Synthesis and Characterization of Novel Aromatic Polyamides with Polyalicyclic Cardo Groups

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ABSTRACT: 5,5-Bis[4-(4-carboxyphenoxy)phenyl]hexahydro-4,7-methanoindan (**3a**) and 5,5-bis[4-(4-aminophenoxy)phenyl]hexahydro-4,7-methanoindan (**3b**) were prepared in two main steps starting from the aromatic nucleophilic halogen-displacement of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with 5,5-bis(4-hydroxyphenyl)hexahydro-4,7-methanoindan in the presence of potassium carbonate in *N,N*-dimethylformamide (DMF). Using triphenyl phosphite and pyridine as condensing agents, two series of polyamides having polyalicyclic cardo units were directly polycondensated from dicarboxylic acid **3a** with various aromatic diamines, or from diamine **3b** with various aromatic dicarboxylic acids in the *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride. High molecular weight polyamides with inherent viscosities between 0.73 and 1.44 dL/g were obtained. All polymers were readily soluble in polar aprotic solvents such as NMP and *N,N*-dimethylacetamide (DMAc) and afforded transparent, flexible, and tough films by solution casting. The glass-transition temperatures (T_g) of these aromatic polyamides were in the range of 219–253°C by DSC, and the 10% weight loss temperatures in nitrogen and air were above 467 and 465°C, respectively. A comparative study of some polyamides with an isomeric repeat unit is also presented. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 4510–4520, 1999

Keywords: 5,5-bis[4-(4-carboxyphenoxy)phenyl]hexahydro-4,7-methanoindan; 5,5-bis[4-(4-aminophenoxy)phenyl]hexahydro-4,7-methanoindan; polyamide; polyalicyclic cardo unit

INTRODUCTION

Aromatic polyamides (aramids) belong to the class of high-performance polymers because of their high thermal and chemical resistance as well as high strength and high modulus in fiber form.[1,2] DuPont developed two aramid fibers, Kevlar® [poly(*p*-phenylene)terephthalamide] and Nomex® [poly(*m*-phenylene)isophthalamide], and began production in the late 1960s. Both aramids exhibit excellent mechanical strength and thermal stability and are suitable for composites. Versatile applications of these polyamides have generally been reduced by the high crystallinity and limited solubility in common solvents. Therefore, various efforts have focused on the synthesis of soluble and/or thermoplastic polyamides without much sacrifice of their excellent properties. Typical approaches were to introduce kinks of flexible linkages,[3–5] bulky groups,[6–16] or cardo groups[17–21] into a polymer backbone. These procedures can be employed to disrupt crystallinity to obtain almost completely amorphous polyamides. In general, amorphous polyamides have relatively low softening temperature and improved solubility compared to crystalline analogs, and they are also of

considerable interest as high-performance engineering plastics. According to these research trends, we previously reported the synthesis of polyamides with good solubility and moldability as well as reasonable thermal stability by introduction of an alicyclic ether-linked diamine or dicarboxylic acid containing the cardo cyclohexane structure.[22,23] From the results of these works, it was known that interchain interaction of the resulting polymers was decreased by the introduction of plasticizing cyclohexylidene units, which resulted in good solubility and lowered T_g's. Recently, we have also demonstrated that incorporating the polyalicyclic groups such as hexahydro-4,7-methanoindan-5,5-diyl in polyimides can hinder chain packing and segmental mobility, raising solubility and maintaining modest glass-transition temperatures.[24,25] The present work deals with the synthesis and basic characterization of some novel polyamides containing both ether and the bulky hexahydro-4,7-methanoindan-5,5-diyl unit in the main chain. It was hoped that incorporation of the polyalicyclic unit would decrease polymer intermolecular interaction and generally disrupt the coplanarity of phenylene units to reduce packing efficiency and the crystallinity, thus leading to an enhanced solubility. It was postulated that the introduction of alicyclic units would provide additional energy dissipation mechanisms involving some conformational transformations that would increase the toughness of these polymers. The alicyclic cardo group was also expected to act as an internal plasticizer and allow the polymer chain more freedom for flow during processing. In addition, the polyamides were expected to maintain good thermal stability because of the multibond of the polyalicyclic structure.

EXPERIMENTAL

Materials

5,5-Bis(4-hydroxyphenyl)hexahydro-4,7-methanoindan (1, from Acros), p-fluorobenzonitrile (from Wako), p-chloronitrobenzene (from Tokyo Chemical Industry; TCI), and hydrazine monohydrate (from Acros) were used as received. p-Phenylenediamine (4a) and benzidine (4c) were purified by vacuum sublimation. m-Phenylenediamine (4b) was purified by vacuum distillation. 4,4′-Oxydianiline (4d, from TCI), 3,4′-oxydianiline (4e, from Mitsui Petrochemical Ind., Tokyo, Japan), 4,4′-methylenedianiline (4f, from TCI), and 1,4-bis(4-aminophenoxy)benzene (4g, from TCI) were used without further purification. 4,4′-Bis(4-aminophenoxy)biphenyl (4h, mp 198–199°C) was prepared by the chloro displacement of p-chloronitrobenzene with 4,4′-biphenol in the presence of potassium carbonate followed by catalytic hydrazine reduction.[26] The aromatic dicarboxylic acids such as terephthalic acid (5a, from Wako), isophthalic acid (5b, from Wako), 4,4′-biphenyldicarboxylic acid (5c, from TCI), and 4,4′-oxydibenzoic acid (5d, from TCI) were used as received. Commercially obtained calcium chloride (CaCl$_2$) was dried under vacuum at 180°C for 10 h. Pyridine was purified by distillation after being refluxed with potassium hydroxide. N-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP, from Fluka) was purified by distillation under reduced pressure.

Monomer Synthesis

5,5-Bis[4-(4-cyanophenoxy)phenyl]Hexahydro-4,7-Methanoindan (2a)

Bisphenol 1 (32 g, 0.1 mol) was dissolved in a mixture of N,N-dimethylformamide (DMF) (200 mL) and toluene (50 mL) in a 250 mL round-bottom flask connected to a Dean–Stark trap and a condenser. Anhydrous potassium carbonate (27.6 g, 0.2 mol) was added to this solution. The suspension solution was heated to reflux, and water was removed by azeotropic distillation with toluene. After water was removed completely, the residual toluene was distilled out from the system. Then, the reaction mixture was cooled to about 60°C, and p-fluorobenzonitrile (24.3 g, 0.2 mol) was added. After refluxing at 150°C for 6 h, the solution was allowed to cool and poured into 500 mL of water. The precipitated white powder was collected by filtration, thoroughly washed with water, and dried. The crude product was recrystallized from acetonitrile to give a white fine granular crystal; yield after recrystallization, 44.8 g, 81%; mp 154–157°C. IR (KBr): 2228 (C≡N stretch) and 1249 cm^{-1} (C—O—C stretch).

^{1}H NMR (CDCl$_3$, δ ppm): 1.01, 1.09 (lump, 3H, H$_{1b, 2b, 3b}$), 1.45, 1.56 (2d, 2H, H$_{6a, 6b}$), 1.66 (lump, 1H, H$_{2a}$), 1.84 (lump, 4H, H$_{1a, 3a, 7, 8}$), 2.18 (s, 1H, H$_9$), 2.31, 2.35 (m, 2H, H$_{10a,10b}$), 2.94 (s, 1H, H$_4$), 6.91, 6.93 (2d, 4H, H$_{13,13'}$), 6.96, 6.98 (2d, 4H, H$_{16,16'}$), 7.27, 7.35 (2d, 4H, H$_{12,12'}$), 7.55, 7.57 (2d, 4H, H$_{17,17'}$) [see Fig. 2(a)].

^{13}C NMR (CDCl$_3$, δ ppm): 26.50 (C^2), 31.29, 31.41, 31.73 (C^1, C^3, C^6), 41.82, 41.88 (C^7, C^9), 43.00 (C^{10}), 47.42 (C^8), 48.95 (C^4), 54.65 (C^5), 105.89, 105.96 (C^{18},C$^{18'}$), 118.26, 118.39 (C^{13}, C$^{13'}$), 119.27 (C≡N), 120.16, 120.36 (C^{16}, C$^{16'}$), 129.35, 130.04 (C^{12}, C$^{12'}$), 134.67, 134.70 (C^{17}, C$^{17'}$), 145.79, 149.88 (C^{11}, C$^{11'}$), 152.70, 153.07 (C^{14}, C$^{14'}$), 162.43, 162.55 (C^{15}, C$^{15'}$) [see Fig. 2(b)].

ANAL. Calcd for C$_{36}$H$_{30}$N$_2$O$_2$ (522.64): C, 82.73%; H, 5.78%; N, 5.36%. Found: C, 82.07%; H, 5.76%; N, 5.34%.

5,5-Bis[4-(4-carboxyphenoxy)phenyl]Hexahydro-4,7-Methanoindan (3a)

A mixture of 87 g (1.56 mol) of potassium hydroxide and 40 g (0.078 mol) of dinitrile compound **2a** in 250 mL of ethanol and 250 mL of distilled water was stirred at a reflux temperature until no further ammonia was generated. The resulting clear solution was filtered while hot to remove any possible insoluble impurities. The filtrate was cooled, and the pH value was adjusted by concentrated hydrochloric acid to 2–3. The white precipitate formed was collected by filtration and dried in vacuum; yield, 42 g (96%); mp 272–275°C (278°C by DSC). IR (KBr): 2500–3500 cm^{-1} (carboxyl O—H stretch), 1688 cm^{-1} (C=O stretch), 1162 cm^{-1} (C—O—C stretch).

^{1}H NMR (DMSO-d_6, δ ppm): 0.94, 1.05 (lump, 3H, H$_{1b, 2b, 3b}$), 1.28, 1.47 (2d, 2H, H$_{6a, 6b}$), 1.59 (lump, 1H, H$_{2a}$), 1.77 (lump, 4H, H$_{1a, 3a, 7, 8}$), 2.08 (s, 1H, H$_9$), 2.23, 2.55 (m, 2H, H$_{10a,10b}$), 3.04 (s, 1H, H$_4$), 6.95, 6.97 (2d, 4H, H$_{13,13'}$), 6.97, 6.99 (2d, 4H, H$_{16,16'}$), 7.36, 7.41 (2d, 4H, H$_{12,12'}$), 7.95, 7.96 (2d, 4H, H$_{17,17'}$) [see Fig. 3(a)].

^{13}C NMR (DMSO-d_6, δ ppm): 26.84 (C^2), 31.50, 31.94 (C^1, C^3, C^6), 41.87, 42.16 (C^7, C^9), 43.35 (C^{10}), 47.71 (C^8), 48.79 (C^4), 54.88 (C^5), 118.27, 118.38 (C^{13}, C$^{13'}$), 120.15, 120.43 (C^{16}, C$^{16'}$), 126.46, 126.57 (C^{18},C$^{18'}$), 129.68, 130.54 (C^{12}, C$^{12'}$), 132.81, 132.94 (C^{17}, C$^{17'}$), 145.63, 149.57 (C^{11}, C$^{11'}$), 153.74, 154.13 (C^{14}, C$^{14'}$), 162.25, 162.42 (C^{15}, C$^{15'}$), 168.49 (—COOH) [see Fig. 3(b)].

ANAL. Calcd for C$_{36}$H$_{32}$O$_6$ (560.64): C, 77.13%; H, 5.75%. Found: C, 76.96%; H, 5.67%.
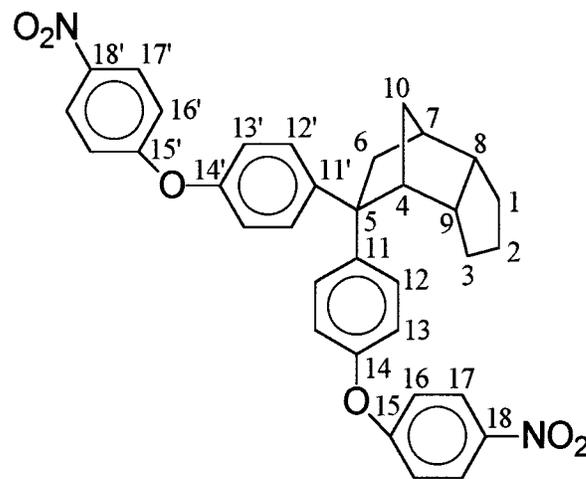
5,5-Bis[4-(4-nitrophenoxy)phenyl]Hexahydro-4,7-Methanoindan (2b)

Bisphenol **1** (32 g, 0.1 mol) and *p*-chloronitrobenzene (31.5 g, 0.2 mol) were dissolved in 150 mL of DMF. Anhydrous K$_2$CO$_3$ (27.3 g, 0.2 mol) was added to this solution, and the suspension was

then refluxed at 150°C for 8 h. After cooling to room temperature, the product was precipitated into 500 mL of water. Recrystallization from DMF/methanol gave light yellow crystals (**2b**) that were isolated by filtration and dried; yield after recrystallization, 45 g, 80%; mp 173–174°C. IR (KBr): 1513, 1344 cm^{-1} (N=O stretch), 1167 cm^{-1} (C—O—C stretch).

^{1}H NMR (DMSO-d_6, δ ppm): 0.96, 1.07 (lump, 3H, H$_{1b, 2b, 3b}$), 1.29, 1.51 (2d, 2H, H$_{6a, 6b}$), 1.62 (lump, 1H, H$_{2a}$), 1.80 (lump, 4H, H$_{1a, 3a, 7, 8}$), 2.12 (s, 1H, H$_9$), 2.25, 2.36 (m, 2H, H$_{10a,10b}$), 3.11 (s, 1H, H$_4$), 7.04, 7.06 (2d, 4H, H$_{13,13'}$), 7.08, 7.10 (2d, 4H, H$_{16,16'}$), 7.45, 7.50 (2d, 4H, H$_{12,12'}$), 8.22, 8.24 (2d, 4H, H$_{17,17'}$).

^{13}C NMR (DMSO-d_6, δ ppm): 26.83 (C^2), 30.66, 31.43, 31.88 (C^1, C^3, C^6), 41.62, 41.96 (C^7, C^9), 43.14 (C^{10}), 47.47 (C^8), 48.50 (C^4), 54.69 (C^5), 117.04, 117.23 (C^{13}, C$^{13'}$), 119.53, 119.74 (C^{16}, C$^{16'}$), 125.93, 125.95 (C^{17}, C$^{17'}$), 128.56, 129.36 (C^{12}, C$^{12'}$), 141.92, 141.97 (C^{18},C$^{18'}$), 144.87, 148.70 (C^{11}, C$^{11'}$), 151.13, 151.48 (C^{14}, C$^{14'}$), 162.37, 162.50 (C^{15}, C$^{15'}$).

ANAL. Calcd for C$_{34}$H$_{30}$N$_2$O$_6$ (562.62): C, 72.58%; H, 5.37%; N, 4.98%. Found: C, 72.23%; H, 5.37%; N, 5.01%.

5,5-Bis[4-(4-aminophenoxy)phenyl]Hexahydro-4,7-Methanoindan (3b)

A mixture of 30 g (0.053 mol) of dinitro compound **2b**, 27 g of hydrazine hydrate, 0.1 g of 10% Pd/C catalyst, and 200 mL of ethanol was refluxed overnight. The resulting solution was filtered hot to remove the catalyst. The filtrate was cooled to room temperature and precipitated into water. The product was collected by filtration and dried;

yield, 23.8 g (89%); mp 183–184°C. IR (KBr): 3372, 3450 cm^{-1} (N—H stretch), 1171 cm^{-1} (C—O—C stretch).

^{1}H NMR (CDCl$_3$, δ ppm): 0.96, 1.04 (lump, 3H, H$_{1b, 2b, 3b}$), 1.41, 1.48 (2d, 2H, H$_{6a, 6b}$), 1.62 (lump, 1H, H$_{2a}$), 1.80 (lump, 4H, H$_{1a, 3a, 7, 8}$), 2.08 (s, 1H, H$_9$), 2.20, 2.27 (m, 2H, H$_{10a,10b}$), 2.84 (s, 1H, H$_4$), 3.35 (-NH$_2$), 6.62, 6.64 (2d, 4H, H$_{17,17'}$), 6.74, 6.76 (2d, 4H, H$_{13,13'}$), 6.82, 6.84 (2d, 4H, H$_{16,16'}$), 7.13, 7.19 (2d, 4H, H$_{12,12'}$).

^{13}C NMR (CDCl$_3$, δ ppm): 27.27 (C^2), 31.88, 32.12, 32.41 (C^1, C^3, C^6), 42.37, 42.39 (C^7, C^9), 43.45 (C^{10}), 47.90 (C^8), 49.38 (C^4), 54.48 (C^5), 116.08, 116.31 (C^{17}, C$^{17'}$), 116.31, 116.51 (C^{13}, C$^{13'}$), 120.95, 121.05 (C^{16}, C$^{16'}$), 127.93, 128.67 (C^{12}, C$^{12'}$), 142.08, 142.34 (C^{18},C$^{18'}$), 142.39, 146.15 (C^{11}, C$^{11'}$), 148.42, 148.51 (C^{15}, C$^{15'}$), 155.68, 156.01 (C^{14}, C$^{14'}$).
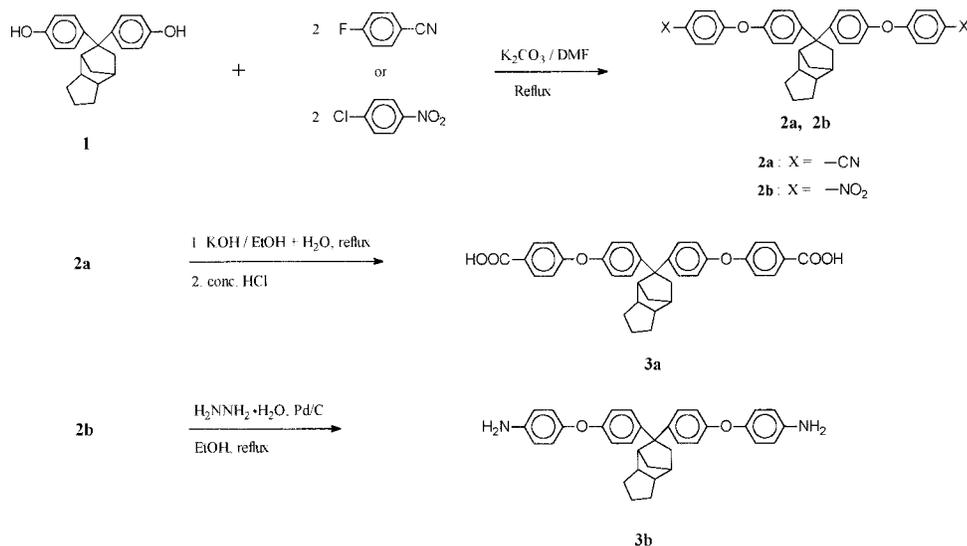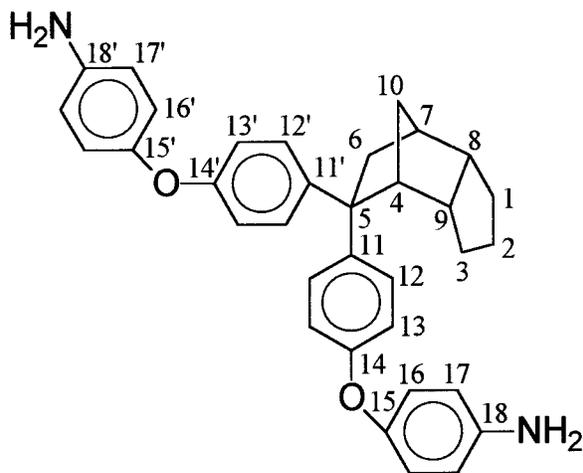
ANAL. Calcd for C$_{34}$H$_{34}$N$_2$O$_2$ (502.65): C, 81.24%; H, 6.82%; N, 5.57%. Found: C, 81.06%; H, 6.84%; N, 5.35%.

General Polymer Synthesis

Synthesis of polyamide **6d** is described as a typical procedure. A mixture of 0.7008 g (1.25 mmol) of diacid **3a**, 0.2503 g (1.25 mmol) of 4,4'-oxydianiline (**4d**), 0.4 g of calcium chloride, 1 mL of triphenyl phosphite, 1 mL of pyridine, and 4 mL of NMP was heated with stirring at 120°C for 3 h. The resulting highly viscous solution was poured slowly into 300 mL of stirring methanol, giving rise to a tough, fiberlike polymer precipitate. The product was isolated by filtration, thoroughly washed by methanol and hot water, and dried. The yield was quantitative. The inherent viscosity of the polyamide (**6d**) was 1.24 dL/g, as measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30°C. IR (film): 3314 (N—H stretch), 2950 (aliphatic C—H stretch), 1669 (C=O stretch), and 1245 cm^{-1} (C—O—C stretch).

All other polyamides were synthesized analogously.

Preparation of Polyamide Films

A solution of polymer was made by dissolving about 0.9 g of the polyamide in 9 mL of hot DMAc to afford an approximate 10 wt % solution. The clear solution was poured into a 9-cm diameter glass culture dish, which was placed in a 90°C
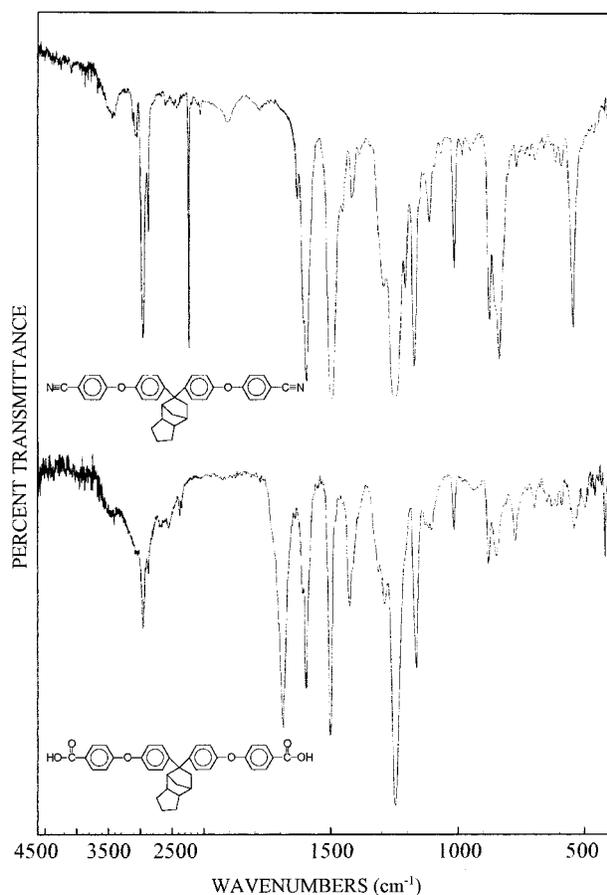

Scheme 1.

Figure 1. IR spectra of 5,5-bis[4-(4-cyanophenoxy)-phenyl]hexahydro-4,7-methanoindan and 5,5-bis[4-(4-carboxyphenoxy)phenyl]hexahydro-4,7-methanoindan.

oven overnight to evaporate the solvent. The semidried polyamide film was stripped off from the glass surface and further dried in vacuum at 160°C for 6 h. The obtained films showed about 0.06 mm thickness and were ready for X-ray diffraction measurements and tensile tests.

Measurements

A JASCO FT/IR-7000 Fourier transform infrared spectrometer was used to record IR spectra on KBr pellets or solution cast films. Elemental analyses were run in a Perkin–Elmer model 2400 CHN analyzer at National Taiwan University, Taipei. ^{1}H- and ^{13}C NMR spectra were acquired on a JEOL EX-400 spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using a Cannon–Fenske capillary viscometer. DSC analyses were performed on a Perkin–Elmer DSC 7 in flowing nitrogen with heating

rates of 20°C/min. Thermomechanical analysis (TMA) measurements were conducted for the polymer films with a Perkin–Elmer TMA 7 instrument using a penetration probe of 1.0-mm diameter and using an applied constant load of 30 mN (stress, 0.038 MPa) with a scan rate of 10°C/min. The TMA experiments were carried out in duplicate from 40 to 300°C. The apparent T_g's were taken as the intersection of the extrapolation of the baseline with the extrapolation of inflection from the second TMA traces. A DuPont 951 Thermogravimetric Analyzer was used for thermogravimetric analysis (TGA) in nitrogen and air with heating rates of 20°C/min. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu Kα radiation (40 kV, 15 mA) with a scanning rate of 2°/min. An Instron Universal Tester Model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the polymer films (0.5-cm wide, 6-cm long, and
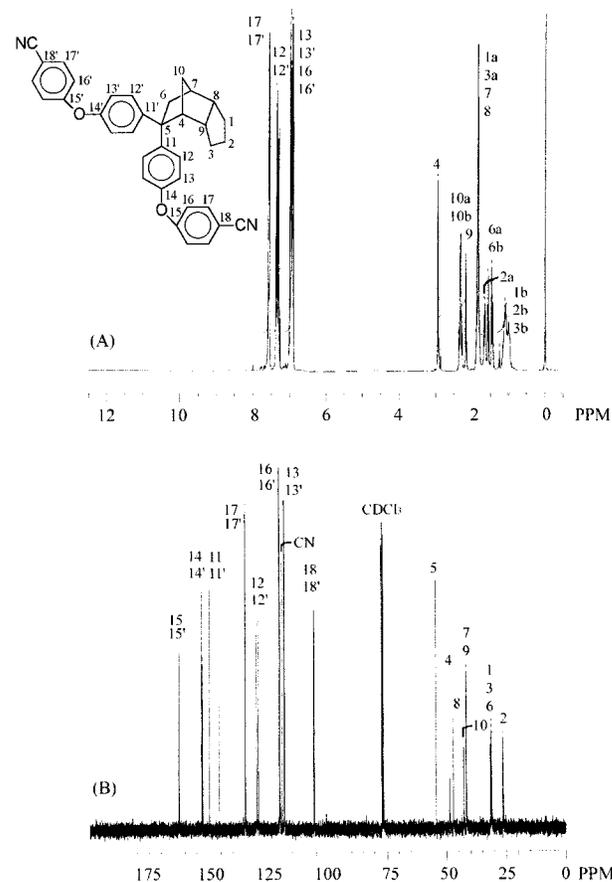

Figure 2. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of 5,5-bis[4-(4-cyanophenoxy)phenyl]hexahydro-4,7-methanoindan in CDCl$_3$.
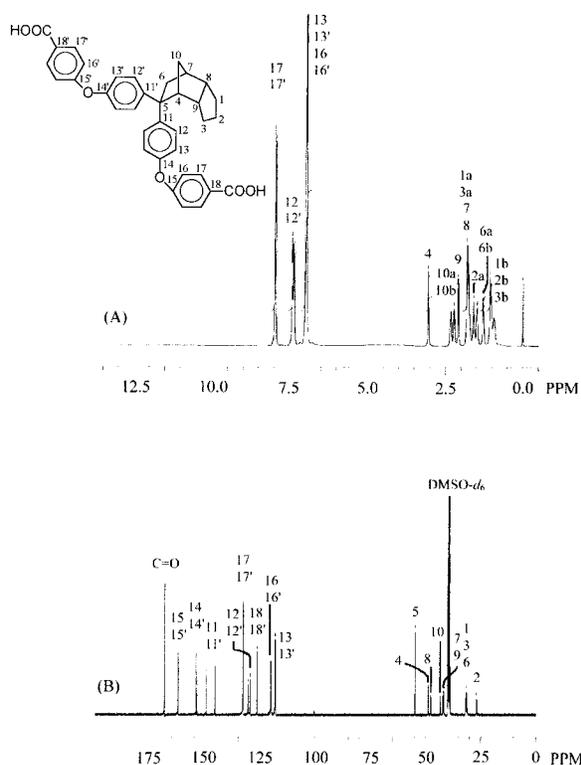
Figure 3. ^{1}H NMR (a) and ^{13}C NMR (b) spectra of 5,5-bis[4-(4-carboxyphenoxy)phenyl]hexahydro-4,7-methanoindan in DMSO-d_6.

about 0.06-mm thick). A crosshead gauge of 2 cm and a strain rate of 5 cm/min were used for this study. An average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

5,5-Bis[4-(4-carboxyphenoxy)phenyl]hexahydro-4,7-methanoindan (**3a**) and 5,5-bis[4-(4-amino-phenoxy)phenyl]hexahydro-4,7-methanoindan (**3b**) were prepared in two steps according to Scheme 1. Intermediate compounds **2a** and **2b** were synthesized by nucleophilic aromatic halogen displacement of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with 5,5-bis(4-hydroxyphenyl)hexahydro-4,7-methanoindan (**1**) in the presence of potassium carbonate in DMF. The dinitrile **2a** was then readily converted into dicarboxylic acid **3a** by alkaline hydrolysis. The diamine **3b** was obtained by catalytic hydrogenation of the dinitro compound **2b** using hydrazine hydrate and Pd/C catalyst in refluxing ethanol.

All the intermediate and monomer structures were confirmed by IR, NMR, and elemental analysis. Figure 1 illustrates the IR spectra of dinitrile **2a** and diacid **3a**. Characteristic bands for C≡N stretch at 2228 and C—O—C at 1249 cm^{-1} are consistent with structure **2a**. After hydrolysis, the CN peak disappeared and typical bands for the carboxyl groups were observed around 1688 (C=O stretch) and 2500–3500 cm^{-1} (hydrogen-bonded O—H). Figures 2 and 3 display the ^{1}H NMR and ^{13}C NMR spectra of dinitrile **2a** in CDCl$_3$ and diacid **3a** in DMSO-d_6, respectively. Assignments of peaks for these spectra are given in the figure. In the ^{1}H NMR spectra the aromatic protons (H$_{17,17'}$) *ortho* to the carboxyl or cyano groups and those (H$_{12,12'}$) *ortho* to the polyalicyclic unit were clearly distinguished, whereas the aromatic protons *ortho* to the ether groups were overlapped. The resonance signals of some aliphatic protons were also overlapped. The ^{13}C NMR spectra of **2a** and **3a** look somewhat complicated owing to the asymmetric structure of aliphatic rings. Thus, some resonance signals could not be clearly assigned. The most powerful features of the ^{13}C spectra are the shifts of the resonance signals for the cyano carbons and its adjacent carbons C^{18} and C$^{18'}$. The C^{18} and C$^{18'}$ of **2a** are shielded by the anisotropic field induced by the π electrons of C≡N, and hence they resonate at higher field than the other aromatic carbons. After hydrolysis, the resonance peaks of C^{18} and C$^{18'}$ moved to lower field (from 105.9 to 126.5 ppm) because of the lack of anisotropic shielding, the original signal at 119.27 ppm assigned to cyano carbons disappeared, and the resonance of carbonyl carbons occurred at the farthest downfield (168.49 ppm). The NMR spectra of dinitro
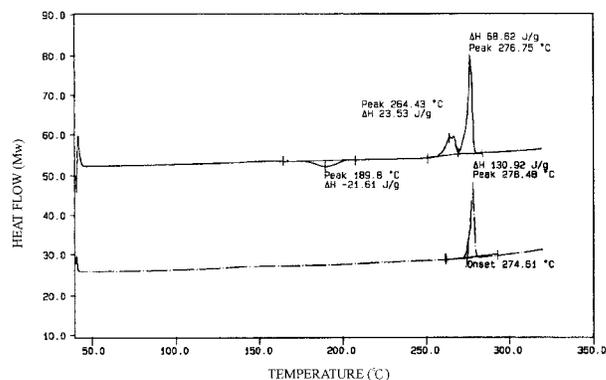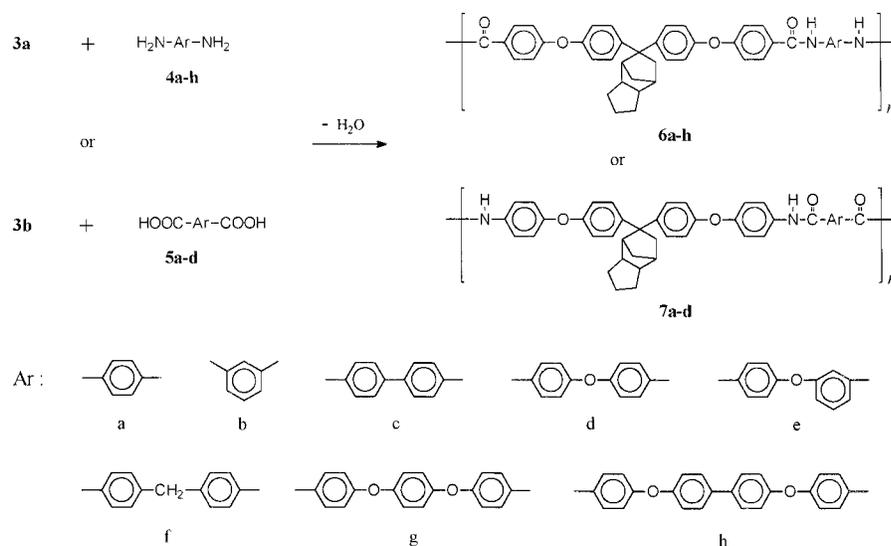

Figure 4. DSC thermograms of diacid 3 (top: as-prepared; bottom: after recrystallization from acetic acid), with a heating rate of 10°C/min.

Scheme 2.

compound **2b** and diamine **3b** are as reported in the experimental section and are in good agreement with the proposed structures.

Moreover, it is worth mentioning that the as-prepared diacid **3a** exhibited three transitions in the temperature range of 50–300°C based on its DSC trace (Fig. 4). The transition at 190°C is probably related to the conformational rearrangements of the alicyclic unit. The main transition at around 277°C could be indicative of a melting transition, and a smaller lower temperature endotherm at 264°C was believed to be a result of solid state polymorphism. However, the recrystallized material showed only one melt at 278°C.

Polymer Synthesis

Polyamides **6a–h** were prepared from the diacid **3a** and diamines **4a–h** (Scheme 2) according to the procedure developed by Yamazaki and coworkers.[27] Synthesis conditions and inherent viscosities of the polyamides are summarized in Table I. All polymerizations proceeded homogeneously throughout the reaction, and highly viscous solutions were obtained. The polyamides were isolated as tough fibers in quantitative yields. Polyamides **6a–h** had inherent viscosities between 0.87 and 1.27 dL/g and could be solution-cast into tough films, indicating high molecular weight polymers. For comparison, some analogous polyamides **7a–d** with comparable inherent viscosities were prepared from diamine **3b** and diacids **5a–d**. The only structure difference be-

tween polyamides **6a–d** and **7a–d** is the orientation of the amide groups. The IR spectra of the polymers exhibited characteristic amide absorptions around 3300 (N—H stretch), 1650–1670 (C=O stretch), and 1520 cm^{-1} (N—H bend). The strong absorption around 1230 cm^{-1} was as-

Table I. Synthesis Conditions and Inherent Viscosities of Polyamides

	Amount of Reagents Used[a]			
Polymer	NMP (mL)	Py (mL)	CaCl$_2$ (g)	η_{inh}[b] (dL/g)
6a	3 + 1[c]	1	0.4	1.24
6b	3	0.8	0.3	0.87
6c	4	1	0.4	1.14
6d	4	1	0.4	1.24
6e	3 + 1	0.8	0.3	1.18
6f	4 + 1	1	0.4	1.28
6g	3 + 3	0.8	0.3	1.29
6h	6	1.5	0.6	1.27
7a	3	0.8	0.3	0.88
7b	2 + 1	0.5	0.2	0.73
7c	3 + 4	0.8	0.3	1.44
7d	3	0.8	0.3	0.75

[a] 1.25 mmol each of the diacid and diamine monomer were used; triphenyl phosphite = 1 mL; reaction temperature = 120°C; time = 3 h. NMP: N-methyl-2-pyrrolidone; Py: pyridine.
[b] Measured in DMAc-5 wt % LiCl at 30°C on 0.5 g/dL.
[c] "3 + 1" means that an initial amount of 3 mL NMP was used and an additional 1 mL of NMP was added when the reaction solution was too viscous to stir.
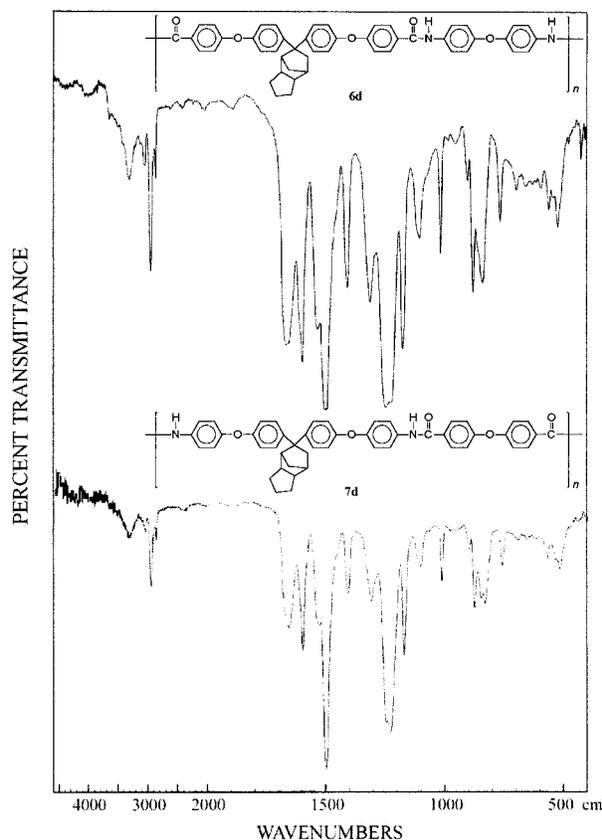
Figure 5. Infrared spectra of isomeric polyamides **6d** and **7d**.

signed to the aryl ether stretching. A typical set of IR spectra of the isomeric polyamides **6d** and **7d** are illustrated in Figure 5. Because of the structural analogy, these two spectra look very similar even in the fingerprint region.

Polymer Properties

The solubility of the polyamides was studied qualitatively, and the results are shown in the Table II. Almost all the polyamides were readily soluble in amide-type polar aprotic solvents (such as NMP, DMAc, and DMF) and *m*-cresol; however, they were not as soluble in DMSO without heating. Polyamides **6b** and **7b** were also soluble in less efficient THF because of the less symmetrical diamine or diacid residues. The polymers with 4,4′-biphenylene groups such as **6c**, **6h**, and **7c** showed somewhat lower solubility. They were insoluble or just soluble in hot DMF or DMSO. The less solubility may indicate stronger hydrogen bonding between chains or better packing efficiency because of the presence of rigid rodlike

4,4′-biphenylene segment. In general, the aliphatic rings containing polyamides showed higher solubility compared to conventional aromatic polyamides. This may be due to the amorphous nature of these polymers as evidenced by X-ray diffractograms discussed subsequently. Furthermore, in comparison with two sets of analogous polyamides **6a–d** and **7a–d**, which had an isomeric repeat unit, they showed a similar solubility behavior. This indicates that the presence of the polyalicyclic structure in either diamine or dicarboxylic acid moiety did not affect noticeably the polymer solubility. Similar results were found for the polyamides derived from 1,1-bis[4-(4-carboxyphenoxy)phenyl]cyclohexane or 1,1-bis[4-(4-aminophenoxy)phenyl]cyclohexane, as described in the previous publications.[22,23]

The crystallinity of the polyamides was measured by wide-angle X-ray diffraction scans. The diffraction patterns indicated that all polyamides, even that obtained from *p*-phenylenediamine and benzidine, were completely amorphous. This is reasonable because the presence of bulky polyalicyclic unit hindered chain packing and reduced intramolecular interactions. Thus, the amorphous nature of these polymers was reflected in their good solubility.

All polymers can be solution cast into transparent (essentially colorless), flexible, and tough films. Their tensile properties are listed in Table III. All polyamides behaved as tough materials. They necked during tensile testing and had moderate elongation to break. The high toughness may be due in part to the energy dissipation mechanisms involving conformational transformations of the cyclic aliphatic unit. In addition, as can be seen from Table III, the isomeric polyamides **6a–d** and **7a–d** exhibited similar tensile properties.

Thermal analysis results are summarized in Table IV. Polyamides **6a–h** and **7a–d** showed T_g values in the range of 219–249°C and 233–253°C, respectively, by DSC. The T_g values generally decreased with the decreasing order of segmental flexibility of the diamine moiety. Polyamides **7a–d** displayed a comparable T_g with analogous **6a–d**, indicating that constitutional isomerism of the recurring unit did not affect significantly the polymer rigidity. No discernible T_g values were observed for the polyamide (**7c**) from 4,4′-biphenylenedicarboxylic acid and **6c** from benzidine by DSC, possibly because of the rigid 4,4′-biphenylene segment. These results are in good agreement with the solubility test results. However,

Table II. Solubility Behavior of Polyamides[a]

Polymer	Solvent[b]					
	NMP	DMAc	DMF	DMSO	*m*-Cresol	THF
6a	+	+	+	+h	+	−
6b	+	+	+	+h	+	+
6c	+	+	−	+h	s	−
6d	+	+	+	+h	+	−
6e	+	+	+	+	+	−
6f	+	+	+	−	+	−
6g	+	+	+	+h	+	−
6h	+	+	−	−	+	−
7a	+	+	+	+h	+	−
7b	+	+	+	+	+	+
7c	+	+	+h	+h	+	−
7d	+	+	+	+h	+	−

[a] +: Soluble; +h: soluble on heating at 100°C; s: swelling; −: insoluble even on heating.
[b] NMP: *N*-methyl-2-pyrrolidone; DMAc: *N,N*-dimethylacetamide; DMF: *N,N*-dimethylform-amide; DMSO: dimethyl sulfoxide; THF: tetrahydrofuran.

the T_g's of these two rigid polymers could be readily determined using thermomechanical analysis (TMA). The T_g's of the other polyamide samples have also been measured using TMA. The trend of T_g variation with the chain flexibility is the same as that seen in the DSC measurements. However, in most cases, T_g's measured by TMA are slightly different from those determined by DSC experiments. This difference may be attributable to the distinctive nature of the testing methods (thermomechanical versus calorimetric

responses). It should be pointed out that the T_g values obtained from TMA experiments might be sensitive to the applied stress. When compared with the corresponding polyamides with the cyclohexylidene cardo group as described in the preceding papers,[22,23] the series of polyamides showed increased T_g's because of the more rigid and bulky methanoindan structure.

Thermal stabilities of these polyamides were evaluated under both nitrogen and air using a 10 wt % loss values (T_d) for comparison. The T_d

Table III. Tensile Properties of Polyamide Films[a]

Polymer	Yield Strength (MPa)	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
6a	85	81	31	1.77
6b	90	88	13	1.81
6c	85	81	21	1.77
6d	93	91	18	1.79
6e	91	89	12	1.78
6f	89	85	17	1.64
6g	91	87	14	1.81
6h	90	88	18	1.67
7a	91	88	18	1.76
7b	101	95	17	1.88
7c	91	89	25	1.82
7d	95	94	14	1.79

[a] Films were cast from slow evaporation of the polymer solutions in DMAc. The cast films were dried under vacuum at 150°C for 6 h prior to the tensile test.

Table IV. Thermal Properties of Polyamides

Polymer	T_g (°C)		$T_d{}^c$ (°C)		Char Yield[d] (%)
	DSC[a]	TMA[b]	In N$_2$	In Air	
6a	249 (214)[f]	275	488	500	60
6b	234 (188)	247	487	487	52
6c	$-$[e] (244)	288	489	511	64
6d	232 (209)	257	491	498	62
6e	223 (195)	242	496	502	61
6f	226 (206)	251	482	509	58
6g	219 (191)	243	484	505	52
6h	230 (199)	254	490	487	60
7a	253 (219)	267	487	481	45
7b	240 (195)	245	480	477	42
7c	$-$ (243)	295	492	491	58
7d	233 (202)	246	478	473	57

[a] The samples were heated to 400°C with a heating rate of 20°C/min and rapidly cooled to 30°C at -100°C/min. The midpoint of baseline shift on the subsequent second DSC heating trace was defined as T_g.

[b] The onset temperature of the probe displacement on the second TMA traces. A penetration probe of 1.0-mm diameter and an applied constant load of 30 mN (stress, 0.038 MPa), and a heating rate of 10°C/min were used in the TMA experiments.

[c] Decomposition temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20°C/min.

[d] Residual weight (%) when heated to 800°C in nitrogen.

[e] No discernible transitions was observed.

[f] Values in parentheses are T_g's of analogous polyamides having cyclohexylidene groups and the corresponding –Ar– unit (see refs. 22 and 23).
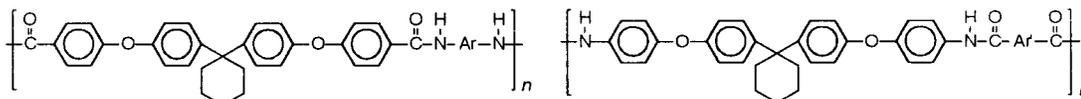
values stayed in the range of 478–496°C in nitrogen and 477–511°C in air, which are reasonable considering the high aliphatic content of these polymers. In some cases the T_d values in air were slightly higher than that in nitrogen, possibly because of the oxidative crosslinking, or an early weight-gained oxidation of the aliphatic groups when thermally degraded in air. In addition, the degradation seems to start by the breaking of the pendant alicyclic groups and, hence, the structure of the diamine or dicarboxylic acid does not seem to influence the thermal stability. The representative TGA thermograms of polyamide **6d** measured in air and in nitrogen are reproduced in Figure 6.
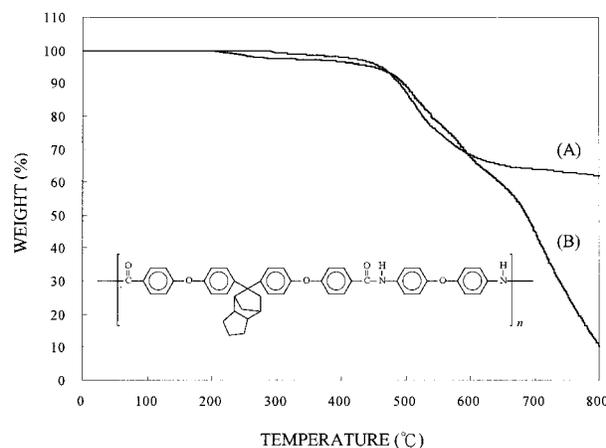
CONCLUSION

Extended dicarboxylic acid **3a** and diamine **3b** were successfully synthesized in high purity and high yields. Polyamides with high molecular weight were synthesized based on these monomers in good yields. The introduction of the methanohexahydroindan cardo group and aryl ether groups into the backbones of aromatic polyamides improves their solubility and toughness. No crystallinity was observed for any of these

Figure 6. Typical TGA curves for polyamide **6d** in nitrogen (a) and in air (b) with a heating rate of 20°C/min.

polymers. The polyamides showed a reasonable level of thermal stability and exhibited moderate T_g's potential for moldability. Overall, internal plasticization through the incorporation of the polyalicyclic groups was shown to be successful.

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