Synthesis and Properties of Aromatic Polyamides Containing the Cyclohexane Structure

SHENG-HUEI HSIAO, CHIN-PING YANG, SHENG-WEN WANG, MING-HUNG CHUANG

Department of Chemical Engineering, Tatung Institute of Technology,
40 Chungshan North Road, Sec. 3, Taipei, Taiwan, Republic of China

ABSTRACT: 1,1-Bis[4-(4-carboxyphenoxy)phenyl]cyclohexane (**III**) and 1,1-bis[4-(4-aminophenoxy)phenyl]cyclohexane (**V**) were prepared in two main steps starting from the aromatic nucleophilic substitution of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with 1,1-bis(4-hydroxyphenyl)cyclohexane in the presence of potassium carbonate in *N,N*-dimethylformamide (DMF). Using triphenyl phosphite and pyridine as condensing agents, two series of polyamides with cyclohexylidene cardo groups were directly polycondensated from dicarboxylic acid **III** with various aromatic diamines or from diamine **V** with various aromatic dicarboxylic acids in an *N*-methyl-2-pyrrolidone (NMP) solution containing dissolved calcium chloride. The polyamides exhibited inherent viscosities in the range of 0.45 to 1.78 dL/g. Almost all of the polymers were readily soluble in polar aprotic solvents such as NMP and *N,N*-dimethylacetamide (DMAc) and could afford transparent, flexible, and tough films by solution casting. The glass transition temperatures (T_g) of these aromatic polyamides were in the range of 180–243°C by DSC, and the 10% weight loss temperatures in nitrogen and air were all above 450°C. © 1999 John Wiley & Sons, Inc. J Polym Sci A: Polym Chem 37: 3575–3583, 1999
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INTRODUCTION

Wholly aromatic polyamides, such as poly(*p*-phenyleneterephthalamide), poly(*m*-phenyleneisophthalamide), and poly(*p*-benzamide), attract much interest because of their high thermal and chemical resistances as well as their high strength and high modulus in fiber form.[1,2] But these materials suffer often poor processibility due to their limited solubility and infusibility caused by the high crystallinity and stiffness of the polymer backbones. Therefore, preparation of soluble and/or thermoplastic polyamides has been a major research interest. Many efforts have been made with the aim of making synthetic modifications of

the rigid backbone by incorporating kinks of flexible linkages,[3–6] the distortion of molecular symmetry by *meta*- or *ortho*-catenated aromatic or heterocyclic units,[7–12] and the introduction of bulky groups into the polymer chain.[13–25] The latter method has found the widest application. In addition to using bulky monomers, any of these procedures can also be used to disrupt crystallinity to obtain almost completely amorphous polyamides. In general, amorphous polyamides have relatively low softening temperature and enhanced solubility compared to crystalline analogs, and they are of considerable interest as high-performance engineering plastics.

Another approach to increasing the solubility of aromatic polyamides is to incorporate cardo groups in the main chain.[26] In previous works[27–30] we described the synthesis of soluble polyamides by introducing cardo groups such as

Correspondence to: S.-H. Hsiao

fluorene, phthalide, and phthalimidine along the polymer backbone. The cardo groups twist the phenylene moieties of the main chain out of a planar conformation, thereby increasing solubility. This study deals with the synthesis and characterization of soluble polyamides containing a cyclohexane ring as a cardo group in the main chain. It was hoped that incorporation of the cyclohexane unit would decrease polymer interchain interaction and generally disrupt the coplanarity of phenylene units to reduce packing efficiency and crystallinity, thus leading to enhanced solubility. It was postulated that the introduction of alicyclic chains along the polyamide backbone would increase the polymer's free volume, resulting in decreased glass transition temperature (T_g). The cyclohexane cardo group was also expected to act as an internal plasticizer and allow the polymer chain more freedom for flow during processing. In addition, arylene ether groups have been inserted in the backbone to contribute to the increased solubility and decreased T_g.

EXPERIMENTAL

Materials

According to a common bisphenol synthesis,[31] 1,1-bis(4-hydroxyphenyl)cyclohexane (**I**) (m.p. 178–180°C) was prepared by the HCl-catalyzed condensation reaction of cyclohexanone with excess phenol. *p*-Phenylenediamine (**VI**$_a$, from TCI) and benzidine (**IV**$_c$, from TCI) were purified by vacuum sublimation. *m*-Phenylenediamine (**VI**$_b$, from Janssen) was purified by vacuum distillation. 4,4′-Oxydianiline (**VI**$_d$, from TCI), 3,4′-oxydianiline (**VI**$_e$, from Mitsui Petrochemical Ind., Tokyo, Japan), 4,4′-methylenedianiline (**VI**$_f$, from TCI), 1,4-bis(4-aminophenoxy)benzene (**VI**$_g$, from TCI), and α,α'-bis(4-aminophenyl)-1,4-diiso-propylbenzene (**VI**$_h$, from Mitsui Petrochemical Ind.) were used without further purification. According to a well-developed procedure,[5,32,33] ether diamines with four or five benzene rings that include 1,1-bis[4-(4-aminophenoxy)phenyl]cyclohexane (**V**, m.p. 156–157°C), 4,4′-bis(4-aminophenoxy)biphenyl (**VI**$_i$, m.p. 198–199°C), bis[4-(4-aminophenoxy)phenyl] sulfone (**VI**$_j$, m.p. 228–230°C), 2,2-bis[4-(4-aminophenoxy)phenyl]propane (**VI**$_k$, m.p. 125–126°C), 1,1-bis[4-(4-aminophenoxy)phenyl]-hexafluoropropane (**VI**$_l$, m.p. 162–163°C), 1,1-bis[4-(4-aminophenoxy)phenyl]-1-phenylethane (**VI**$_m$, m.p. 68°C), and α,α'-bis[4-(4-aminophe-noxy)phenyl]-1,4-diisopropylbenzene (**VI**$_n$, m.p. 187–189°C) were prepared by the chloro displacement reaction of *p*-chloronitrobenzene (from TCI) with the corresponding bisphenol precursors in the presence of potassium carbonate followed by catalytic hydrazine reduction. Aromatic dicarboxylic acids such as terephthalic acid (**VIII**$_a$, from Wako), isophthalic acid (**VIII**$_b$, from Wako), 4,4′-biphenyldicarboxylic acid (**VIII**$_c$, from TCI), 4,4′-oxydibenzoic acid (**VIII**$_d$, from TCI), 5-*tert*-butylisophthalic acid (**VIII**$_e$, from Aldrich), 4,4′-sulfonyldibenzoic acid (**VIII**$_f$, from New Japan Chemical Co.) 4,4′-hexafluoroisopropylidenedibenzoic acid (**VIII**$_g$, from Chriskev), 2,6-naphthalenedicarboxylic acid (**VIII**$_h$, from TCI), and 1,4-naphthalenedicarboxylic acid (**VIII**$_i$, from Wako) were used as received. Commercially obtained anhydrous calcium chloride ($CaCl_2$) was dried under vacuum at 200°C for 10 h. Pyridine was purified by distillation after being refluxed with KOH. *N*-Methyl-2-pyrrolidone (NMP) was distilled over calcium hydride under reduced pressure and stored over 4 Å molecular sieves. Similarly, triphenyl phosphite (TPP, from Fluka) was purified by distillation under reduced pressure.

Monomer Synthesis

1,1-Bis[4-(4-cyanophenoxy)phenyl]cyclohexane (II)

In a 300-mL flask equipped with a Dean–Stark trap and a condenser, cyclohexane-diphenol **I** (15 g, 0.057 mol) was dissolved in a mixture of DMF (100 mL) and toluene (70 mL). Anhydrous potassium carbonate (15.5 g, 0.11 mol) was added to this solution. The suspension solution was heated to reflux, and water was removed by azeotropic distillation with toluene. After the water was completely removed, the residual toluene was distilled out from the system. Then the reaction mixture was cooled to about 60°C, and *p*-fluorobenzonitrile (13.6 g, 0.112 mol) was added. After refluxing 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 (25.2 g, 96% yield) was purified by recrystallization from acetonitrile; yield, 21.3 g (85%); m.p. 154–156°C. IR (KBr): 2228 (C≡N stretch) and 1249 cm^{-1} (C—O—C stretch). ^{1}H-NMR (CDCl$_3$): δ(ppm) 7.58 (d, 4H, H$_g$), 7.32 (d, 4H, H$_d$), 6.98 (two overlapped AB doublets, 8H, H$_e$ + H$_f$), 2.29 (s, 4H, H$_a$), 1.59 (s, 6H, H$_b$ + H$_c$). ^{13}C-NMR (CDCl$_3$): δ(ppm) 161.50 (C^9), 152.32 (C^8), 145.15

(C^5), 134.01 (C^{11}), 127.78 (C^6), 119.91 (C^7), 118.74 (C≡N), 117.88 (C^{10}), 105.54 (C^{12}), 45.55 (C^1), 37.18 (C^2), 26.15 (C^4), 22.75 (C^3).
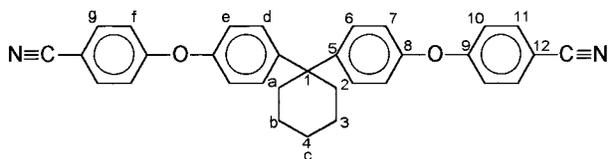
ANAL calcd for $C_{32}H_{26}N_2O_2$ (470.57): C, 81.68%; H, 5.57%, N, 5.95%. Found: C, 81.18%; H, 5.74%,;N, 5.91%.

1,1-Bis[4-(4-carboxyphenoxy)phenyl]-cyclohexane (III)

Bis(ether nitrile) **II** (20.8 g, 0.044 mol), potassium hydroxide (50 g, 0.44 mol), ethanol (150 mL), and water (150 mL) were introduced into a 500-mL flask, and the suspension was refluxed for 50 h. The resulting clear solution was filtered while hot to remove any possible impurities. After cooling to room temperature, the filtrate was acidified by concentrated HCl to pH = 2~3. The precipitated white powder was isolated by filtration, washed repeatedly with water, and dried under vacuum at 150°C for 6 h; yield, 21.6 g (96%); m.p. 247–249°C. IR (KBr): 2500–3500 (H-bonded O—H stretch), 1690 (C=O stretch), and 1251 cm^{-1} (C—O—C stretch). ^{1}H-NMR (DMSO-d_6): δ(ppm) 7.94 (d, 4H H_g), 7.37 (d, 4H, H_d), 7.02 (two overlapped AB doublets, 8H, H_e + H_f), 2.27 (s, 4H, H_a), 1.48 (s, 6H, H_b + H_c). ^{13}C-NMR (DMSO-d_6): δ(ppm) 166.75 (C=O), 160.88 (C^9), 152.72 (C^8), 144.34 (C^5), 131.65 (C^{11}), 128.62 (C^6), 125.20 (C^{12}), 119.45 (C^7), 117.21 (C^{10}), 45.02 (C^1), 36.37 (C^2), 26.15 (C^4), 22.49 (C^3).
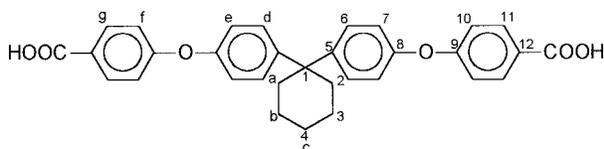
ANAL calcd for $C_{32}H_{28}O_6$ (508.57): C, 75.57%; H, 5.55%. Found: C, 75.30%; H, 5.51%.

Polymerization

A typical synthesis for polyamide **VII**$_a$ is as follows. A mixture of bis(ether-carboxylic acid) **III** (0.6357 g, 1.25 mmol), *p*-phenylene-diamine (**VI**$_a$) (0.1315 g, 1.25 mmol), CaCl$_2$ (0.3 g), TPP (0.9

mL), pyridine (0.8 mL), and NMP (2 mL) was heated at 120°C for 3 h. The obtained viscous polymer solution was poured slowly into 300 mL of stirring methanol to precipitate a white fiber-like product, which was isolated by filtration, thoroughly washed first with methanol and then with boiling water, and dried at 150°C under vacuum. The yield was almost quantitative. The inherent viscosity of the polymer (**VII**$_a$) was 0.75 dL/g, as measured at a concentration of 0.5 g/dL in DMAc containing 5 wt % LiCl at 30°C. The IR spectrum exhibited absorptions at 3500 (N—H stretch), 1651 (C=O stretch), and 1243 cm^{-1} (C—O—C stretch).

ANAL calcd for $(C_{38}H_{32}N_2O_4)_n$ (580.68)$_n$: C, 78.60%; H, 5.95%; N, 4.82%. Found: C, 77.60%; H, 6.13%; N, 4.30%.

Measurements

Elemental analyses were run on a Perkin-Elmer 2400 C, H, N analyzer. Inherent viscosities of the polymers were measured with a Cannon-Fenske viscometer at 30°C. IR spectra were obtained on a Jasco FT/IR-7000 Fourier transform spectrometer on KBr pellets or solution-cast films. Solution ^{1}H- and ^{13}C-NMR spectra were recorded on a Jeol EX-400 FT-NMR spectrometer. Differential scanning calorimetry (DSC) analyses were performed on a Perkin-Elmer differential scanning calorimeter, DSC 7, coupled to a Perkin-Elmer thermal analysis controller, TAC 7/DX, at a scan rate of 10°C/min in flowing nitrogen (30 cm^3/min). T_g's were read at the middle of the change in the heat capacity, and were taken from the second heating scan after quick cooling from 400°C. Thermogravimetric analyses (TGA) were conducted on a DuPont 951 thermogravimetric analyzer coupled to a DuPont 2000 thermal analyst. Experiments were performed with 9–11 mg of samples heated in flowing nitrogen or air (50 cm^3/min) at a scan rate of 20°C/min. The measurements were taken after an initial 250°C/10 min drying step. Dynamic mechanical analysis (DMA) measurements were performed on a TA Instruments DMA 2980. Wide-angle X-ray diffraction patterns were recorded on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu Kα radiation (1.5418 Å). The scanning rate was 2°/min over a 2θ range of 5–40°. Tensile properties of solution-cast films were determined from stress–strain curves obtained using an Instron 1130 universal tester with a load cell of 5 kg. A gauge length of 2
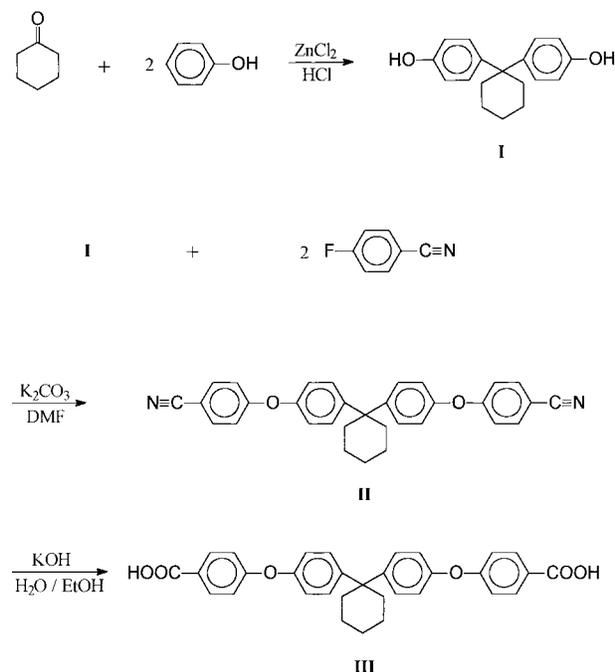
Scheme 1.   Synthesis of diacid **III**.

cm and an extension rate of 5 cm/min were used for this study. Measurements were performed with film specimens (length 6 cm, width 0.5 cm, thickness about 0.1 mm), and an average of at least five individual determinations was used.

RESULTS AND DISCUSSION

Monomer Synthesis

1,1-Bis(4-hydroxyphenyl)cyclohexane (**I**), prepared by a HCl-catalyzed condensation reaction of cyclohexanone with excess phenol, was used as the starting material. 1,1-Bis[4-(4-carboxyphenoxy)phenyl]cyclohexane (**III**) was synthesized according to the reaction sequence of Scheme 1. The intermediate bis(ether nitrile) **II** was obtained from the nucleophilic fluoro displacement of *p*-fluorobenzonitrile with the potassium phenolate of cyclohexane-bisphenol **I** in DMF. The bis(ether nitrile) **II** was then readily converted into bis(ether-carboxylic acid) **III** in high purity and high yield by alkaline hydrolysis. In addition, 1,1-bis[4-(4-amino-phenoxy)phenyl]cyclohexane (**V**) was prepared in two steps according to Scheme 2. The intermediate dinitro compound **IV** was synthesized by nucleophic aromatic chloro displacement of bisphenol **I** with the *p*-chloronitrobenzene in the presence of potassium carbonate in DMF.
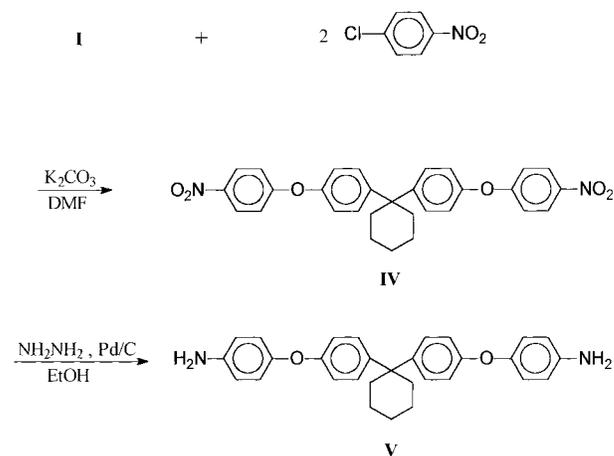
The diamine **V** was obtained in high purity and high yield using hydrazine hydrate and the Pd/C catalyst in refluxing ethanol.

The monomer structures were confirmed by elemental analyses as well as IR and NMR spectroscopy. Figure 1 presents the ^{1}H-NMR and ^{13}C-NMR spectra of dicarboxylic acid **III** in DMSO-d_6 solution. Assignments of peaks for both spectra are shown. In the ^{1}H-NMR spectrum, the carboxyl protons were exchangeable with D$_2$O. The aromatic protons (H$_g$) *ortho* to the carboxyl groups and those (H$_d$) *ortho* to the cyclohexylidene unit were clearly distinguished, whereas the aromatic protons (H$_e$ and H$_f$) *ortho* to the ether groups were overlapped. The resonance signals of cyclohexane protons H$_b$ and H$_c$ were also overlapped. However, all carbon nuclei in diacid **III** gave well-separated peaks in the ^{13}C-NMR spectrum. The resonance of carbonyl carbon occurred at the farthest downfield of 166.75 ppm.

Figure 2 shows the ^{1}H-NMR and ^{13}C-NMR spectra of diamine **V** in DMSO-d_6 solution and the assignments to all carbons and protons. All expected absorptions are observed. In the ^{1}H-NMR spectrum, the absorption signals of aromatic protons appear in the range of δ 6.50–7.20 ppm, the cycloalkane protons give unresolvable "lumps" centered at 1.42 and 2.17 ppm, and the resonance at 4.92 ppm is due to the amino protons. Furthermore, in the ^{13}C-NMR spectrum, the C^9 and C^{12} carbons are partially overlapped, whereas the other carbon nuclei show well-separated peaks.

Polymer Synthesis

Two series of aromatic polyamides, **VII**$_{a-n}$ and **IX**$_{a-i}$, were synthesized from bis(ether-carboxylic
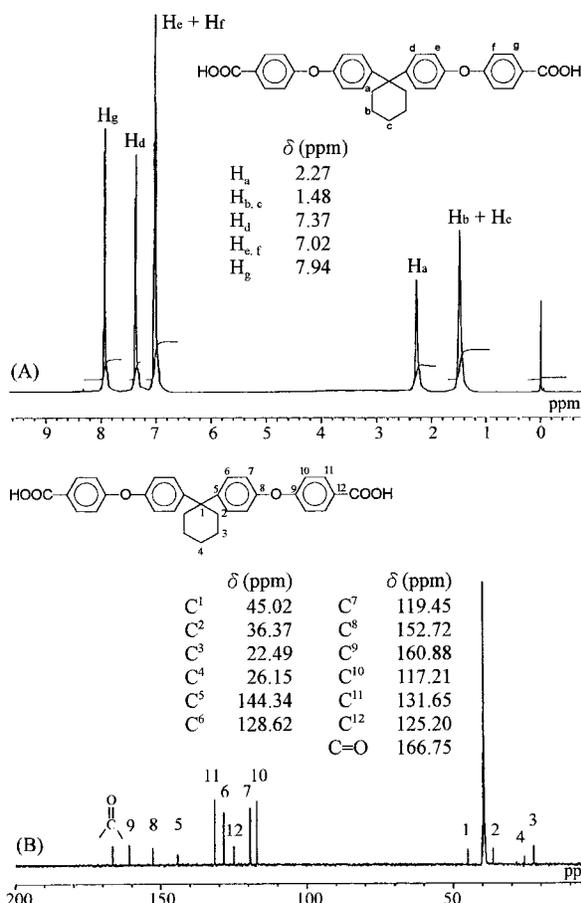

Scheme 2.   Synthesis of diamine **V**.

	δ (ppm)		δ (ppm)
H_a	2.27		
$H_{b,c}$	1.48		
H_d	7.37		
$H_{e,f}$	7.02		
H_g	7.94		

	δ (ppm)		δ (ppm)
C^1	45.02	C^7	119.45
C^2	36.37	C^8	152.72
C^3	22.49	C^9	160.88
C^4	26.15	C^{10}	117.21
C^5	144.34	C^{11}	131.65
C^6	128.62	C^{12}	125.20
		C=O	166.75

Figure 1. ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of dicarboxylic acid **III** in DMSO-d_6 solution.

acid) **III** with various aromatic diamines **VI**$_{a-n}$ (Scheme 3) and from bis(ether amine) **V** with various commercially available dicarboxylic acids **VIII**$_{a-n}$ (Scheme 4) by means of the TPP/pyridine-activated polycondensation technique.[34] All polyamidations proceeded in homogeneous and transparent solutions and resulted in highly viscous polymer solutions, indicative of the formation of high molecular weights. As shown in Table I, the inherent viscosities of these polyamides obtained exceeded 0.45 dL/g and ranged up to 1.78 dL/g. In general, the molecular weight of the polymer obtained from the phosphorylation reaction is highly dependent on the reactant concentration. According to our earlier work,[4–10] it was repeatly observed that the higher the concentration of monomers, the higher the final inherent viscosity if no precipitation or gelation of the product from the reaction medium occurred. It was anticipitated that the kinked cyclohexylidene group and flexible ether group–containing polyamides would

have enhanced solubility in the reaction media, and thus a higher reactant concentration could be tolerated during the polymerization. In some cases, higher polymer viscosities could be obtained by using a higher initial reactant concentration and then adding an additional amount of solvent to the highly viscous reaction medium before the formation of swollen gel.

The molecular structure of the polyamides were verified by FTIR based on characteristic absorptions observed around 3300 (N—H stretch), 1650 (C=O), 1510 (N—H bend), and 1230 cm^{-1} (C—O—C stretch). Elemental analyses are in good agreement with the proposed structures, missing only the values found for the C-percentages, which are always lower than the theoretical ones. This certainly can be due to the very aromatic nature of these polymers, which commonly leave a slight coal residue in the standard conditions of microanalysis. On the other hand, mois-

	δ (ppm)
H_a	2.17
$H_{b,c}$	1.42
H_d	7.17
$H_{e,f}$	6.72
H_g	6.57
-NH$_2$	4.92

	δ (ppm)		δ (ppm)
C^1	44.42	C^7	115.94
C^2	36.37	C^8	156.47
C^3	22.46	C^9	145.50
C^4	25.73	C^{10}	120.90
C^5	141.52	C^{11}	114.82
C^6	127.86	C^{12}	145.37

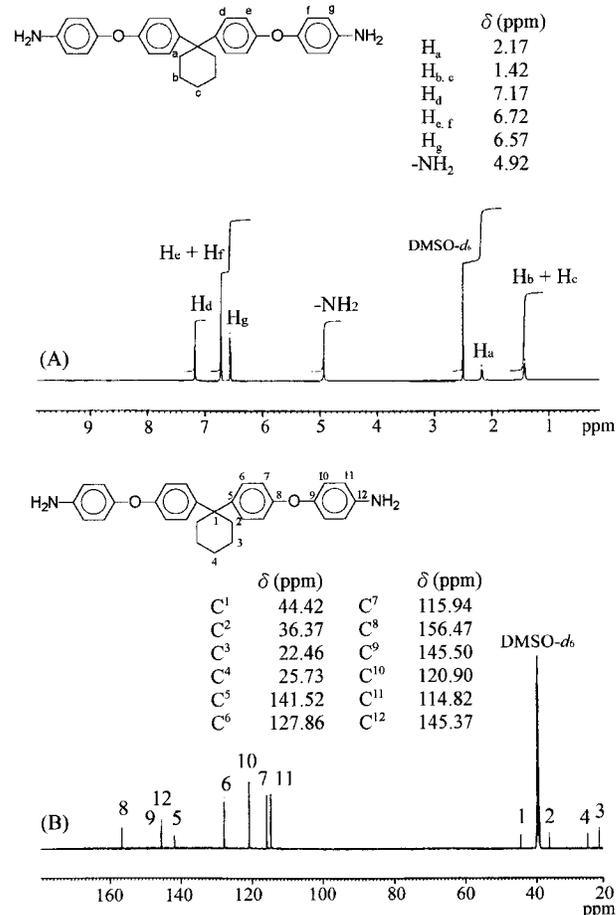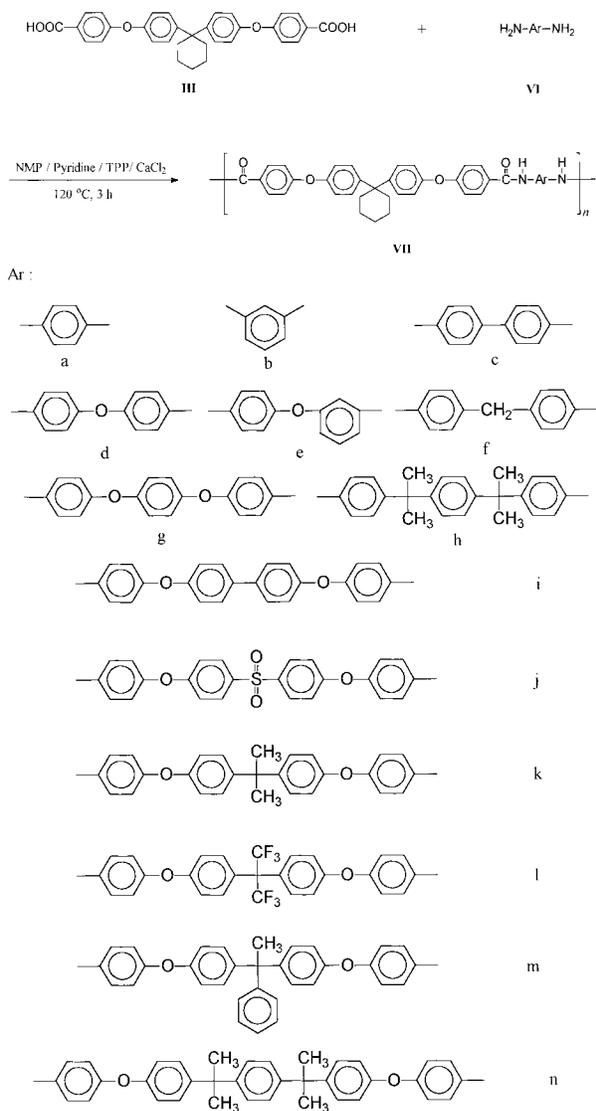**Figure 2.** ^{1}H-NMR (a) and ^{13}C-NMR (b) spectra of diamine **V** in DMSO-d_6 solution.

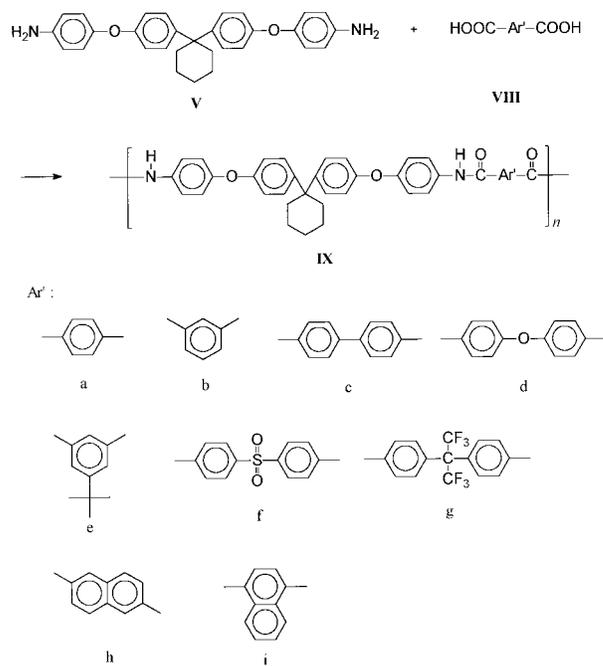**Scheme 3.** Sythesis of polyamides **VIIa–n**.

ture absorption could also give rise to slight differences in the values of the elemental analyses.

Polymer Characterization

The qualitative solubility of the polyamides in various organic solvents is also shown in Table I. Almost all of the polyamides were readily soluble in amide-type polar solvents such as NMP, DMAc, and DMF. Most polyamides of the VII_{a-n} series and some of those of the IX_{a-i} series were not as soluble in DMSO and *m*-cresol without heating. Polyamides VII_{l-n} were also soluble in less efficient THF, due to the flexible diamine residues, and polyamides IX_f and IX_g were also

soluble in THF, attributable to the presence of sulfonyl and hexafluoroisopropylidene linkages in the dicarboxylic acid moiety. The polymers containing a 4,4′-biphenylene unit, such as VII_c, VII_g, and IX_c had somewhat limited solubility. They were insoluble or just swelled in DMF, DMSO, *m*-cresol, and THF. The lower solubility of these three polymers may indicate strong hydrogen bonding between chains or good packing ability due to the presence of rigid rod-like 4,4′-biphenylene segments. In general, the cyclohexylidene-containing polyamides showed higher solubility than the conventional aromatic polyamides. In addition, in comparison with two sets of analogous polyamides of VII_{a-d} and IX_{a-d}, which had an isomeric repeat unit, they revealed similar solubility behavior. This indicates that the presence of cyclohexylidene in either diamine or dicarboxylic acid moiety did not noticeably affect polymer solubility.

X-ray diffraction confirmed that all polyamides were amorphous. One factor contributing to the enhanced solubility was the characteristic amorphous nature, caused in part by the introduction of the cyclohexylidene cardo group and flexible ether linkage. Strong, transparent films could be easily obtained from DMAc solutions of these polymers. The mechanical properties of these polyamide films, shown in Table I, are good and

Scheme 4. Synthesis of polyamides **IXa–i**.

Table I. Inherent Viscosities, Solubility Behavior, and Tensile Properties of Polyamides

Polymer Code	η_{inh}[a] (dL/g)	Solubility[b]						Tensile Properties[c]		
		NMP	DMAc	DMF	DMSO	m-Cresol	THF	Tensile Strength (MPa)	Elongation to Break (%)	Tensile Modulus (GPa)
VII$_a$	0.75	+	+	+	+h	+h	−	85	9	2.4
VII$_b$	0.89	+	+	+	+	+	−	62	4	2.1
VII$_c$	1.78	+	+h	−	−	−	−	109	6	2.8
VII$_d$	1.61	+	+	+	+h	+h	s	90	9	2.1
VII$_e$	1.60	+	+	+	+h	s	s	81	10	2.0
VII$_f$	1.59	+	+	+	+h	+h	s	76	9	1.7
VII$_g$	1.43	+	+	+	+h	s	−	76	17	1.9
VII$_h$	1.31	+	+	+	+h	+h	+h	85	13	2.9
VII$_i$	0.72	+	+h	s	s	s	−	70	14	1.7
VII$_j$	0.80	+	+	+	+h	+h	s	75	11	1.7
VII$_k$	1.29	+	+	+h	s	s	s	74	12	1.9
VII$_l$	0.93	+	+	+	+h	s	+	77	11	2.0
VII$_m$	0.69	+	+	+	+h	+h	+	72	18	1.7
VII$_n$	0.79	+	+	+	+h	+	+	83	9	1.9
IX$_a$	1.04	+	+	+	+	+	−	79	16	1.8
IX$_b$	0.45	+	+	+	+	+	s	90	9	2.0
IX$_c$	1.01	+	+	s	−	−	−	81	14	1.9
IX$_d$	0.98	+	+	+	+h	+	s	93	16	1.9
IX$_e$	0.51	+	+	+	+h	+	−	83	7	2.0
IX$_f$	0.98	+	+	+	+	+	+	78	9	2.0
IX$_g$	0.71	+	+	+	+	+	+	86	11	1.7
IX$_h$	1.20	+	+	+	+	+	−	99	16	2.3
IX$_i$	0.88	+	+	+	+	+	−	100	8	2.3

[a] Measured in DMAc-5 wt % LiCl at 30°C on 0.5 g/dL.

[b] NMP, N-methyl-2-pyrrolidone; DMAc, N,N-dimethylacetamide; DMF, N,N-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran. +, soluble at room temperature; +h, soluble on heating; s, swelling; −, insoluble even on heating.

[c] 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.

do not indicate any clear dependence on the structure of diamine or the dicarboxylic acid.

The thermal properties of polyamides evaluated by DSC and TGA are summarized in Table II. Polyamides **VII**$_{a-n}$ showed T_g values of 180–214°C by DSC, following the decreasing order of segment flexibility of the diamine moiety. The lowest T_g of 180°C was observed for polyamide **VII**$_n$ derived from the multiring flexible diamine **VI**$_n$. No T_g values were observed for the polyamide (**VII**$_c$) of benzidine by DSC. Thus the DMA measurements were conducted for polyamide **VII**$_c$. The DMA curves indicated a clear T_g around 220°C for polymer **VII**$_c$. The T_g values for the **IX**$_{a-i}$ series were 195–243°C. The highest T_g, 243°C, was observed for polyamide **IX**$_c$ derived from 4,4′-biphenyldicarboxylic acid; the lowest T_g, 195°C, was observed for polyamide **IX**$_b$ derived for iso-

phthalic acid. A 24°C difference in T_g between polyamides **IX**$_b$ and **IX**$_e$ was observed as a result of an increased rotational barrier due to the *tert*-butyl group of diacid **VIII**$_e$. When the two sets of isomeric polyamides are compared, **IX**$_{a-d}$ displays a comparable T_g with the corresponding **VII**$_{a-d}$ by means of DSC, thus indicating that constitutional isomerism of the recurring unit did not significantly affect polymer rigidity.

In general, all polyamides exhibited good thermal stability, and the onset of decomposition occurred around 400°C in air and in nitrogen. Their 10% weight loss temperatures (T_d) were 453–502°C and 453–492°C in air and in nitrogen, respectively, which are reasonable values considering the aliphatic content of these polymers. It is worth mentioning that in almost all cases, the T_d values were higher in air than in nitrogen, possi-

Table II. Thermal Properties of Polyamides

Polymer	$T_g{}^a$ (°C)	$T_d{}^b$ (°C) In N_2	In Air	Char Yield^c (%)
VII$_a$	214	470	481	59
VII$_b$	188	472	490	46
VII$_c$	220^d	460	473	56
VII$_d$	209	485	494	53
VII$_e$	195	482	495	50
VII$_f$	206	483	488	48
VII$_g$	191	492	499	53
VII$_h$	199	467	478	36
VII$_i$	199	481	493	62
VII$_j$	199	486	495	50
VII$_k$	189	489	502	43
VII$_l$	196	489	498	51
VII$_m$	195	482	501	49
VII$_n$	180	466	486	41
IX$_a$	219	470	480	62
IX$_b$	195	483	492	59
IX$_c$	243 (364)^e	485	486	55
IX$_d$	202	474	488	59
IX$_e$	219	477	487	64
IX$_f$	221	463	473	51
IX$_g$	220	483	499	56
IX$_h$	215	469	481	58
IX$_i$	214	453	453	52

^{a} Baseline shifts in the second heating DSC traces, with a heating rate of 10°C/min.
^{b} Decomposition temperatures at which 10% weight loss was recorded by TGA at a heating rate of 20°C/min.
^{c} Residual weight (%) when heated to 800°C at a scan rate of 20°C/min in nitrogen.
^{d} Measured by DMA at a scan rate of 2°C/min.
^{e} Peak temperature of the endotherm observed on the first DSC heating trace.

bly due to oxidative crosslinking or an early weight-gained oxidation of the aliphatic segments when thermally degraded in air. Char yields at 800°C in nitrogen of the polyamides were in the range of 36–62%, with **VII**$_h$ having the lowest char yield, due to the presence of two less-stable isopropylidene linkages in its diamine moiety.

CONCLUSIONS

The effect of ether-linked cyclohexylidene cardo monomers on the properties of various aromatic polyamides has been demonstrated. Polymers in general showed a reasonable level of thermal stability and moderate T_g values, demonstrating good potential for moldability. Overall, internal plasticization through the incorporation of the cyclohexylidene unit was shown to be successful. The pendent alicyclic cardo chains influenced polyamide properties as desired by enhancing solubility and reducing the T_g.

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