# Synthesis and Properties of Organosoluble Poly(ether imide)s Containing 4,4'(Octahydro-4,7-methano-5H-inden-5-ylidene) Cardo Group

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ABSTRACT: A series of organosoluble aromatic poly(ether imide)s (PEIs) **VIIa-k** were synthesized from 4,4'-[(octahydro-4,7-methano-5H-inden-5-ylidene)bis(1,4-phenylene)dioxy] diphthalic dianhydride (**IV**) and various aromatic diamines. PEIs synthesized through two-stage polymerization had inherent viscosities of 0.51–0.64 dL/g. This series of polymers could also be synthesized from **IV** and diamines in a small amount of refluxing *m*-cresol in a one-step process and had inherent viscosities of 0.65–0.87 dL/g. For the low melting point diamines (**Vj** and **Vk**), polymers could be obtained by bulk polymerization and had inherent viscosities of 0.36 and 0.41 dL/g. Polymers showed good organosolubility and could be cast into transparent, flexible, and tough polyimide films with good tensile properties. These PEIs had glass transition temperatures among 203–281°C. Thermogravimetric analyses established that these polymers were fairly stable up to 430°C, and the 10% weight loss temperatures were recorded in the range of 473–503°C in nitrogen and 481–512°C in air atmosphere. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 987–996, 1999

**Key words:** 4,4′(octahydro-4,7-methano-5H-inden-5-ylidene); bis(ether anhydride); poly(ether imide)s

# **INTRODUCTION**

As high-performance polymers, polyimides are widely used in electrical materials, adhesives, composite materials, and fiber, as well in as film materials, due to their excellent heat resistance, electrical insulating properties, and mechanical characteristics.<sup>1,2</sup> Without a carefully designed structure, that polyimides were often insoluble and intractable in the fully imidized form presented serious processing difficulties. Therefore,

much effort has been made to synthesize soluble, tractable polyimides without sacrificing their desired properties. Structural modifications, such as the incorporation of flexible bridging linkages<sup>3-7</sup> or *meta* or *ortho*-oriented phenylene rings<sup>8,9</sup> into the polymer backbone and the introduction of bulky substituents<sup>10–13</sup> along the polymer skeleton have been used to enhance the solubility and to lower the phase transition temperatures. Another approach to enhance solubility and processibility is to utilize alicyclic dianhydrides to replace the aromatic anhydrides.<sup>14–16</sup> In introducing flexible linkages into the polymer chain, ether linkages are the most popularly used. The introduction of ether linkages could be made by introducing ether linkages to either diamine or dianhydride monomers.<sup>17,18</sup> The polyimides syn-

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thesized by the polymerization of bis(ether anhydride)s and diamines are always called poly-(ether imide)s (PEIs).<sup>19,20</sup> Bis(ether anhydride)s are always formed by a nitro displacement reaction between the diol and a suitable nitrophthalic acid derivative (often a nitrophthalodinitrile).<sup>21,22</sup>

In this study, bis(ether anhydride) (**IV**), which contained the 4,4'(octahydro-4,7-methano-5H-inden-5-ylidene) cardo group, was prepared from 4,4'(octahydro-4,7-methano-5H-inden-5-ylidene)bisphenol  $(\mathbf{I})^{23,24}$  and 4-nitrophthalonitrile. Although the synthesis of IV and two of its PEIs has been reported recently, the structure of IV and the physical properties of other PEIs are not clearly known.<sup>25</sup> A series of soluble aromatic PEIs VII containing the 4,4'(octahydro-4,7-methano-5H-inden-5-ylidene) cardo side group were synthesized by the polymerization of IV with 11 aromatic diamines. This series of PEIs has good solubility, and their structures are confirmed by the two-dimensional (2-D) <sup>1</sup>H-<sup>13</sup>C correlated spectroscopy (COSY) nuclear magnetic resonance (NMR) spectrum. The synthesis of the polymers and their physical properties are also reported in this study.

# **EXPERIMENTAL**

## **Materials**

4,4'(Octahydro-4,7-methano-5H-inden-5-ylidene)bisphenol (I), 4-nitrophthalonitrile (from TCI), potassium hydroxide (from Wako), and acetic anhydride (from TCI) were used as received.

*p*-Phenylene diamine (**Va**; TCI) was purified by vacuum sublimation. *m*-Phenylene diamine (**Vb**; TCI) was purified by vacuum distillation. The other diamines 4,4'-diaminophenyl methane (**Vc**; from TCI), 4,4'-diaminophenyl ether (**Vdi**; from TCI), 3,4'-diaminophenyl ether (**Ve**; from Mitsui Toatsu), 1,4-(aminophenoxy)benzene (**Vf**; from TCI), 1,3-(aminophenoxy)benzene (**Vg**; from Chriskev) 2,2-bis[4-(aminophenoxy)phenyl]propane (**Vh**; from Chriskev), and 2,2-bis[4-(4-aminophenoxy)phenyl]sulfone (**Vi**; from Chriskev) were used as received. 2,2-Bis[3-(4-aminophenoxy)phenyl]sulfone (**Vj**) and 1,3-bis{2-[4-(4-aminophenoxy)-phenyl]isopropyl}benzene (**Vk**) were synthesized according to the method in the literature.<sup>26</sup>

N,N-Dimethylacetamide (DMAc) and N,N-dimethylforamide (DMF) were purified by distillation under reduced pressure over calcium hydride and stored over 4-Å molecular sieves.

### **Monomer Synthesis**

# *4,4' -[(Octahydro-4,7-methano-5H-inden-5-ylidene) bis(1,4-phenylene)dioxy] diphthalodinitrile (II)*

This compound was synthesized by the reaction of 4,4'(octahydro-4,7-methano-5H-inden-5-ylidene)bisphenol (I) 9.6 g (0.03 mol) and 4-nitrophthalonitrile 10.38 g (0.06 mol) in the presence of potassium carbonate (8.28 g, 0.06 mol) in N,Ndimethylforamide (50 mL) at room temperature for 24 h. Then the reaction mixture was poured into 400 mL of water, and the precipitation solid was filtered and washed with ethanol and hot water. The dry crude product was recrystallized from CH<sub>3</sub>CN/EtOH (100 mL/100 mL) to yield 15.26 g (89% yield) of white crystal. (mp 138–140°C).

IR (KBr): 2231 cm<sup>-1</sup> (C=N); 1251 cm<sup>-1</sup> (C-O). Element analysis ( $C_{38}H_{28}N_4O_2$ ). Calcd: C, 79.70; H, 4.93; N, 9.78. Found: C, 79.53; H, 4.99; N, 9.81.

# 4,4' -[(Octahydro-4,7-methano-5H-inden-5ylidene)bis(1,4-phenylene)dioxy] diphthalic acid (III)

In a 500-mL flask, a suspension of bis(ether dinitrile) II (11.44 g, 0.02 mol) and KOH (17.92 g, 0.32 mol) in an ethanol–water (100 mL/100 mL) cosolvent was boiled under reflux. The suspension turned into a clear solution after about 4 h. Reflux was continued for 2 days until the evolution of ammonia had ceased. The resulting hot, clear solution was filtered to remove any possible insoluble impurities. The solution was cooled and acidified by concentrated HCl to about pH 3 and a large amount of the product precipitated. The precipitation solid was filtered and washed with water. After being dried, 11.20 g (87%) of III was yielded (mp 145–147°C).

IR (KBr): 3600–2500 cm<sup>-1</sup> (O—H); 1715 cm<sup>-1</sup> (C=O); 1248 cm<sup>-1</sup> (C=O). Element analysis (C<sub>38</sub>H<sub>32</sub>O<sub>10</sub>). Calcd: C, 70.36; H, 4.97. Found: C, 70.11; H, 5.09.

# 4,4'-[(Octahydro-4,7-methano-5H-inden-5ylidene)bis(1,4-phenylene)dioxy] diphthalic dianhydride (IV)

In a 200-mL flask, 10.4 g (0.016 mol) of bis(ether diacid) **III** was dispersed in 50 mL of acetic anhydride. The suspension was heated to reflux until turning into a clear solution. The heating was kept for half an hour. The resulting hot, clear solution was filtered to remove any insoluble im-

purities. After being cooled, the white crystal was phased out of the solution, then the solid was filtered and washed with dry toluene. After being dried in vacuum, 7.8 (78%) of chemical cyclization bis(ether anhydride) **IVc** was obtained (mp 165–167°C). The dehydration of **III** through direct heating at 170°C under nitrogen provided the heating cyclization bis(ether anhydride) **IVh** (mp 162–165°C).

IR (KBr): 1850 cm $^{-1}$  (asym C=O); 1776 cm $^{-1}$  (sym C=O); 1276 cm $^{-1}$  (C=O-C). <sup>1</sup>H-NMR (400 MHz,  $CDCl_3$ ):  $\delta = 1.03$  (3H, m, H-14b, 15b, 16b); 1.50 (1H, d, J = 10.1 Hz, H-19b; 1.57 (1H, d, J = 10.1 Hz, H-19a); 1.66 (1H, m, H-15a); 1.86 (4H, m, H-14a, 15a, 17, 18); 2.28 (1H, m, H-13); 2.36 (2H, m, H-20a, 20b); 2.96 (1H, s, H-12); 6.96 (4H, dd, J = 8.8, 3.2 Hz, H-8, 8'); 7.40 (8H, m, H-9, 9', 3, 3', 5, 5'); 7.90 (2H, dd, J = 8.2, 1.2 Hz, H-6, 6'). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 27.11$  (C-15); 31.92 (C-16, C-19); 32.30 (C-14); 42.31 (C-13); 42.39 (C-18); 43.50 (C-20); 47.84 (C-17); 49.34 (C-12); 55.15 (C-11); 112.37; 112.56 (C-3, C-3'); 120.08; 120.28 (C-8, C-8'); 124.05 (C-1, C-1'); 124.94; 125.02 (C-5, C-5'); 127.61 (C-6, C-6'); 129.23; 129.90 (C-9, C-9'); 133.85 (C-2, C-2'); 145.98; 149.97 (C-10, C-10'); 151.20; 151.57 (C-7, C-7'); 162.19; 162.69 (C-4, C-4'); 165.01; 165.18 (C=0).



Element analysis (C $_{38}\rm{H}_{28}\rm{O}_8$ ). Calcd: C, 74.50; H, 4.61. Found: C, 74.31; H, 4.72.

## Polycondensation

#### **Two-Stage Polymerization**

A typical example of polymerization of series **VII** is as follows. Into a solution of *p*-phenylene diamine, 0.108 g (1.0 mmol) in 7.25 mL of DMAc, 0.612 g (1.0 mmol) of **IV** was added portionwise within 30 min. The reaction mixture was kept stirred for 2 h. The inherent viscosity of the obtained poly(amic acid) (**VIa**) was achieved 0.81 dL/g.

## **Thermal Cyclization**

The poly(amic acid) solution was spread on a glass plate and baked at 80°C to remove the sol-

vent. The semidried poly(amic acid) film was further dried and transformed into polyimide by sequential heating at 120, 140, 160, 180, 220, and 250°C, each for 20 min. The PEI (**VIIa**) film was stripped from the glass substrate by soaking in hot water and dried at 100°C under vacuum. The inherent viscosity of the obtained PEI (**VIIa**) was 0.52 dL/g, measured at a concentration of 0.5 g/dL at 30°C in DMAc.

## m-Cresol One-Step Polymerization

In a 25-mL flask, 0.306 g of **IV** was added into a *m*-cresol (0.31 mL) solution containing 0.054 g of *p*-phenylene diamine. The reaction solution was kept stirred for half an hour at 60°C. The reaction temperature was raised by sequential heating at 120, 140, 160, and 180°C, each for 20 min. At the end, the reaction solution was heated at 220°C for 2 h to provide **VIIa.** The other PEIs (**VIIb–VIIi**) were prepared by the same procedure from **IV** and other aromatic diamines (**Vb–Vi**).

## **Bulk Polymerization**

0.13 g of 2,2-bis[3-(4-aminophenoxy)phenyl]sulfone (**Vj**) and 0.184 g of **IV** were added into a 25-mL flask and were premixed at 120°C for 30 min. After being premixed, the reaction temperature was raised by sequential heating at 150 and 180°C, each for 20 min. At the end, the reaction solution was heated at 220°C for 2 h to provide **VIIj.** 

NMR spectrum of VIIa. <sup>1</sup>H-NMR (400 MHz, CDCl<sub>3</sub>): δ = 0.94-1.05 (3H, m, H-14b, 15b, 16b), 1.42 (1H, d, J = 10.1 Hz, H-19b), 1.50 (1H, d, J = 10.1 Hz, H-19a), 1.59 (1H, m, H-15a), 1.80 (4H, m, H-14a, 15a, 17, 18), 2.23 (1H, m, H-13), 2.26–2.33 (2H, m, H-20a, 20b), 2.91 (1H, s, H-12), 6.90 (4H, dd, J = 8.8, 3.2 Hz, H-8, 8'), 7.27(4H, m, H-3, 3', 5, 5'), 7.34 (4H, m, H-9, 9') 7.50 (4H, s, H-22, 22'), 7.90 (2H, dd, J = 8.2, 1.2 Hz, H-6, 6'). <sup>13</sup>C-NMR (400 MHz, CDCl<sub>3</sub>):  $\delta = 27.33$  (C-15), 31.13 (C-16, C-19), 32.50 (C-14), 42.48 (C-13), 42.55 (C-18), 43.63 (C-20), 47.98 (C-17), 49.50 (C-12), 55.16 (C-11), 111.80, 112.01 (C-3, C-3'), 119.63, 119.88 (C-8, C-8'), 122.96, 123.10 (C-5, C-5') 124.70, 124.80 (C-1, C-1') 125.64 (C-6, C-6'), 126.65 (C-22, C-22') 129.23, 129.90 (C-9, C-9'), 130.96 (C-2, C-2') 133.90 (C-21, C-21') 145.12, 149.14 (C-10, C-10'), 151.63, 152.63 (C-7, C-7'), 163.36, 163.55 (C-4, C-4') 166.15, 166.23 (C=O).



## Measurements

Melting points were measured in capillaries on a Yamato mp apparatus (Model MP-21) without correction. <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra were recorded on a JEOL-400 Fourier transform (FT)-NMR spectrometer operated at 30°C with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were recorded on a Jasco FT/ IR-7000 Fourier transform infrared (FTIR) spectrometer. Elemental analyses were run in a Perkin-Elmer model 2400 C, H, N analyzer. The inherent viscosities of all the poly(amic acid)s were measured at 0.5 g/dL concentration with a Cannon-Fenske viscometer at 30°C. Thermogravimetric analysis (TGA) was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Experiments were carried out on  $10 \pm 2$  mg samples heated in flowing nitrogen or air (50 cm<sup>3</sup>/min) at a heating rate of 20°C/min. The differential scanning calorimetry (DSC) traces were performed on a Sinku-Riko DSC-7000 differential scanning calorimeter coupled to a TA 7000 thermal analyzer in flowing nitrogen (30 cm<sup>3</sup>/min) at a heating rate of 15°C/ min. The wide-angle X-ray diffraction (WAXRD) patterns were obtained on a Rigaku Geiger D-Max IIIa X-ray diffractometer, using Ni-filtered  $\text{Cu-K}_{\alpha}$  radiation (40 kV, 15 mA) with film specimens of about 0.1 mm in thickness. The scanning rate was 2°/min. An Instron universal test Model 1130 with a load cell of 5 kg was used to study the stress-strain behavior of the samples.

# **RESULTS AND DISCUSSIONS**

#### **Polymer Synthesis**

According to the reported method,<sup>25</sup> bis(ether anhydride) (**IV**) was synthesized in a three-stage route starting from the nitro displacement reaction of nitrophthalonitrile with bisphenol (**I**) (Scheme 1). 4,4'(Octahydro-4,7-methano-5H-inden-5-ylidene) cardo group-containing aromatic PEIS **VIIa-k** were prepared from **IV** and eleven aromatic diamines, as shown in Scheme 2.

The inherent viscosities of all poly(amic acid)s, together with their corresponding PEIs, are summarized in Table I. By the conventional two-step procedure, the inherent viscosities of these polymers in the amic acid stage were in the range of 0.48–0.81 dL/g, and their corresponding PEIs had inherent viscosities of 0.51–0.64 dL/g. This series of polymers could also be synthesized from



**IV** and diamines in a small amount of m-cresol (50 wt % of polymer concentration) in one-step polymerization caused by their high solubility. Polymerized from the chemical dehydrated dian-





hydride (**IVc**) with diamines, polymers exhibited inherent viscosities of 0.65–0.87 dL/g. PEIs synthesized from the heating dehydrated dianhydride (**IVh**) had inherent viscosities of 0.51–0.66 dL/g. Because the purity of **IVh** was lower than that of **IVc**, polymers synthesized from **IVh** showed lower viscosities than those synthesized from **IVc**. For the low-melting-point diamines (**Vj** and **Vk**), polymers (**VIIj** and **VIIk**) could be obtained by bulk polymerization and had inherent viscosities of 0.36 and 0.41 dL/g. The viscosities of these polymers could not be promoted were because the complete premix of monomers was difficult under bulk polymerization. This problem could be solved by adding a suitable amount of m-cresol to the reaction mixture, and the viscosities of these polymers would be higher than 0.7 dL/g. During the polymerization, this series of PEIs formed a clear solution in a small amount of the solvent (such as m-cresol) and was suitable for direct processing. For the poor solubility of normal polyimides, structure identification by the nuclear magnetic resonance (NMR) spectrum is difficult. In this study, polymers had good solubility in a low polarity solvent and could be easily identified by the NMR spectrum. The <sup>1</sup>H-NMR spectrum data of **VIIa** was shown in the experimental section. The 14 protons of the alignatic

	Polyamic Acid <sup>a</sup>		1		Elemental Analysis $(\%)^{g}$		
Diamines	Code	$\eta_{\rm inh}~(\rm dL/g)^c$	Polyimide <sup>b</sup> Code	$\eta_{\rm inh}\;(dL/g)^{\rm d}$	С	Н	Ν
Va	VIa	0.81	VIIa	0.52 (0.87)	77.59	4.38	4.01
				$(0.66)^{\rm e}$	(77.41)	(4.43)	(4.10)
Vb	VIb	0.65	VIIb	0.48 (0.65)	77.32	4.46	4.25
				$(0.51)^{\rm e}$	(77.41)	(4.43)	(4.10)
Vc	VIc	0.56	VIIc	0.57 (0.79)	79.45	4.83	3.51
				$(0.57)^{\rm e}$	(79.20)	(4.70)	(3.62)
Vd	VId	0.61	VIId	0.60	77.35	4.52	3.56
					(77.51)	(4.42)	(3.69)
Ve	VIe	0.48	VIIe	0.51	77.55	4.44	3.48
					(77.51)	(4.42)	(3.69)
Vf	VIf	0.53	VIIf	0.52	77.48	4.66	3.35
					(77.59)	(4.42)	(3.23)
Vg	VIg	0.55	VIIg	0.55	77.78	4.55	3.28
5	C		0		(77.59)	(4.42)	(3.23)
Vh	VIh	0.62	VIIh	0.64	79.06	4.98	2.78
					(79.25)	(4.91)	(2.86)
Vi	VIi	0.72	VIIi	0.62	73.66	4.38	2.67
					(73.94)	(4.20)	(2.78)
Vj <sup>f</sup>	VIj	_	VIIj	0.36 (0.81)	73.56	4.26	2.71
Ū.	Ū		Ū.		(73.94)	(4.20)	(2.78)
$\mathbf{V}\mathbf{k}^{\mathrm{f}}$	VIk	_	VIIk	0.41 (0.76)	78.65	6.13	2.72
					(78.74)	(6.22)	(2.70)

Table I Synthesis of Polymers VI and VII from Dianhydrides IV and Various Aromatic Diamines

<sup>a</sup> Polymerization was carried out with equimolar quantities of IV and aromatic diamines to obtain 10 wt % poly(amic acid) solution.

<sup>b</sup> Obtained by thermal cyclization from the corresponding poly(amic acid)s.

<sup>c</sup> Inherent viscosity measured in DMAc at a concentration of 0.5 g/dL at 30°C.

<sup>d</sup> Data in parentheses are obtained by the m-cresol method, and  $\mathbf{IVc}$  was used as reactant.

<sup>e</sup> Obtained by the *m*-cresol method, and **IVh** was used as reactant.

<sup>f</sup> Obtained by the bulk polymerization method.

<sup>g</sup> Data in parentheses are calculated values.

ring present in the upfield and 18 protons of aromatic rings present in the downfield were in agreement with the predict structure of VIIa. The <sup>13</sup>C-NMR spectra revealed nine peaks in the upfield as a result of the overlap of  $C_{16}$  and  $C_{19}$ . The 2-D <sup>1</sup>H-<sup>13</sup>C COSY spectrum of **VIIa** is shown in Figure 1, with the aid of clear carbon and proton spectrum assignment. From the correlation of <sup>1</sup>H-NMR and <sup>13</sup>C-NMR spectra, the proton and carbon position of the polymer could be easily pointed out. The protons  $H_{8,8'}$  present at 6.96 ppm and their corresponding carbons  $C_{8.8'}$  appear at 119.63 and 119.88 ppm. The carbons appear at 125.64 ppm and correlate with the most downfield protons are  $C_{6.6'}$ . The protons  $H_{22,22'}$  appeared at 7.50 as a single peak, and their corresponding carbons  $C_{22,22'}$ were present at 126.65 ppm. The other protons and carbons are assigned, as shown in Figure 1

and in the experimental section. The element analysis values of these poly(ether imide)s, which are also shown in Table I, are generally in good agreement with their theoretical values.

## **Properties of Polymers**

The solubility (Table II) of the PEIs was tested qualitatively in various solvents at a concentration of 1 wt %. Polymers were easily dissolved in all of the test solvents, except DMSO, at room temperature. Polymers showed good solubility in the volatile low polar solvent, such as  $CH_2Cl_2$  and THF, caused by the containing of the nonpolar aliphatic ring. **VIIa** derived from the rigid *p*-phenylene diamine was easily dissolved in the test solvent, clearly proving that this series of PEIs had a high solubility. The crystallinity of PEI films, by casting from their DMAc solutions, was



Figure 1 <sup>1</sup>H-<sup>13</sup>C COSY spectrum of VIIa.

evaluated by XRD measurement with scattering angles  $2\theta$  from 5–40°. All the polymers showed an amorphous characteristic and exhibited no observable reflection peak in the testing range. The X-ray results were consistent with the solubility behavior of the resulting polymers. The good solubility is governed by the structure modification through the incorporation of bulky polycyclic group into the polyimides structures. All the polymers could be solution cast into transparent, flexible, and tough PEI films. Their tensile properties are also shown in Table III. The polymer films **VIIa-k** have a tensile strength of 80.9–128.3 MPa, elongation at break of 7.6–30.5%, and initial modulus of 1.83–2.96 GPa. The film **VIIc** behaves as the most tough material and possesses the highest tensile strength and initial modulus. Polymers **VIIh**, **VIIi**, and **VIIk** 

Polymer	$\operatorname{Solvent}^{\operatorname{a}}$							
	DMAc <sup>b</sup>	NMP	DMF	DMSO	Ру	m-Cresol	THF	$\mathrm{CH}_2\mathrm{Cl}_2$
VIIa	+	+	<u>+</u>	_	<u>+</u>	+	+	+
VIIb	+	+	+	_	+	+	+	+
VIIc	+	+	+	_	+	+	+	+
VIId	+	+	<u>+</u>	_	+	+	+	+
VIIe	+	+	<u>+</u>	_	+	+	+	+
VIIf	+	+	<u>+</u>	_	+	+	+	+
VIIg	+	+	+	<u>±</u>	+	+	+	+
VIIh	+	+	+	<u>+</u>	+	+	+	+
VIIi	+	+	+	<u>+</u>	+	+	+	+
VIIj	+	+	+	+	+	+	+	+
VIIk	+	+	+	+	+	+	+	+

Table IISolubility of Polyimides

<sup>a</sup> Solubility: (+) soluble at room temperature;  $(\pm)$  partial soluble; (-) insoluble.

<sup>b</sup> DMAc: N,N-dimethylacetamide, NMP: N-methyl-2-pyrrolidone, DMF: N,N-dimethylformamide, Py: pyridine.

exhibited higher elongations than other polymers were because of the lower packing density in the molecular chains. Synthesized by bulk polymerization, **VIIi** and **VIIk** also showed good mechanical properties.

The thermal behavior of the polymers was evaluated by DSC and TGA. Table IV summarizes the thermal properties of all the PEIs. The decomposition temperatures of **VIIa-k** at 10% weight loss ( $T_{10}$ ) were observed in the range of 481–512°C in air and 473–503°C in nitrogen, de-

Polymer <sup>a</sup>	Strength at Break (MPa)	Elongation at Break (%)	Initial Modulus (GPa)
VIIa	109.1	11.1	2.09
VIIb	92.1	8.8	1.83
VIIc	128.3	10.9	2.96
VIId	118.2	9.7	2.24
VIIe	107.1	8.0	2.40
VIIf	119.9	7.6	2.57
VIIg	80.9	7.6	2.59
VIIh	89.9	30.5	2.25
VIIi	107.5	10.6	2.34
VIIj <sup>b</sup>	84.3	25.4	2.14
VIIj <sup>c</sup>	93.5	23.4	2.31
VIIk <sup>b</sup>	87.7	27.8	2.09
$\mathbf{VIIk}^{\mathrm{c}}$	92.4	25.8	2.23

Table III Tensile Properties of Polyimides

<sup>a</sup> Films were casted from polymer solution of DMAc.

 $^{\rm b}$  Polymers were obtained by the bulk polymerization method.

<sup>c</sup> Polymers were obtained by the *m*-cresol method.

pending on the diamines used. The char yields of PEIs at 800°C in nitrogen ranged between 48– 54%. Figure 2 shows the TG curves of VIIa with a heating rate of 20°C/min under nitrogen and air atmosphere. It is observed that a high thermal stability occurs below 430°C under nitrogen and air atmosphere. Polymer VIIa shows a higher thermal stability than any other polymers caused by its highest symmetric linear structure. The lower thermal stability of VIIh and VIIk is brought about by the easy degradation of the isopropyl group. The  $T_{10}$  of **VIId**, which contains the para ether linkage in the main chain, is 14°C higher than meta linkage isomer **VIIe.** The  $T_{10}$ 's of the polymers were higher under the air than under nitrogen because of the oxygen absorption of the aliphatic ring during the initial oxidative degradation.

DSC measurements were conducted with a heating rate of 15°C/min. Glass transition temperature  $(T_g's)$  of the PEIs could be easily observed at midpoint of the transition on the DSC curve measured in the second heating traces of DSC. The  $T_g$ 's of PEIs (**VIIa-k**) were recorded in the range of 203–283°C. The highest  $T_g$  of **VIIa**, which contained *p*-phenylene in the polymer chain, was due to its high symmetric structure. The decreasing of  $T_g$ 's followed the introduction of flexible linkages. The  $T_g$  of **VIIa** was about 50°C higher than that of VIIf-h. Polymers VIIj and VIIk, which contained higher meta linkage density than the other polymers, showed lower  $T_g$ 's than the other polymers. Their  $T_g$ 's were close to 200°C.

			TGA			
	DSC	Decomp Temperat				
Polymer	$T_g^{\ a}_{(^\circ\mathrm{C})}$	In Air	In $N_2$	Wt $\%$ Residue at 800°C in N <sub>2</sub>		
VIIa	283	505	503	53.0		
VIIb	253	504	490	52.8		
VIIc	238	508	494	54.1		
VIId	242	512	496	51.3		
VIIe	228	496	482	48.4		
VIIf	223	499	491	53.6		
VIIg	221	488	485	52.1		
VIIh	220	486	476	48.8		
VIIi	218	502	494	52.1		
VIIj	207	486	482	51.3		
VIIk	203	481	473	49.8		

Table IV Thermal Properties of Polyimides

<sup>a</sup> From the second heating, DSC traces conducted at a heating of 20°C/min in nitrogen, and  $T_g$ was defined as the midpoint of the transition. <sup>b</sup> Temperature at which a 10% weight loss was recorded by TGA at a heating rate of 20°C/min.

# **CONCLUSIONS**

A series of soluble aromatic PEIs VIIa-k containing the polycyclic cardo group were synthesized

by polymerization of **IV** with various aromatic diamines. This series of PEIs could be synthesized by various methods, such as two-stage polymerization, m-cresol one-step polymerization,



Figure 2 TGA curves of polyimide VIIa at a heating rate of 20°C/min under a nitrogen (---) and an air (---) atmosphere.

and bulk polymerization. The structures of poly-(ether imide)s are also confirmed by the 2-D  $^{1}$ H– $^{13}$ C COSY spectrum. Polymers showed good organosolubility and tensile properties. The incorporation of the alicyclic pandent group did not induce much decrease in the thermal stability of polymers. Depending on these properties, this series of poly(ether imide)s are an easily produced mechanical plastics with good physical properties.

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