

## Synthesis and Characterization of New Soluble Cardo Polyamides Derived from 2,2-Bis[4-(4-carboxyphenoxy)phenyl]norbornane

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Aromatic polyamides have been reported for high temperature resistance and excellent mechanical properties.<sup>1,2</sup> However, wholly aromatic polyamides, particularly those with *para* substituted rings, are quite intrac-table materials that do not melt and only dissolve in strong mineral acids such as concentrated sulfuric acid or in very polar aprotic solvents containing salts. Therefore, many efforts have been made to chemically modify the structures of these polymers to improve solubility and/or lowering transition temperatures to a range that facilitates processing in a melt. Several studies have been made to improve the solubility of polyamides such as addition of pendent groups to the polymeric backbone<sup>3–5</sup> and incorporation of bulky substituents<sup>6–10</sup> within the parent chain.

Another successful approach to improve the processability of aromatic polyamide without extreme loss of outstanding properties is to introduce cardo, *i.e.*, pendent loops, along the polymer backbone.<sup>11</sup> The introduction of cardo groups creates amorphous polymers with characteristic features such as improved solubility and enhanced thermal stability as well as better mechanical and thermal properties.<sup>11,12</sup> Our previous studies reported that incorporating cardo groups such as cyclododecylidene<sup>13</sup>, adamantane<sup>14,15</sup>, tricyclo[5.2.1.0<sup>2,6</sup>]decane<sup>16</sup> into the backbone of polyamides resulted in polymers with enhanced solubility, processability and good thermal stability.<sup>13–16</sup> The solubility and glass transition temperature of the polymers increased with stiffness and bulkiness of the cardo groups.<sup>13–16</sup>

The present study reports the synthesis of novel polyamides with pendent norbornyl groups along the polymer chain. The new dicarboxylic acid, 2,2-bis[4-(4-carboxyphenoxy)phenyl]norbornane (BCAPN), containing norbornyl group was synthesized and polymerized with various diamines to prepare novel polyamides. The incorporation of stiff and bulky norbornyl group into polyamide backbones showed increase the solubility, thermal and mechanical properties of the polymers. The characterization of new polymers such as crystallinity, thermal, physical, and mechanical properties was made.

## EXPERIMENTAL

### Materials

Norcamphor (from Aldrich), *p*-chlorobenzonitrile (from ACROS), anhydrous potassium carbonate (from Merck), hydrazine monohydrate (from Merck), and 10% palladium on activated carbon (Pd/C, from Merck) were used as received. 1,3-Phenylenediamine (**DA1**, from Merck) was purified by vacuum sublimation. 3,3',5,5'-Tetramethyl-2,2-bis[4-(4-aminophenoxy)phenyl]propane<sup>17</sup> (**DA2**), 2,2-bis[4-(4-aminophenoxy)phenyl]adamantane<sup>14</sup> (**DA3**), 5,5-bis[4-(4-aminophenoxy)phenyl]-4,7-methanohexahydroindane<sup>16</sup> (**DA4**) were synthesized and purified according to the method previously reported.<sup>14,16,17</sup>

### Monomer Synthesis

*2,2-Bis(4-hydroxyphenyl)norbornane (BHPN)*. Norcamphor 11.0 g (0.1 mol), 75 g (0.8 mol) of phenol and 1 mL of 3-mercaptopropionic acid were introduced into a three-neck flask equipped with a condenser, magnetic stirrer, gas inlet, and thermometer. The reaction was heated to 80°C and purged with hydrogen chloride gas. After 30 min, a dark red foamy material was obtained. The addition of hydrogen chloride gas was stopped and the reaction mixture was cooled. The mixture was allowed to stand at room temperature for 12 h during which time the mixture solidified. The solid mass was dispersed in 1 L water and the mixture was steam distilled to remove excess phenol and 3-mercaptopropionic acid leaving an aqueous suspension. The solid residue was collected from the mixture by filtration, and was recrystallized from toluene twice. The yield of BHPN was 70%; mp 196–197°C (literature<sup>11</sup>: 199–200°C).

*2,2-Bis[4-(4-cyanophenoxy)phenyl]norbornane (BCYPN)*. A mixture of BHPN (10.3 g, 35 mmol), *p*-chlorobenzonitrile (9.7 g, 72 mmol), potassium carbonate (4.3 g, 77 mmol) and dry *N,N*-dimethylformamide (DMF, 20 mL) was refluxed for 8 h, cooled and poured into methanol-water (1:1 by volume). The crude product was recrystallized from ethanol twice. The yield was

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76%; mp 142–144°C; Infrared (IR) (KBr,  $\text{cm}^{-1}$ ): 2216 (CN), 1243 (COC);  $^1\text{H}$  Nuclear magnetic resonance (NMR) (400 MHz in Dimethyl sulfoxide ( $\text{DMSO}-d_6$ ), ppm):  $\delta=7.80\text{--}7.77$  (dd, 4H); 7.45–7.38 (dd, 4H); 7.03–6.97 (m, 8H); 3.3–1.1 (m, 10H);  $^{13}\text{C}$  NMR (99 MHz in  $\text{DMSO}-d_6$ , ppm):  $\delta=162.4, 153.0, 152.8, 149.9, 146.1, 135.7, 130.5, 129.5, 120.7, 120.5, 119.6, 118.8, 105.7, 105.7, 55.6, 44.0, 43.3, 37.6, 37.5, 29.1, 24.1$ . Anal. calcd for  $\text{C}_{33}\text{H}_{26}\text{O}_2\text{N}_2$ : C, 82.13%; H, 5.43%; N, 5.81%; found: C, 81.95%; H, 5.27%; N, 5.63%.

**2,2-Bis[4-(4-carboxyphenoxy)phenyl]norbornane (BCAPN)**. A mixture of 3.57 g (7.4 mmol) of dinitrile compound (BCYPN), 8.3 g of potassium hydroxide in 80 mL of ethanol and 80 mL of distilled water was stirred at 130°C. Hydrogen peroxide (30 mL) was added dropwise over a period of 0.5 h to the suspension solution. After 4 days, the solution became clear and then was cooled, pH was adjusted by hydrochloric acid to near 3. The white precipitate formed was collected by filtration, washed with methanol several times and reprecipitated from *N,N*-dimethylacetamide (DMAc) solution into methanol. The system was dried under vacuum at 80°C for 24 h. The yield was 87%; mp 273°C (by Differential Scanning Calorimeter (DSC)); IR (KBr,  $\text{cm}^{-1}$ ): 2500–3600 (C(O)O–H str.), 1674 (C=O str.), 1239 (C–O str.).  $^1\text{H}$  NMR (400 MHz in  $\text{DMSO}-d_6$ , ppm):  $\delta=12.79$  (s, 2H); 7.93–7.91 (dd, 4H); 7.42–7.35 (dd, 4H); 7.03–6.94 (m, 8H); 3.30–1.02 (m, 10H);  $^{13}\text{C}$  NMR (99 MHz in  $\text{DMSO}-d_6$ , ppm):  $\delta=168.2, 162.3, 162.2, 153.8, 153.5, 149.5, 145.6, 132.7, 130.4, 129.4, 126.2, 126.1, 120.3, 120.1, 118.1, 55.6, 44.1, 43.4, 37.6, 37.5, 29.2, 24.1, 18.3$ . Anal. calcd for  $\text{C}_{33}\text{H}_{28}\text{O}_6$ : C, 76.14%; H, 6.43%; found: C, 75.98%; H, 6.23%.

#### Preparation of Polymer

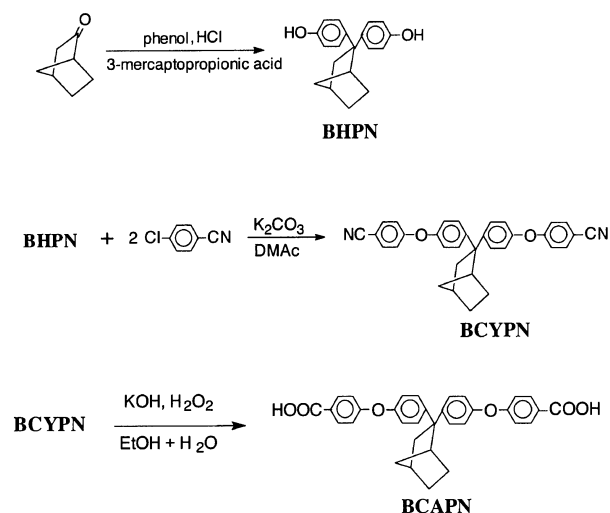
A mixture of 0.625 g (1.2 mmol) of dicarboxylic acid BCAPN, 0.129 g (1.2 mmol) of diamine **DA1**, 0.3 g of calcium chloride, 0.9 mL of triphenyl phosphite (TPP), 0.9 mL of pyridine, and 5.0 mL of *N*-methyl-2-pyrrolidinone (NMP) was heated with stirring at 100°C for 2 h. After cooling, the reaction mixture was poured into excess methanol with constant stirring to produce a white stringy precipitate that was washed thoroughly with methanol and hot water. It was then extracted with hot acetone using a Soxhlet extractor and dried at 100°C under vacuum for 24 h. The inherent viscosity of the polymer in DMAc was  $1.49\text{ dL g}^{-1}$ , as measured at  $0.5\text{ g dL}^{-1}$  at 30°C. IR (film,  $\text{cm}^{-1}$ ): 1650 (C=O), 3284 (N–H).

Other polyamides were prepared by similar procedure.

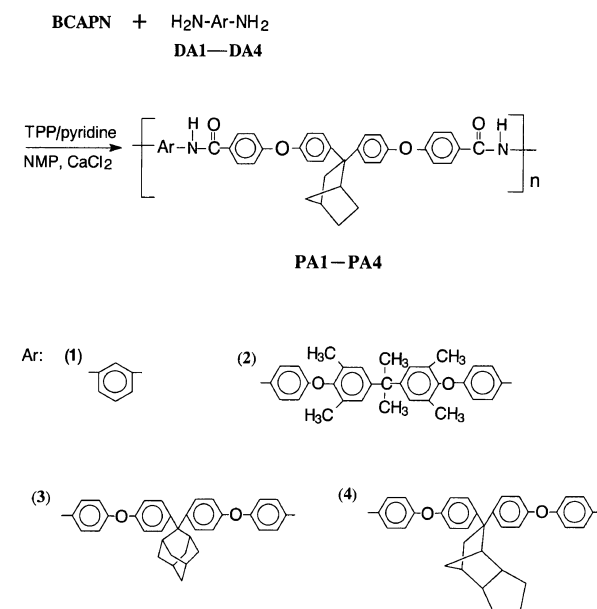
## RESULTS AND DISCUSSION

#### Synthesis of Dicarboxylic Acid

The synthetic route of the new norbornyl-containing dicarboxylic acid monomer, 2,2-bis[4-(4-carboxyphenoxy)phenyl]norbornane (BCAPN), is shown in Scheme 1. The bisphenol compound, 2,2-bis(4-hydroxyphenyl)norbornane (BHPN) was prepared by acid-catalyzed condensation from norcamphor with excess phenol in the presence of hydrogen chloride. BHPN was reacted with *p*-chlorobenzonitrile in the presence of potassium carbonate to afford the dinitrile compound, 2,2-bis[4-(4-cyanophenoxy)phenyl]norbornane (BCYPN), which was



**Scheme 1.** Route for synthesis of 2,2-bis[4-(4-carboxyphenoxy)phenyl]norbornane (BCAPN).



**Scheme 2.** Preparation of new cardo polyamides.

purified by recrystallization from ethanol twice. Hydrolysis of the dinitrile compound BCYPN to the dicarboxylic acid compound, 2,2-bis[4-(4-carboxyphenoxy)phenyl]norbornane (BCAPN), was accomplished by potassium hydroxide as well as hydrogen peroxide in a mixture of ethanol and water. It was purified by reprecipitation from DMAc into methanol. Nitriles can be hydrolyzed to give either amides or carboxylic acids. The amide is formed initially, but since amides are hydrolyzed with acid or base, carboxylic acid is the more common product. When carboxylic acid is desired, the reagent of choice is a basic aqueous solution containing 6 to 12% hydrogen peroxide, although acid-catalyzed hydrolysis is frequently carried out.<sup>18</sup> The structures of the synthetic compounds were identified by elemental analysis, IR, and NMR spectroscopy. The cyano group of compound BCYPN appeared from the peak at  $2216\text{ cm}^{-1}$  in the IR spectrum. In the IR spectrum of BCAPN, cyano

**Table I.** Preparation, average molecular weights, and elemental analysis data for various polyamides

Polymer Code	$\eta_{\text{inh}}^{\text{a}}$ dL g <sup>-1</sup>	Yield %	IR/cm <sup>-1</sup>		Elemental analysis/%				
			N-H	C=O	C	H	N	Moisture Intake in%	
<b>PA1</b>	1.49	99	3284	1650	Calcd	77.37	5.56	4.63	2.10
					Found	77.85	5.68	4.51	
<b>PA2</b>	0.93	98	3286	1648	Calcd	77.72	6.35	2.81	2.56
					Found	77.99	6.38	2.68	
<b>PA3</b>	1.14	97	3279	1651	Calcd	78.91	5.99	2.53	2.40
					Found	79.01	6.08	2.48	
<b>PA4</b>	0.98	98	3280	1655	Calcd	78.62	6.04	2.68	2.46
					Found	78.89	6.10	2.55	

<sup>a</sup> Measured in DMAc at 0.5 g dL<sup>-1</sup> at 30 °C.

stretching vibration disappeared, but broad C(O)O-H absorption appeared in the region of 2500–3600 cm<sup>-1</sup> and C=O stretching absorption appeared at 1674 cm<sup>-1</sup>. NMR spectra data are listed in the experimental section. In the <sup>13</sup>C NMR spectrum, the carbon of the carboxyl group had resonance at 168.2 ppm. A broad peak attributed to the carboxylic acid proton was observed around 12.8 ppm in the <sup>1</sup>H NMR spectrum, thus indicating the new dicarboxylic acid monomer prepared in this study to be consistent with the proposed structure.

#### Synthesis of Polyamides

New polyamides (**PA1**–**PA4**) were prepared by phosphorylation polycondensation of dicarboxylic acid BCAPN with aromatic diamines using triphenyl phosphite (TPP) and pyridine as condensing agents (Scheme 2). All polymerizations readily proceeded in homogeneous solution, indicating good polymer solubility in the polymerization media. Tough and stringy precipitates formed when viscous polymer solutions were trickled into the stirring methanol. All polymers were obtained in high yield (above 97%) and inherent viscosities of 0.93–1.49 dL g<sup>-1</sup> as measured in DMAc solution (Table I). Transparent, tough and flexible polymer films were obtained by casting from DMAc solution. IR spectra of the polyamides showed characteristic absorptions of amide groups at 1648–1650 and 3279–3286 cm<sup>-1</sup> (Table I).

Elemental analysis results of the polyamides are listed in Table I. Carbon of polyamides was less than that calculated for the proposed structures. Such difference may be attributed to amide group hygroscopic characteristics.<sup>3</sup> Absorbed water of the polyamides ranged from 2.40–2.56%. Corrected values correlated well with those calculated after found values had been corrected.

#### Polymer Characterization

Crystallinity of the cardo polyamides was estimated by wide-angle X-Ray diffractograms. Entire polymers exhibited amorphous patterns. The amorphous behavior of the cardo polyamides was attributed to bulky pendent groups which increased significantly disorder in polymer chains and therefore caused less chain packing. The norbornyl group decreased intermolecular force such as hydrogen bonding between polymer chains, causing decrease in crystallinity.<sup>19</sup>

Solubility of all polyamides is summarized in Table II.

Most of the polyamides exhibited good solubility in solvents such as NMP, DMAc, DMF, DMSO, pyridine,

and cyclohexanone at room temperature or on heating at 70 °C, due to the pendent norbornyl group in the polymer backbone. Norbornyl groups disturbed dense chain packing of the polymer chain; consequently, solvent molecules penetrated easily to solubilize the chains. Polymer **PA2** containing no ether group showed less solubility than the other polyamides. The solubility of two analogous poly **Ref 1** with adamantyl group and **Ref 2** with tricyclo[5.2.1.0<sup>2,6</sup>] group<sup>15–16</sup> is listed in Table II. Polymer **PA3** with a norbornyl group showed better solubility than **Ref 1** or **Ref 2**.

Thermal properties of the polyamides are summarized in Table III.

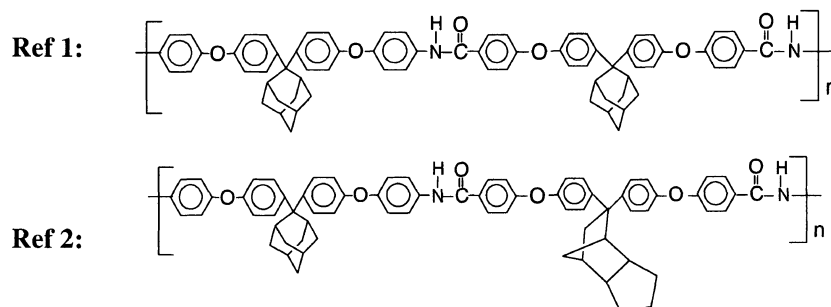
All polymers displayed distinct glass transition with the second heating of DSC traces, whereas endotherms or exotherms were completely lacking. These polyamides had glass transition temperatures ( $T_g$ s) of 231–266 °C. Polymer **PA3** containing a pendent adamantane group exhibited the highest  $T_g$ . In general, chain rigidity increased due to the pendent cardo group, which restricted free rotation of the polymer backbone. Hence, the obtained polymers showed high glass transition temperature. Polymer **PA2** bearing a *meta*-linkage showed lower  $T_g$  than the other polyamides. TGA traces reveal all cardo polyamides not to decompose around or below 450 °C in nitrogen or air. Decomposition temperatures of 10% weight loss ( $T_{d10}$ ) were from 468–523 °C and 503–553 °C in nitrogen and air, respectively.  $T_{d10}$  of the polymers in air was higher than in nitrogen. The higher  $T_{d10}$  in air may reflect oxidation of alicyclic norbornyl groups, to form carbonyl groups, and cause weight gain.<sup>19</sup> Adamantane-containing polymer **PA3** showed the highest  $T_{d10}$  since adamantane is generally recognized as a highly thermally stable unit.<sup>9</sup> Table II, it shows **PA3** to exhibit higher  $T_{d10}$  than **Ref 2**.

The mechanical properties of the polymer films are summarized in Table III. The polymer films had tensile strength of 99–130 MPa, elongation at break of 9–15% and tensile modulus of 2.1–3.2 GPa. Polyamide **PA2** film containing flexible isopropylidene unit exhibited a yield point on stress-strain curves while the others did not. Polymer **PA1** derived from 1,3-phenylenediamine showed the best mechanical properties. This may be due to **PA1** being derived from **DA1**, which has no ether group and shows more stiffness than the others. Table II, shows **PA3** to exhibit better mechanical properties than **Ref 1** or **Ref 2**.

**Table II.** Solubility of various polyamides<sup>a</sup>

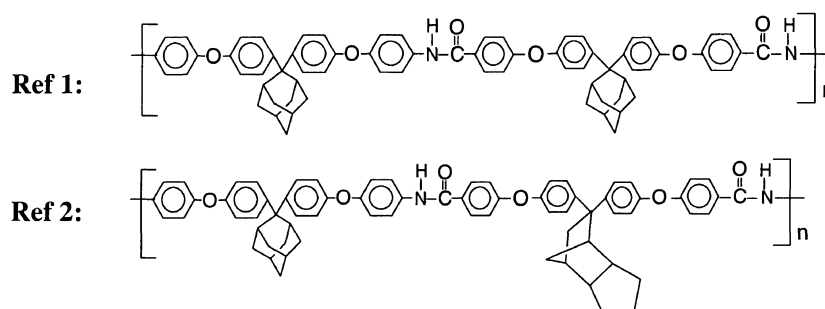
Polymer Code	Solubility <sup>b</sup>							
	NMP	DMAc	DMF	DMSO	Pyridine	Cyclohexanone	THF	Chloroform
<b>PA1</b>	++	++	+–	+–	++	+	–	–
<b>PA2</b>	++	++	++	+	++	++	++	+–
<b>PA3</b>	++	++	++	+	++	++	+	–
<b>PA4</b>	++	++	++	+	++	++	+	–
<b>Ref 1</b>	++	++	++	+	+	+	+–	–
<b>Ref 2</b>	++	++	++	+	++	+	+–	–

<sup>a</sup> Measured at 0.5 g dL<sup>-1</sup> at 30°C. <sup>b</sup> Solubility: ++: soluble at room temperature; +: soluble on heat at 70°C; +–: partial soluble at 70°C; –: insoluble at 70°C. Abbreviations: NMP: *N*-methyl-2-pyrrolidinone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylformamide; DMSO: dimethylsulfoxide; THF: tetrahydrofuran.

**Table III.** Thermal and mechanical properties of various polyamides

Polymer Code	DSC	TGA		Yield point	Tensile strength	Elongation at break	Tensile modulus
	$T_g$ <sup>a</sup> /°C	$T_{d_{10}}$ <sup>b</sup> /°C					
		In N <sub>2</sub>	In Air	MPa	MPa	%	GPa
<b>PA1</b>	231	468	507	— <sup>c</sup>	130	15	3.2
<b>PA2</b>	251	479	506	116	103	10	2.1
<b>PA3</b>	266	523	537	— <sup>c</sup>	91	10	2.4
<b>PA4</b>	261	498	503	— <sup>c</sup>	90	10	2.4
<b>Ref 1</b>	275	536	553	— <sup>c</sup>	89	9	2.2
<b>Ref 2</b>	269	515	523	— <sup>c</sup>	78	8	2.0

<sup>a</sup> Glass transition temperature ( $T_g$ ) (°C) measured by DSC at heating rate of 20°C min<sup>-1</sup>. <sup>b</sup> Temperature at which 10% weight loss was recorded on TGA at a heating rate of 20°C min<sup>-1</sup>. <sup>c</sup> No yield point observed from stress-strain curve.



## CONCLUSIONS

The authors synthesized a new norbornyl-containing dicarboxylic acid, BCAPN. Novel cardo polyamides were prepared by direct polymerization from BCAPN with various diamines. Due to the incorporation of pendent norbornyl and cardo groups, polyamides were amorphous with excellent solubility and thermal stability, high glass transition temperature as well as mechanical

properties. The polymer containing adamantane showed high thermal stability. The polymer from 1,3-phenylenediamine showed excellent mechanical properties. Accordingly, the present polyamides may be considered as new processable high-temperature materials.

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