

NOTES

Synthesis and Characterization of New Cardo Polyimides Containing Pendent Norbornane Group

Der-Jang LIAW[†] and Been-Yang LIAW

*Department of Chemical Engineering,
National Taiwan University of Science and Technology,
Taipei, Taiwan 106, Republic of China*

(Received May 26, 1999)

KEY WORDS 2,2-Bis[4-(4-aminophenoxy)phenyl]norbornane / Polyimide / Cardo Group / Solubility / Thermal Property / Tensile Property / Crystallinity /

Outstanding properties of aromatic polyimides such as excellent thermo-oxidative stability and superior chemical resistance has led to the use of polyimides as insulating materials for electronics, semipermeable membranes for gas separation and high-temperature adhesives and coatings.¹ In general, aromatic polyimides are insoluble and intractable or only processable under extreme conditions. A great deal of research on the polyimides has been made on increasing processability with minimal effect on thermal stability as well as improvement of their specific properties, such as the introduction of bulky substituent^{2–6} or pendent groups^{7–10} along the polymer backbone to improving processability of the polyimides while maintaining thermal stability.

The introduction of cardo (Latin meaning loop) groups into the backbone of polymers is another approach for improving solubility and thereby processability. Cardo polymers exhibit valuable properties: increased thermal stability with increased solubility in organic solvents because the specific contribution of the cardo group.^{11–14} Previously we found several means for the introduction of cardo groups such as alicyclic cyclododecylidene,¹⁵ polyalicyclic adamantane¹⁶ and tricyclo[5.2.1.0^{2,6}]decane¹⁷ groups in the polymer backbone. The solubility of polyimide was enhanced while high glass transition temperature and thermal stability were maintained.^{15–17}

A new family of cardo polyimides derived from a norbornane-containing diamine, 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane (BAPN), was synthesized. The synthesis and characterization of the new polyimides are discussed.

EXPERIMENTAL

Synthesis of Monomer

2,2-Bis[4-(4-nitrophenoxy)phenyl]norbornane (BNPN). A mixture of 2,2-bis(4-hydroxyphenyl)norbornane (BHPN) (3.0 g, 10.7 mmol), *p*-chloronitrobenzene (3.4 g, 21.4 mmol), potassium carbonate (3.37 g) and *N,N*-dimethylformamide (DMF, 16 mL) was refluxed for 8 h. The mixture was cooled and poured into methanol–water

(1:1 by volume). The crude product, 2,2-bis[4-(4-nitrophenoxy)phenyl]norbornane (BNPN), was recrystallized from DMF to provide yellow needles (mp 153–155°C) in 83% yield. IR (KBr): 1577 and 1336 cm⁻¹ (NO₂), and 1240 cm⁻¹ (C–O–C); ¹H NMR (dimethyl sulfoxide (DMSO)-*d*₆, ppm): δ = 8.23–8.19 (m, 4H, 7.48–7.42 (dd, 4H); 7.08–7.02 (m, 8H); 3.34–1.13 (m, 10H). *Anal.* Calcd for C₃₁H₂₆O₆N₂: C, 71.25%; H, 5.01%; N, 5.36%; found: C, 70.95%; H, 4.97%; N, 5.10%.

2,2-Bis[4-(4-aminophenoxy)phenyl]norbornane (BAPN). Hydrazine monohydrate (10 mL) was added dropwise to a mixture of BNPN (4.0 g, 7.6 mmol), ethanol (20 mL), and a catalytic amount of 10% palladium on activated carbon (Pd/C, 0.05 g) at the boiling temperature. The reaction mixture was refluxed for 24 h and filtered to remove Pd/C. After cooling, the precipitated crystals, 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane (BAPN), were isolated by filtration and recrystallized from ethanol. The yield was 79%; mp 149–150°C.

Anal. Calcd for C₃₁H₃₀O₂N₂: C, 80.49%; H, 6.54%; N, 6.06%; found: C, 80.32%; H, 6.40%; N, 6.32%.

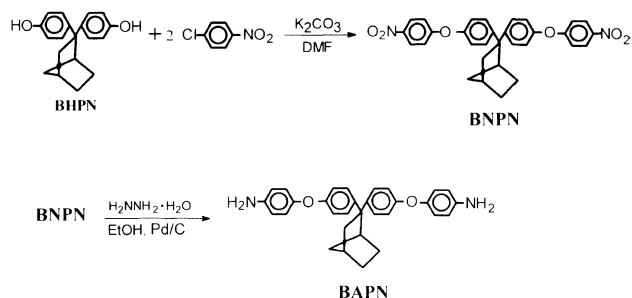
Preparation of Polymers

Aromatic dianhydride (1.3 mmol) was added in one portion to a solution of diamine BAPN (0.601 g, 1.3 mmol) in 7 mL *N,N*-dimethylacetamide (DMAc) at room temperature under argon atmosphere. The solution was stirred for another 3 h to obtain viscous polyamic acid solution. The viscous polyamic acid solution was cast on a glass plate and preheated at 80°C for 12 h to remove DMAc. The polyamic acid film was heated from 100 to 300°C for 3 h, and the temperature was held at 300°C for 1 h under vacuum. The polyamic acid film was converted to brown, tough and flexible polyimide film. Chemical cyclodehydration was carried out by adding extra DMAc, 0.5 mL of acetic anhydride and 0.4 mL pyridine to the above polyamic acid solution with stirring at room temperature for 1 h and heating at 100°C for 3 h, and subsequently poured into methanol to afford polyimide powder.

[†] To whom correspondence should be addressed (Phone: 886-2-27376638 or 886-2-27335050, Fax: 886-2-23781441 or 886-2-27376644, e-mail: liaw@ch.ntust.edu.tw).

RESULTS AND DISCUSSION

Scheme 1 illustrates the synthetic procedure of the new diamine monomer BAPN. The bisphenol compound



Scheme 1. Synthesis of 2,2-bis[4-(4-aminophenoxy)phenyl]norbornane (BAPN).

BHPN was synthesized from reaction of norcamphor with excess phenol using hydrogen chloride as catalyst as well as 3-mercaptopropionic acid as cocatalyst. The dinitro compound BNPN was obtained through aromatic nucleophilic substitution of BHPN with *p*-chloronitrobenzene in the presence of potassium carbonate. The catalytic hydrogenation of compound BNPN to diamine BAPN was accomplished using hydrazine monohydrate as well as a catalytic amount of Pd/C. The chemical structures of compounds BNPN and BAPN were established by elemental analysis, IR spectroscopy and NMR analysis. Figures 1(A) and 1(B) show the ^{13}C and ^1H NMR spectra of the new diamine BAPN, respectively.

Cardo polyimides were prepared from diamine BAPN and commercially available aromatic dianhydrides (DAa—DAe) through ring-opening polyaddition and

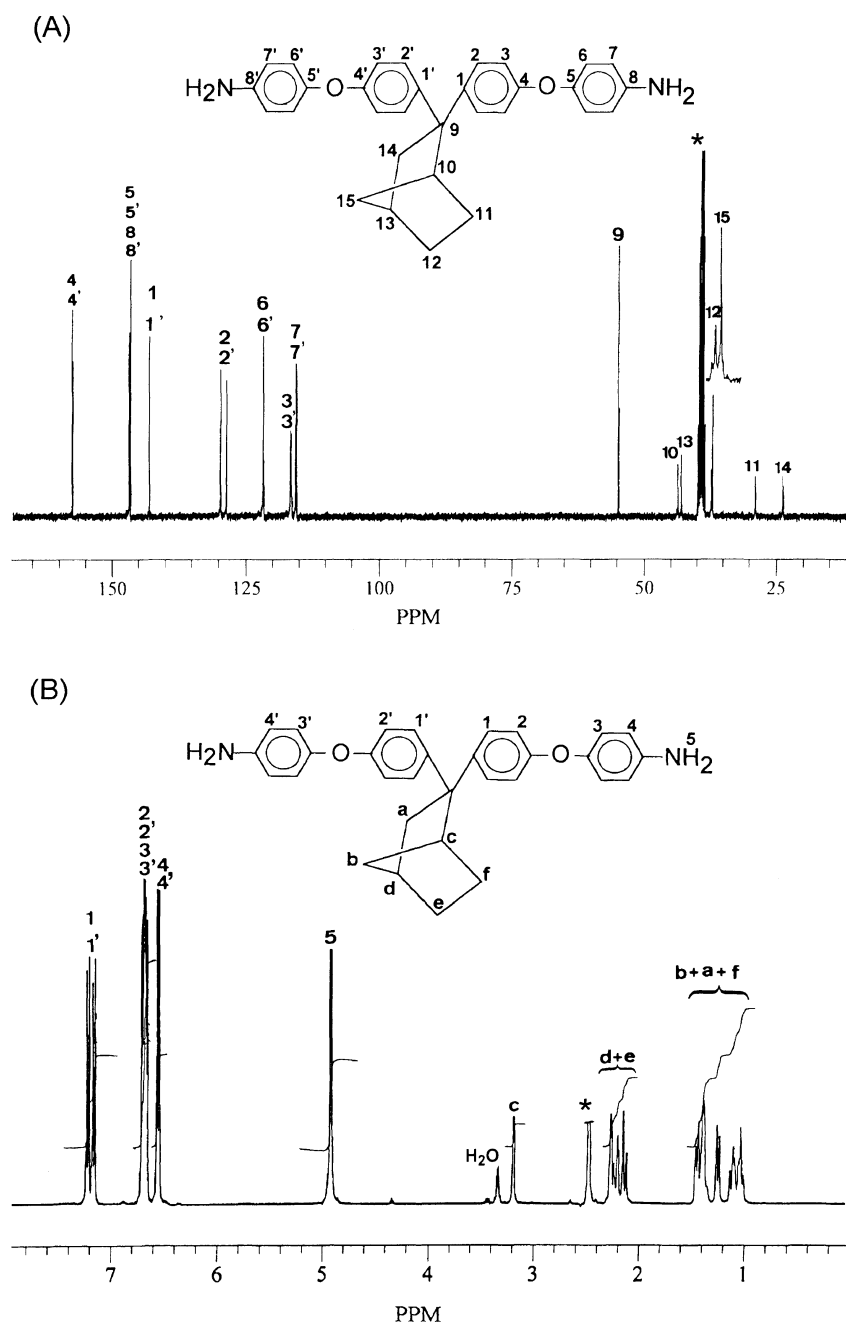
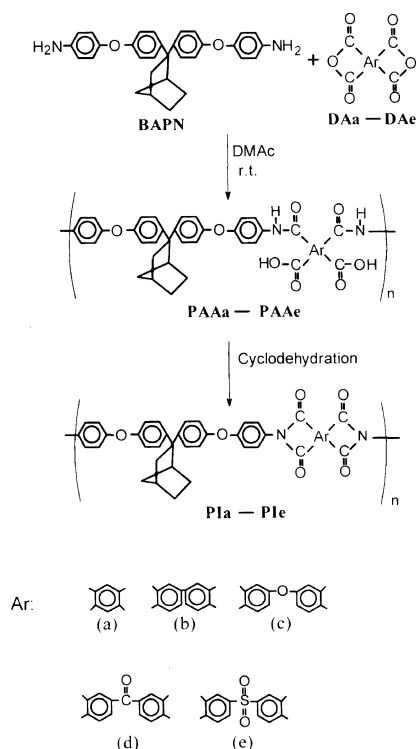


Figure 1. NMR spectra of BAPN in $\text{DMSO}-d_6$: (A) ^{13}C NMR and (B) ^1H NMR (*: solvent peak).

subsequent cyclodehydration as shown in Scheme 2. The ring-opening polyaddition in DMAc at room temperature afforded viscous polyamic acid solutions. The



Scheme 2. Preparation of cardo polyimides.

inherent viscosity of polyamic acid was 1.02–1.82 dL g⁻¹ (Table I). The polyamic acids were cast on a glass plate and preheated to give the polyamic acid films. Thermal conversion to polyimides was carried out by successive heating of the films to 300°C under vacuum. Brownish, transparent and fingernail creasable films were obtained. Chemical cyclodehydration of polyamic acids with a dehydrating agent such as a mixture of acetic anhydride and pyridine was effective in obtaining polyimides. The resulting polyimides which dissolved in *N*-methyl-2-pyrrolidone (NMP) had inherent viscosity of 0.70–0.85 dL g⁻¹. The solution cyclodehydration method using xylene as an azeotropic reagent was also carried out in the case of polymerization of PIa. PIa precipitation occurred during solution cyclodehydration while gelation, during chemical imidization.

The crystallinity of these new cardo polyimides was estimated by wide-angle X-ray diffractograms. All cardo polyimides exhibited amorphous patterns. The amorphous behavior of the cardo polyimides is due to bulky planar substituents, which disrupt the symmetry of macromolecules and prevent ordering. A cardo group also decreased the intermolecular force between the polymer chains, causing decrease in crystallinity.

The solubility behavior of the polyimides obtained by chemical cyclodehydration is listed in Table I. Polymers PIc and PIE derived from ether- and sulfonyl-contained dianhydride, respectively, showed good solubility in NMP, DMAc, *N,N*-dimethylformamide, pyridine, cyclohexanone, and tetrahydrofuran at room temperature or

Table I. Synthesis and solubility of polyimides

Polyamic acid		Polyimide ^b									
Code	η_{inh}^a dL g ⁻¹	Code	η_{inh}^c dL g ⁻¹	Remark ^e	Solubility ^f						
					NMP	DMAc	DMF	DMSO	Py	Cyclohexanone	THF
PAAa	1.82	PIa	— ^d	G	—	—	—	—	—	—	—
PAAb	1.02	PIb	0.70	P	++	—	—	—	++	—	—
PAAc	1.51	PIc	0.85	S	++	++	++	+	++	+	++
PAAc	1.42	PIc	0.85	S	++	++	++	+	++	+	++
PAAc	1.42	PIc	0.85	S	++	++	++	+	++	+	++
PAAc	1.42	PIc	0.85	S	++	++	++	+	++	+	++
PAAe	1.54	PIe	0.80	S	++	++	++	++	++	++	++

^a Measured in DMAc at 0.5 g dL⁻¹ at 30°C. ^b Obtained by chemical imidization from the corresponding polyamic acids. ^c Measured in NMP at 0.5 g dL⁻¹ at 30°C. ^d Could not dissolved in NMP. ^e Features of the polymerization mixture: G, gelation; P, polymer precipitation; S, homogeneous solution. ^f Solubility: ++, soluble at room temperature; +, soluble on heating; +-, partial soluble on heating; —, insoluble; Abbreviations: NMP, *N*-methyl-2-pyrrolidone; DMAc, *N,N*-dimethylacetamide; DMF, *N,N*-dimethylformamide; DMSO, dimethylsulfoxide; Py, pyridine; THF, tetrahydrofuran.

Table II. Thermal and tensile properties of polyimides

Polymer code	DSC		TGA		Tensile strength	Elongation at break	Tensile modulus
	T_g^a °C	°C	$T_{d10}^{c/\circ C}$				
			In N ₂	In air	MPa	%	GPa
PIa	— ^b	—	513	532	145	9	2.7
PIb	283	—	526	547	128	19	2.3
PIc	261	—	522	549	141	8	2.6
PIc	269	—	526	551	156	7	2.8
PIe	288	—	500	511	144	6	2.3

^a Glass transition temperature (T_g) measured on DSC at heating rate of 20°C min⁻¹. ^b Not detectable by DSC. ^c Temperature at which 10% weight loss was recorded on TGA at heating rate of 20°C min⁻¹.

upon heating at 70°C. Other polyimides derived from rigid and symmetric dianhydrides exhibited limited solubility. The polymer derived from dianhydride DAb dissolved in NMP and pyridine. The good solubility of these polyimides was due to the presence of the bulky pendent group, which did not allow for dense chain packing and decreased crystallinity.

The thermal behavior of the norbornane-containing cardo polyimides is summarized in Table II. These polyimides, except PIa, displayed distinct glass transition with the second heating of DSC traces, whereas endotherms or exotherms were completely lacking. These polyimides had glass transition temperatures (T_g s) of 261–288°C, depending on dianhydride component structure. Thermogravimetric analysis (TGA) traces revealed that all the polyimides not to decompose around or below 500°C in nitrogen and air. Decomposition temperatures of 10% weight loss (T_{d10}) were 500–526 and 511–551°C in nitrogen and air, respectively.

The tensile properties of the tough polyimide films obtained by thermal cyclodehydration are summarized in Table II. Tensile strength was 128–156 MPa, elongation at break, 6–19% and tensile modulus, 2.3–2.8 GPa. This demonstrates that these polyimide films are strong materials.

Acknowledgment. The authors thank the National Science Council of the Republic of China for support of this work under grant NSC 89-2216-E011-008.

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