) and 12.2 g (70 mmol) of 4-nitrophthalonitrile were dissolved in 80 mL of dry DMF. Anhydrous potassium carbonate (10.1 g, 73 mmol) was added and the suspension was stirred at room temperature for 2 days. The reaction mixture was then poured into 500 mL of water to give a pale-yellow solid product, which was washed repeatedly with water and methanol, filtered out, and dried. The crude product was then recrystallized from acetonitrile twice to obtain yellow crystals of bis(ether dinitrile) (**2A**) in 83% yield. mp 227−228 °C. IR (KBr): 2222 ($C\equiv N$) and 1240 cm^{-1} (C−O). ^{1}H NMR ($CDCl_3$): δ (ppm) 7.80 (d, 2H), 7.37 (d, 4H), 7.29 (t, 2H), 7.05 (s, 2H), 7.01 (d, 2H), 2.15 (s, 6H). ^{13}C NMR ($CDCl_3$): δ (ppm) 162.8, 153.8, 139.9, 139.1, 136.2, 132.2, 122.4, 122.3, 122.0, 118.3, 118.1, 115.9, 115.5, 109.2, 19.4. Anal. Calcd for $C_{30}H_{18}O_2N_4$: C, 77.24%; H, 3.89%; N, 12.01%. Found: C, 77.14%; H, 4.07%; N, 11.93%.

*Bis[4-(3,4-dicyanophenoxy)phenyl]diphenylmethane (**2B**).* The synthetic procedure of **2B** was similar to that of **2A** using bis(4-hydroxyphenyl)diphenylmethane (**1B**) as the diol compound. The crude product was also recrystallized from acetonitrile twice to obtain brown crystals of bis(ether dinitrile) (**2B**) in 86% yield. mp 219−220 °C. IR (KBr): 2224 ($C\equiv N$) and 1244 cm^{-1} (C−O). ^{1}H NMR (DMSO-d_6): δ (ppm) 8.06 (d, 2H), 7.78 (s, 2H), 7.41 (dd, 2H), 7.32−7.20 (m, 14H), 7.10 (d, 4H). ^{13}C NMR (DMSO-d_6): δ (ppm) 162.3, 153.3, 147.5, 145.0, 137.5, 133.8, 131.6, 129.1, 127.4, 123.9, 123.3, 120.4, 117.8, 116.9, 116.4, 109.3, 64.1. Anal. Calcd for $C_{41}H_{24}O_2N_4$: C, 81.44%; H, 4.00%; N, 9.26%. Found: C, 81.27%; H, 4.40%; N, 9.45%.

*2,2′-Dimethyl-4,4′-bis[4-(3,4-dicarboxyphenoxy)]biphenyl (**3A**).* In a 100-mL round-bottomed flask, 5.41 g (11.6 mmol) of bis(ether dinitrile) (**2A**) was suspended in a solution of 12.9 g (0.23 mol) potassium hydroxide in 40 mL/40 mL of water−ethanol. The solid bis(ether dinitrile) could be dissolved within 1 h. Reflux was continued for 2 days until the evolution of ammonia had ceased. After filtration and removal of the residue ethanol under reduced pressure, the cooled filtrate was diluted with 200 mL of water and acidified by concentrated HCl. The precipitated bis(ether diacid) (**3A**) was filtered off and washed thoroughly with distilled water until the filtrate was neutral. The yield was 92%. The compound had an endothermic peak due to thermal cyclodehydration at about 165 °C (by DSC). IR (KBr): 2500−3600 (C(O)O−H), 1690 (C=O), and 1271 cm^{-1} (C−O−C). ^{1}H NMR (DMSO-d_6): δ (ppm) 7.79 (d, 2H), 7.15−

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6.98 (m, 10H), 2.02 (s, 6H). ^{13}C NMR (DMSO-d_6): δ (ppm) 170.2, 169.2, 160.8, 155.7, 139.4, 137.9, 137.8, 132.7, 132.3, 129.9, 121.9, 120.0, 117.9, 117.8, 19.4. Anal. Calcd for $C_{30}H_{22}O_{10}$: C, 57.41%; H, 4.09%. Found: C, 57.86%; H, 3.71%.

*Bis[4-(3,4-dicarboxylphenoxy)phenyl]diphenylmethane (**3B**).* The synthetic procedure of **3B** was similar to that of **3A** using **2B** as the bis(ether dinitrile) compound. The product was obtained in 91% yield. mp 168−170 °C. IR (KBr): 2500−3600 (C(O)O−H), 1710 (C=O), and 1227 cm^{-1} (C−O−C). ^{1}H NMR (DMSO-d_6): δ (ppm) 169.9, 169.2, 160.3, 154.8, 147.6, 143.9, 138.0, 136.9, 133.6, 131.6, 129.1, 127.9, 127.4, 120.2, 119.8, 118.9, 64.0. ^{13}C NMR (DMSO-d_6): δ (ppm) 7.85−7.67 (m, 2H), 7.33−7.00 (m, 24H). Anal. Calcd for $C_{41}H_{28}O_{10}$: C, 81.44%; H, 4.00%. Found: C, 81.27%; H, 4.40%.

*2,2′-Dimethyl-4,4′-bis[4-(3,4-dicarboxyphenoxy)]biphenyl Dianhydride (**4A**).* In a 100-mL round-bottomed flask, 3.7 g (6.8 mmol) of bis(ether diacid) (**3A**) was suspended in 35 mL of glacial acetic acid and 25 mL of acetic anhydride. The mixture was boiled under reflux for 24 h. Then, the mixture was filtered and left to crystallize overnight. The precipitated product was filtered out and further recrystallized from acetic anhydride. The obtained brown crystals were filtered out, washed with dry toluene, and dried at 100 °C for 24 h under vacuum to give bis(ether anhydride) (**4A**). Yield: 81%. mp 217−218 °C. IR (KBr): 1837, 1767 (C=O), 1272 cm^{-1} (C°-O). ^{1}H NMR (DMSO-d_6): δ (ppm) 7.79 (d, 2H), 7.18−6.97 (m, 10H), 2.02 (s, 6H). ^{13}C NMR (DMSO-d_6): δ (ppm) 170.3, 169.2, 160.8, 155.8, 139.5, 138.0, 137.9, 132.7, 132.3, 126.9, 122.0, 120.0, 118.0, 117.9, 19.9. Anal. Calcd for $C_{30}H_{18}O_8$: C, 71.15%; H,3.58%. Found: C, 70.79%; H, 3.77%.

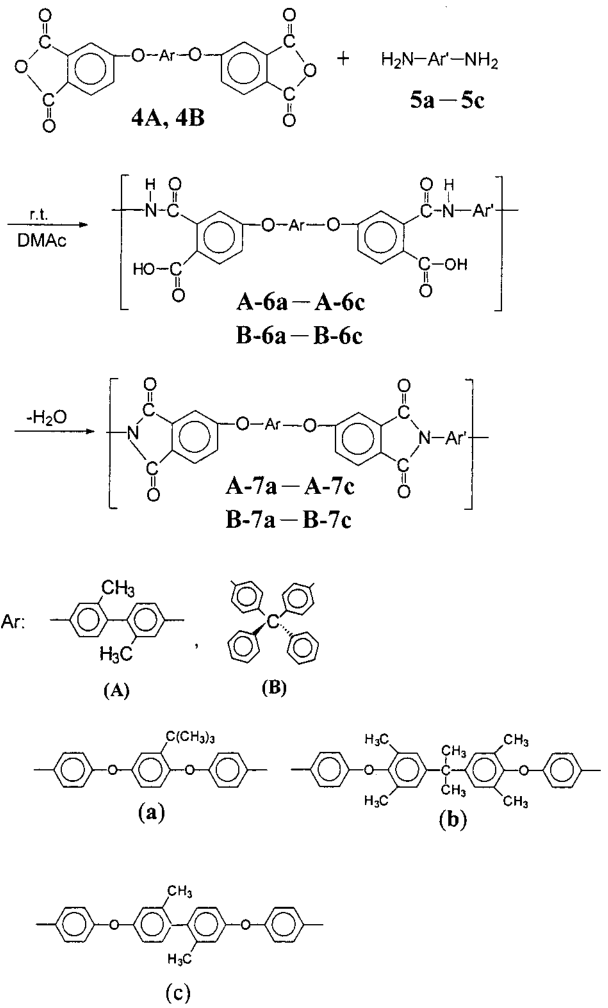
*Bis[4-(3,4-dicarboxylphenoxy)phenyl]diphenylmethane dianhydride (**4B**).* The synthetic procedure of **4B** was similar to that of **4A** using **3B** as the bis(ether diacid) compound. The product was obtained in 84% yield: mp 262 °C (by DSC). IR (KBr): 1842, 1764 (C=O), 1262 cm^{-1} (C−O). ^{1}H NMR (DMF-d_7): 8.00 (dd, 2H), 7.61 (d, 2H), 7.53 (s, 2H), 7.39−7.13 (m, 18H). ^{13}C NMR (DMF-d_7): δ (ppm) 171.1, 170.0, 166.6, 155.0, 148.7, 146.2, 136.3, 134.9, 136.7, 129.8, 129.7, 128.3, 127.0, 126.9, 121.4, 114.6, 65.3. Anal. Calcd for $C_{41}H_{24}O_8$: C, 74.19%; H, 3.85%. Found: C, 73.33%; H, 4.30%.

Polymerization Procedures. See Scheme 2. To a stirred solution of 3,3′,5,5′-tetramethyl-2,2-bis[4-(4-aminophenoxy)-phenyl]propane (**5b**) (0.513 g, 0.11 mmol) in DMAc (5 mL) was gradually added bis(ether anhydride) (**4A**) (0.557 g, 0.11 mmol). The mixture was stirred at room temperature for 2 h under an argon atmosphere to form the poly(ether amic acid) precursor (**A-6b**). Chemical imidization was carried out by adding an extra 3 mL of DMAc, 1 mL of acetic anhydride, and 0.5 mL of pyridine into the above-mentioned **A-6b** solution with stirring at room temperature for 1 h and then heating at 100 °C for 3 h. The homogeneous solution was subsequently poured into methanol and the yellow solid precipitate was filtered off, washed with methanol and hot water, and then dried at 100 °C for 24 h to afford poly(ether imide) **A-7b**. The inherent viscosity of the polymer in *N*,*N*-dimethylacetamide (DMAc) was 0.80 dL·g^{-1}, measured at a concentration of 0.5 g·dL^{-1} at 30 °C. ^{1}H NMR (DMSO-d_7): 7.90 (s, 2H), 7.39−7.12 (m, 30H), 6.87 (s, 4H), 2.05 (s, 12H), 1.67 (s, 6H). ^{13}C NMR (DMSO-d_7): δ (ppm) 169.1, 168.9, 165.3, 159.6, 155.6, 150.9, 149.9, 148.7, 145.7, 136.5, 134.8, 132.7, 132.1, 130.9, 129.8, 129.5, 128.2, 127.7, 127.5, 124.9, 121.1, 116.4, 113.5, 65.3, 42.8, 30.8, 16.4.

All other poly(ether imide)s were prepared using a similar procedure.

Instruments. Melting points were measured in capillaries on a Büchi apparatus (Model BUCHI 535). IR spectra were recorded in the range 4000−400 cm^{-1} on a JASCO IR-700 spectrometer. ^{13}C and ^{1}H NMR spectra were obtained using a JEOL EX-400 operating at 100.40 MHz for carbon and 399.65 MHz for proton. The inherent viscosities of all poly(ether imide)s were measured using an Ubbelohode viscometer. Elemental analysis was made (Perkin-Elmer 2400 instrument). Weight-averaged ($\bar{M}_w$, g/mol) and number-averaged molecular weight ($\bar{M}_n$, g/mol) were determined by gel permeation chromatography (GPC). Four Waters (Ultrastyragel) columns 300 × 7.7 mm (guard, 10^5, 10^4, 10^3, 500 Å in a series) were used for GPC analysis with tetrahydrofuran (THF) (1 mL·min^{-1}) as the eluent. The eluents were monitored with a UV detector (Gilson model 116) at 254 nm. Polystyrene was used as the standard. Wide-angle X-ray diffraction patterns were performed at room temperature with film specimens on an X-ray diffractometer (Philips model PW 1710) using Ni filtered Cu Kα radiation (30 kV, 20 mA). Thermogravimetric data were obtained on a TGA 2050 thermogravimetric analyzer (TA Instruments) in flowing nitrogen or air (100 cm^3·min^{-1}) at a heating rate of 20 °C·min^{-1}. Differential scanning calorimetry (DSC) analysis was performed on a DuPont 2000 differential scanning calorimeter at a heating rate of 20 °C·min^{-1}. The glass transition temperature (T_g) was taken at the inflection point. Tensile properties were determined from stress−strain curves obtained with a Orientec Tensilon with a load cell of 10 kg. Isothermal gravimetric analysis (IGA) was performed on a ULVAC thermogravimetric analyzer (model 7000). A gauge of 3 cm and a strain rate of 2 cm·min^{-1} were used for this study. Measurements were performed at room temperature with five film specimens (4-mm wide, 5-cm long, and ca. 0.1-mm thick).

Scheme 2. Preparation of Various New Poly(ether imide)s



Results and Discussion

Monomer Synthesis. As shown in Scheme 1, the bis(ether anhydride)s were prepared by a three-stage synthetic procedure starting from the nucleophilic nitrodisplacement reaction of diols (**1A** and **1B**) and 4-nitrophthalonitrile in dry DMF in the presence of potassium carbonate at room temperature. It was preferable that

Table 1. Inherent Viscosities and Average Molecular Weights of Various Poly(ether imide)s

polymer code	η_{inh}[a] (dL·g^{-1})	$\bar{M}_{\mathrm{n}} \times 10^{-4}$ [b]	$\bar{M}_{\mathrm{w}} \times 10^{-4}$ [b]	PDI[b]
A-7a	0.81	4.5	7.9	1.8
A-7b	0.80	3.4	8.2	2.4
A-7c	0.65	1.7[c]	3.1[c]	1.6[c]
B-7a	0.56	2.3	5.2	2.2
B-7b	0.55	2.5	5.8	2.3
B-7c	0.65	2.7	6.2	2.3

[a] Inherent viscosity measured in DMAc at a concentration of 0.5 g·dL^{-1} at 30 °C. [b] Measured by GPC in THF; polystyrene was used as the standard. [c] Polymer was measured from the soluble part in THF.

the nitrodisplacement reaction be carried out at low temperature (at room temperature) than in higher temperature (higher than 100 °C) because the products (**2A** and **2B**) always showed dark color when they were obtained at high temperature. The resulting bis(ether dinitrile)s **2A** and **2B** were hydrolyzed in an alkaline solution to obtain the bis(ether diacid)s **3A** and **3B**, respectively. The hydrolysis procedure of **2A** was performed in 2 days. However, the hydrolysis procedure of bis(ether dinitrile) **2B** needed a longer time due to the poorer solubility of **2B** than **2A**. After complete hydrolysis, the solution became clear. Before acidification by aqeous HCl, the removal of the residual ethanol is necessary. The presence of the residual ethanol in the aqueous solution always resulted in viscous product during acidification. The bis(ether diacid)s were then cyclodehydrated to the bis(ether anhydride)s **4A** and **4B**. The structure of these synthesized compounds was confirmed by elemental analysis, IR, and NMR spectroscopy. For instance, the IR spectrum of the bis(ether anhydride) **4A** shows characteristic cyclic anhydride absorption at 1837 and 1767 cm^{-1} attributed to the asymmetrical and symmetrical stretching vibrations of C═O of the anhydride group. The NMR spectra data are listed in the Experimental Section. It was found that the NMR spectra provided clear evidence that the bis(ether anhydride) monomers prepared herein were correlated with the proposed structure.

Preparation of Poly(ether imide)s. The poly(ether imide)s were prepared by the conventional two-step polymerization method, as shown in Scheme 2, involving ring-opening polyaddition forming poly(ether amic acid)s and subsequently chemical cyclodehydration. In general, the thermal cyclodehydration of the poly(amic acid) film is also performed under reduced pressure at high temperature (about 300 °C). However, the high-temperature thermal cyclodehydration may result in poorer solubility of polymer than chemical cyclodehydration.[29] Because the aim of this study is to prepare organosoluble poly(ether imide)s, chemical cyclodehydration was adopted herein. The poly(ether amic acid) precursors were prepared by adding the bis(ether anhydride) (**4A** and **4B**) to the diamine solution gradually. To the obtained viscous poly(ether amic acid) solutions were then added dehydrating agents such as a mixture of acetic anhydride and pyridine to yield various poly(ether imide)s. The resulting poly(ether imide)s had inherent viscosities of 0.55−0.81 dL·g^{-1} (Table 1). The poly(ether imide)s, except polymer **A-7c**, exhibited number-averaged molecular weights ($\bar{M}_{\mathrm{n}}$) and weight-averaged molecular weights ($\bar{M}_{\mathrm{w}}$) above 23 000 and 52 000 g/mol, respectively, measured by GPC by using polystyrene as the standard. All the polymer films could be obtained by solution cast from their DMAc solution. All polymer films were tough, transparent, and flexible. These films were subjected to a tensile test.

Polymer Characterization. The crystallinity of the polymers was examined by wide-angle X-ray diffraction diagrams. All polymers showed the fair amorphous patterns in the region of $2\theta = 8°$ and 40°, indicating that the polymers were amorphous. This observation is reasonable because the presence of noncoplanar conformation of a 2,2′-dimethyl-substituted biphenylene unit and bulky phenyl groups on the diphenylmethylene linkage decreased the intermolecular forces between the polymer chains, causing a decrease in crystallinity. In general, the presence of the biphenylene unit in the polymer backbone led to a rigid-rod polymer with high crystallinity and poor solubility. However, the incorporation of the 2,2′-dimethyl substituent on the 4,4′-biphenylene unit effectively reduced the packing of the polymer chains.[13−18] It should be noted that the polymer chain containing symmetric substituents always leads to better packing of the polymer chain.[30,31] The diphenyl substituents on the methylene group could also be considered symmetric substituents on the polymer backbone. However, the diphenylmethylene linkage will be present as a kink conformation, thus, the rigidity of the polymer chain was lowered. The crystallinity of the polymer-containing kink linkage was thus reduced.[28]

The solubility of these poly(ether imide)s in several organic solvents at 5.0% (w/v) is also summarized in Table 2. Almost all the poly(ether imide)s were soluble in the test solvents including *N*-methyl-2-pyrrolidinone, *N*,*N*-dimethylacetamide (DMAc), pyridine, cyclohexanone, tetrahydrofuran, and even chloroform at room temperature. The good solubility of these poly(ether imide)s was possibly governed by the presence of a flexible ether group, noncoplanar biphenylene, and kink linkage, which reduced the polymer chain interaction and rigidity. The comparison of the polymer solubility between these poly(ether imide)s indicated that the diphenylmethylene-containing poly(ether imide)s showed slightly better solubility than 2,2′-dimethyl-4,4′-biphenylene unit containing poly(ether imide)s. It demonstrated that the kink unit was more effective for improving the solubility of the polymers than the noncoplanar 2,2′-dimethyl-4,4′-biphenylene unit.

The thermal properties of the poly(ether imide)s are tabulated in Table 3. Glass transition temperatures (T_{g}'s) of the poly(ether imide)s, determined by means of a differential scanning calorimeter (DSC), were found to be in the range of 224−256 °C. No melting endotherm peak was observed from DSC traces. This also verified the amorphous nature of the poly(ether imide)s. Obviously, the polymers containing a 2,2′-dimethyl-4,4′-bipheylene unit exhibited a higher T_{g} value than those bearing a kink linkage. This is because the polymers with a biphenylene unit exhibited higher rigidity than those with kink linkages. The thermogravimetric (TG) analysis revealed that these poly(ether imide)s showed

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Table 2. Solubility of Various New Poly(ether imide)s[a]

polymer code	solubility in the solvent below[b]						
	NMP	DMAc	DMF	pyridine	cyclohexanone	THF	chloroform
A-7a	++	++	++	++	+	++	++
A-7b	++	++	++	++	+	+−	+−
A-7c	++	++	++	++	+	++	++
B-7a	++	++	++	++	++	++	++
B-7b	++	++	++	++	++	++	++
B-7c	++	++	++	++	++	++	++

[a] Solubility: ++, soluble at room temperature; +, soluble upon heating at 70 °C; + −, partially soluble at 70 °C. [b] Abbreviations: NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N*,*N*-dimethylacetamide; DMF, *N*,*N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

Table 3. Thermal Properties of Various New Poly(ether imide)s

polymer code	T_g [a] (°C)	Td_{10} [b] (°C)	char yield[c] (%)	wt loss[d] (%)
A-7a	247	518	49	7.0
A-7b	239	493	42	8.4
A-7c	256	535	64	7.9
B-7a	229	501	52	8.8
B-7b	224	489	42	10.5
B-7c	233	531	58	9.0

[a] From the second heating trace of DSC measurements conducted at a heating rate of 20 °C·min^{-1}. [b] Temperature at 10% weight loss (Td_{10}) determined by TGA in nitrogen at a heating rate of 20 °C·min^{-1}. [c] Char yield at 800 °C in nitrogen. [d] Weight loss after 20 h of isothermal aging at 350 °C in static air.

Table 4. Mechanical Properties of Various New Poly(ether imide)s

polymer code	tensile strength (MPa)	elongation at break (%)	initial modulus (GPa)
A-7a	103	7	2.5
A-7b	112	6	2.5
A-7c	116	6	2.7
B-7a	84	12	1.9
B-7b	98	9	2.0
B-7c	91	8	2.3

good thermal stability. They were stable up to the temperature above 450 °C. The temperatures at 10% weight loss (Td_{10}) of these polymers reached 489−535 °C in a nitrogen atmosphere. It was observed that polymers with 2,2′-dimethyl-4,4′-biphenylene having a biphenylene unit showed higher Td_{10} values than those with diphenylmethylene linkages. Upon comparison of these polymers **A-7a**−**A-7c** derived from the diamines (a)−(c), it was observed that the polymer-containing 2,2′-dimethyl-4,4′-bipheylene unit (**A-7c**) exhibited the higher Td_{10} value than that bearing an asymmetric *tert*-butyl substitution group (**A-7a**) and the polymer-containing tetramethyl substituent (**A-7b**) showed the lowest Td_{10} value in the polymer series (**A-7a**−**A-7c**). Like the similar observations reported in our previous study, the noncoplanar conformation can impart greater thermal stability of the polymer than the *tert*-butyl substitution and tetramethyl substituent groups.[7,18] In addition, the polymer-containing 2,2′-dimethyl-4,4′-bipheylene unit (**B-7c**) exhibited the higher Td_{10} value than that bearing the asymmetric *tert*-butyl substitution group (**B-7a**) and the polymer-containing tetramethyl substituent (**B-7b**) showed the lowest Td_{10} value in the polymer series (**B-7a**−**B-7c**). In our previous research, it had been observed that the solubility of the polymer was improved by the noncoplanar conformation of 2,2′-dimethyl-substituted biphenylene in the polymer backbone,which reduced the polymer chain interaction and rigidity.[17] Like the similar observations found in our previous work, the incorporation of the methyl substituent on the 2,2′-dimethyl-4,4′-biphenylene unit did not significantly sacrifice the thermal stability of the polymer but enhanced the processability.[18] According to the results in our previous study, the tetramethyl substituents on the phenylene unit not only effectively improved the polymer solubility but also enhanced the thermo-oxidative stability of the polymers, compared with the polymer having no tetramethyl substituents on the phenylene units.[19] The results of the TGA measurement of these polymers indicated that polymers with noncoplanar biphenylene groups exhibited higher thermal stability than those with kink diphenylmethylene linkages. The isothermal gravimetric analysis (IGA) results demonstrated that these poly(ether imide)s showed good thermo-oxidative stability. In general, the IGA results were in agreement with the TGA data. Specifically, following 20 h of isothermal aging at 350 °C in static air, the polymer showed weight losses of 7.0−10.5% (Table 3). Upon comparing the weight loss value, it is seen that the polyimides containing the 2,2′-dimethyl-4,4′-biphenylene unit were somewhat more thermally stable than those containing the diphenylmethylene unit. The lower weight loss of 2,2′-dimethyl-4,4′-biphenylene unit containing poly(ether imide)s in air may reflect the oxidation of the methyl group of the polymer backbone to form a carbonyl group (C═O) and then cause weight gain.[18,32] Upon comparison with the thermal properties, all the polyimides exhibited higher T_g values than the commercial available polyimide Ultem 1000 (T_g = 215 °C). All the polymides herein have also showed better thermal properties than the results reported in our previous studies.[33−35] These polyimides could be considered as new processable high-performance polymeric materials.

The mechanical properties of the two series of poly(ether imide) films prepared by solution casting from the DMAc solution are summarized in Table 4. These tough and flexible films had tensile strengths of 84−116 MPa, elongation at break of 6−12%, and initial modulus of 1.9−2.7 GPa. The films showed strong and tough natures. It could be concluded that the polymer films with 2,2′-dimethyl-4,4′-biphenylene units are stronger than those with kink diphenylmethylene linkages. It is quite reasonable that the poly(ether imide) having the 4,4′-biphenylene unit showed a rodlike nature and

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led to a higher rigidity of the polymer chain than the kink linkage. Upon comparison with the mechanical properties, polyimides (**A-7b**−**A-7c**) also showed higher tensile strength than commercial available polyimide Ultem 1000 (105 MPa). All the polyimides herein have also showed better mechanical properties than the results reported in our previous studies.[33−35]

Conclusions

Two new bis(ether anhydride)s bearing noncoplanar a 2,2′-dimethyl-4,4′-biphenylene unit and kink diphenylmethylene linkage were successfully prepared in three steps. A series of poly(ether imide)s with moderate molecular weights were obtained from such bis(ether anhydride)s monomers and various diamines. These poly(ether imide)s were easily soluble in various organic solvents including common organic solvents such as cyclohexanone and chloroform. On the other hand, these poly(ether imide)s had high thermal stability and mechanical properties. Thus, these new soluble poly(ether imide)s could be considered as new processable high-performance polymeric materials. The results presented here also demonstrated that polymers with a noncoplanar 2,2′-dimethyl-4,4′-biphenylene unit showed higher thermal stability and mechanical properties than those with kink diphenylmethylene linkages. However, the latter exhibited higher solubility than the former.

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