Preparation and characterization of aromatic polyamides from 4,4′-(2,6-naphthylenedioxy)dibenzoic acid and aromatic diamines

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SUMMARY: A new aromatic dicarboxylic acid, 4,4′-(2,6-naphthylenedioxy)dibenzoic acid (**3**), was synthesized by the fluoro-displacement reaction of *p*-fluorobenzonitrile with 2,6-naphthalenediol in the presence of potassium carbonate, followed by alkaline hydrolysis. A series of aromatic polyamides having inherent viscosities of 1.30–2.19 dL/g were prepared by the triphenyl phosphite activated polycondensation from the diacid **3** with sixteen aromatic diamines. Most of the resulting polymers were noncrystalline and readily soluble in a variety of polar solvents such as *N,N*-dimethylacetamide (DMAc) and *N*-methyl-2-pyrrolidone (NMP). Except for those polymers derived from *p*-phenylenediamine, benzidine, and 4,4′-bis(*p*-aminophenoxy)biphenyl, transparent, tough, and flexible films were cast from the DMAc or NMP solutions. The films had tensile strengths ranging from 70 to 91 MPa, elongations at break from 6 to 50%, and initial moduli from 1.35 to 2.32 GPa. The polyamides exhibit glass transition temperatures in the range of 178–300 °C. Almost all polymers are stable up to 400 °C, with 10% weight loss being recorded above 500 °C, in air and nitrogen atmosphere.

Introduction

Wholly aromatic polyamides (aramids) are well accepted as thermally stable polymers with a favorable balance of physical and chemical properties[1, 2]. One of the problems is their poor processability caused by low solubility in organic solvents and high melting or softening temperatures. Therefore, considerable effort has been made to modify their chemical structure to improve the processing characteristics of the relatively intractable polymers. Introduction of flexibilizing groups as well as bulky groups into the polymer backbone, or attachment of bulky side groups, results in aramids soluble in organic solvents[3–6]. We also have already reported the synthesis of new aromatic polyamides and polyimides, soluble in organic solvents and having high glass transition temperatures, by the incorporation of biphenyl-2,2′-diyl or 1,1-binaphthyl-2,2′-diyl units having kinked, cranked and twisted non-coplanar structures into the polymer backbone[7–9]. Recently, in continuation of these studies, we became interested in the potential usefulness of naphthyl-containing structures as simultaneously bulky and symmetrical units in the polymer main chain. We have already reported that the aramids containing 1,5-, 1,4-, 2,7-, or 2,3-naphthylenedioxy units show improved solubility with retention of moderately high thermal stability[10–13]. In order to get more insight into the effect of different naphthalene catenation positions on properties of aramids, 4,4′-(2,6-naphthylenedioxy)dibenzoic acid was synthesized in the present study. The novel aromatic polyamides were prepared by direct polycondensation of the diacid with various aromatic diamines. The solubility, tensile properties, crystallinity, and thermal properties of the obtained polymers were also investigated.

Experimental part

Materials

2,6-Naphthalenediol (**1**) and *p*-fluorobenzonitrile (both from TCI) were used without previous purification. *p*-Phenylenediamine (**4a**) and *m*-phenylenediamine (**4b**) were purified by distillation under reduced pressure before use. The reagent-grade aromatic diamines such as benzidine (**4c**), 4,4′-oxydianiline (**4d**), 3,4′-oxydianiline (**4e**), 4,4′-methylenedianiline (**4f**), and 1,4-bis(*p*-aminophenoxy)benzene (**4g**) were used as received. *a,a*′-Bis(*p*-aminophenyl)-1,4-diisopropylbenzene (**4h**) and *a,a*′-bis(*p*-aminophenyl)-1,3-diisopropylbenzene (**4i**) were purified by recrystallization from ethanol. According to a reported method[14, 15], 4,4′-bis(*p*-aminophenoxy)biphenyl (**4j**), 4,4′-bis(*p*-aminophenoxy)-3,3′,5,5′-tetramethylbiphenyl (**4k**), 2,2-bis[*p*-(*p*-aminophenoxy)phenyl]propane (**4l**), 1,1-bis[*p*-(*p*-aminophenoxy)phenyl]-1-phenylethane (**4m**), 2,2-bis[*p*-(*p*-aminophenoxy)phenyl]hexafluoropropane (**4n**), bis[*p*-(*p*-aminophenoxy)phenyl] sulfone (**4o**), and *a,a*′-bis[*p*-(*p*-aminophenoxy)phenyl]-1,4-diisopropylbenzene (**4p**), were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenols and *p*-chloronitrobenzene in the presence of potassium carbonate, giving the dinitro compounds, and subsequent reduction using hydrazine as the reducing agent and palladium as the cata-

lyst. NMP and pyridine were purified by distillation under reduced pressure over calcium hydride. Anhydrous calcium chloride was dried in a vacuum oven at $180\,°C$ for 10 h. Triphenyl phosphite (TPP; from Fluka) was used as received.

4,4′-(2,6-Naphthylenedioxy)dibenzonitrile (2)

In a three-neck flask equipped with a nitrogen inlet, a Dean-Stark trap and a condensor, were placed 16.02 g (100 mmol) of 2,6-naphthalenediol and 27.64 g (200 mmol) of potassium carbonate with 100 mL of toluene and 200 mL of NMP. The mixture was heated with stirring at $140\,°C$ for 6 h under nitrogen to facilitate dehydration. After the toluene had been removed, the mixture was cooled and then 24.22 g (200 mmol) of p-fluorobenzonitrile was added. The reaction was carried out at $170\,°C$ for 10 h, and then the reaction mixture was allowed to cool and poured into 3 L of cold water. The product was filtrated and recrystallized from acetonitrile to afford 21.75 g (60% yield) of yellowish needles, m.p. 251–$252\,°C$ (by DSC).

IR (KBr): 2224 (C≡N), 1245, 1118 cm^{-1} (C—O).

EIMS: $m/z = 362$ (M$^+$, 100%), 260 (10%), 102 (10%).

^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 105.36$ (C^9), 116.24 (C^2), 117.77 (C^7), 118.12 (C≡N), 120.81 (C^5), 129.50 (C^3), 131.14 (C^4), 133.87 (C^8), 151.73 (C^6), 160.84 (C^1) (shown in Fig. 1).

Crystal data: C$_{24}$H$_{14}$N$_2$O$_2$, pale-yellow crystal, $0.25 \times 0.50 \times 0.50$ mm, monoclinic $P2_1/c$ with $a = 9.282(4)$ Å, $b = 8.189(3)$ Å, $c = 12.145(8)$ Å, $\beta = 96.75(4)$ with $D_c = 1.313$ g/mL for $Z = 2$, $V = 916.8(8)$ Å^3, $T = 25\,°C$, λ (Cu-K_a) = 1.5418 Å, $\mu = 6.429$ cm^{-1}, $R_w = 0.077$ for 1300 observed reflections.

C$_{24}$H$_{14}$N$_2$O$_2$(362.38) Calc. C 79.54 H 3.89 N 7.73
                                      Found C 79.26 H 4.09 N 7.66

4,4′-(2,6-Naphthylenedioxy)dibenzoic acid (3)

4,4′-(2,6-Naphthylenedioxy)dibenzoic acid (3) was synthesized by the hydrolysis of dinitrile compound 2. The procedure was modified from the method of Heath and Wirth[16]. A mixture of 45.0 g of potassium hydroxide and 20.0 g of dinitrile compound 2 in 250 mL of ethanol and 250 mL of distilled water was stirred at ca. $100\,°C$ under nitrogen atmosphere until no further ammonia was generated. The solution was cooled, and the pH value was adjusted by hydrochloric acid to near 3. The white precipitate formed was collected by filtration and dried in vacuum. The yield was 100% of white powder without further purification, m.p. 352–$353\,°C$ (by DSC).

IR (KBr): 1680 cm^{-1} (C=O).

EMIS: $m/z = 400$ (M$^+$, 100%), 65 (15%).

^{13}C NMR (100 MHz, DMSO-d_6): $\delta = 116.07$ (C^2), 117.43 (C^7), 121.25 (C^5), 125.45 (C^9), 129.90 (C^3), 131.31 (C^4), 131.76 (C^8), 152.54 (C^6), 161.06 (C^1), 166.80 (carbonyl carbon) (shown in Fig. 1).

C$_{24}$H$_{16}$O$_6$ (400.39) Calc. C 71.99 H 4.02
                                  Found C 71.25 H 3.97

Polymer synthesis

A typical example of polycondensation is as follows: A mixture of 0.25 g (1.25 mmol) of diamine 4d, 0.50 g (1.25 mmol) of diacid 3, 0.5 g of calcium chloride, 8 mL of NMP, 1 mL of pyridine, and 0.9 mL of triphenyl phosphite was heated at $100\,°C$ for 3 h. The reaction mixture was slowly poured into 300 mL of methanol. The precipitated fiber-like polymer was collected by filtration, washed thoroughly with hot methanol, and dried at $100\,°C$ in vacuum. The yield was quantitative. The inherent viscosity of the polymer was 2.19 dL/g, measured at a concentration of 0.5 g/dL in DMAc containing 5 wt.-% LiCl at $30\,°C$.

IR (film): 3306 (N—H), 1653 (C=O), 1400–1600 (arom. C=C), 1250 cm^{-1} (C—O).

All other polymers were synthesized analogously.

Preparation of polyamide films

A solution of polymer was made by dissloving about 0.8 g of the polymer in 8 mL of hot DMAc or NMP 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 $80\,°C$ oven overnight to remove the solvent. The semi-dried polyamide film was stripped off from the glass surface and further dried in vacuum at $150\,°C$ for 6 h. The obtained films showed about 0.1 mm thickness and were ready for X-ray diffraction measurements and tensile tests.

Measurements

Infrared spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. Elemental analyses were run in a Perkin-Elmer model 2400 C, H, N analyzer. ^{13}C NMR spectra were measured on a Jeol EX-400 Fourier transform nuclear magnetic resonance spectrometer with perdeuterodimethyl sulfoxide (DMSO-d_6) as an external reference, working at 100 MHz. The X-ray crystallographic data were collected on a CAD-4 diffractometer. MS spectra were obtained by using a Jeol JMS-D300 mass spectrometer. The inherent viscosities were determined at 0.5 g/dL concentration using a Cannon-Fenske viscometer. Thermogravimetric analysis was conducted with a Rigaku thermoflex TG 8110 coupled to a Rigaku TAS-100 thermal analysis station. Measurements were carried out on 10 ± 2 mg samples heated in flowing nitrogen or air (50 cm^3/min) at a heating rate of $20\,°C$/min. Differential scanning calorimetry (DSC) analyses were performed on a Sinku Riko DSC-7000 differential scanning calorimeter coupled to a Sinku Riko TA-7000 thermal analysis controller in flowing nitrogen (30 cm^3/min) at a heating rate of $20\,°C$/min. Wide-angle X-ray diffractograms were obtained on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu-K_a radiation (40 kV, 15 mA), and the scanning rate was $2\,°$/min. Measurements were performed with film specimens of about 0.1 mm in thickness or powder. An Instron Universal Tester Model 1130 with a load cell 5 kg was used to study the stress-strain behavior of the samples at a drawing speed of 5 cm/min. Measurements were performed at room temperature (ca. $20\,°C$) with film specimens (0.5 cm wide, 6 cm long, and

about 0.1 mm thick), and an average of at least individual determinations was used.

Results and discussion

Monomer synthesis

The naphthalene unit-containing new polymer-forming dicarboxylic acid, 4,4′-(2,6-naphthylenedioxy)dibenzoic acid (3), was successfully synthesized from 2,6-naphthalenediol (1) and p-fluorobenzonitrile as starting materials by the nucleophilic fluoro-displacement reaction followed by alkaline hydrolysis according to the synthetic route shown in Scheme 1. The chemical structures of all synthesized compounds were confirmed by means of ele-
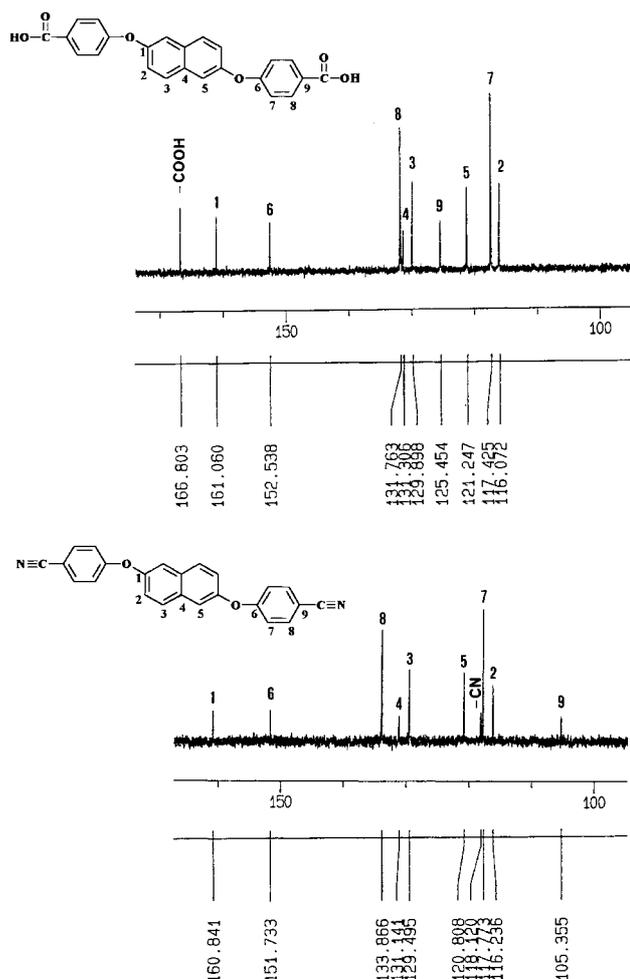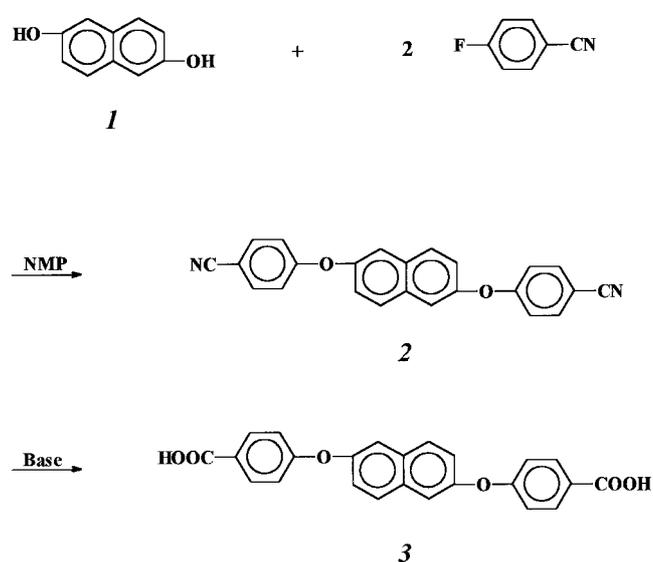
Scheme 1:

mental analysis, the characteristic peaks in the NMR spectra, and the characteristic absorption bands in the IR spectroscopic techniques. Concerning the synthesis of diacid 3, the disappearance of characteristic cyano stretching bands at around 2228 cm^{-1} on the IR spectra revealed completion of the hydrolysis of dicyano compound 2. The elemental analyses of all of these com-

pounds were also in good agreement with the calculated values for the proposed structures. According to the basis of the shielding effect of carbon the positions of chemical shifts for carbons were readily assigned from ^{13}C NMR experiments of compounds 2 and 3, as shown in Fig. 1. The ^{13}C NMR spectra of 2 and 3 exhibited exactly 10 peaks due to symmetry and were consistent with the cal-

Fig. 1. ^{13}C NMR spectra of 4,4′-(2,6-naphthylenedioxy)dibenzonitrile in CDCl$_3$ and 4,4′-(2,6-naphthylenedioxy)dibenzoic acid in DMSO-d_6
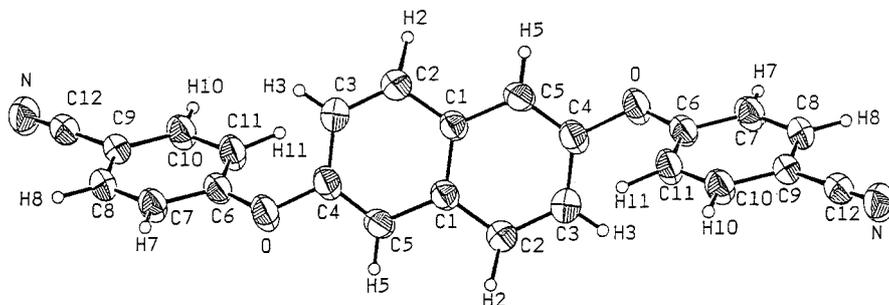

Fig. 2.   X-ray crystal structure of 4,4′-(2,6-naphthylenedioxy)dibenzonitrile

Tab. 1. Selected bond distances (in Å) and bond angles (in degree) of dinitrile 2[a]

O-C4	1.388(5)[b]	C5-H5	0.900(4)
O-C6	1.377(5)	C6-C7	1.391(6)
N-C12	1.138(7)	C6-C11	1.366(7)
C1-C1	1.408(8)	C7-C8	1.370(7)
C1-C2	1.422(6)	C7-H7	0.910(4)
C1-C5	1.420(6)	C8-C9	1.377(7)
C2-C1	1.422(6)	C8-H8	0.990(4)
C2-C3	1.376(6)	C9-C10	1.396(6)
C2-H2	1.120(6)	C9-C12	1.452(7)
C3-C4	1.382(7)	C10-C11	1.390(7)
C3-H3	0.900(5)	C10-H10	1.030(4)
C4-C5	1.353(7)	C11-H11	1.050(4)
C4-O-C6	118.7(3)	C7-C6-C11	120.8(4)
C1-C1-C2	119.0(4)	C6-C7-C8	119.4(4)
C1-C1-C5	119.8(4)	C6-C7-H7	118.4(22)
C2-C1-C5	121.2(4)	C8-C7-H7	122.1(22)
C1-C2-C3	119.0(4)	C7-C8-C9	120.3(4)
C1-C2-H2	106.0(3)	C7-C8-H8	116.4(24)
C3-C2-H2	119.0(3)	C9-C8-H8	123.3(24)
C2-C3-C4	121.2(4)	C8-C9-C10	120.6(4)
C2-C3-H3	120.0(3)	C8-C9-C12	120.9(4)
C4-C3-H3	118.0(3)	C10-C9-C12	118.4(4)
O-C4-C3	120.3(4)	C9-C10-C11	118.5(4)
O-C4-C5	117.9(4)	C9-C10-H10	121.3(21)
C3-C4-C5	121.6(4)	C11-C10-H10	120.1(21)
C1-C5-C4	119.3(4)	C6-C11-C10	120.3(4)
C1-C5-H5	118.9(23)	C6-C11-H11	124.0(3)
C4-C5-H5	121.7(23)	C10-C11-H11	114.0(3)
O-C6-C7	115.3(4)	N-C12-C9	178.1(6)
O-C6-C11	123.8(4)		

[a] The atom labeling used here is the same as in Fig. 2.
[b] Estimated standard deviations in the least significant figure are given in parentheses.

culated values. The structure of 2 was also confirmed by X-ray diffraction analysis. X-ray crystal data (shown in Tab. 1) for 2 were acquired from a single crystal, as obtained by slow crystallization of an acetonitrile solution of 2. The structure of 2 exhibits symmetrical and bulky molecular characteristics (Fig. 2). The complete X-ray structure determinations are available as supporting information.

Polymer synthesis

The direct polycondensation of aromatic diamines with dicarboxylic acids using a mixture of triphenyl phosphite and pyridine as condensing agent is a convenient method for the preparation of polyamides on a laboratory scale[17–20]. A series of new aramids (5a–p) were prepared from the diacid (3) and various aromatic diamines (4a–p) by this direct polycondensation technique (Scheme 2). The reaction conditions and the results are summarized in Tab. 2. The solubility of the polymer in the reaction medium and the state of stirring affected the inherent viscosity of the resulting aramids significantly. In general, the

molecular weight of the polymers obtained from the phosphorylation reaction is highly dependent on the reactant concentration. Higher molecular weights of these polymers could be obtained by using a higher initial reactant concentration and then adding a proper amount of supplemental NMP into the viscous reaction medium before the formation of swollen gel. According to the reaction conditions listed in Tab. 2, this series of polyamides generally remained soluble in the reaction medium during the polymerization, except those prepared from benzidine (4c) and 4,4′-bis(p-aminophenoxy)biphenyl (4j). Aramids 5a–p were successfully obtained in almost quantitative yields with inherent viscosities of 1.30–2.19 dL/g (as measured in DMAc containing 5 wt.-% LiCl dissolved). Aramids 5c and 5j were insoluble in all the available organic solvents but were soluble in concentrated sulfuric acid. As shown in Tab. 2, in many cases the inherent viscosity values of these aramids measured in sulfuric acid were comparable to or slightly lower than those measured in DMAc-5 wt.-% LiCl. However, it is worth noting that sulfuric acid dissolved but simultaneously degraded polyamides 5h, 5i, 5l, 5m, and 5p. These five polyamides with inherent viscosities of 1.30–1.71 in DMAc-5 wt.-% LiCl when dissolved in concentrated sulfuric acid had inherent viscosities ranging from 0.06 to 0.28. The degradation of these polymers is likely to be related to the presence of isopropylidene (—C(CH$_3$)$_2$—) or phenylethylidene (—C(C$_6$H$_5$)(CH$_3$)—) linkages between phenylene units along the macromolecular backbone.

The structures of these polyamides were confirmed by IR spectroscopy. The characteristic absorptions of the amide group were observed at 3340–3350 (N—H) and 1650–1660 cm^{-1} (C=O), and that of aryl ether stretching appeared near 1250 cm^{-1}.

Polymer characterization

The solubility behavior of these aramids was qualitatively tested in various solvents. All the polyamides except polymers 5a, 5c and 5j were highly soluble in polar solvents such as DMAc, NMP, and m-cresol. The polyamides obtained from flexibilizing group-linked "multiring" diamines such as 4l–p dissolved even in less polar solvents like tetrahydrofuran (THF). Polymers 5a, 5c and 5j had poor solubility due to their symmetrical and rigid p-phenylene or biphenylylene diamine components. X-ray diffraction results, as discussed below, revealed that polymers 5a, 5c and 5j had higher crystallization tendency than the other polyamides. The solubility behavior was consistent with the results of X-ray diffraction studies. Thus, the solubility of aramids was significantly improved by the introduction of the bulky and symmetrical 2,6-naphthyl unit into the polymer backbone.

Scheme 2:
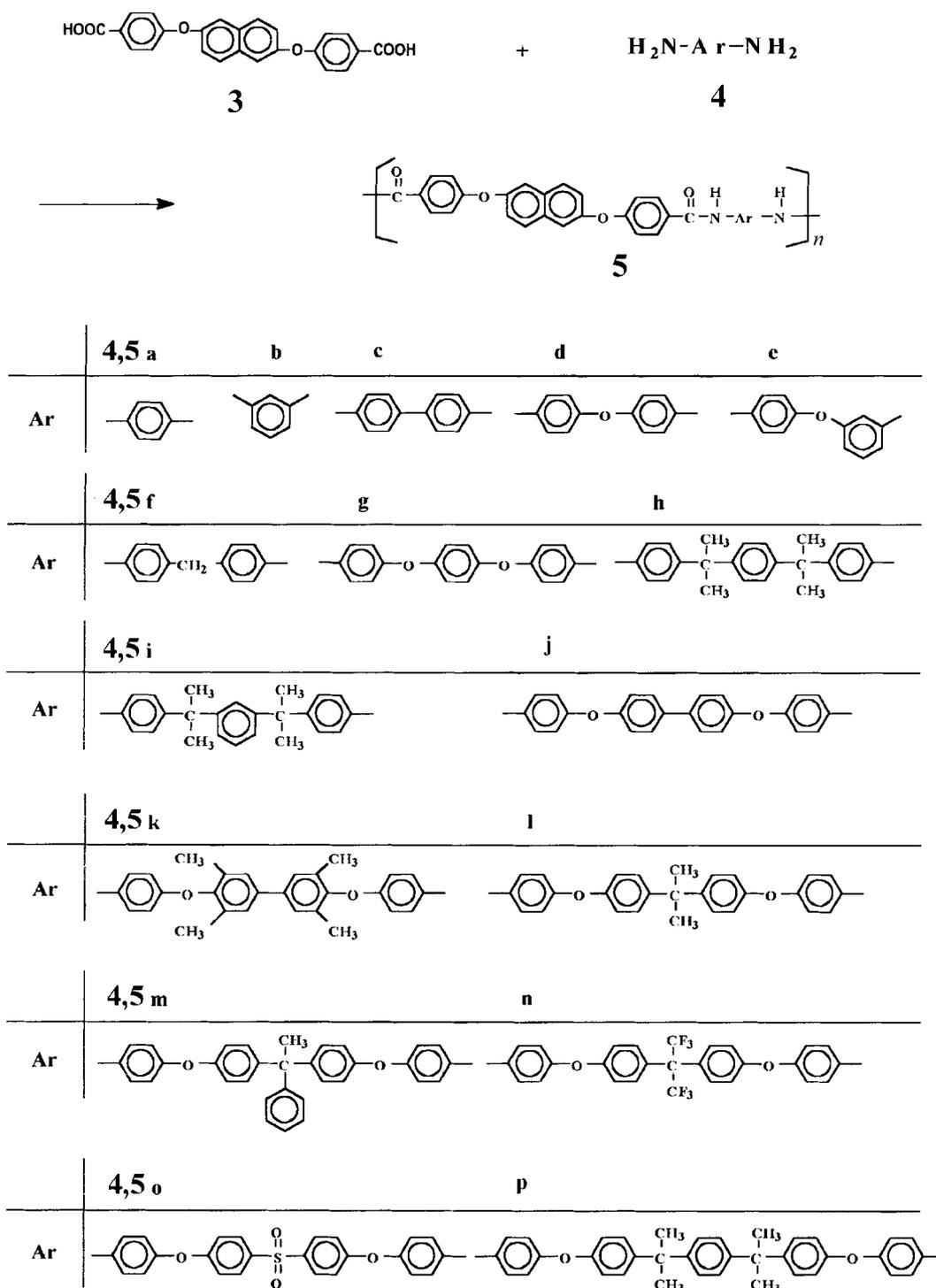
As-prepared powders and films were structurally characterized by X-ray diffraction studies. Typical diffraction patterns for some representative polyamides are reproduced in Fig. 3. The results revealed that polyamides **5a**, **5c** and **5j** had a fair degree of crystallinity, whereas all of the other polymers were completely amorphous. Thus, the amorphous nature of these polymers was reflected in their excellent solubility, and this could be attributed in part to the introduction of the crank shaft-like 2,6-naphthyl unit and the flexible ether group along the polymer backbone.

The mechanical properties of the solution cast films of the polyamides from DMAc solutions are given in Tab. 3. The tensile strength, elongation at break, and tensile mod-

Tab. 2. Synthesis conditions and inherent viscosities of polyamides

Polymer code	Amount of reagents used[a]			η_{inh}[d] in dL/g	
	NMP in mL	pyridine in mL	CaCl$_2$ in g	in DMAc-5% LiCl	in conc. H$_2$SO$_4$
5a	10	2.5	0.6 (+ 0.6 g LiCl)	1.43	1.34
5b	5	1.3	0.6	1.30	1.27
5c	10 + 5[b]	2.5	0.9	–[e]	0.64
5d	4 + 4[c]	1.0	0.5	2.19	1.80
5e	4	1.0	0.5	1.50	0.73
5f	4 + 2[c]	1.0	0.5	1.47	1.22
5g	5 + 2[c]	1.3	0.6	1.56	1.43
5h	5	1.3	0.6	1.30	0.07
5i	4	1.0	0.5	1.45	0.28
5j	5 + 15[b]	1.3	0.6 (+ 0.5 g LiCl)	–[e]	1.34
5k	8	1.8	0.9	1.65	1.50
5l	5	1.3	0.6	1.64	0.06
5m	5 + 2[c]	1.3	0.6	1.39	0.10
5n	5 + 4[c]	1.3	0.6	1.72	1.71
5o	5 + 2[c]	1.3	0.6	1.39	1.53
5p	5 + 4[c]	1.3	0.6	1.71	0.06

[a] The polymerization was carried out with 1.25 mmol of each monomer, 2.5 mmol (about 0.9 mL) of triphenyl phosphite, and the amount of reagents used as indicated.
[b] The polymer precipitated during the reaction and could not be redissolved by further addition of NMP.
[c] An initial amount of NMP was used, and an additional amount was supplemented when the reaction medium was too viscous to stir.
[d] Measured on a concentration of 0.5g/dL at 30 °C.
[e] Insoluble.

Tab. 3. Tensile and thermal properties of polyamides

Polymer	Tensile properties of polymer films[a]			T_g[b]/°C	T_d[d]/°C		Char yield[e] in %
	tensile strength in MPa	elongation at break in %	tensile modulus in GPa		in air	in N$_2$	
5a	–	–	–	222 (465)[c]	487	506	52.8
5b	91	6	2.23	218 (364)	505	510	64.4
5c	–	–	–	295	493	526	64.5
5d	–	–	–	230	510	508	65.0
5e	88	9	2.30	195	522	533	68.1
5f	90	28	2.16	247	513	519	66.6
5g	–	–	–	222 (423)	512	512	61.5
5h	80	8	2.32	205	459	451	55.7
5i	77	6	1.83	178	495	493	55.8
5j	–	–	–	265 (438)	494	521	56.0
5k	83	50	1.63	300	500	500	69.0
5l	74	11	1.83	216	520	519	64.4
5m	74	17	1.35	208	517	515	68.7
5n	70	21	1.75	203	520	529	58.4
5o	72	16	1.78	235	511	516	63.2
5p	82	10	1.93	197	518	520	62.0

[a] Films were cast from slow evaporation of polymer solutions in DMAc.
[b] Temperatures at the midpoint of baseline shift on the second heating DSC traces, with a heating rate of 20 °C/min.
[c] Values in parentheses are the peak temperatures of melting endotherms on the first heating DSC traces before 480 °C.
[d] Decomposition temperature at which 10% weight loss was recorded by thermogravimetry conducted at a heating rate of 20 °C/min.
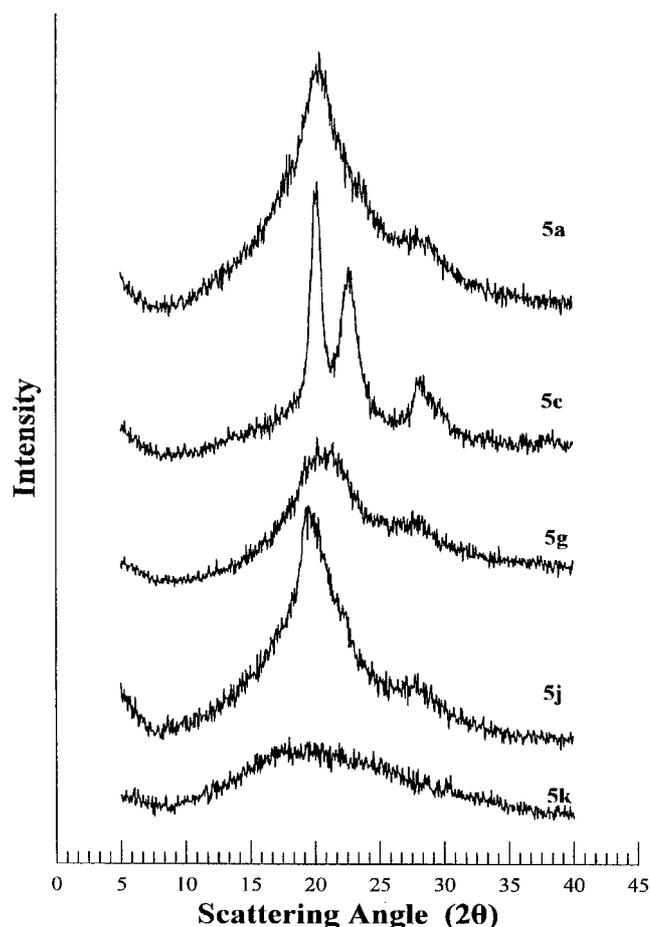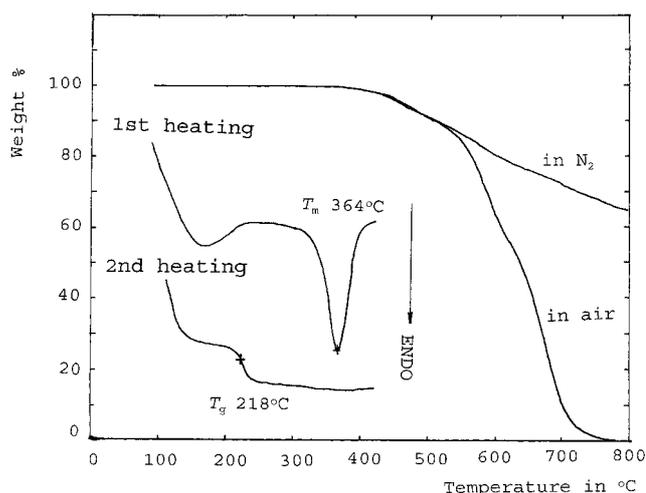[e] Residual weight in % at 800 °C in nitrogen.

Fig. 3. Wide-angle X-ray diffractograms of some polyamides

Fig. 4. DSC and TG thermograms of polyamide **5b**, at a heating rate of 20 °C/min

Tab. 4. Glass transition temperatures of isomeric polyamides

-Ar-	$T_g{}^{a)}$ in °C of polyamides having various naphthalene catenation positions				
	2,6	1,5	2,7	1,4	2,3
(benzene)	218	234	168	224	221
–⬡–O–⬡–	230	230	–	240	231
–⬡–O–(naphthalene)	195	227	164	233	183
–⬡–CH₂–⬡–	247	237	–	220	202
(naphthalene)–O–⬡–O–⬡–	222	235	191	220	213

a) The samples were first heated to 400 °C at a heating rate of 20 °C/min in nitrogen, and subsequently quenched to room temperature. T_g was read at the middle of the baseline shift on the second DSC heating trace.

ulus of polymer **5** films were in the ranges 70 to 91 MPa, 6–50% and 1.35 to 2.32 GPa, respectively.

The thermal behavior of the polymers was evaluated by means of DSC and TG. Fig. 4 shows typical DSC and TG curves of a representative polyamide **5b**, and the thermal behavior data of all the polymers are summarized in Tab. 3. The influence of residual water or solvent and history of thermal annealing are sometimes observed in the first heating scanning of DSC. Quenching from elevated temperatures to room temperature yields predominantly amorphous samples so that discernible baseline shifts could be easily measured in the DSC charts of the second heating trace. The glass transition temperatures (T_g), defined by the midpoint of the baseline shift, of polymers **5a–p** were observed in the range of 195–300 °C, depending on the structure of the diamine component, and decreased with decreasing rigidity and symmetry of the polymer backbone (Tab. 3). Some of the polyamides showed a medium broad endotherm in their first DSC heating traces. However, in all cases rapid cooling and reheating showed a strong T_g and disappearance of the melting transition, and this may indicate a low crystallization rate.

The T_g data of some isomeric polyamides with different naphthalene catenation positions are shown in Tab. 4. There is no clear dependence on the isomeric attachment in the naphthalene unit, but it is possible to recognize some trends. For example, the T_g values are higher for the more symmetric systems. Generally speaking the T_g values of the 2,6 polymers are similar to those of 1,5 polymers and are higher than those of 2,7 polymers, and those of 1,4 polymers are higher than of 2,3 polymers.

The thermal stability of the polyamides **5** was studied by thermogravimetric analysis (TG). Typical TG curves in both air and nitrogen atmospheres of representative polymer **5b** are illustrated Fig. 4. The temperatures of

10% weight loss in nitrogen and air atmosphere were determined from original thermograms and tabulated in Tab. 3. In general, all the polymers exhibit good thermal stability with no significant weight loss up to temperatures of approximately 400 °C in both air and nitrogen atmospheres, and the temperatures at 10% weight loss were above 500 °C on the TG curves. The amount of carbonized residue (char yield) of polyamides in nitrogen atmosphere was in the range of 50–70 wt.-% even at 800 °C, showing high intrinsic fire resistance.

Conclusions

New soluble aromatic polyamides containing 2,6-naphthyl units were successfully synthesized by the direct polycondensation of 4,4-(2,6-naphthylenedioxy)dibenzoic acid and various aromatic diamines using triphenyl phosphite and pyridine as condensing agent. Thus polyamides having high molecular weight up to inherent viscosities 2.19 dL/g were obtained. The polymers with bulky and symmetrical 2,6-naphthyl units and flexible ether linkages in the polyamide backbone showed excellent solubility in various organic solvents, good thermal stability, and could be cast into transparent, tough, and flexible films. Thus, these aramids are considered to be promising soluble high-performance polymeric materials.

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