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Synthesis and characterization of aromatic polyamides and polyimides from trimethyl- and di-*t*-butylhydroquinone-based ether-linked diamines

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1,4-Bis(4-aminophenoxy)trimethylbenzene (**3a**) and 1,4-bis(4-aminophenoxy)-2,5-di-*t*-butylbenzene (**3b**) were synthesized in two steps from the hydroquinones via nucleophilic aromatic substitution and catalytic reduction. Aromatic polyamides were synthesized from these diamines by direct polycondensation with various diacid chlorides or by reaction with diacids, triphenyl phosphite and pyridine in *N*-methyl-2-pyrrolidinone (NMP). Aromatic polyimides were synthesized from the trimethyl monomer using commercial dianhydrides in two-step polycondensations. Characterization of polymers was accomplished by ^{1}H n.m.r., ^{13}C n.m.r., *FT*i.r., d.s.c. and t.g.a. Intrinsic viscosities of polyamides were between 0.30 and 0.73 dl g^{-1} in NMP for the trimethyl polymers and between 0.57 and 1.47 dl g^{-1} in 5% LiCl/NMP for the di-*t*-butyl polyamides. Viscosities of the poly(amic acid)s ranged from 0.45 to 0.85 dl g^{-1}. Polyamides displayed T_g values of 237–305°C and 5% weight loss values above 402°C in N_2. T_g values of polyimides varied between 235 and 300°C, with 5% weight loss values above 435°C in N_2. Most polyimides were only soluble in H_2SO_4, while polyamides were soluble in polar aprotics such as NMP, *N,N*-dimethylacetamide and dimethyl sulfoxide. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: polyamides; polyimides; ether-linked diamines)

INTRODUCTION

Aromatic polyimides and polyamides are important classes of high-performance polymers due to their excellent thermo-oxidative stability, mechanical strength, electrical properties, and high radiation and solvent resistance[1–3]. However, rigidity of the backbone, strong hydrogen bonding (in polyamides) and charge transfer complex formation (in polyimides) result in insolubility in most organic solvents and high softening temperatures. These properties make them generally difficult or too expensive to process, thus restricting their applications.

In the last few decades, many studies have focused on designing the chemical structure of the rigid-aromatic backbone in order to obtain aromatic polymers that are processible with conventional techniques, such as melt processing or solvent casting, while maintaining desirable properties. The majority of these studies involved three main structure modifications: incorporation of thermally stable flexible or non-symmetrical linkages in the backbone; introduction of polar or non-polar bulky substituents; or disruption of symmetry and recurring regularity through copolymerization[4].

Incorporation of aryl ether units is a successful method for improving solubility with slight reduction in thermal properties. This trade-off is a natural outcome of the flexible linkages, which inhibit packing and decrease the co-planarity of the aromatic rings, thus reducing the inter- and intra-chain interactions to enhance solubility. However,

lowering the segmental rotational barrier and increasing the degrees of freedom also lowers the T_g. On the other hand, incorporation of bulky pendent groups can impart a significant increase in both T_g and thermo-oxidative stability by restricting segmental mobility, while providing good solubility due to decreased packing and crystallinity. Combining these two structural modifications minimizes the trade-off between processability and properties of wholly aromatic polymers.

The magnitude and nature of property alteration also depends on which monomer unit is carrying these structural features, especially in polyimides. Modifications in the anhydride moiety may decrease charge transfer complex formation by separating the aromatic rings and reducing co-planarity[5]. For example, Eastmond and Paprotny[6–8] studied a series of poly(ether imide)s with isomeric and alkane-substituted ether-linked aryl dianhydrides. Linkage groups were based on trimethylhydroquinone (TMHQ) and di-*t*-butylhydroquinone (DTBHQ). These materials gave enhanced solubility and acceptable thermal properties. On the other hand, structure alteration in the diamine has additional consequences. Recently, polyimides were reported from di-*t*-butylhydroquinone- and *t*-butylhydro-quinone-based diamines that showed some enhancement in solubility with less rigid anhydrides and some crystallinity with the former diamine due to its symmetry[9,10]. A relative decrease in T_g and crystallinity was seen with the latter due to its non-symmetric nature. Previously, we showed that polyimides with excellent solubility and high thermo-oxidative stability could be achieved with small, *ortho*-substituted diamines such as mesitylene diamine or an

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isomeric mixture of diethyl toluene diamines[11]. These results support the idea that substituents that hinder rotation around the N–C bond have a dramatic effect on polymer properties[12].

Similar structure modifications have also been demonstrated as successful methods to improve polyamide processability. Yang and Lin[13,14] synthesized aromatic polyamides and polyimides with diamines containing backbone cardo groups, such as fluorene and phthalimidine, and obtained excellent solubility and good thermal properties. More recently, Hsiao *et al.*[15,16] demonstrated that incorporation of large spiro segments into the diamine segment improved processability significantly without an unacceptable loss of thermal properties in both polyamides and polyimides. Hsiao and Chang[17] synthesized soluble polyamides with good thermal properties from methyl- and phenyl-substituted ether-linked dibenzoic acids.

We became interested in the ability to influence chain flexibility with the extended diamines 1,4-bis(4-aminophenoxy)trimethylbenzene (**3a**) and 1,4-bis(4-aminophenoxy)-2,5-di-*t*-butylbenzene (**3b**), which incorporate trimethylhydroquinone and di-*t*-butylhydroquinone moieties. Here we describe the synthesis of **3a** and **3b**, the synthesis of novel polyamides from **3a** and **3b**, and polyimides from **3a**. It was hoped that incorporation of these hindered diamines, with strategically placed substitution sites, would decrease polymer inter- and intra-chain interactions in polyimides, decrease hydrogen bonding in polyamides, and generally disturb the co-planarity of aromatic units to reduce packing efficiency and cystallinity. This should promote solubility while maintaining high T_g through controlled segmental mobility.

3a

3b
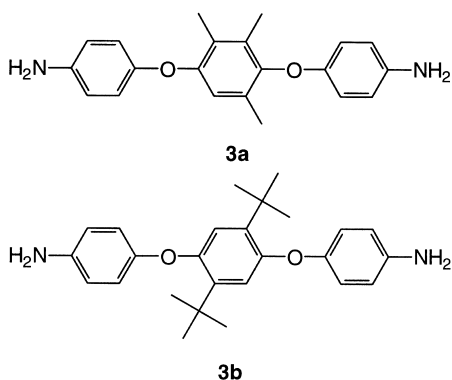
EXPERIMENTAL

Materials

All chemicals were purchased from Aldrich unless specified otherwise. Trimethylhydroquinone (TMHQ), 2,5-di-*t*-butylhydroquinone (DTBHQ), *p*-fluoronitrobenzene (PFNB), 10% palladium on activated carbon, hydrazine hydrate, (hexafluoroisopropylidine)-2,2-bis(benzoic acid) (6FDCA), 5-*t*-butylisophthalic acid (TBIPA), 4,4′-dicarboxydiphenylsulfone (DCDPS; purchased from TCI), 4,4′-oxybis(benzoic acid) (donated by Amoco) and anhydrous K_2CO_3 were used without further purification, but all diacids were dried at 100°C under vacuum prior to use. Isophthaloyl dichloride (IPDC) was recrystallized from hexanes and dried under vacuum at room temperature. Terephthalic acid was stirred with NaOH overnight, filtered and precipitated with concentrated HCl; the isolated terephthalic acid was then dried under vacuum at 100°C overnight. LiCl was dried at 130°C under vacuum. Pyridine was purified by distillation

after being refluxed with KOH. *N*-Methyl-2-pyrrolidinone (NMP) and *N,N*-dimethylacetamide (DMAc) were distilled over CaH_2 under reduced pressure. Similarly, triphenylphosphite (TPP) was purified by distillation under reduced pressure. All solvents were stored over 4 Å molecular sieves. 3,3′,4,4′-Diphenylsulfonetetracarboxylic dianhydride (DSDA), pyromellitic dianhydride and 3,3′,4,4′-biphenyltetracarboxylic dianhydride were purchased from Chriskev and dried under vacuum at 120°C prior to use. 3,3′,4,4′-Oxydiphthalic dianhydride (ODPA; Chriskev) was sublimed at 250°C under reduced pressure. (Hexafluoroisopropylidene)-2,2-diphthalic anhydride (6FDA) was donated by Air Products and Chemical Company and was used after drying at 120°C under vacuum. Bisphenol A dianhydride (BPADA) was donated by General Electric Company and recrystallized from toluene. 3,3′,4,4′-Benzophenonetetracarboxylic dianhydride was recrystallized from acetic anhydride and sublimed twice at 250°C and 1 mmHg.

Characterization

I.r. spectra were obtained on an ATI-Mattson Galaxy 5020 spectrometer on KBr pellets or solution cast films. Solution ^1H and ^{13}C n.m.r. spectra were recorded on a Bruker AC-300 spectrometer at 300.133 and 75.47 MHz frequencies with standard acquisition parameters. Solid-state ^{13}C n.m.r. spectra were acquired on Bruker MSL-400 and MSL-200 spectrometers at 100.61 and 50.32 MHz, respectively, using cross-polarization/magic angle spinning (CP/MAS) and high-power proton decoupling with sample spinning rates greater than 4.0 kHz. D.s.c. analyses were performed on a TA Instrument 2920 with heating rates of 10°C min^{-1} for normal scans and 2°C min^{-1} with a modulation amplitude of ± 1°C every 60 s for modulated d.s.c. T.g.a. experiments were performed in N_2 and air with heating rates of 20°C min^{-1} with a TA Instrument 2960. The intrinsic viscosities of poly(amic acid)s and **3a** polyamides were measured in NMP; 5% w/v LiCl/NMP solvent was used for viscosity measurements of **3b** polyamides.

Monomer synthesis

*1,4-Bis(4-nitrophenoxy)trimethylbenzene (**2a**).* TMHQ (**1a**; 12.06 g, 76.88 mmol) was dissolved in 200 ml of DMAc under N_2 in a 500-ml round-bottomed flask. Anhydrous K_2CO_3 (23.18 g, 166.87 mmol) was added to this solution and stirred for 10 min; a purple colour was observed for a few seconds and then faded away. PFNB (23.74 g, 166.59 mmol) was added to the reaction mixture and it was refluxed overnight (14 h). The progress of the reaction was followed by thin layer chromatography (hexane/toluene, 1:1 v/v). After cooling to room temperature, the product mixture was precipitated into water to give a brown powder. Recrystallization from acetic anhydride gave a light yellow powder (**2a**) that was isolated by filtration, washed with water and dried under vacuum at 50°C for 5 h; yield 24.33 g, 95%; m.p. 197–199°C; i.r. (KBr): 3112–3083 (symmetric and asymmetric aromatic C–H stretch), 2958–2840 (symmetric and asymmetric aliphatic C–H stretch), 1587 (C=C stretch), 1502 and 1346 (symmetric and asymmetric NO_2 stretch), 1236–1108 cm^{-1} (C–O–C stretch). Calc. for $C_{21}H_{18}N_2O_6$ (394.38): C, 63.96%; H, 4.60%; N, 7.10%. Found: C, 63.88%; H, 4.74%; N, 7.22%.

*1,4-Bis(4-aminophenoxy)trimethylbenzene (**3a**).* Intermediate **2a** (0.22 g, 0.56 mmol) was refluxed in 10 ml absolute ethanol in the presence of 10% Pd/C catalyst (0.02 g) in a 50-ml round-bottomed flask equipped with an addition

funnel and condenser under N_2. Hydrazine hydrate (1 ml) was added dropwise to the mixture at 100°C; it was refluxed overnight then filtered hot to remove the catalyst. Upon cooling, a white powder precipitated (**3a**), that was isolated by filtration, recrystallized from ethanol and dried in a vacuum oven at 40°C overnight; yield 0.167 g, 89%; m.p. 191–192°C; i.r. (KBr): 3423 and 3347 (N–H stretch), 1209 cm^{-1} (C–O–C stretch). Calc. for $C_{21}H_{22}N_2O_2$ (334.41): C, 75.42%; H, 6.63%; N, 8.83%. Found: C, 75.50%; H, 6.43%; N, 8.65%.

1,4-Bis(4-nitrophenoxy)-2,5-di-t-butylbenzene (**2b**). Compound **2b** was synthesized similarly to **2a** starting from DTBHQ (**1b**; 1.10 g, 4.96 mmol) and PFNB (1.50 g, 10.55 mmol) in the presence of K_2CO_3 (1.47 g, 10.62 mmol) in 15 ml DMAc. After overnight reaction and cooling to room temperature, the product was filtered, along with the inorganic salts, from the reaction mixture. Crude product was refluxed in water 1 h, and pure **3b** was isolated as a pale yellow powder after hot filtration; yield 1.78 g, 89%; m.p. 275°C; i.r. (KBr): 1511 and 1340 (symmetric and asymmetric NO_2 stretch), 1243 cm^{-1} (C–O–C stretch); ^1H n.m.r. (CDCl$_3$): δ 8.27–8.24 (d, 4H), 7.06–7.03 (d, 4H), 6.97 (s, 2H), 1.28 (s, 18H); ^{13}C n.m.r. (CDCl$_3$): δ 163.6, 150.0, 142.7, 141.7, 126.3, 121.5, 117.1, 34.7, 30.2 ppm. Calc. for $C_{26}H_{28}N_2O_6$ (464.51): C, 67.23%; H, 6.08%; N, 6.03%. Found: C, 67.15%; H, 5.99%; N, 6.21%.

1,4-Bis(4-aminophenoxy)-2,5-di-t-butylbenzene (**3b**). Intermediate **2b** (5.23 g, 11.30 mmol) was reduced to **3b** with hydrazine hydrate (28 ml) in 330 ml absolute ethanol in the presence of 10% Pd/C catalyst (0.056 g) as described above for **3a**, filtered hot to remove the catalyst, then crystallized by cooling and isolated by filtration as pale yellow needles; 93% yield without further purification; m.p. 247–248°C; i.r. (film from CH$_2$Cl$_2$ on NaCl disc): 3405–3315 (symmetric and asymmetric N–H stretch), 1201 cm^{-1} (C–O–C stretch); ^1H n.m.r. (deuterated dimethyl sulfoxide, DMSO-d_6): δ 6.69–6.66–6.64 (s and d, 6H), 6.58–6.55 (d, 4H), 4.85 (s, 4H of –NH$_2$), 1.22 (s, 18H); ^{13}C n.m.r. (DMSO-d_6): δ 150.8, 147.3, 144.3, 137.4, 119.3, 116.9, 114.9, 33.9, 29.6 ppm. Calc. for $C_{26}H_{32}N_2O_2$ (404.55): C, 77.19%; H, 7.97%; N, 6.92%. Found: C, 77.33%; H, 7.78%; N, 7.09%.

General polyimide synthesis

A typical synthesis of polyimides was as follows. Monomer **3a** (1.08 g, 3.25 mmol) was dissolved in 9 ml of NMP in a 100-ml three-necked round-bottomed flask under N_2, equipped with a mechanical stirrer, a xylene-filled Dean–Stark trap and a condenser. DSDA (1.16 g, 3.25 mmol) was added to the amine solution and stirred for 2 h to form poly(amic acid). At this stage, the viscosity of the mixture increased rapidly as the dianhydride dissolved, and this was true for all polyimide syntheses. Poly(amic acid) was cyclized to the polyimide by azeotropic distillation of water with 3 ml xylenes over 5 h. The polymer precipitated during cyclization. After cooling to room temperature, the polymerization mixture was poured into 100 ml methanol to remove solvent from the powdery yellow polymer (**4d**), which was isolated by filtration and dried at 100°C under vacuum; yield 2.07 g; *ca.* 100%. All analyses were done after samples were dried further at 300°C under nitrogen for 1 h; i.r. (KBr): 3486 (OH stretch of residual amic acid), 3070 and 2923 (aromatic C–H and aliphatic C–H stretch), 1781–1718 (C=O stretch), 1380

(C–N stretch), 1228 cm^{-1} (C–O–C stretch); ^{13}C n.m.r. (CP/MAS): δ 12.8, 16.1, 113.1,113.8, 117.0, 122.3, 124.7, 130.4, 131.8, 135.3, 146.2, 147.2, 149.3, 158.6, 159.4, 166.0 ppm.

Polyimide **4a**. ^{13}C n.m.r. (CP/MAS): δ 13.5, 17.0, 118.3, 123.4, 128.9, 136.3, 150.8, 168.0 ppm; i.r. (KBr): 3478, 3079, 2923, 1776, 1724, 1606, 1506, 1376, 1228, 1114, 817 cm^{-1}.

Polyimide **4b**. ^{13}C n.m.r. (CP/MAS): δ 13.3, 18.1, 113.4, 117.9, 124.3, 132.2, 139.5, 147.6, 158.7, 167.2 ppm; i.r. (KBr): 3471, 3052, 2921, 1776, 1712, 1606, 1506, 1373, 1226, 110, 829, 736 cm^{-1}.

Polyimide **4c**. ^{13}C n.m.r. (CP/MAS): δ 13.5, 16.3, 113.4, 117.3, 122.8, 125.6, 129.0, 131.1, 138.3, 148.2, 149.7, 155.4, 167.5 ppm; i.r. (KBr): 3064, 2923, 1778, 1718, 1608, 1508, 1378, 1234, 1085, 817 cm^{-1}.

Polyimide **4e**. ^{13}C n.m.r. (CP/MAS): δ 13.06, 117.1, 124.3, 129,9, 148.9, 158.9, 165.9 ppm; i.r. (KBr): 3482, 3058, 2923, 1779, 1718, 1608, 1506, 1374, 1225, 1089, 829, 717 cm^{-1}.

Polyimide **4f**. ^{13}C n.m.r. (CP/MAS): δ 11.9, 65.3, 115.5, 125.2, 132.4, 138.6, 148.5, 158.1, 165.5 ppm; i.r. (KBr): 3490, 3066, 2929, 1785, 1727, 1608, 1508, 1382, 1228, 1093, 831, 715 cm^{-1}.

Polyimide **4g**. ^1H n.m.r. (CDCl$_3$): δ 1.55, 175, 2.12, 6.89, 7.01, 7.25, 7.86 ppm; ^{13}C n.m.r. (CDCl$_3$): δ 12.8, 13.4, 16.6, 31.2, 42.8,112.1, 116.1, 117.1, 121.1, 121.9, 123.8, 125.2, 125.8, 128.1, 128.9, 130.1, 133.2, 124.4, 147.7, 150.5, 152.9, 157.6, 158.3, 163.9, 167.2 ppm; i.r. (film on salt window): 2962, 2873, 1774, 1720, 1602, 1504, 1378, 1216, 1078, 835 cm^{-1}.

General polyamide synthesis

Synthesis of polyamide **6c** is described as a typical procedure. A mixture of TBIPA (0.65 g, 2.92 mmol), **3b** (1.18 g, 2.92 mmol), LiCl (0.86 g) and pyridine (0.6 ml, 7.45 mmol) was heated to 100°C with stirring in NMP (17 ml), then TPP (1.68 ml, 6.41 mmol) was added to the solution. After 4 h of stirring at this temperature, it was cooled to room temperature and precipitated into methanol. The polymer (**6c**) was isolated as a yellow powder and refluxed in acetone for 1.5 h, filtered and dried at 100°C under vacuum; yield 1.62 g, 94%; intrinsic viscosity 0.99 dl g^{-1} in NMP/5% LiCl at 35°C; ^{13}C n.m.r. (CP/MAS): δ 30.4, 34.6, 121.1, 126.7, 134.3, 140.2, 152.3, 156.1, 167.1 ppm; i.r. (KBr): 3311 (N–H stretch), 1652 (C=O stretch, amide I), 1506 (N–H bend, amide II), 1373 (C–N stretch, amide III), 1211 cm^{-1} (C–O–C stretch).

Polyamides from IPDC were synthesized as follows. For example, **3a** (1.06 g, 3.18 mmol) was dissolved in 10 ml NMP under N_2 in a 100-ml round-bottomed flask equipped with an addition funnel and a condenser. Pyridine (0.57 ml, 7.08 mmol) was added to the solution and cooled to 0°C in an ice bath. IPDC (0.64 g, 3.18 mmol) was dissolved in 10 ml NMP and added dropwise to the polymerization mixture from the addition funnel with fast stirring. The reaction mixture was stirred for 4 h at 0°C and 7 h at room temperature, and then added into a large excess of methanol to give a white powdery product (**5b**). The crude product was filtered, refluxed in acetone for 1 h, filtered and dried at 100°C under vacuum; yield 1.34 g, 90%, intrinsic viscosity

(measured in NMP at 35°C) 0.46 dl g^{-1}; ^{1}H n.m.r. (DMSO-d_6): δ 2.02, 2.06, 2.10, 6.79, 6.79, 692, 7.70, 774, 7.79, 8.11, 8.14, 8.51, 8.62, 10.37, 10.41 ppm; ^{13}C n.m.r. (DMSO-d_6): δ 12.4, 12.8, 16.0, 114.3, 116.9, 119.6, 122.4, 126.9, 127.3, 128.5, 129.2, 130.4, 131.4, 132.9, 133.7, 135.2, 146.8, 150.5, 153.8, 164.7, 164.8 ppm; i.r. (KBr): 3274 (N–H stretch), 1668 (C=O stretch, amide I), 1506 (N–H bend, amide II), 1373 (C–N stretch, amide III), 1213 cm^{-1} (C–O–C stretch).

Polyamide **5a**. ^{13}C n.m.r. (CP/MAS): δ 13.2, 117.5, 124.7, 130.6, 147.6, 158.5, 166.3 ppm; i.r. (KBr): 3313, 3050, 2921, 1646, 1504, 1403, 1311, 1207, 1072, 821 cm^{-1}.

Polyamide **5c**. ^{1}H n.m.r. (DMSO-d_6): δ 1.37, 2.02, 2.06, 2.10, 6.78, 6.92, 7.74, 8.10, 8.38, 10.41 ppm; ^{13}C n.m.r. (DMSO-d_6): δ 12.3, 12.8, 16.0, 30.9, 34.8, 114.2, 116.9, 119.6, 122.4, 124.2, 127.3, 129.1, 131.4, 132.9, 133.7, 134.9, 146.7, 150.6, 151.2, 153.8, 165.1 ppm; i.r. (KBr): 3315, 3046, 2960, 1666, 1598, 1502, 1405, 1309, 1211, 1076, 873, 821 cm^{-1}.

Polyamide **5d**. ^{1}H n.m.r. (swelled in DMSO-d_6): δ 2.01, 2.05, 2.10, 6.76, 6.92, 7.19, 7.46, 7.73, 8.03, 10.20 ppm; ^{13}C n.m.r. (swelled in DMSO-d_6): δ 12.3, 12.8, 15.9, 114.2, 116.9, 118.4, 119.6, 122.2, 129.1, 130.0, 131.4, 133.0, 145.5, 150.6, 153.7, 158.5, 164.4 ppm; i.r. (KBr): 3064, 2923, 1778, 1718, 1608, 1508, 1378, 1234, 1085 cm^{-1}.

Polyamide **5e**. ^{1}H n.m.r. (DMSO-d_6): δ 2.32, 3.54, 7.09, 7.96, 8.83, 9.03 ppm; ^{13}C n.m.r. (DMSO-d_6): δ 12.3, 12.8, 15.9, 114.3, 116.9, 119.6, 122.1, 127.3, 127.6, 129.0, 131.4, 132.6, 133.4, 139.8, 142.8, 146.7, 150.5, 154.0, 163.8 ppm; i.r. (KBr): 3347, 3043, 2923, 2871, 1662, 1504, 1405, 1317, 1209, 1157, 1084, 829 cm^{-1}.

Polyamide **5f**. ^{1}H n.m.r. (DMSO-d_6): δ 2.02, 2.06, 2.11, 6.79, 6.93, 7.52, 7.74, 8.05, 10.44–10.39 ppm; ^{13}C n.m.r. (DMSO-d_6): δ 12.4, 12.8, 15.9, 63.4, 63.9, 64.3, 114.3, 116.9, 118.1, 119.6, 122.1, 125.7, 127.3, 128.1, 129.2, 129.7, 131.4, 132.9, 133.7, 134.8, 137.3, 146.7, 150.6, 153.9, 156.1, 164.4 ppm; i.r. (film): 3393, 3048, 2925, 2875, 1670, 1610, 1540, 1505, 1407, 1311, 1213, 823 cm^{-1}.

Polyamide **6a**. ^{13}C n.m.r. (CP/MAS): δ 30.4, 34.4, 121.6, 126.1, 134.2, 138.6, 154.9, 167.3 ppm; i.r. (KBr): 3326, 3045, 2966, 2867, 1656, 1600, 1492, 1407, 1373, 1328, 1209, 1132, 881, 831 cm^{-1}.

Polyamide **6b**. ^{13}C n.m.r. (CP/MAS): δ 30.0, 34.4, 122.1, 128.8, 136.6, 154.7, 156.4, 165.9 ppm; i.r. (KBr): 3313, 3058, 2968, 2869, 1658, 1506, 1403, 1369, 1213, 1120, 829 cm^{-1}.

Polyamide **6d**. ^{13}C n.m.r. (CP/MAS): δ 30.3, 34.4, 121.6, 130.9, 140.1, 149.1, 152.9, 155.2, 157.1, 161.6, 164.2, 166.8 ppm; i.r. (KBr): 3430, 3353, 3043, 2958, 1664, 1596, 1502, 1407, 1371, 1318, 1213, 1118, 881, 837 cm^{-1}.

Polyamide **6e**. ^{13}C n.m.r. (CP/MAS): δ 30.3, 34.5, 121.3, 128.3, 140.5, 154.9, 164.9 ppm; i.r. (KBr): 3353, 3058, 2958, 2871, 1671, 1604, 1506, 1407, 1375, 1331, 1213, 1174, 1093, 883 cm^{-1}.

Polyamide **6f**. ^{13}C n.m.r. (CP/MAS): δ 30.0, 34.4, 64.8, 121.4, 127.8, 129.9, 135.6, 149.9, 155.9, 164.4 ppm; i.r. (KBr): 3289, 3056, 2958, 2871, 1670, 1608, 1508, 1414, 1375, 1324, 1253, 1213, 1176, 1123, 883 cm^{-1}.

RESULTS AND DISCUSSION

Monomer synthesis

1,4-Bis(4-aminophenoxy)trimethylbenzene (**3a**) and 1,4-bis(4-aminophenoxy)-2,5-di-*t*-butylbenzene (**3b**) were prepared in two steps according to *Figure 1*. Compounds **2a** and **2b** were synthesized by nucleophilic aromatic substitution of trimethylhydroquinone and di-*t*-butylhydroquinone respectively, with *p*-fluoronitrobenzene in the presence of anhydrous potassium carbonate in DMAc. The corresponding diamines were obtained in high purity by using hydrazine hydrate and Pd/C catalyst in refluxing ethanol. 4,4′-Oxydianiline was isolated as a by-product from both reactions. Although this material was not mentioned by Liaw and Liaw[10] in their synthesis of **3b** from *p*-chloronitrobenzene, we also observed it in the reaction
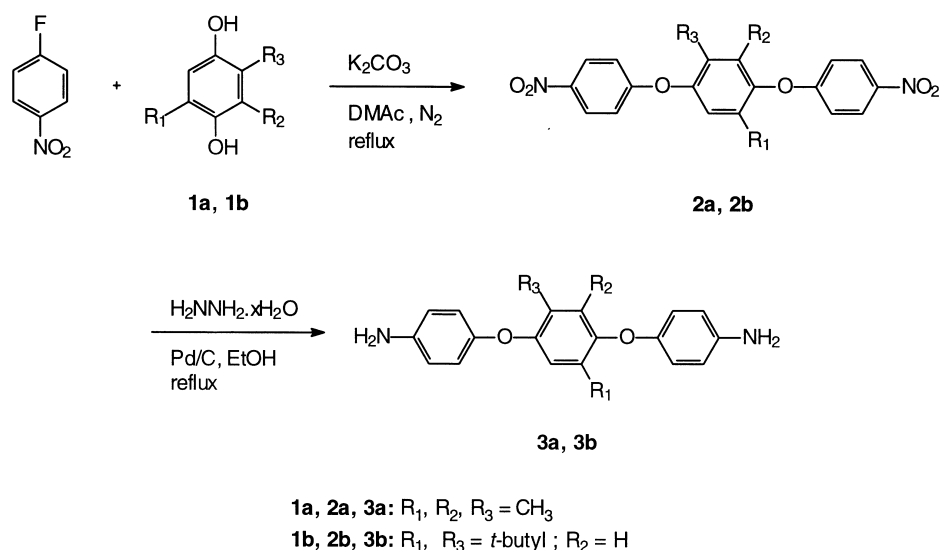

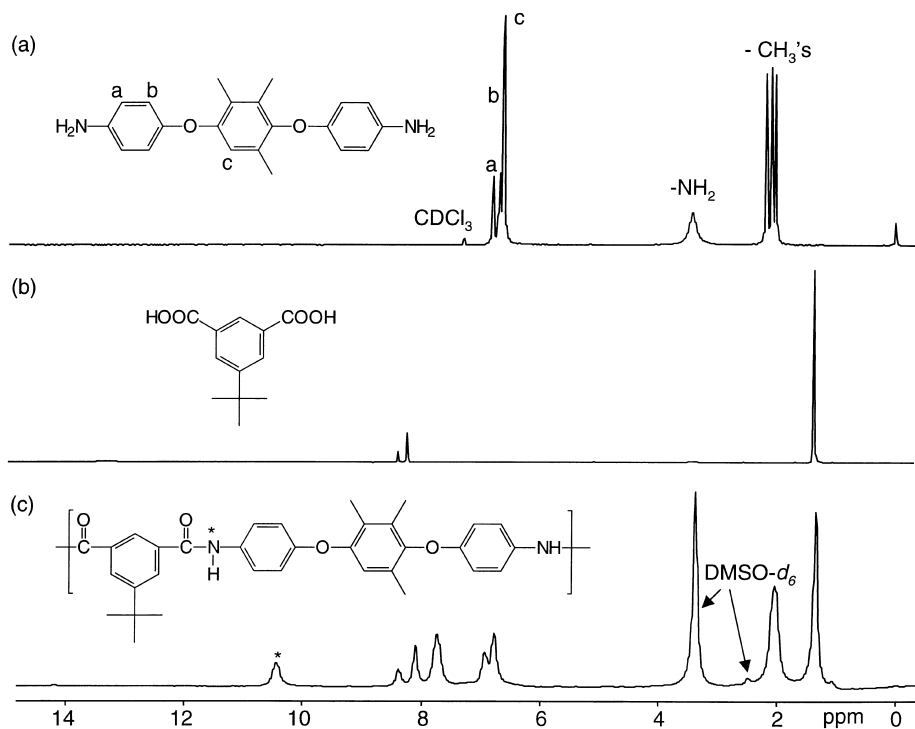**Figure 1** Synthesis of dinitro and diamino compounds

Figure 2 (a) ^{1}H n.m.r. (CDCl$_3$) spectrum of **3a**. (b) ^{1}H n.m.r. (DMSO-d_6) spectrum of TBIPA. (c) ^{1}H n.m.r. (DMSO-d_6) spectrum of **5c**

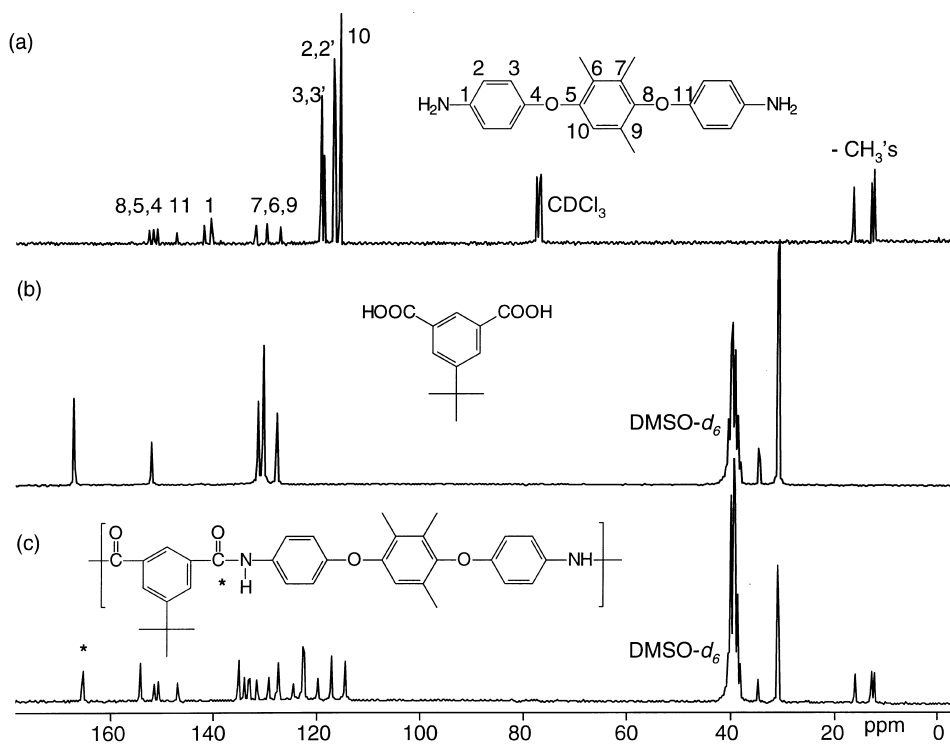**Figure 3** (a) ^{13}C n.m.r. (CDCl$_3$) spectrum of **3a**. (b) ^{13}C n.m.r. (DMSO-d_6) spectrum of TBIPA. (c) ^{13}C n.m.r. (DMSO-d_6) spectrum of **5c**

with the chloro substrate, which gave the desired products in much lower yields.

All the structures were confirmed by *FT*i.r., n.m.r. and elemental analysis. The dinitro compounds **2a** and **2b** displayed characteristic absorption bands corresponding to symmetric and asymmetric NO$_2$ stretching at 1502 and 1346 cm^{-1}, respectively, which disappeared after reduction. The diamine compounds showed typical N–H stretching bands at 3423 and 3347 cm^{-1}. Both the diamine and dinitro compounds showed the –C–O–C– stretching band around 1230–1209 cm^{-1}, confirming the presence of the aromatic ether linkage. The ^{1}H and ^{13}C n.m.r. spectra of the diamine **3a** are given in *Figures 2 and 3*, respectively. The signal at 3.40 ppm in *Figure 2* is unique to amine protons. The n.m.r. spectrum of diamine **3b** is as reported[10].
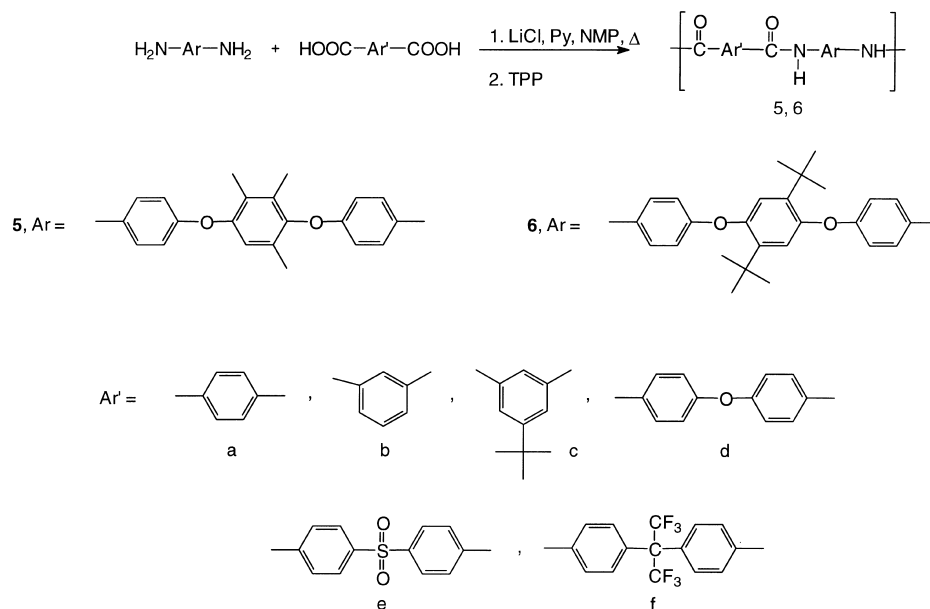
Figure 4 Synthesis of aromatic polyimides from **3a**
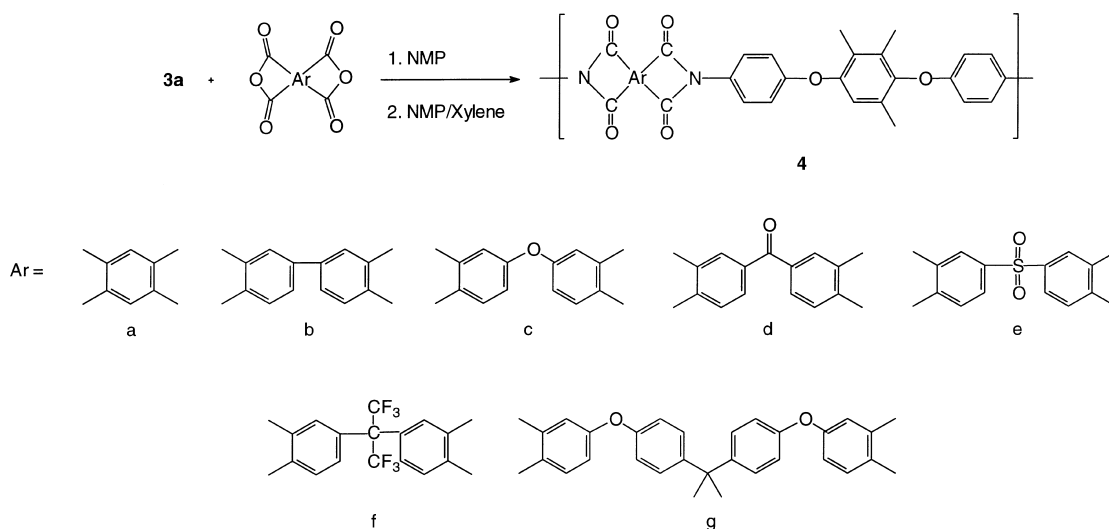
Figure 5 Synthesis of aromatic polyamides from **3a** and **3b**

Polymer synthesis

Polyimides. All aromatic poly(ether)imides were prepared by two-step polycondensation (*Figure 4*) from **3a** and various commercially available dianhydrides in NMP. Solid dianhydrides were added to the diamine solutions at ambient temperature to give poly(amic acids)s. All polymerizations showed large increases in viscosity in just a few minutes after the dianhydride dissolved; in fact, the stir shaft stopped completely in a couple of hours, indicating that high molecular weight polymer had formed. Polyimides **4a–e** precipitated from solution during imidization. The only exceptions were polyimides of 6FDA and BPADA, which were stirred as viscous poly(amic acid) solutions overnight and stayed in solution during cyclization. *FT*i.r. bands at 1774 and 1720 cm^{-1} for imide carbonyl and 1378 cm^{-1} for C–N stretches verified the imide formation. A weak OH stretch for uncyclized amic acid units was observed around 3400 cm^{-1} for some of the polyimides that precipitated during imidization due to inherent insolubility in the reaction medium. The chemical structure of

polyimide **4g** was confirmed by solution n.m.r. in chloroform; all other polyimides were characterized by solid state ^{13}C n.m.r. spectroscopy, which showed disappearance of a peak at 141.7 ppm shift for the amine *ipso* carbon and downfield shifts of the unique carbon of trimethylhydroquinone (C-10). Intrinsic viscosities of poly(amic acid)s in NMP ranged from 0.45 to 0.85 dl g^{-1} at 35°C, confirming the formation of moderate to high molecular weight products.

Polyamides. Two series of aromatic polyamides, **5a–f** and **6a–f**, were synthesized using the Yamazaki[18] phosphorylation polycondensation procedure from dicarboxylic acids and extended diamines **3a** and **3b** (*Figure 5*). Polymers **5b** and **6b**, however, were prepared from isophthaloyl dichloride and the corresponding diamines in the presence of pyridine at low temperatures. All polyamidations proceeded in homogeneous, transparent and viscous solutions throughout the reaction, and the polyamides were isolated as fibres or powders in quantitative yields. Intrinsic viscosities for **5a–f** ranged from 0.30 to 0.73 dl g^{-1} in NMP, and for

6a–f were between 0.57 and 1.47 dl g^{-1} in 5% LiCl/NMP, indicating moderate to high molecular weight polyamides. Polyamide structures were verified by *FT*i.r. based on characteristic absorption bands observed around 3300 (N–H stretch), 1660 (C=O stretch), 1506 (N–H bending) and 1373 cm^{-1} (C–N stretch). Solution ^{1}H and ^{13}C n.m.r. spectra in DMSO-d_6 confirmed the chemical structures of **5a–f** with amide proton chemical shifts observed at *ca.* 10 ppm, and downfield shifts of the unique proton of the central ring (H-3). Disappearance of the NH$_2$ peak at 3.4 ppm indicates complete conversion of the amine groups into amides. Similarly, disappearance of the amine-bearing carbon peak at 144 ppm and appearance of the amide carbonyl peak at around 167 ppm in solid-state ^{13}C n.m.r. spectra were evidence for chemical structure verification of polyamides **6a–f**. Example spectra are shown in *Figures 2 and 3*.

Polymer properties

Polyimides. The solubility of the polyimides was determined qualitatively (*Table 1*). All except **4g** showed poor solubility in common organic solvents such as chloroform, DMSO and NMP. However, even the solubility of **4g** could not be totally attributed to the diamine structure, as BPADA is a very flexible anhydride, which should enhance solubility over more rigid dianhydrides. The solubility behaviour of these polymers is similar to the polyimides prepared from **3b**. Liaw and Liaw assumed that the high symmetry of the polyimide backbone containing the 2,5-di-*t*-butylhydroquinone unit leads to facile packing and, hence, the insolubility[10]. Although the aromatic rings of diamine **3a** cannot be co-planar, poor solubility of the prepared polyimides indicates either strong intermolecular interactions or good packing ability. Polyimides **4a**, **4c**, **4d** and **4g** were soluble in concentrated sulfuric acid, but small insoluble pieces were observed in some of the samples prepared for viscosity measurements; therefore, instead of polyimides, viscosities of the corresponding poly(amic acid) solutions were measured in NMP.

No glass transition was detected for **4a**, **4b**, **4d** and **4e**, even with modulated d.s.c., up to the decomposition temperatures (*Table 2*). Polyimides **4g**, **4c** and **4f** showed T_g values between 235 and 300°C, following the decreasing order of chain flexibility and steric hindrance of the dianhydrides, BPADA, ODPA and 6FDA. These values are 18–23°C higher than the analogous polyimides obtained from **3b** and *t*-butylhydroquinone-centred diamines[9,10].

Decomposition temperatures ranged from 435 to 482°C in nitrogen and 410 to 462°C in air, which are reasonable values considering the aliphatic content of these polymers. T.g.a. traces showed two-step transitions at later stages of decomposition in nitrogen and at much earlier stages but with slower decomposition rates in air, probably due to free radical formation on the methyl sites, resulting in cross-linking. Char yields were in the range of 31–48%, with **4e** having the lowest char yield and the lowest decomposition temperature, as is typical for sulfone-linked polyimides[9,11,19].

Polyamides. Polyamides prepared from **3a** showed excellent solubility in NMP, DMAc and DMSO (with heating). Polyamides from **3b** were not as soluble without added LiCl, indicating strong hydrogen bonding between chains. Polymers from terephthalic acid, the most rigid and smallest diacid monomer evaluated, were insoluble due to symmetry and the higher density of hydrogen bonding per repeat unit. Polyamides derived from 6FDCA were partially soluble in tetrahydrofuran and acetone, probably due to their non-planar structures and low cohesive energies caused by the CF$_3$ groups. The slight solubility differences between the **5a–f** and **6a–f** series are believed to be related to the molecular symmetry in **3b**, similar to the behaviour in the polyimides. Molecular symmetry allows better packing, stronger inter-chain interactions and therefore lower solubility for the **6a–f** series.

The thermal properties of the polymers were determined using d.s.c. and t.g.a. (*Table 3*). No T_g values were observed for the polyamides of terephthalic acid by d.s.c. Polyamides from DCDPS showed the highest T_g values in both series. When the two sets of polyamides are compared, **3a** polyamides showed slightly higher T_g values (3–8°C). This might be a consequence of higher restriction of mobility in TMHQ, which has three aliphatic groups hindering rotation at the ether sites in **3a**, in comparison to the disubstituted DTBHQ centre in **3b**.

Table 1 Solubility behaviour^a of synthesized polyimides and polyamides

Polymer	Solvent^b					
	CHCl$_3$	THF	NMP	DMAc	DMSO	H$_2$SO$_4$
4a	−	−	−	−	−	+
4b	−	−	−	−	−	δ
4c	−	−	δh	δh	δh	+
4d	−	−	−	−	−	+
4e	−	−	δh	δh	δh	+
4f	−	−	+ h	−	−	−
4g	+	δ	+	+ g	+ h	+
5a	−	−	− ^{c}	− ^{c}	−	
5b	−	−	+	+	+	
5c	−	−	+	+ h	+ h	
5d	−	−	+	+	+ h	
5e	−	−	+	−	+ h	
5f	−	δ	+	+	+	
6a	−	−	δ ^{c}	−	−	
6b	−	−	+ ^{c}	+	−	
6c	−	−	+ ^{c}	+	−	
6d	−	−	+ ^{c}	+ h	−	
6e	−	−	+ ^{c}	+	+ h	
6f	−	δ	+ ^{c}	+	−	

^{a} + , soluble; + h, soluble on heating; − , insoluble; δ, partially soluble; δh, partially soluble on heating
^{b}THF, tetrahydrofuran; NMP, *N*-methyl-2-pyrrolidinone; DMAc, *N,N*-dimethylacetamide; DMSO, dimethyl sulfoxide
^{c}With 5% w/v LiCl

Table 2 Thermal properties of **3a** polyimides

Polymer	T_g (°C)^a	T_{dec} (°C)^b		Char yield^c (%)	[η] (dl g^{-1})
		N$_2$	Air		
4a	ND^d	482	423	39	0.52
4b	ND^d	476	426	49	0.71
4c	261^d	451	422	42	0.55
4d	ND	465	447	43	0.74
4e	ND^d	435	410	32	0.45
4f	300	470	462	39	0.85
4g	235	471	447	36	0.54

ND, none detected up to decomposition temperature by d.s.c.
$^a T_g$ reported as inflection point of the second d.s.c. trace at a heating rate of 10°C min^{-1} in N$_2$
$^b T_{dec}$ reported as the 5% weight loss recorded by t.g.a. at a heating rate of 20°C min^{-1}
^{c}Residual wt% at 1000°C in N$_2$
^{d}Recorded as modulated d.s.c. at a heating rate of 2°C min^{-1}, with modulation amplitude of ± 1°C every 60 s

Table 3 Thermal properties and viscosity of polyamides

Polymer	T_g (°C)[a]	T_{dec} (°C)[b]		Char yield[c]	$[\eta]$
		N$_2$	Air	(%)	(dl g^{-1})
5a	ND[d]	439	423	57	—
5b	237	418	424	34	0.30[e]
5c	292 (280, 347)[f]	402	388	43	0.46[e]
5d	283 (345)[f]	415	401	49	0.73[e]
5e	305 (315)[f]	406	425	33	0.73[e]
5f	294	422	431	52	0.46[e]
6a	ND[d]	435	419	46	—
6b	300	463	407	28	0.57[g]
6c	292 (293)[f]	449	405	30	0.99[g]
6d	276 (305)[f]	458	426	39	1.47[g]
6e	302 (295)[f]	430	417	46	0.57[g]
6f	286	457	442	43	1.29[g]

ND, none detected up to decomposition temperature by d.s.c.
[a] T_g reported as inflection point of the second d.s.c. trace at a heating rate of 10°C min^{-1} in N$_2$
[b] T_{dec} reported as the 5% weight loss recorded by t.g.a. at a heating rate of 20°C min^{-1}
[c] Residual wt% at 1000°C in N$_2$
[d] Recorded as modulated d.s.c. at a heating rate of 2°C min^{-1}, with modulation amplitude of ± 1 every 60 s
[e] Measured in NMP
[f] Values in parentheses correspond to the endotherms in the first d.s.c. trace
[g] Measured in NMP/5 wt% LiCl

Polymers **6a–f** showed T_g values between 276 and 302°C. The glass transition temperatures for **5a–f** were between 237 and 305°C. A 55°C difference in T_g between **5b** and **5c** was observed as a result of an increased rotational barrier due to the *t*-butyl group of TBIPA. However, similar behaviour was not observed between **6b** and **6c**. The higher T_g values of **6e**, **5e** and **5f** are believed to be due, respectively, to the increased intermolecular interactions of the sulfone units and increased steric hindrance due to the hexafluorisopropylidene groups.

Polyamides **5a–f** and **6a–f** were stable in nitrogen up to 400°C and 430°C, respectively. Polyamides **5b**, **5e** and **5f** showed slightly higher stability in air than in nitrogen, possibly due to oxidative cross-linking. Slightly higher decomposition temperatures for the **6a–f** series in comparison to the **5a–f** series might be a result of strong interactions and better packing due to the symmetrical nature of the central unit. However, char yields for **5a–f** were higher than **6a–f** due to the higher aliphatic content of diamine **3b**. An interesting point is that the sulfone-containing polyamide **5e** gave the lowest char yield in its series, as was seen in polyimides, but it is not possible to generalize this behaviour to all sulfone-linked polyamides, since **6e** did not show the same trend.

CONCLUSION

Extended diamines **3a** and **3b**, containing TMHQ and DTBHQ units, were successfully synthesized in high purity and high yields. Soluble polyamides with high T_g values, good thermal stability and moderate to high molecular weights were synthesized from these diamines in good yields. Polyimides were synthesized from **3b** with high T_g values from flexible dianhydrides and no detectable T_g values for rigid ones. Incorporation of methyl substituents and disruption of ring–ring co-planarity did not enhance polyimide solubility.

Overall, our observations suggest that methyl and *t*-butyl groups on the central ring did not inhibit polymerization, and large viscosity increases occurred in very short reaction times during polymerization. It was also demonstrated that multiple substitutions at the flexible ether linkages increased rotational barriers and formed more rigid (although non-co-planar) segments that enhance T_g values.

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