

Synthesis and properties of *ortho*-linked polyamides based on a bis(ether-carboxylic acid) or a bis(ether amine) derived from 4-*tert*-butylcatechol

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Abstract

4-*tert*-Butyl-1,2-bis(4-carboxyphenoxy)benzene (**2a**) and 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**2b**) were synthesized through the aromatic nucleophilic substitution reaction of 4-*tert*-butylcatechol with *p*-fluorobenzonitrile or *p*-chloronitrobenzene in the presence of potassium carbonate in *N,N*-dimethylformamide. Two series of polyamides with flexible main-chain ether linkages and *ortho*-phenylene units were prepared from dicarboxylic acid **2a** with various aromatic diamines or from diamine **2b** with various aromatic dicarboxylic acids via the phosphorylation reaction with triphenyl phosphite and pyridine. The inherent viscosities of these new polyamides were in the range of 0.52–2.60 dl g⁻¹. Almost all the polyamides were noncrystalline and readily soluble in a variety of polar solvents and afforded transparent, flexible and tough films by solution casting. They have useful levels of thermal stability, associated with relatively high glass transition temperatures (most > 200°C) and 10% weight loss temperatures in excess of 480°C in nitrogen or in air. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: *Ortho*-linked; Polyamide; 4-*tert*-Butylcatechol

1. Introduction

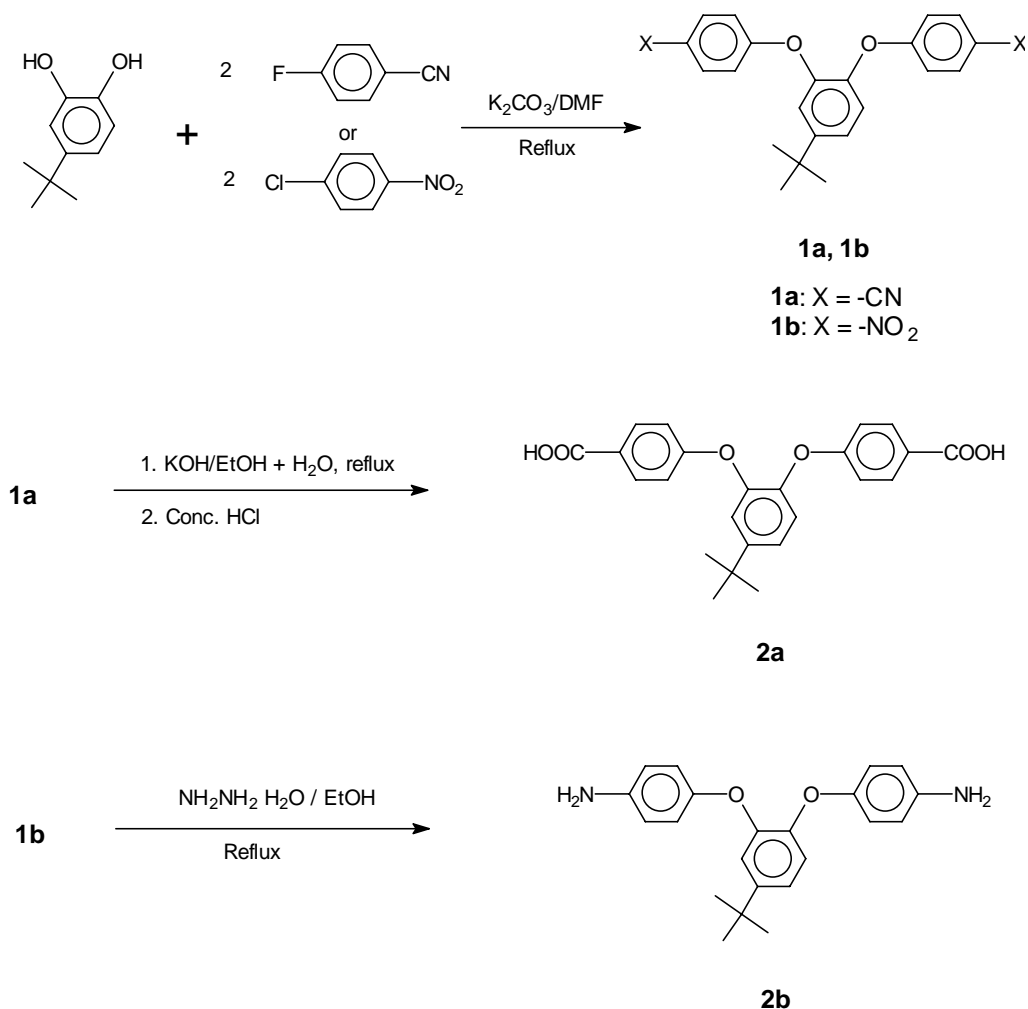
Rigid-rod aromatic polyamides (aramids), such as poly(*p*-phenyleneterephthalamide) and poly(*p*-benzamide), have already reported for their high temperature resistance and excellent mechanical strength, giving easily lyotropic solutions [1–5]. Fibers obtained from anisotropic solutions of these materials have been used in applications where high thermal stability and mechanical strength are required [6]. Their relatively high stiffness favors high melting temperatures and limited solubility, which restrict synthesis and applications especially of high molecular weight materials. Therefore, the interest was focused on the preparation of aramids with improved processability either by introducing flexible linkages [7–9] or bulky groups [10–15] in the main chain or by attachment of pendant alicyclic groups [16–21]. These modifications lower the melting temperature and lead to soluble and amorphous polymers. In general, amorphous polyamides have lower softening temperature and improved solubility compared to crystalline analogues, thus they may

open applications in the area of films, coatings, engineering plastics, polymer blends, and composites.

An alternative to improve the tractability of aramids is the incorporation of less symmetric units such as *meta*- or *ortho*-catenated aromatic rings in the polymer backbone [22–27]. There are many polyamides with *ortho*-linked main-chain units derived from 1,2-bis(4-carboxyphenoxy)benzene, 2,3-bis(4-carboxyphenoxy)naphthalene, 1,2-bis(4-aminophenoxy)benzene, and 2,3-bis(4-aminophenoxy)naphthalene have been prepared in this laboratory [24–27]. We found that *ortho*-linked polyamides are far more processable than their *para*- or *meta*-linked analogues. Properties are slightly inferior to but comparable with their *para*- or *meta*-linked analogues. However, we also discovered that some polyamides derived from more rigid monomers like terephthalic acid and *p*-phenylenediamine were crystalline and insoluble in organic solvents, even though they had *ortho*-linked main chain structure. Several previous articles have demonstrated that introducing a *tert*-butyl substituted monomer into the polymer backbone improved solubility and processability without an unacceptable loss of thermal properties in many polymer systems such as polyarylates [28], polyamides [29–33], polyimides [31,34], and poly(amide-imide)s [35,36]. Recently, we

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Scheme 1.

have demonstrated that the combination of *ortho*-phenylene units and the bulky *tert*-butyl group could further improve processability in polyimides [37]. We have now investigated the possibility of transferring the improved processability achieved in polyimides to aramids. We used the bis(ether-carboxylic acid) **2a** and bis(ether amine) **2b** extended from 4-*tert*-butylcatechol in the synthesis of new poly(ether amide)s and now report their basic properties. It was hoped that incorporation of bulky *tert*-butyl group would further decrease hydrogen bonding and intermolecular interactions between polyamide chains and reduce packing efficiency and crystallinity. This should promote solubility while maintaining high T_g through controlled segmental mobility. The introduction of pendant *tert*-butyl group may be more advantageous than the attachment of pendant alicyclic cardo groups [16–21] because it minimizes and even avoids the weakening of inherent thermal and mechanical properties of the polyamides. In addition, the *tert*-butyl substituted polyamides were also expected to exhibit higher thermo-oxidative stability

than the polyamides with other alkyl substituents such as methyl group [31] because of the lack of benzylic hydrogens.

2. Experimental

2.1. Materials

4-*tert*-Butylcatechol (Acros), *p*-fluorobenzonitrile (TCI), *p*-chloronitrobenzene (TCI), potassium carbonate (Wako), hydrazine monohydrate (Acros), 10% palladium on activated carbon (Pd/C) (Fluka) were used as-received. *p*-Phenylenediamine (**3a**) and benzidine (**3c**) were purified by vacuum sublimation. *m*-Phenylenediamine (**3b**) was purified by vacuum distillation. The other reagent-grade diamines such as 4,4'-oxydianiline (**3d**) (TCI), 1,4-bis(*p*-aminophenoxy)benzene (**3e**) (TCI), and 1,3-bis(4-aminophenoxy)benzene (**3f**) (TCI) were used as received. According to a well-developed procedure [38],

Table 1
Bond lengths (Å) and bond angles (°) for dinitrile **1a** (the atom labeling used here is the same as in Fig. 1)

O1–C1	1.404(5)	C8–C9	1.374(7)
O1–C7	1.377(5)	C9–C10	1.369(7)
O2–C6	1.386(5)	C10–C11	1.439(7)
O2–C14	1.365(6)	C10–C12	1.382(6)
N1–C11	1.134(7)	C12–C13	1.381(6)
N2–C18	1.136(8)	C14–C15	1.371(7)
C1–C2	1.363(7)	C14–C20	1.388(6)
C1–C6	1.369(6)	C15–C16	1.365(8)
C2–C3	1.381(7)	C16–C17	1.390(8)
C3–C4	1.379(6)	C17–C18	1.431(8)
C4–C5	1.396(6)	C17–C19	1.378(7)
C4–C21	1.534(6)	C19–C20	1.372(7)
C5–C6	1.385(6)	C21–C22	1.415(9)
C7–C8	1.382(6)	C21–C23	1.547(10)
C7–C13	1.364(7)	C21–C24	1.460(9)
C1–O1–C7	117.3(3)	C11–C10–C12	119.5(5)
C6–O2–C14	120.5(3)	N1–C11–C10	178.6(6)
O1–C1–C2	120.5(4)	C10–C12–C13	119.9(4)
O1–C1–C6	119.0(4)	C7–C13–C12	119.5(4)
C2–C1–C6	120.5(4)	O2–C14–C15	116.3(4)
C1–C2–C3	119.8(4)	O2–C14–C20	123.1(4)
C2–C3–C4	121.5(4)	C15–C14–C20	120.5(4)
C3–C4–C5	117.6(4)	C14–C15–C16	120.1(4)
C3–C4–C21	122.5(4)	C15–C16–C17	120.3(4)
C5–C4–C21	119.9(4)	C16–C17–C18	119.9(5)
C4–C5–C6	120.8(4)	C16–C17–C19	119.0(4)
O2–C6–C1	118.0(4)	C18–C17–C19	121.0(5)
O2–C6–C5	122.1(4)	N2–C18–C17	178.0(6)
C1–C6–C5	119.8(4)	C17–C19–C20	121.1(4)
O1–C7–C8	115.8(4)	C14–C20–C19	118.9(4)
O1–C7–C13	123.3(4)	C4–C21–C22	114.0(5)
C8–C7–C13	120.9(4)	C4–C21–C23	107.3(4)
C7–C8–C9	119.2(4)	C4–C21–C24	112.3(4)
C8–C9–C10	120.6(4)	C22–C21–C23	107.3(8)
C9–C10–C11	120.6(4)	C22–C21–C24	113.3(7)
C9–C10–C12	119.8(4)	C23–C21–C24	101.6(6)

1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**2a**) (m.p. 130–131°C, lit. [39] 131–132°C), 4,4'-bis(*p*-aminophenoxy)-biphenyl (**3g**) (m.p. 198–199°C) and bis[4-(4-aminophenoxy)phenyl] ether (**3h**) (m.p. 128–129°C) were prepared by the aromatic nucleophilic substitution reaction of the corresponding bisphenol precursors and *p*-chloronitrobenzene in the presence of potassium carbonate and subsequent reduction of the intermediate bis(*p*-nitrophenoxy) compounds using hydrazine monohydrate as the reducing agent and Pd/C as the catalyst. Aromatic dicarboxylic acids such as terephthalic acid (**5a**) (Fluka), isophthalic acid (**5b**) (Fluka), 4,4'-biphenyldicarboxylic acid (**5c**) (TCI), 4,4'-oxydibenzoic acid (**5d**) (TCI), 5-*tert*-butylisophthalic acid (**5e**) (Aldrich), 2,2-bis(4-carboxyphenyl)-1,1,1,3,3,3-hexafluoropropane (**5f**) (Chriskev), 4,4'-sulfonyldibenzoic acid (**5g**) (New Japan Chemical Co.), 2,6-naphthalenedicarboxylic acid (**5h**) (TCI), and 1,4-naphthalenedicarboxylic acid (**5i**) (TCI) were used without further purification. *N,N*-Dimethylformamide (DMF) (Fluka), *N*-methyl-2-pyrrolidone (NMP) (Fluka),

Table 2
Bond lengths (Å) and bond angles (°) for diamine **2b** (the atom labeling used here is the same as in Fig. 1)

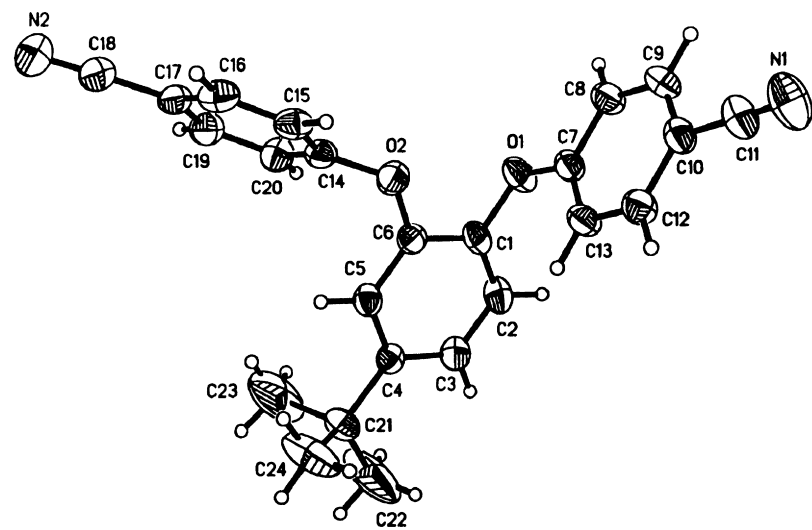
O1–C1	1.378(3)	O1–C7	1.398(3)
O2–C6	1.385(3)	O2–C13	1.405(3)
N1–C10	1.403(3)	N2–C16	1.398(3)
C1–C2	1.374(3)	C1–C6	1.389(3)
C2–C3	1.396(3)	C3–C4	1.383(4)
C3–C19	1.523(4)	C4–C5	1.380(4)
C5–C6	1.368(4)	C7–C8	1.366(3)
C7–C12	1.376(3)	C8–C9	1.374(3)
C9–C10	1.378(3)	C10–C11	1.385(3)
C11–C12	1.385(3)	C13–C14	1.356(3)
C13–C18	1.366(4)	C14–C15	1.387(3)
C15–C16	1.374(4)	C16–C17	1.381(4)
C17–C18	1.382(4)	C19–C21	1.507(4)
C19–C20	1.522(4)	C19–C22	1.533(4)
C1–O1–C7	120.6(2)	C6–O2–C13	115.8(2)
C2–O1–O1	124.7(2)	C2–C1–C6	119.6(2)
O1–C1–C6	115.5(2)	C1–C2–C3	122.5(2)
C4–C3–C2	116.4(2)	C4–C3–C19	122.1(2)
C2–C3–C19	121.4(2)	C5–C4–C3	121.6(3)
C6–C5–C4	121.1(3)	C5–C6–O2	122.5(2)
C5–C6–C1	118.8(2)	O2–C6–C1	118.7(2)
C8–C7–C12	120.3(2)	C8–C7–O1	117.1(2)
C12–C7–O1	122.3(2)	C7–C8–C9	120.2(2)
C8–C9–C10	120.9(2)	C9–C10–C11	118.2(2)
C9–C10–N1	122.0(2)	C11–C10–N1	119.8(2)
C12–C11–C10	121.2(2)	C7–C12–C11	119.0(2)
C14–C13–C18	120.1(2)	C14–C13–O2	119.5(2)
C18–C13–O2	120.3(2)	C13–C14–C15	120.2(3)
C16–C15–C14	120.8(2)	C15–C16–C17	118.2(2)
C15–C16–N2	120.9(2)	C17–C16–N2	120.8(3)
C16–C17–C18	120.7(3)	C13–C18–C17	120.0(3)
C21–C19–C20	107.8(3)	C21–C19–C3	112.0(3)
C20–C19–C3	111.7(2)	C21–C19–C22	108.9(3)
C20–C19–C22	107.1(3)	C3–C19–C22	109.2(2)

N,N-dimethylacetamide (DMAc) (Fluka), and pyridine (Py) (Wako) were purified by distillation under reduced pressure over calcium hydride and stored over 4 Å molecular sieves. Triphenyl phosphite (TPP) (TCI) was purified by vacuum distillation. Commercially obtained calcium chloride (Wako) was dried under vacuum at 180°C for 10 h.

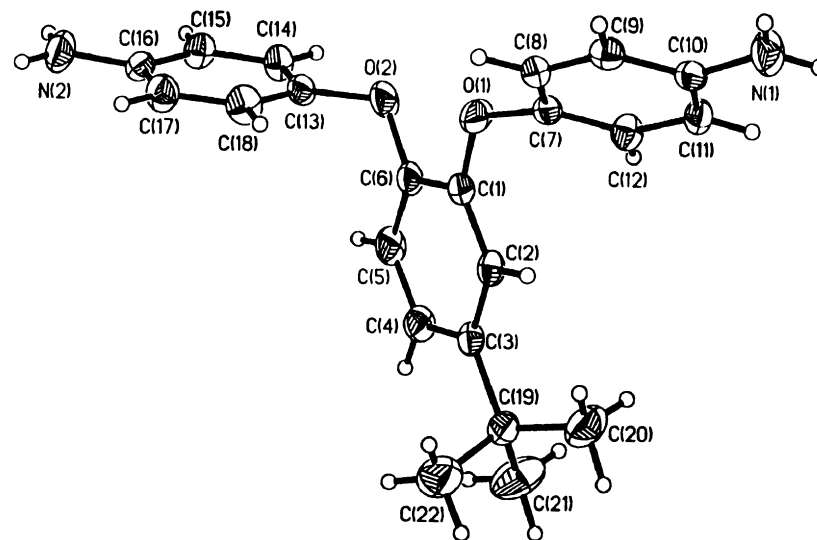
2.2. Monomer synthesis

2.2.1. 4-*tert*-Butyl-1,2-bis(4-cyanophenoxy)benzene (**1a**)

4-*tert*-Butylcatechol (33.2 g, 0.2 mol) and potassium carbonate (55 g, 0.4 mol) were added into a mixture of DMF (100 ml) and toluene (50 ml) in a 500-ml round-bottomed flask. The suspension mixture was heated at reflux temperature to remove the water azeotropically by using a Dean–Stark trap. After the water was removed completely, *p*-fluorobenzonitrile (48.4 g, 0.4 mol) was added, and the suspension mixture was heated to reflux temperature and held for 8 h. Then, the mixture was allowed to cool and subsequently poured into 700 ml water to precipitate white solid. The crude product was recrystallized by

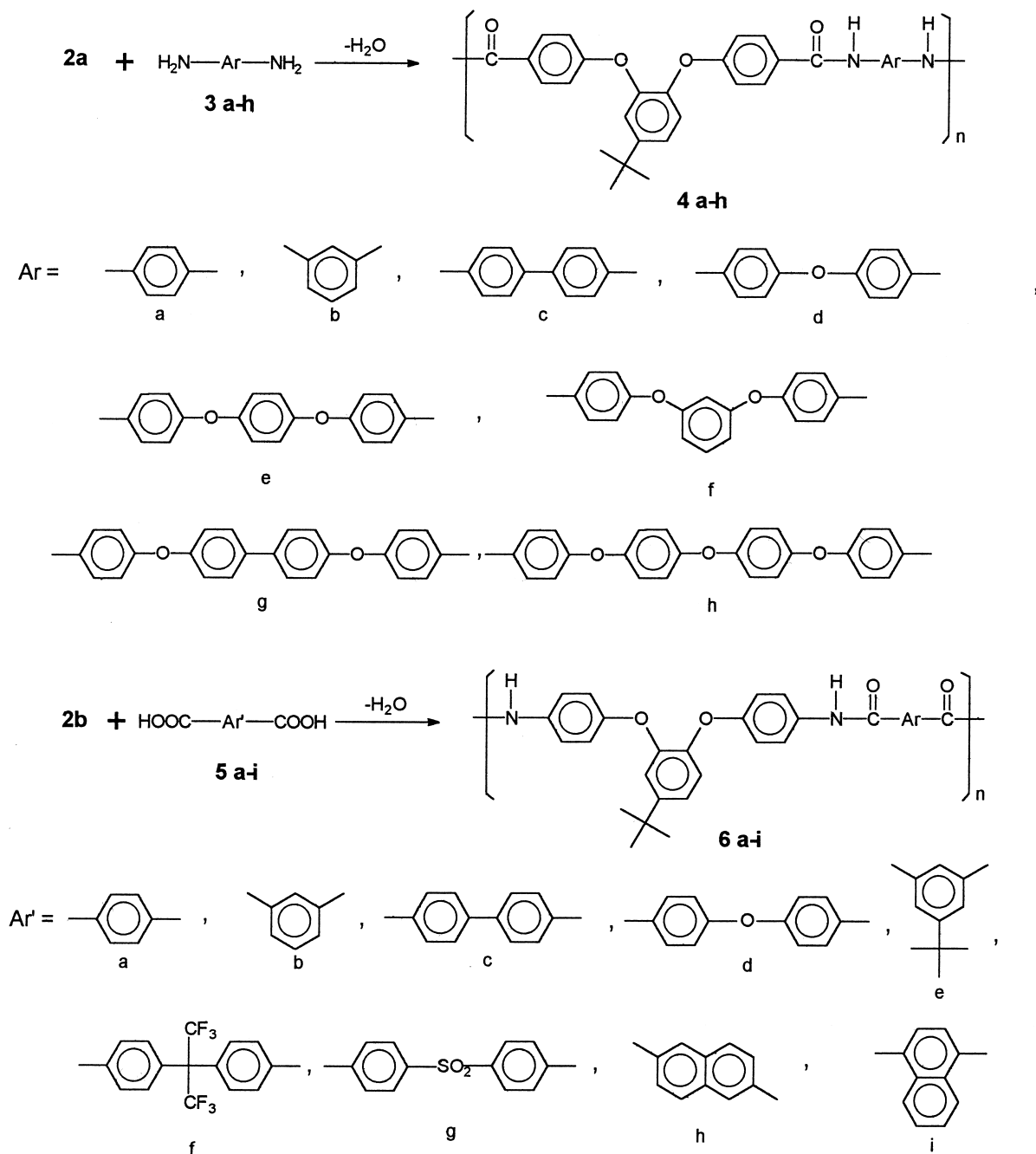


(a)



(b)

Fig. 1. X-ray structures of (a) dinitrile **1a** and (b) diamine **2b**.



Scheme 2.

methanol to give pure 1,2-bis(4-cyanophenoxy)-4-*tert*-butylbenzene (**1a**); m.p. 120–121°C (lit. [23] 119–120°C); yield, 58.9 g (80%).

IR (KBr): 2964 (aliphatic C–H str.), 2228 (C≡N str.), and 1236 cm⁻¹ (C–O str.).

¹H NMR (400 MHz, in DMSO-*d*₆): δ 7.52 (two overlapped AB doublets, H_c + H_c', 4H), 7.34 (d, H_b, 1H), 7.26 (m, H_a, 1H), 7.16 (d, H_c, 1H), 6.83 (two overlapped AB doublets, H_d + H_d', 4H), 1.35 (s, –CH₃, 9H).

¹³C NMR (100 MHz, in DMSO-*d*₆): δ 161.76, 161.71

(C⁹, C^{9'}), 151.62 (C⁴), 144.60 (C²), 143.79 (C¹), 134.96, 134.43 (C¹¹, C^{11'}), 124.29 (C⁶), 123.00 (C³), 120.81 (C⁵), 119.01 (C≡N), 117.11, 116.96 (C¹⁰, C^{10'}), 106.00, 105.94 (C¹², C^{12'}), 34.01 (C⁷), 30.48 ppm (C⁸).

Crystal data: C₂₄N₂₀N₂O₂, colorless crystal, 0.30 × 0.35 × 0.45 mm³, triclinic P-1 with *a* = 9.5720(16), *b* = 9.8773(18), *c* = 11.965(3) Å, α = 111.071(16), β = 105.164(16), γ = 92.282(14)° with *D*_c = 1.214 g cm⁻³ for *Z* = 2 and *V* = 1007.5(3) Å³. μ = 0.595 cm⁻¹, *R*_w = 0.068 for 2245 observed reflections.

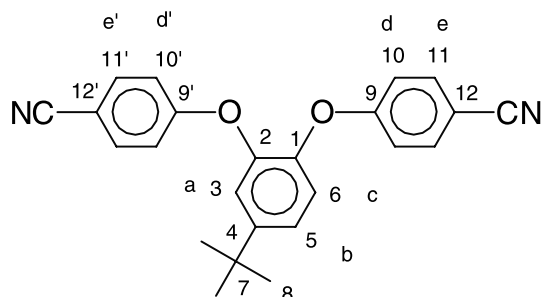
Table 3
Synthesis conditions, inherent viscosity, and film quality of polyamides

Polymer code	Amount of reagents used ^a			η_{inh} (dl g ⁻¹) ^b	Film quality ^c
	NMP (ml)	Pyridine (ml)	CaCl ₂ (g)		
4a	3 + 4	1	0.3	1.41	Flexible
4b	2	0.5	0.2	1.15	Flexible
4c	10 + 2	1	0.3	1.41	Flexible
4d	4 + 2	1	0.4	1.51	Flexible
4e	4 + 6	1	0.4	2.20	Flexible
4f	4 + 6	1	0.4	1.90	Flexible
4g	5 + 5	1.2	0.5	2.60	Flexible
4h	4	1	0.5	1.20	Flexible
6a	3	1	0.3	0.80	Flexible
6b	2	0.5	0.2	0.62	Flexible
6c	3	0.8	0.3	0.84	Flexible
6d	2	0.5	0.2	0.84	Flexible
6e	2	0.5	0.2	0.52	Flexible
6f	3	0.8	0.3	0.58	Flexible
6g	2	0.5	0.2	0.67	Flexible
6h	3	0.8	0.3	0.92	Flexible
6i	2	0.5	0.2	0.71	Brittle

^a The polymerisation was carried out with 2 mmol of each monomer, 2 mmol (about 1.6 ml) of triphenyl phosphite, and the amount of reagents used as indicated at 120°C for 3 h.

^b Measured in DMAc containing 5 wt% LiCl on 0.5 g dl⁻¹ at 30°C by Cannon–Fenske viscometer.

^c Films were cast by slow evaporation of solutions in DMAc.



Anal. calcd for C₂₄H₂₀N₂O₂ (368.43): C, 78.24; H, 5.47; N, 7.60%. Found: C, 78.20; H, 5.72; N, 7.60%.

2.2.2. 4-tert-Butyl-1,2-bis(4-carboxyphenoxy)benzene (2a)

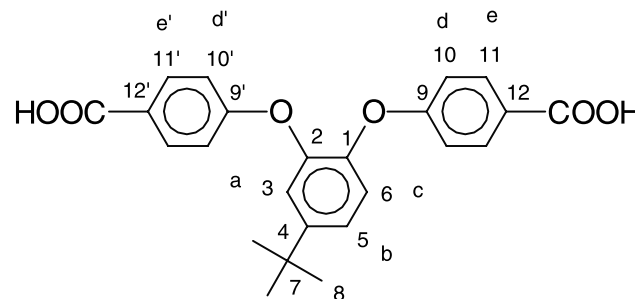
A suspension of the intermediate dinitrile **1a** (35 g, 0.095 mol) in 400 ml of 1:1 volume mixture of water and ethanol containing potassium hydroxide (53.3 g, 0.95 mol) was heated to reflux for 25 h. The resulting clear solution was acidified to pH = 2–3 by concentrated HCl. The white precipitate was filtered off, washed with water to neutral and dried to give 35.8 g (93%) of diacid **2a** with a melting point of 231–232°C (lit. [23] 231–232°C).

IR (KBr): 2500–3500 (O–H str.), 2968 (aliphatic C–H str.), 1690 (C=O str.), and 1226 cm⁻¹ (C–O str.).

¹H NMR (400 MHz, in DMSO-*d*₆): δ 7.90 (two overlapped AB doublets, H_c + H_{c'}, 4H), 7.33 (d, H_b, 1H), 7.26 (m, H_a, 1H), 7.16 (d, H_c, 1H), 6.84 (two overlapped AB doublets, H_d + H_{d'}, 4H), 1.32 (s, –CH₃, 9H).

¹³C NMR (100 MHz, in DMSO-*d*₆): δ 168.38 (C=O), 162.25, 162.21 (C⁹, C^{9'}), 150.78 (C⁴), 144.89 (C²), 132.39 (C¹¹, C^{11'}), 126.32, 126.20 (C¹², C^{12'}), 124.09 (C⁶), 143.79 (C¹), 134.96, 134.43 (C¹¹, C^{11'}), 123.00 (C³), 120.82 (C⁵), 116.70, 116.46 (C¹⁰, C^{10'}), 34.22 (C⁷), 30.86 ppm (C⁸).

Anal. calcd for C₂₄H₂₂O₆ (406.43): C, 70.92; H, 5.54%. Found: C, 69.73; H, 5.30%.



2.3. Polymer synthesis

A typical polymerization procedure of polyamide **4a** is as follows. A mixture of diacid **2a** (0.8129 g, 2 mmol), *p*-phenylenediamine (0.2163 g, 2 mmol), calcium chloride (0.2 g), triphenyl phosphite (TPP) (1.6 ml), pyridine (1 ml), and *N*-methyl-2-pyrrolidone (NMP) (3 ml) was heated and stirred at 110°C. After reaction for about 1 h, the solution became too viscous for magnetic stirrer to work; thus, additional 4 ml of NMP was added into the reaction medium. After a further 2 h of stirring at this temperature,

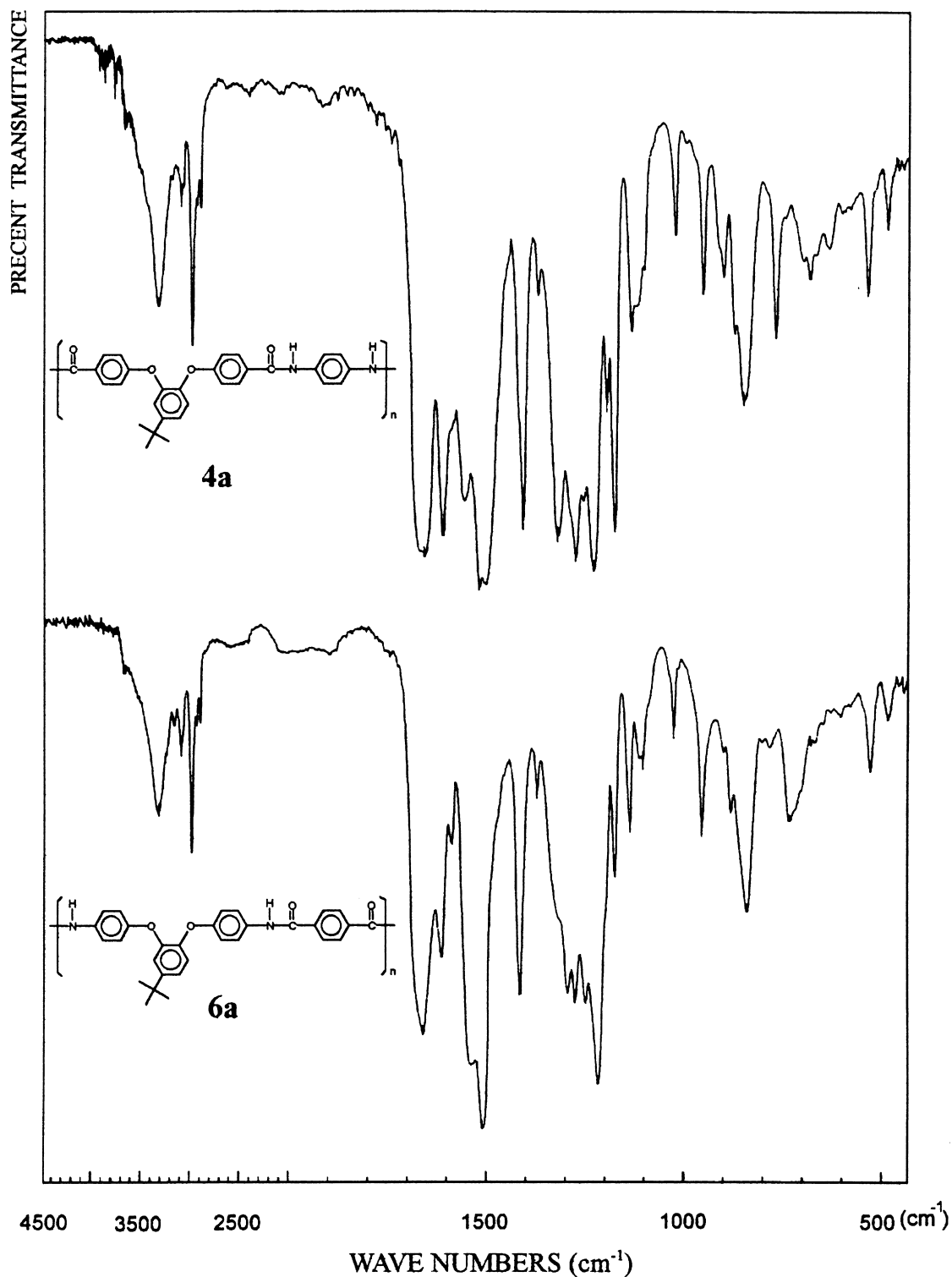


Fig. 2. FT-i.r. spectra of isomeric polyamides **4a** and **6a**.

the obtained polymer solution was poured slowly into 300 ml of methanol giving rise to a fiber-like precipitate which was washed thoroughly with methanol and hot water, collected by filtration, and dried under vacuum at

100°C. The yield of the obtained polymer (**4a**) was 1.04 g (99%), and the inherent viscosity was 1.41 dl g⁻¹, as measured in DMAc containing 5% LiCl at a concentration of 0.5 g dl⁻¹ at 30°C.

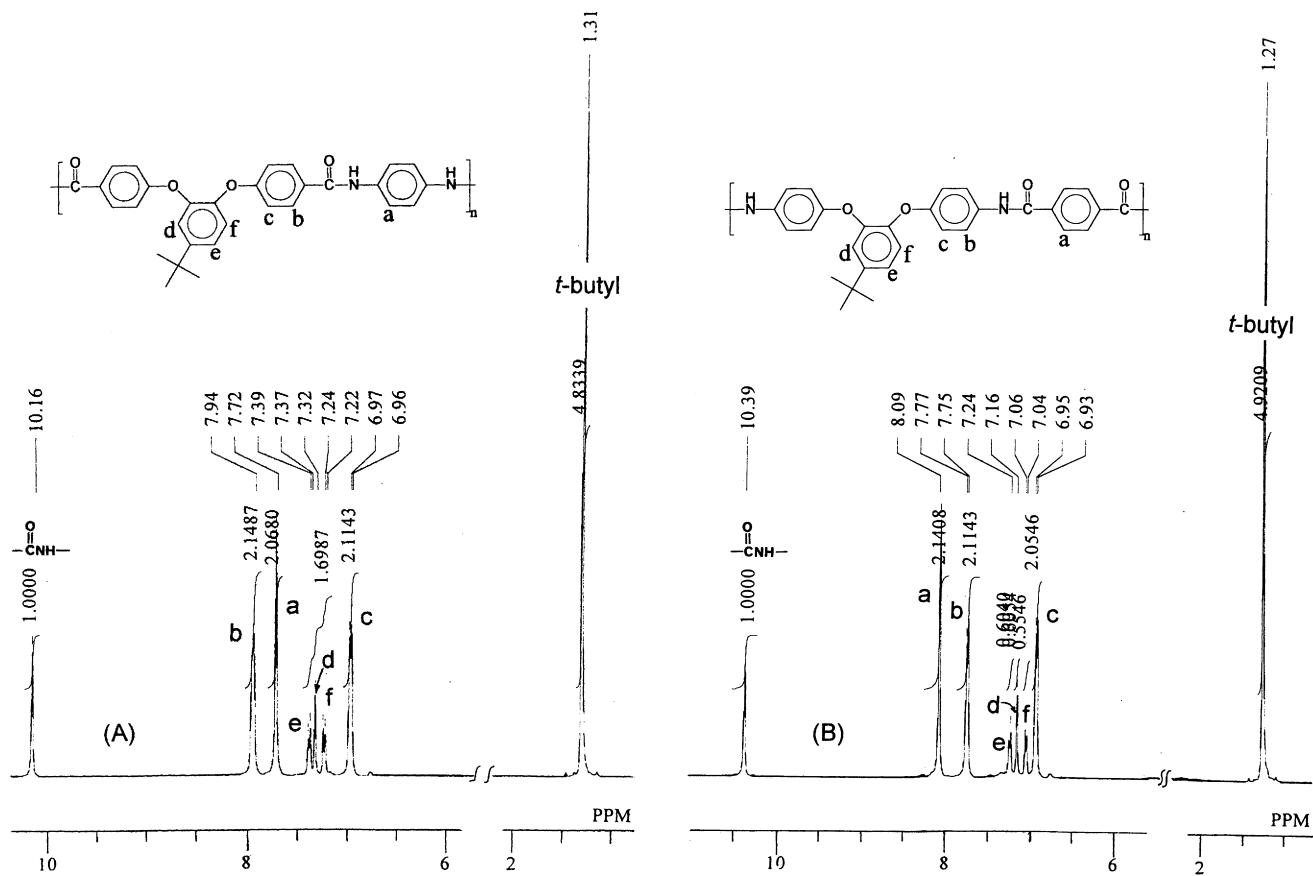


Fig. 3. (A) $^1\text{H-NMR}$ (DMSO- d_6) spectrum of **4a**. (B) $^1\text{H-NMR}$ (DMSO- d_6) spectrum of **6a**.

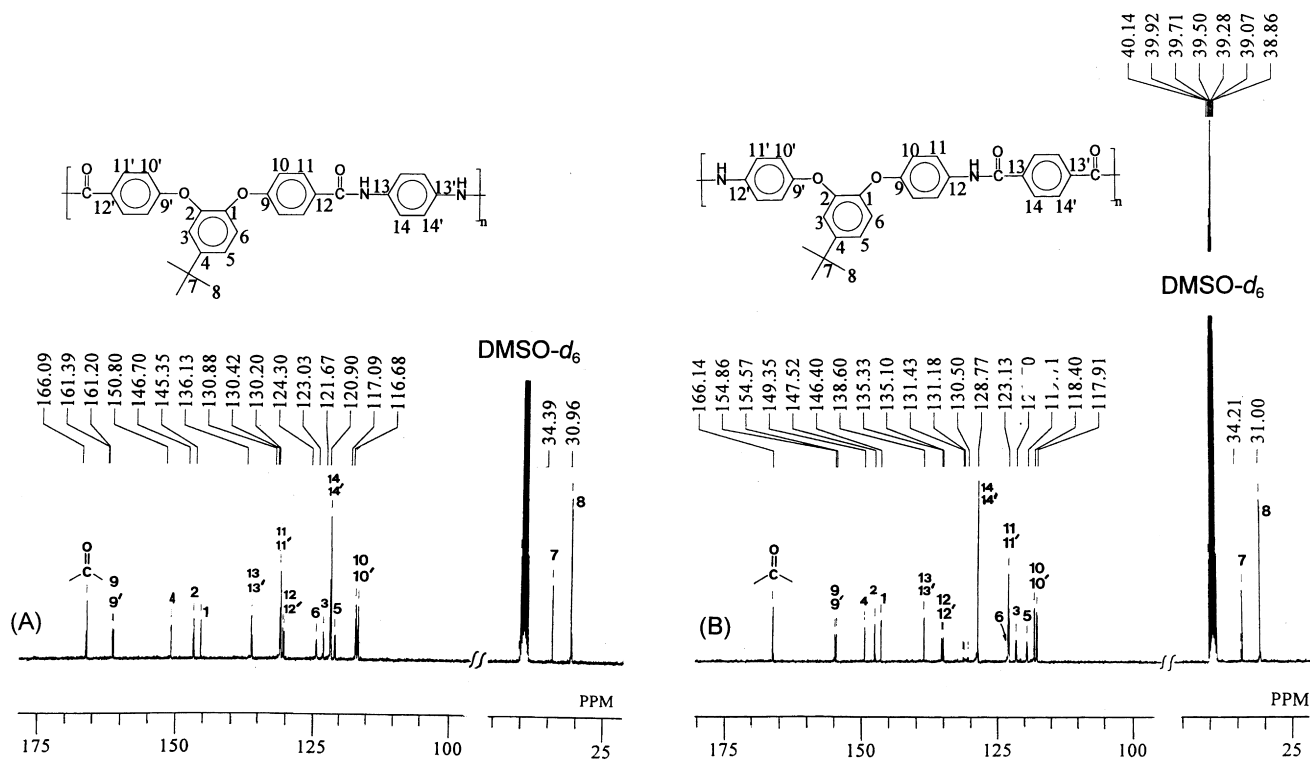


Fig. 4. (A) $^{13}\text{C-NMR}$ (DMSO- d_6) spectrum of **4a**. (B) $^{13}\text{C-NMR}$ (DMSO- d_6) spectrum of **6a**.

Table 4

Solubility behavior and tensile properties of polyamides (qualitative solubility was determined using 10 mg of polymer in 1 ml of solvent. + : soluble at room temperature; – insoluble even on heating)

Polymer code	Solvents ^a						Tensile properties of polyamide films		
	DMF	DMSO	DMAc	NMP	<i>m</i> -cresol	THF	Tensile strength (MPa)	Elongation at break point (%)	Initial modulus (GPa)
4a	+	+	+	+	–	–	75	25	1.78
4b	+	+	+	+	+	+	104	10	2.29
4c	–	–	–	+	–	–	79	6	2.99
4d	+	+	+	+	+	+	83	27	1.77
4e	+	+	+	+	+	+	83	46	1.79
4f	+	+	+	+	+	+	75	32	1.39
4g	+	+	+	+	+	+	91	35	1.73
4h	+	+	+	+	+	+	78	8	1.51
6a	+	+	+	+	–	–	61	4	1.78
6b	+	+	+	+	+	+	89	8	2.28
6c	+	+	+	+	+	–	79	8	2.22
6d	+	+	+	+	+	+	93	13	2.60
6e	+	+	+	+	+	+	54	5	2.27
6f	+	+	+	+	+	+	48	4	1.08
6g	+	+	+	+	+	–	82	10	1.83
6h	+	+	+	+	+	–	92	13	2.05
6i	–	–	–	+	–	–	–	–	–

^a DMAc, *N,N*-dimethylacetamide; NMP, *N*-methyl-2-pyrrolidone; DMF, *N,N*-dimethylformamide; DMSO, dimethyl sulfoxide; THF, tetrahydrofuran.

Anal. Calcd for $(C_{30}H_{26}N_2O_4)_n$ (478.55)_n: C, 75.30; H, 5.48; N, 5.85%. Found: C, 74.55; H, 5.60; N, 5.58%. All other polyamides were synthesized by using a similar procedure as above.

2.4. Preparation of polyamide films

A solution of polymer was made by dissolving about 1.0 g of the polymer in 10 ml of hot DMAc to afford an approximate 10 wt% solution. After the polymer was dissolved completely, the solution was poured into a 9-cm glass culture dish, which was placed in a 90°C oven overnight to remove the most of solvent. The semi-dried polyamide film was stripped off from the glass surface and further dried in a vacuum oven at 160°C for 8 h. The obtained films had about 0.08 mm in thickness and were used for X-ray diffraction measurements, tensile tests, solubility tests, and thermal analysis.

2.5. Measurements

IR spectra were recorded on a Jasco FT/IR-7000 Fourier transform infrared spectrometer. NMR spectra were obtained on a Jeol EX-400 spectrometer. The X-ray crystallographic data were collected on an Enraf-Norius FR 590 CAD-4 diffractometer. The molecular structure was solved on a VAX-3300 computer using NRCC SDP (Structure Determination Package) software. The inherent viscosity was measured with a Cannon-Fenske viscometer at 30°C. Differential scanning calorimetry (DSC) was performed with a Perkin–Elmer DSC 7 coupled to a Thermal Analysis Controller TAC 7/DX. Heating rate was 20°C min^{–1}. Glass

transition temperatures (T_g s) were read at the middle of the change in the heat capacity and were taken from the second heating scan after quenching from 400°C. Thermo-mechanical analysis (TMA) was recorded on a Perkin–Elmer TMA 7 using a 30 mN loaded penetration probe at a scan rate of 10°C min^{–1}. The TMA experiments were conducted in duplicate from 30 to 300°C. The apparent T_g s were read at the onset temperatures of probe displacement on the second TMA traces. Thermogravimetric analysis (TGA) was conducted with a TA Instruments TGA 2050. Experiments were carried out on approximately 10 mg of samples in flowing nitrogen or air (flow rate 50 cm³ min^{–1}) at a heating rate of 20°C min^{–1}. Wide angle X-ray diffraction measurements were performed at room temperature (about 25°C) on a Siemens Kristalloflex D5000 X-ray diffractometer, using Ni-filtered Cu K_α radiation (40 kV, 20 mA). The scanning rate was 2°/min over a range of $2\theta = 5$ –45°. An Instron universal testing machine model 1130 with a load cell 5 kg was used to study the stress–strain behavior of the polyamide films (6 cm long, 0.5 cm wide, and approximately 0.08 mm thick). Specimens of 2 cm gauge length were clamped between the jaws of the instrument and elongated at a constant rate of 5 cm min^{–1} at room temperature. Reported data are averages of at least five replica tests.

3. Results and discussion

3.1. Monomer synthesis

4-*tert*-Butyl-1,2-bis(4-carboxyphenoxy)benzene (**2a**) and

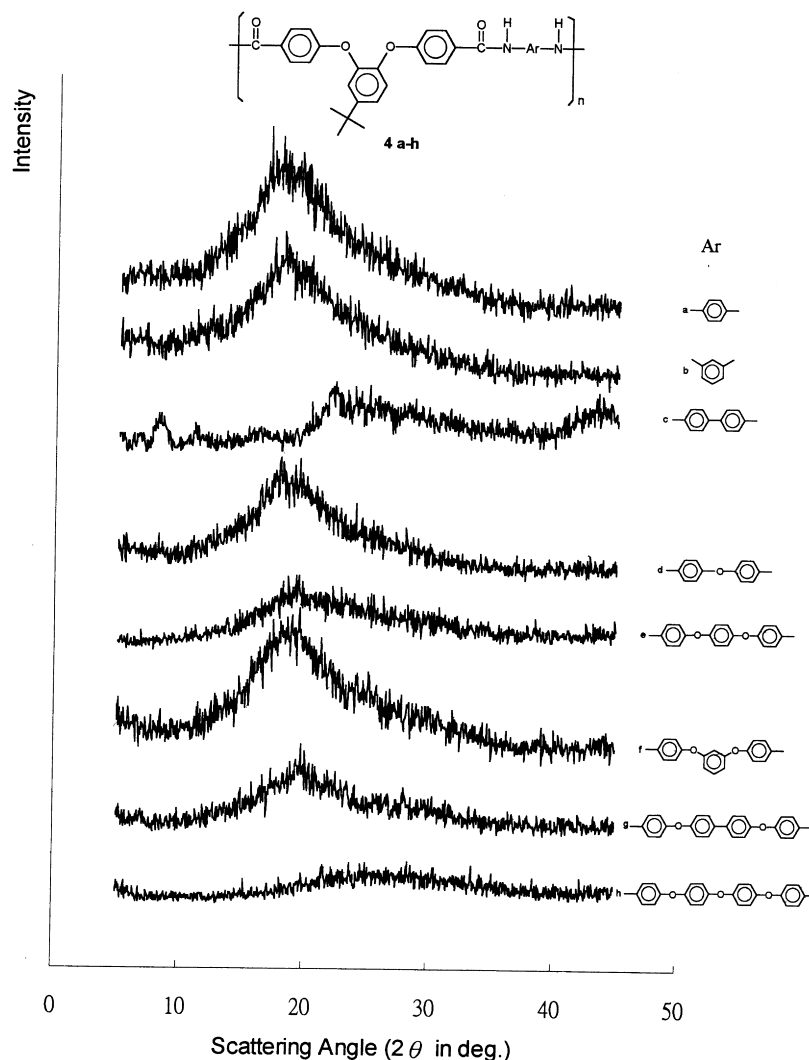


Fig. 5. X-ray diffraction patterns of polyamides **4a-h**.

1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**2b**) were prepared according to the synthetic routes outlined in Scheme 1. Intermediate compounds **1a** and **1b** were synthesized by nucleophilic aromatic halo-displacement of *p*-fluorobenzonitrile and *p*-chloronitrobenzene, respectively, with 4-*tert*-butylcatechol in DMF in the presence of potassium carbonate. The dinitrile **1a** was then readily converted into dicarboxylic acid **2a** by alkaline hydrolysis. The diamine **2b** was obtained by catalytic reduction of the intermediate dinitro compound **1b** using hydrazine hydrate and Pd/C in refluxing ethanol. IR, NMR, and elemental analysis confirmed the structures of all intermediates and monomers. Characterization data of compounds **1b** and **2b** have been given in a separate paper [37].

The structures of dinitrile **1a** and diamine **2b** were also confirmed by X-ray diffraction analysis. X-ray crystal data (shown in Tables 1 and 2) for **1a** and **2b** were acquired from

the single crystals obtained by slow crystallization of an acetonitrile solution of **1a** and an ethanol solution of **2b**. As shown in Fig. 1, **1a** and **2b** display a bent structure, and the three benzene rings are not in the same plane. Eastmond and Paprotny [40] used molecular modeling and obtained similar conformations of diphenoxyphenyl units present in catechol-based bis(ether anhydride) and poly(ether imide)s.

3.2. 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 [41]. Two series of aramids **4a-h** and **6a-i** (Scheme 2) were prepared from diacid **2a** with various aromatic diamines (**3a-h**) and from diamine **2b** with various aromatic diacids

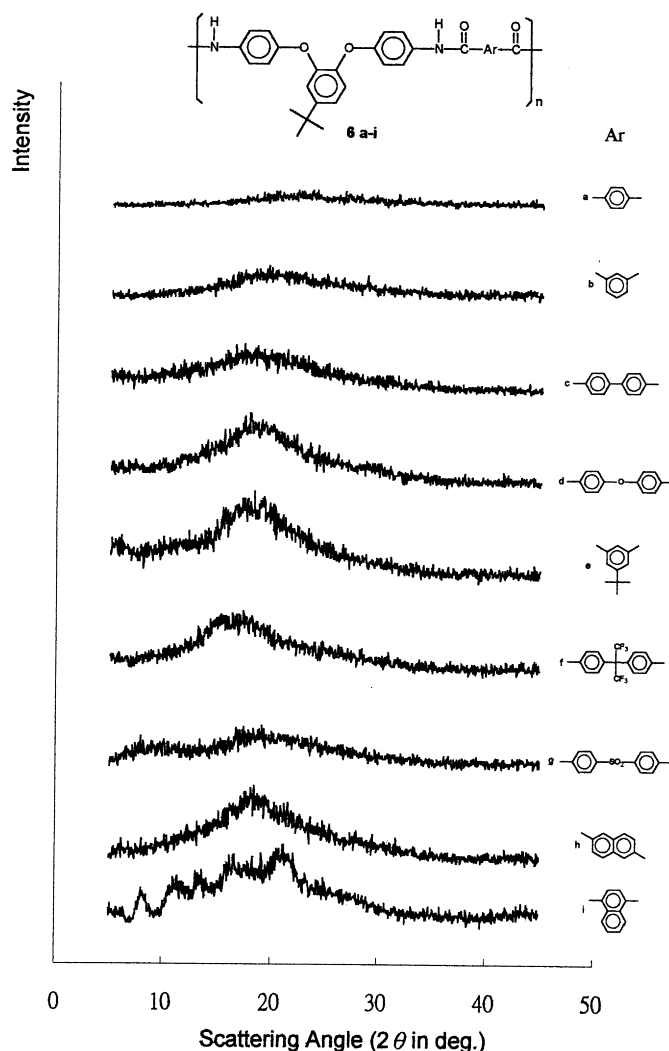


Fig. 6. X-ray diffraction patterns of polyamides **6a-i**.

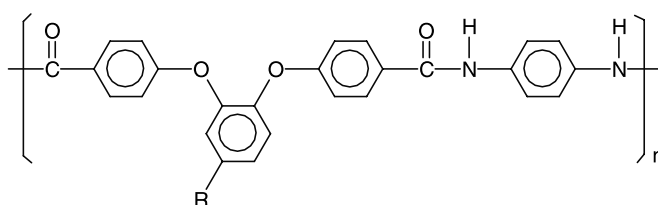
(**5a-i**) by the so-called phosphorylation technique developed by Yamazaki et al. [41,42]. By using the reaction conditions listed in Table 3, all of the reaction solutions were homogeneously transparent throughout the reaction and became highly viscous, indicative of the formation of high molecular weights. As shown in Table 3, the inherent viscosities of polyamides **4a-h** were above 1.15 dl g^{-1} and up to 2.60 dl g^{-1} . However, polyamides of the **6a-i** series had lower inherent viscosities and molecular weights. None of the **6a-i** series had inherent viscosities in excess of unity. The reasons for the lower molecular weights are not clear. It is uncertain at this stage as to whether or not the orientation of the amide linkages in **6a-i** restricts chain conformations in such a way as to favor the formation of cyclic polymers or if the reason is monomer purity. However, all the polyamides had enough molecular weights to permit the casting of flexible and tough films. The brittle nature associated with the casting film of polyamide **6i** is attributed to high crystallinity, as evidenced by the X-ray

diffraction experiments discussed subsequently. All structural features of these polyamides were confirmed by FT-IR spectroscopy. They exhibit characteristic absorptions of the amide group around $3300\text{--}3330 \text{ cm}^{-1}$ (N-H str.) and $1650\text{--}1660 \text{ cm}^{-1}$ (C=O str.). The absorption of aryl ether stretching appeared near 1220 cm^{-1} . Fig. 2 shows a typical set of FT-IR spectra for polyamides **4a** and **6a**, which have an isomeric repeat unit. The chemical structures of **4a** and **6a** were also confirmed by solution NMR in dimethyl- d_6 sulfoxide (DMSO- d_6) (Figs. 3 and 4).

3.3. Polymer characterization

The solubility behavior of these aramids was qualitatively tested in various organic solvents, and the results are summarized in Table 4. Mainly due to the presence of 1,2-phenylenedioxy moiety and pendant *tert*-butyl group, almost all polyamides exhibited high solubility in polar aprotic solvents such as DMF, DMSO, DMAc, and NMP.

Table 5
Effect of the *tert*-butyl group on the properties of the polyamides



R	η_{inh} (dl g ⁻¹)	Film quality	Solubility			WAXD pattern
			NMP	DMAc	DMF	
-H	0.63	Brittle	-	-	-	semi-crystalline
<i>t</i> -butyl	1.41	Flexible	+	+	+	amorphous

-H	1.36	Slightly brittle	+	-	-	semi-crystalline
<i>t</i> -butyl	0.80	Flexible	+	+	+	amorphous

The polyamides containing additional flexible diamine or diacid residue dissolved even in less polar solvents like *m*-cresol and THF. An unfavorable result was found in the cases of polyamides **4c** and **6i**; they were insoluble in the solvents tested except NMP. This can be attributed to their crystalline nature, as evidenced by the X-ray diffraction patterns.

As mentioned earlier, all the polyamides (except **6i**) could be solution-cast into transparent, flexible, and tough films. These tough films were subjected to tensile test, and the results are also summarized in Table 4. The tensile strengths, elongations at break point, and the initial moduli of these polyamides were in the range of 48–104 MPa, 4–46%, and 1.08–2.99 GPa, respectively. Some polyamides such as **4a** and **4d–g** behaved as tough materials. They revealed a well-defined yield point on their stress–strain curves and exhibited moderate elongations to break.

All the polymers were structurally characterized by X-ray diffraction studies. The diffraction patterns of aramids **4a–h** and **6a–i** were, respectively, illustrated in Figs. 5 and 6. The results revealed that aramids **4c** and **6i** had a fair degree of crystallinity, whereas all of the others showed amorphous patterns. Thus, the amorphous nature of most aramids was reflected in their excellent solubility, and the crystalline polyamides **4c** and **6i** were less soluble. Moreover, the effect of the introduction of the *tert*-butyl group on the properties of these polyamides can be seen from the data summarized in Table 5 and the wide-angle X-ray diffraction (WAXD) patterns illustrated in Fig. 7. As shown in Table 5, the

polyamides bearing the *tert*-butyl group exhibited much better solubility than the corresponding ones without the *tert*-butyl group and could afford flexible and strong films by solvent-casting. The polyamides containing the *tert*-butyl group displayed a nearly completely amorphous pattern, whereas the corresponding analogues without the *tert*-butyl group revealed a semi-crystalline pattern (Fig. 7).

The thermal properties of the polyamides are summarized in Table 6. No discernible glass transitions were detected for polyamides **4a**, **4c**, and **6i** by DSC, probably due to the rigid nature or a high crystallization tendency of their polymer chains. However, the T_g s of these rigid polyamides could be readily determined in the TMA experiments. The other polyamides showed T_g values between 191 and 253°C by DSC, following the decreasing order of chain flexibility, steric hindrance, and polarity of the –Ar– moieties. The lowest T_g of 191°C was observed for polyamide **4h** derived from the multiring flexible diamine **3h**. The higher T_g value of polyamide **6g** is believed to be due to the increased intermolecular interactions of the polar sulfonyl groups. The T_g s of the polyamide samples have also been measured using TMA. The trend of T_g variation with the chain flexibility is similar to that observed in the DSC measurements. However, in most cases T_g s obtained by TMA are slightly lower than that measured by DSC experiments. This difference may be attributable to different heating rates, and more fundamentally, the distinctive nature of the testing techniques (thermomechanical versus calorimetric responses). Recently, Eastmond et al. [23] also prepared

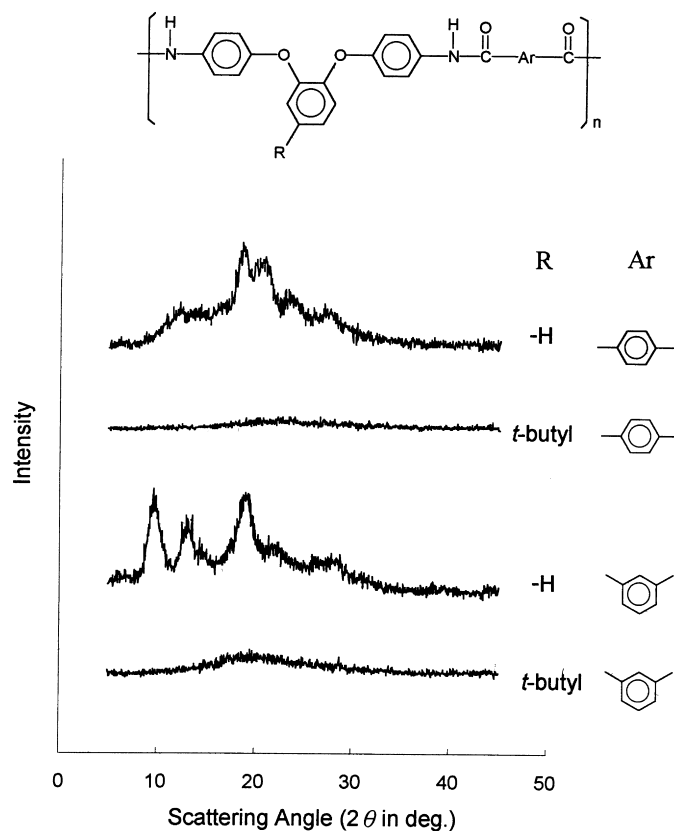


Fig. 7. Effect of the *tert*-butyl group on the crystallinity of the polyamides.

polyamides **4a** (with η_{inh} of 0.70 dl g^{-1}) and **4b** (with η_{inh} of 0.54 dl g^{-1}) from the acid chloride of diacid **2a** with *p*- or *m*-phenylenediamine. They reported that polymer **4a** had a weak, broad and ill-defined T_g at about 230°C and polymer **4b** had a stronger and more well-defined T_g at 217°C . The T_g s of our polyamides **4a** and **4b** measured by TMA experiments are virtually identical with that reported by Eastmond

et al. by means of DSC [17]. However, we failed to observe a T_g for polymer **4a** by DSC, and we also found that our polyamide **4b** had a T_g at 230°C by DSC, which is higher than that reported by Eastmond et al. by 13°C . The difference may be due to different molecular weights and/or different heating history. Polyamides **6b** and **6d** showed T_g values comparable to those of analogous **4b** and **4d** by

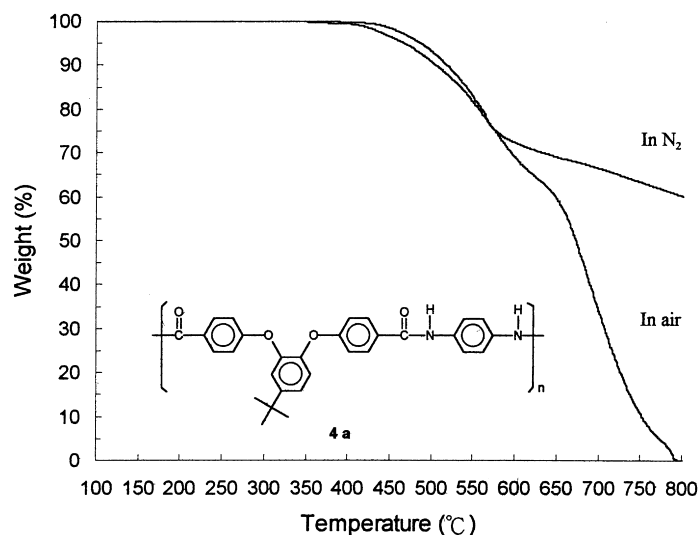


Fig. 8. TGA thermograms of polyamide **4a** at a heating rate of $20^\circ\text{C min}^{-1}$.

Table 6
Thermal properties of polyamides

Polymer code	T_g (°C)		T_d (°C) ^c		Char yield (%) ^d
	DSC ^a	TMA ^b	In N ₂	In air	
4a	– ^e	231	526	514	67.2
4b	230	218	507	485	62.4
4c	– ^e	255	514	501	63.7
4d	200	202	518	512	54.6
4e	203	184	527	528	54.2
4f	204	186	517	515	56.2
4g	230	205	532	524	57.1
4h	191	183	523	519	51.6
6a	218	209	509	503	69.2
6b	225	214	507	499	64.1
6c	220	219	488	492	62.1
6d	192	206	509	505	65.2
6e	235	208	496	496	61.1
6f	202	214	503	503	63.8
6g	253	229	492	492	62.0
6h	209	203	510	510	67.6
6i	– ^e	239	498	498	66.5

^a The samples were heated to 400°C with a heating rate of 20°C min⁻¹ and rapidly cooled to 30°C at –100°C min⁻¹. The midpoint of baseline shift on the subsequent DSC heating trace was defined as T_g .

^b The onset temperature of the probe displacement on the second TMA trace. A penetration probe of 1.0-mm diameter, an applied constant load of 30 mN, and a heating rate of 10°C min⁻¹ were used in the TMA experiments.

^c Decomposition temperature at which 10% weight loss were recorded by TGA at a heating rate of 20°C min⁻¹.

^d Residual wt% at 800°C in nitrogen.

^e No discernible transition were observed.

means of DSC or TMA, thus probably indicating that constitutional isomerism of the repeat unit did not affect significantly the polymer stiffness for the polyamides with a more flexible backbone. However, the semi-rigid polyamides **4a** and **4c** showed higher T_g values than their corresponding

analogs **6a** and **6c**. The only structural difference between these polyamides is the orientation of the amide groups. This result suggests that the incorporation of rigid *p*-phenylene or 4,4'-biphenylene units in the diamine moiety increased the chain stiffness. This result is contrary to that observed for the polyamides based on the bis(ether amine) or bis(ether-carboxylic acid) derived from *tert*-butylhydroquinone reported in one of our recent publications [33]. The reasons for these different behaviors of these polymers may be complicated and need further study.

All polyamides were stable up to 400°C in nitrogen or in air. Typical TGA curves are illustrated in Figs. 8 and 9. Decomposition temperatures at 10% weight loss were recorded in the range of 488–532°C in nitrogen and 485–528°C in air (see Table 6), which are reasonable values considering the aliphatic content of these polyamides. Most of these polyamides showed a good thermal stability in air comparable with that in nitrogen atmosphere before 600°C, indicating that these *tert*-butyl-substituted polyamides had good thermo-oxidative stability.

4. Conclusions

We have demonstrated that 4-*tert*-butyl-1,2-bis(4-carboxyphenoxy)benzene (**2a**) and 1,2-bis(4-aminophenoxy)-4-*tert*-butylbenzene (**2b**) can be readily prepared from 4-*tert*-butylcatechol by reacting with *p*-fluorobenzonitrile or *p*-chloronitrobenzene in DMF, in the presence of potassium carbonate; the intermediate dinitrile and dinitro compounds so formed were hydrolyzed or reduced to the corresponding diacid **2a** or diamine **2b**. These monomers allow the synthesis of novel high-molecular-weight aramids in which *ortho*-phenylene units are enchain through ether linkages and the bulky *tert*-butyl groups are pendent to the

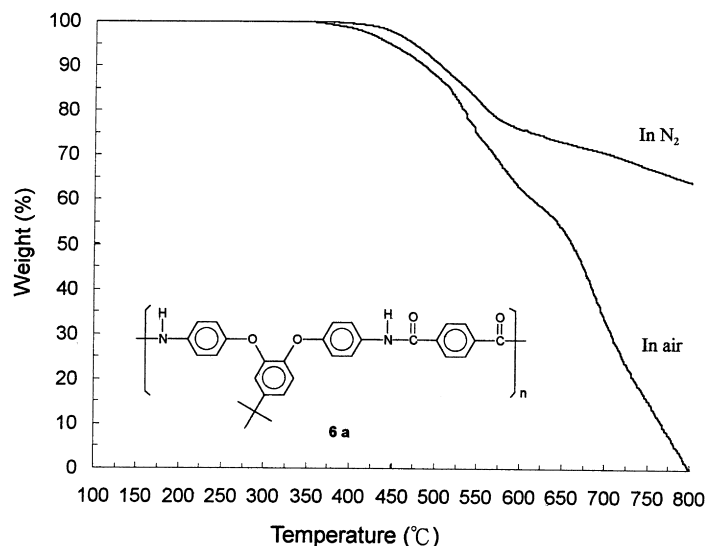


Fig. 9. TGA thermograms of polyamide **6a** at a heating rate of 20°C min⁻¹.

polymer backbone. These polymers are significantly more flexible and, therefore, more soluble than conventional aromatic polyamides and analogous *ortho*-linked polyamides without the *tert*-butyl group. The polyamides have moderate T_g s (most above 200°C) and are all thermally stable up to 400°C. Thus, they considered to be promising soluble high-performance polymeric materials.

Acknowledgements

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