ELSEVIER

Polymer 40 (1999) 3107–3117

polymer

Wholly aromatic polyamides and polyimides prepared from 3,3″-di(4-aminophenyl)-5,5″-di(4-biphenylyl)-*p*-terphenyl and 3,3″-di(4-aminophenyl)-5,5″,6,6″-tetraphenyl-*p*-terphenyl

John A. Mikroyannidis

Chemical Technology Laboratory, Department of Chemistry, University of Patras, GR-26500 Patras, Greece

Received 24 March 1998; revised 17 June 1998; accepted 17 June 1998

Abstract

3,3″-Di(4-aminophenyl)-5,5″-di(4-biphenylyl)-*p*-terphenyl and 3,3″-di(4-aminophenyl)-5,5″,6,6″-tetraphenyl-*p*-terphenyl as well as the corresponding acid chlorides were synthesized through pyrylium salts. The polyamides and polyimides prepared from them were characterized by inherent viscosity, elemental analyses, FTIR, UV–vis, ^{1}H-NMR, ^{13}C-NMR, X-ray diffraction, DSC, TMA, TGA, isothermal gravimetric analysis and moisture absorption. The polymers were amorphous and dissolved in polar aprotic solvents and CCl_3COOH. They did not show melting and their I_g values ranged from 212 to 305°C. No weight loss was observed up to 357–386°C in air and the anaerobic char yields were 61–75% at 800°C. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Polyamides; Polyimides; Synthesis

1. Introduction

Over the past few years much interest has been devoted to the study of rigid-rod polymers, mainly because of their superior heat resistance and mechanical strength. However, their infusibility and limited solubility usually make them inaccessible for processing by conventional methods. To improve the solubility of these materials, several approaches, such as the introduction of bulky side groups along the main chain, have been used [1]. Many rigid-rod polyamides, mainly poly(terephthalamides), bearing aromatic side groups have been synthesized [2–7]. In addition, certain rigid-rod polyimides carrying aromatic pendent groups [8,9] as well as a combination of aromatic and aliphatic side groups [10,11] have been synthesized.

Recently, a synthetic route using pyrylium salts has been developed in our laboratory for the preparation of rigid-rod polyamides and polyimides. They contain long aliphatic or bulky aromatic pendent groups along the polymer backbone to enhance the solubility. Specifically, soluble rigid-rod polyamides and polyimides have been synthesized from substituted aromatic diamines of *p*-terphenyl [12,13] or biphenyl [14]. In addition, we have prepared blue-light-emitting, rigid-rod polyamides and polyimides starting from an aromatic diamine of *p*-quinquephenyl bearing phenyl or 4-biphenylyl side groups [15]. More recently, soluble phenyl- or alkoxyphenyl-substituted rigid-rod polyamides and polyimides containing *m*-terphenyls in the main chain have been synthesized [16].

In connection with our interest in preparing soluble polymers with highly aromatic backbones and with wholly aromatic pendent groups, we prepared a new series of polyamides and polyimides bearing substituted *p*-terphenyl moieties in the main chain. The polymers of the present investigation are expected to be not at all rigid-rod, because they contain *m*-substituted phenyl rings. More particularly, these polymers contain the amide or imide linkages on the pendent phenyls, which are situated at positions 3 and 3″ of *p*-terphenyl. In contrast, these linkages were attached to the terminal rings of *p*-terphenyl in our previous work [12,13]. Thus, the influence of the position of the amide or imide linkages on the polymer properties can be studied. Moreover, the *p*-terphenyl segment carries two 4-biphenylyl side groups at positions 5 and 5″ or four phenyl side groups at positions 5, 5″, 6 and 6″ to reduce molecular symmetry and improve the solubility. The side groups twist the oligophenylene moieties of the main chain out of a planar conformation, thereby increasing solubility.

0032-3861/99/$ - see front matter © 1999 Published by Elsevier Science Ltd. All rights reserved.

PII: S0032-3861(98)00489-3

2. Experimental

2.1. Characterization methods

Melting temperatures were determined on an electrothermal melting point apparatus IA6304 and are uncorrected. IR spectra were recorded on a Perkin-Elmer 16PC FTIR spectrometer with KBr pellets. ^{1}H-NMR spectra were obtained using a Brucker spectrometer (400 MHz) and a Varian T60A spectrometer (60 MHz). ^{13}C-NMR (100 MHz) spectra were obtained with a Brucker spectrometer. Chemical shifts (δ values) are given in ppm with tetramethylsilane as an internal standard. UV–vis spectra were recorded on a Beckman DU-640 spectrometer with spectograde DMF. DSC and TGA were performed on a DuPont 990 thermal analyzer system. Ground polymer samples of about 10 mg each were examined by TGA and isothermal gravimetric analysis (IGA), and the weight loss comparisons were made between comparable specimens. Dynamic TGA measurements were made at a heating rate of 20°C/min in atmospheres of N_2 or air at a flow rate of 60 cm^3/min. Thermomechanical analysis (TMA) was recorded on a DuPont 943 TMA using a loaded penetration probe at a scan rate of 20°C/min in N_2 with a flow rate of 60 cm^3/min. The TMA experiments were conducted at least in duplicate to assure the accuracy of the results. The TMA specimens were pellets of 8 mm diameter and 2 mm thickness prepared by pressing polymer powder for 3 min under 5–7 kpsi pressure at ambient temperature. The inherent viscosities of polymers were determined for solutions of 0.5 g/100 ml in CCl_3COOH or DMAc at 30°C using an Ubbelohde suspended level viscometer. Elemental analyses were carried out with a Hewlett-Packard model 185 analyzer. The wide-angle X-ray diffraction patterns were obtained for powder specimens on an X-ray PW-1840 Philips diffractometer.

To determine the equilibrium water absorption, polymer samples were previously conditioned at 120°C in an oven for 12 h. They were subsequently placed in a desiccator where 65% r.h. (relative humidity) was maintained by means of a saturated aqueous solution of $NaNO_2$ at 20°C, and were periodically weighed.

2.2. Reagents and solvents

1,4-Benzenedicarboxaldehyde was recrystallized from distilled water. 4-Nitroacetophenone, 4-phenylacetophenone and deoxybenzoin were recrystallized from 95% ethanol. 4-Methylacetophenone was distilled under reduced pressure. Terephthaloyl chloride was recrystallized from *n*-hexane. 1,4-Diaminobenzene was sublimed at about 110°C under vacuum (2–3 mm). Pyromellitic dianhydride (PMDA) and benzophenone tetracarboxylic dianhydride (BTDA) were recrystallized from acetic anhydride. Dimethylacetamide (DMAc) was distilled over CaH_2. Triethylamine was dried by distillation over KOH. Thionyl chloride was purified by distillation. Acetic anhydride, 1,2-dichloroethane and boron trifluoride etherate were used as supplied.

2.3. Preparation of monomers

2.3.1. Preparation of diamines (Scheme 1)

*2.3.1.1. 1,4-Phenylene-bis[2-(4-nitrophenylcarbonyl)ethene] (**1**)*

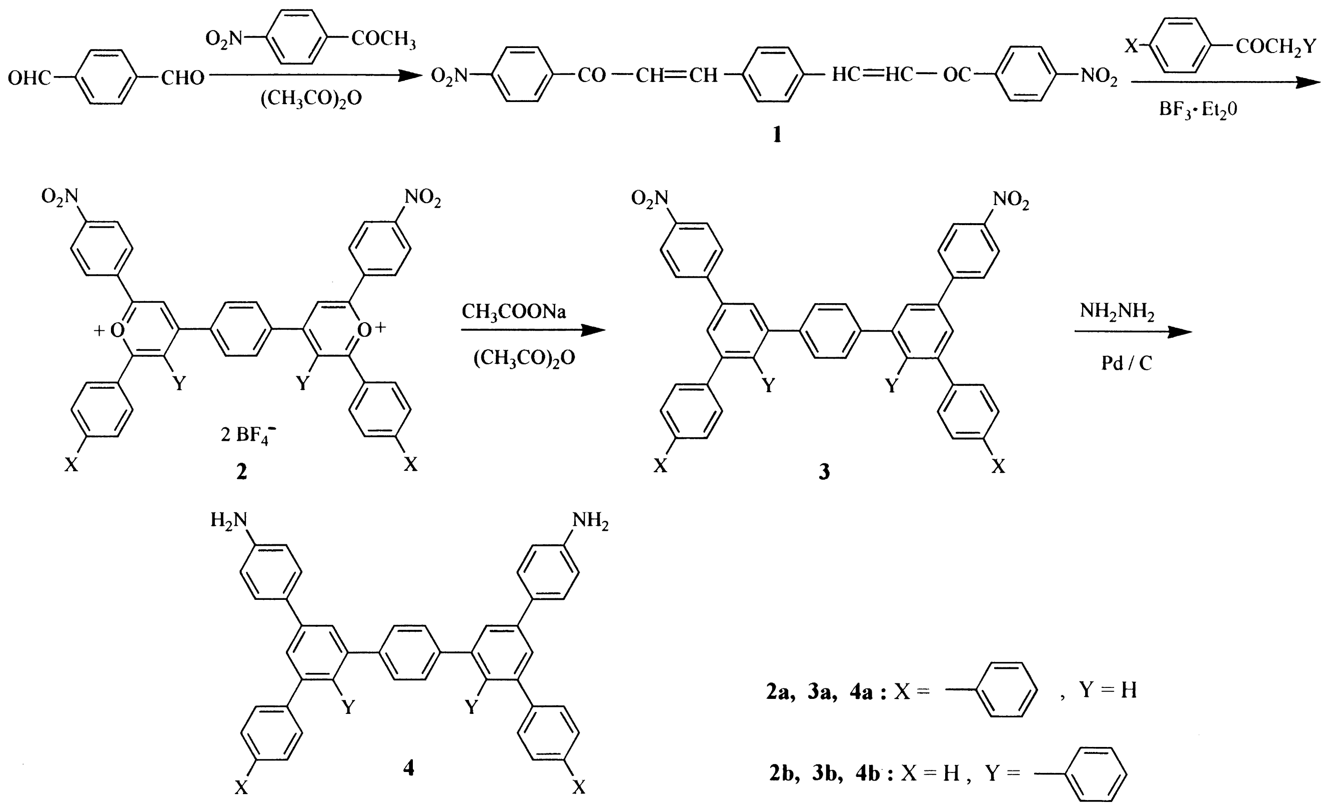
A mixture of 1,4-benzenedicarboxaldehyde (4.02 g, 30.00 mmol), 4-nitroacetophenone (9.91 g, 60.00 mmol) and acetic anhydride (20 ml) was stirred and refluxed for 35 h. Upon cooling to 0°C, a light yellow solid precipitated which was filtered, washed thoroughly with water and dried to afford **1**. It was purified by recrystallization from DMF (10.18 g, 79%, m.p. 283–285°C). IR (KBr, cm^{-1}): 1756 (C=O); 1666 (olefinic); 1516, 1334 (NO_2). ^{1}H-NMR (DMSO-d_6): 8.69–8.22 (m, 4H, aromatic *ortho* to NO_2); 8.12 (m, 4H, aromatic *meta* to NO_2); 7.85–7.42 (m, 4H, other aromatic and 4H, olefinic).

*2.3.1.2. 4,4′-(1,4-Phenylene)bis{[2-(4-nitrophenyl)-6-(4-biphenylyl)]pyrylium tetrafluoroborate} (**2a**)*

A flask was charged with a mixture of **1** (1.10 g, 2.57 mmol), 4-phenylacetophenone (1.02 g, 5.14 mmol) and 1,2-dichloroethane (10 ml). The mixture was heated at about 60°C and boron trifluoride etherate (1.8 ml, 14.33 mmol) diluted with 1,2-dichloroethane (5 ml) was added dropwise to the vigorously stirred mixture. It was refluxed overnight under N_2. It was concentrated under vacuum and a mixture of ethyl acetate/ether (2:1 v/v) was added to the residue. The dark red solid obtained was filtered, washed with ether and dried to afford **2a** (1.72 g, 70%, m.p. 231–233°C). IR (KBr, cm^{-1}): 1623, 1594, 1488, 1460 (aromatic and pyrylium structure); 1522, 1344 (NO_2); 1058 (br, BF_4^-). ^{1}H-NMR (DMSO-d_6): 8.84–8.28 (m, 4H, aromatic *meta* O^+ and 4H, aromatic *ortho* to NO_2); 7.96–7.23 (m, 26H, other aromatic).

*2.3.1.3. 4,4′-(1,4-Phenylene)bis{[2-(4-nitrophenyl)-5,6-diphenyl]pyrylium tetrafluoroborate} (**2b**)*

Compound **2b** was prepared according to the procedure described for **2a** from the reaction of **1** (1.19 g, 2.78 mmol) with deoxybenzoin (1.09 g, 2.56 mmol) and boron trifluoride etherate (0.90 ml, 7.17 mmol) in 1,2-dichloroethane (10 ml). The reaction mixture was concentrated under vacuum and ether was added to the residue. The red-brown precipitate was filtered, washed with ether and dried to afford **2b** (1.70 g, 64%, m.p. 167–169°C (decomposition)). IR (KBr, cm^{-1}): 1620, 1590, 1482, 1462 (aromatic and pyrylium structure); 1526, 1346 (NO_2); 1058 (br, BF_4^-). ^{1}H-NMR (DMSO-d_6): 8.86–8.30 (m, 2H, aromatic *meta* to O^+ and 4H, aromatic *ortho* to NO_2); 7.98–7.25 (m, 28H, other aromatic).



Scheme 1.

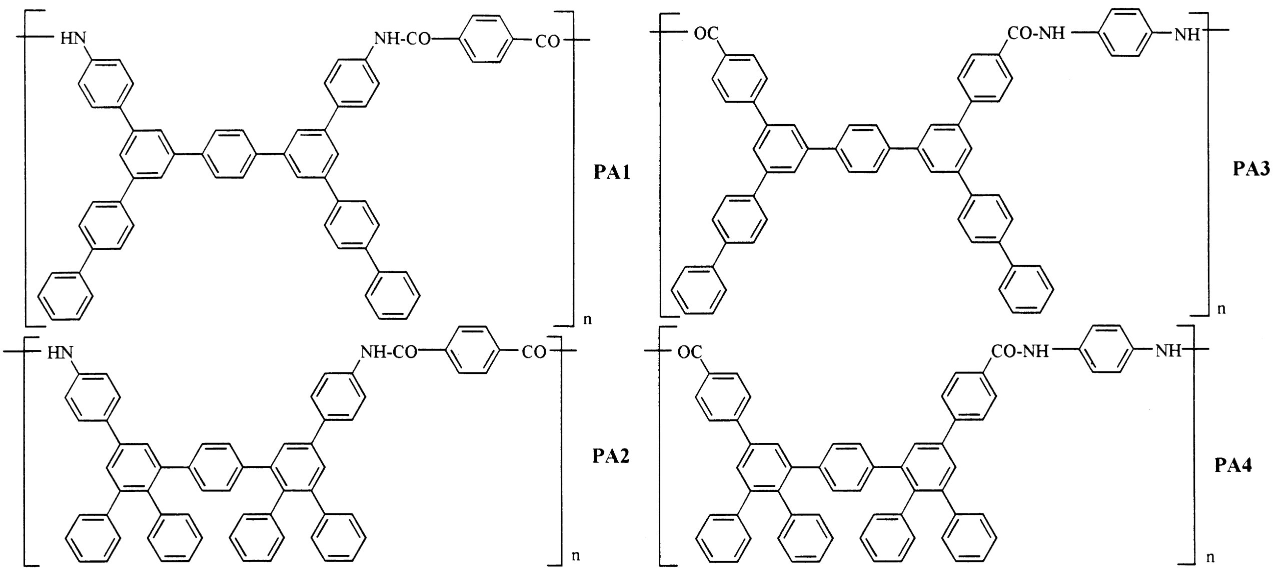


CHART 1

2.3.1.4. 3,3″-Di(4-nitrophenyl)-5,5″-di(4-biphenylyl)-p-terphenyl (3a)

A mixture of **2a** (0.80 g, 0.84 mmol), fused CH_3COONa (0.27 g, 3.36 mmol) and acetic anhydride (3 ml) was refluxed for 3 h. It was subsequently cooled to −10°C overnight and the precipitate was filtered, washed with water, then with methanol and dried to afford **3a** as a light brown solid. It was recrystallized from 1,2-dichlorobenzene (0.53 g, 82%, m.p. 223–225°C). IR (KBr, cm^{-1}): 1598 (aromatic); 1519, 1344 (NO_2). ^1H-NMR (DMSO-d_6): 8.35–8.24 (m, 4H, aromatic *ortho* to NO_2); 7.84–7.22 (m, 32H, other aromatic).

*2.3.1.5. 3,3″-Di(4-nitrophenyl)-5,5″,6,6″-tetraphenyl-p-terphenyl (**3b**)*

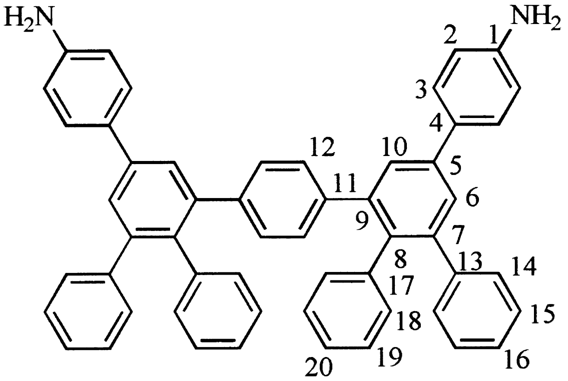
Compound **3b** was prepared as a brown-yellow solid in 91% yield (0.95 g) from the reaction of **2b** (1.28 g, 1.34 mmol) with fused CH_3COONa (0.44 g, 5.35 mmol) and acetic anhydride (4 ml) according to the procedure described for **3a**. It was recrystallized from a mixture of 1,4-dioxane/water (2:1 v/v), m.p. 216–218°C. IR (KBr, cm^{-1}): 1598 (aromatic); 1520, 1344 (NO_2). ^{1}H-NMR (DMSO-d_6): 8.36–8.23 (m, 4H, aromatic *ortho* to NO_2); 7.86–7.18 (m, 32H, other aromatic).

*2.3.1.6. 3,3″-Di(4-aminophenyl)-5,5″-di(4-biphenylyl)-p-terphenyl (**4a**)*

A flask was charged with a mixture of **3a** (1.12 g, 1.44 mmol), 1,4-dioxane (15 ml) and a catalytic amount of palladium 10% on activated carbon. Hydrazine hydrate (7 ml) was added dropwise to the stirred mixture at 101°C and refluxing was continued for 24 h. The mixture was subsequently filtered and the filtrate was poured into water. The precipitate was filtered and dried to afford **4a** as a light yellow-brown solid. It was recrystallized from chlorobenzene (0.94 g, 91%, m.p. 264–266°C). Anal. Calcd for $C_{54}H_{40}N_2$: C, 90.47%; H, 5.62%; N, 3.91%. Found: C, 89.96%; H, 5.57%; N, 3.95%. IR (KBr, cm^{-1}): 3448–3380 (N–H stretching); 1619 (N–H deformation); 1598, 1514, 1448 (aromatic); 1282 (C–N stretching). ^{1}H-NMR (DMSO-d_6): 7.93–7.32 (m, 10H, aromatic of *p*-terphenyl and 18H, aromatic of 4-biphenyls); 6.70 (m, 4H, aromatic *meta* to NH_2); 6.59 (m, 4H, aromatic *ortho* to NH_2); 5.16 (br, 4H, NH_2). The ^{13}C-NMR spectrum is shown in Fig. 1.

*2.3.1.7. 3,3″-Di(4-aminophenyl)-5,5″,6,6″-tetraphenyl-p-terphenyl (**4b**)*

Compound **4b** was prepared as a light yellow-brown solid in 74% yield (1.56 g) by catalytic hydrogenation of **3b** (2.30 g, 2.96 mmol) utilizing hydrazine hydrate (10 ml) in 1,4-dioxane (30 ml) and refluxing for 38 h. It was recrystallized from chlorobenzene (m.p. 144–146°C). Anal. Calcd for $C_{54}H_{40}N_2$: C, 90.47%; H, 5.62%; N, 3.91%. Found: C, 89.92%; H, 5.67%; N, 3.97%. IR (KBr, cm^{-1}): 3372 (N–H stretching); 1620 (N–H deformation); 1606, 1514, 1446 (aromatic); 1288 (C–N stretching). ^{1}H-NMR (DMSO-d_6): 7.63–6.84 (m, 8H, aromatic of *p*-terphenyl and 20H, aromatic of side phenyls at positions 5, 5″, 6 and 6″); 6.57 (m, 4H, aromatic *meta* to NH_2); 6.40 (m, 4H, aromatic *ortho* to NH_2); 6.40 (m, 4H, aromatic *ortho* to NH_2); 5.17 (br, 4H, NH_2).



^{13}C-NMR (DMSO-d_6): 149.78 (1); 142.12, 139.20 (5, 7, 8, 9, 11, 13, 17); 131.08 (4); 128.63, 128.38, 128.28, 128.15, 127.99, 126.87, 126.67, 126.51, 125.93, 124.97 (3, 6, 10, 12, 14, 15, 16, 18, 19, 20); 114.28 (2).

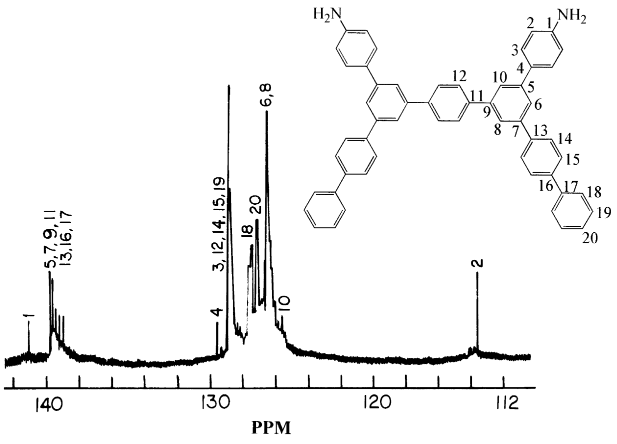


Fig. 1. ^{13}C-NMR spectrum of **4a** in DMSO-d_6 solution.

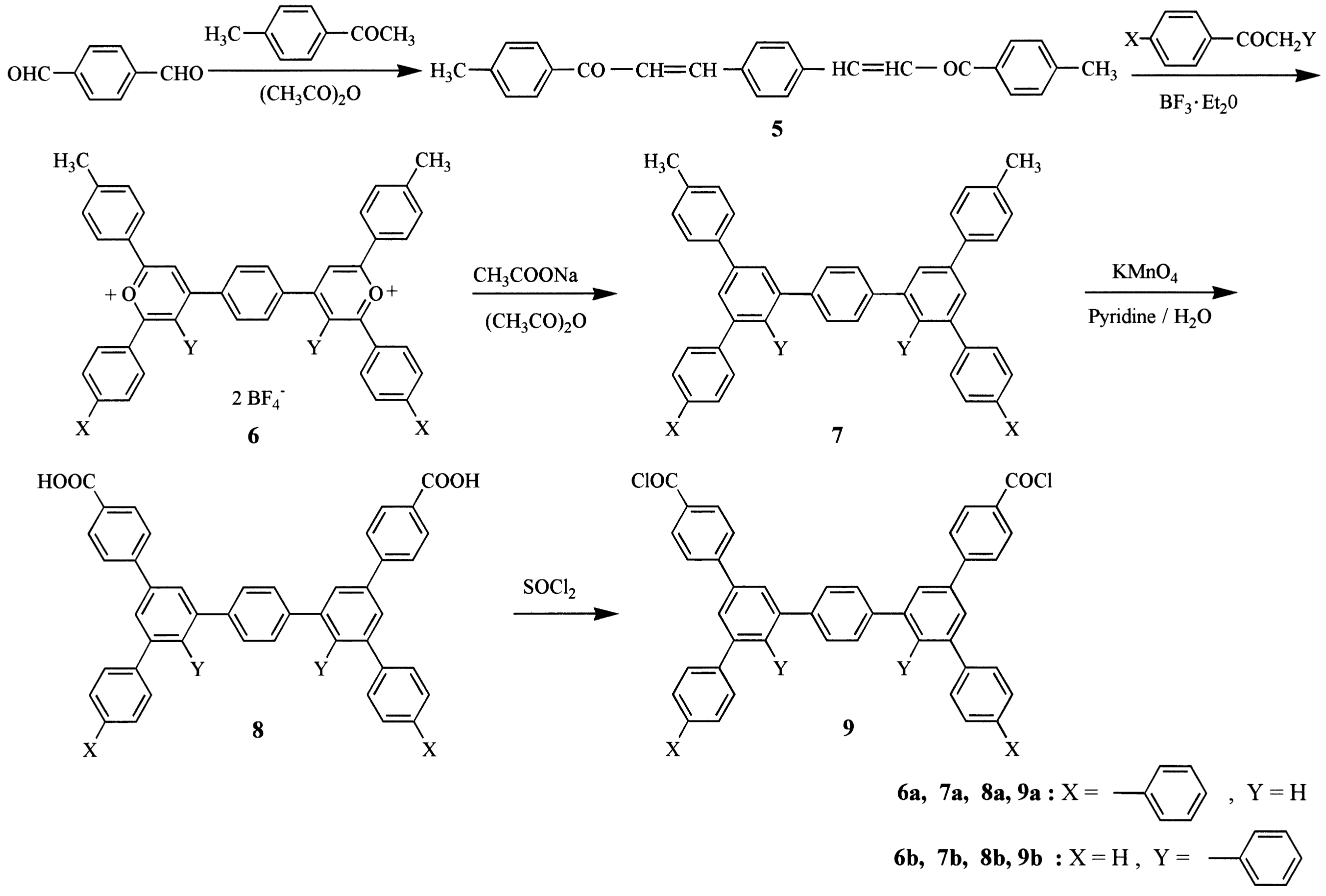
2.3.2. Preparation of dicarboxylic acids (Scheme 2)

*2.3.2.1. 1,4-Phenylene-bis[2-(4-methylphenylcarbonyl) ethene] (**5**)*

A mixture of 1,4-benzenedicarboxaldehyde (4.02 g, 30.00 mmol), 4-methylacetophenone (8.05 g, 60.00 mmol) and acetic anhydride was refluxed for 45 h. It was subsequently cooled to 0°C and the light yellow solid obtained was filtered, washed thoroughly with water and dried to afford **5**. A purified sample was obtained by recrystallization from DMF (6.81 g, 62%, m.p. 230–232°C). IR (KBr, cm^{-1}): 2920, 2860 (C–H aliphatic stretching); 1758 (C=O); 1660 (olefinic); 1464 (C–H aliphatic bending). ^{1}H-NMR (DMSO-d_6): 7.78–7.14 (m, 12H, aromatic and 4H, olefinic); 2.32 (s, 6H, CH_3).

*2.3.2.2. 4,4′-(1,4-Phenylene)bis{[2-(4-methylphenyl)-6-(4-biphenylyl)pyrylium tetrafluoroborate} (**6a**)*

A flask was charged with a mixture of **5** (2.00 g, 5.46 mmol), 4-phenylacetophenone (2.12 g, 10.92 mmol) and 1,2-dichloroethane (16 ml). The mixture was heated at about 60°C and boron trifluoride etherate (2.00 ml, 15.92 mmol) diluted with 1,2-dichloroethane (5 ml) was added dropwise to the mixture. It was refluxed overnight under N_2. The red solution obtained was concentrated under vacuum and ether was added to the residue. Compound **6a** precipitated as a dark red solid which was filtered, washed with ether and



Scheme 2.

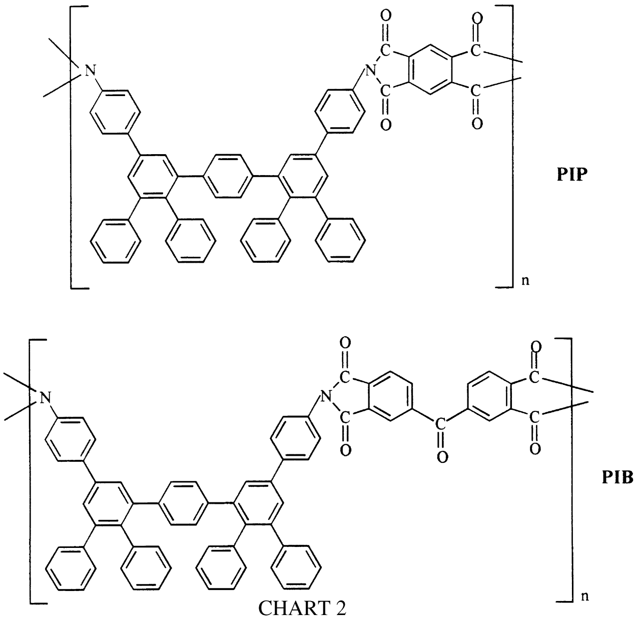


CHART 2

dried. It was recrystallized from chlorobenzene (3.28 g, 67%, m.p. 147–149°C). IR (KBr, cm^{-1}): 2920, 2854 (C–H aliphatic stretching); 1622, 1598, 1488 (aromatic and pyrylium structure); 1460 (C–H aliphatic bending); 1060 (br, BF_4^-). ^1H-NMR (DMSO-d_6): 8.85–8.40 (m, 4H, aromatic *meta* to O^+); 7.76–7.12 (m, 30H, other aromatic); 2.35 (s, 6H, CH_3).

*2.3.2.3. 4,4′-(1,4-Phenylene)bis{[2-(4-methylphenyl)-5, 6-diphenyl]pyrylium tetrafluoroborate} (**6b**)*

Compound **6b** was prepared according to the procedure described for **6a** by reacting **5** (2.00 g, 5.46 mmol) with deoxybenzoin (2.14 g, 10.92 mmol) and boron trifluoride etherate (2.503 ml, 19.20 mmol) in 1,2-dichloroethane (15 ml). The resulting solution was concentrated under vacuum and the residue was stirred first with ether and then with petroleum ether. The dark red-yellow solid thus obtained was filtered, washed with petroleum ether and dried to afford **6b**. It was purified by recrystallization from a mixture of ethyl acetate/ether (2:1 v/v) (2.34 g, 48%, m.p. 90–92°C). IR (KBr, cm^{-1}): 2920, 2857 (C–H aliphatic stretching); 1620, 1598, 1480 (aromatic and pyrylium structure); 1462 (C–H aliphatic bending); 1056 (br, BF_4^-). ^1H-NMR (DMSO-d_6): 8.84–8.45 (m, 2H, aromatic *meta* to O^+); 7.75–7.10 (m, 32H, other aromatic); 2.34 (s, 6H, CH_3).

*2.3.2.4. 3,3″-Di(4-methylphenyl)-5,5″-di(4-biphenylyl)-p-terphenyl (**7a**)*

A mixture of **6a** (3.24 g, 3.62 mmol), fused CH_3COONa (1.19 g, 14.49 mmol) and acetic anhydride (7 ml) was refluxed for 4 h. It was subsequently cooled at −10°C overnight and the precipitate was filtered, washed with water, then with methanol and dried to afford **7a**. It was recrystallized from a mixture of ethyl acetate/ether (2:1 v/v) (2.30 g, 89%, m.p. 167–169°C). IR (KBr, cm^{-1}): 2918, 2855 (C–H aliphatic stretching); 1602, 1512 (aromatic); 1486 (C–H aliphatic bending). ^{1}H-NMR (DMSO-d_6): 7.78–7.10 (m, 36H, aromatic); 2.34 (s, 6H, CH_3).

*2.3.2.5. 3,3″-Di(4-methylphenyl)-5,5″,6,6″-tetraphenyl-p-terphenyl (**7b**)*

Compound **7b** was prepared as a pale brown solid in 65% yield (1.23 g) from the reaction of **6b** (2.37 g, 2.65 mmol) with fused CH_3COONa (0.87 g, 2.65 mmol) and acetic anhydride (6 ml) according to the procedure described for **7a**. It was recrystallized from a mixture of acetone/ethanol (3:1 v/v) (95%, m.p. 148–150°C). IR (KBr, cm^{-1}): 2918, 2857 (C–H aliphatic stretching); 1604, 1512 (aromatic); 1446 (C–H aliphatic bending). ^{1}H-NMR (DMSO-d_6): 7.75–7.08 (m, 36H, aromatic); 2.35 (s, 6H, CH_3).

*2.3.2.6. 3,3″-Di(4-carboxyphenyl)-5,5″-di(4-biphenylyl)-p-terphenyl (**8a**)*

A flask was charged with a solution of **7a** (2.40 g, 3.36 mmol) in a mixture of pyridine (10 ml) and water (1 ml). Potassium permanganate (1.54 g, 9.74 mmol) was added to the solution and it was refluxed. Over a period of 8 h, potassium permanganate (3.02 g, 19.32 mmol) and water (7 ml) were added in portions to the refluxing solution. Refluxing was continued overnight. After cooling to room temperature, the mixture was filtered and manganese dioxide was washed thoroughly with boiling water. The combined filtrates were acidified with hydrochloric acid. The pale yellow precipitate was filtered, washed with water and dried to afford **8a**. It was recrystallized from 95% ethanol (1.46 g, 56%, m.p. 148–150°C). IR (KBr, cm^{-1}): 2542–3060 (O–H stretching); 1686 (C=O); 1606, 1512, 1486 (aromatic); 1420, 1286 (C–O stretching and O–H deformation). ^{1}H-NMR (DMSO-d_6): 12.80 (br, 2H, COOH); 8.12 (m, 4H, aromatic *ortho* to COOH); 7.72–7.23 (m, 32H, other aromatic).

*2.3.2.7. 3,3″-Di(4-carboxyphenyl)-5,5″,6,6″-tetraphenyl-p-terphenyl (**8b**)*

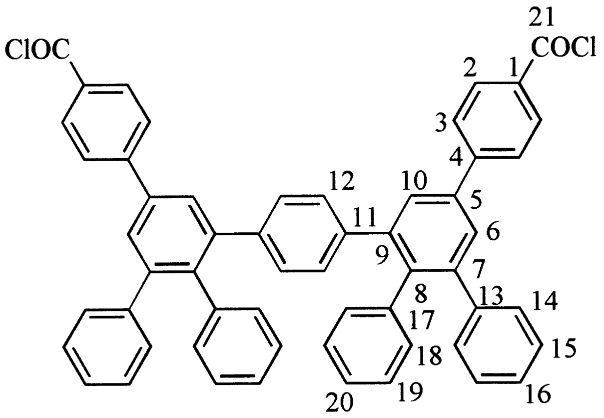
Compound **8b** was prepared as a pale yellow solid in 60% yield (1.57 g) from **7b** (2.40 g, 3.36 mmol) utilizing, in total, pyridine (10 ml), water (8 ml) and potassium permanganate (4.56 g, 28.86 mmol) according to the procedure described for **8a**. It was recrystallized from a mixture of glacial acetic acid/water (3:1 v/v) (m.p. 186–188°C). IR (KBr, cm^{-1}): 2548–3062 (O–H stretching); 1688 (C=O); 1604, 1510, 1488 (aromatic); 1422, 1286 (C–O stretching and O–H deformation). ^{1}H-NMR (DMSO-d_6): 12.67 (br, 2H, COOH); 8.10 (m, 4H, aromatic *ortho* to COOH); 7.75–7.28 (m, 32H, other aromatic).

*2.3.2.8. 3,3″-Di(4-chlorocarbonylphenyl)-5,5″-di(4-biphenylyl)-p-terphenyl (**9a**)*

A mixture of **8a** (1.43 g, 1.85 mmol), thionyl chloride (15 ml) and DMF (0.5 ml) was refluxed overnight. The resulting solution was concentrated under vacuum and the residue was stirred with a mixture of ether/petroleum ether (1:6 v/v). The pale yellow-brown solid thus obtained was filtered, washed with petroleum ether and dried to afford **9a**. It was recrystallized from a mixture of carbon tetrachloride/petroleum ether (1:2 v/v) (1.03 g, 69%, m.p. 159–161°C). Anal. Calcd for $C_{56}H_{36}Cl_2O_2$: C, 82.85%; H, 4.47%. Found: C, 82.08%; H, 4.51%. IR (KBr, cm^{-1}): 1772, 1702 (C=O); 1600, 1486 (aromatic); 1206, 1176 (–C–C=O stretching). ^{1}H-NMR (DMSO-d_6): 8.05 (m, 4H, aromatic *ortho* to C=O); 7.73–7.39 (m, 28H, other aromatic). The ^{13}C-NMR spectrum is shown in Fig. 2.

*2.3.2.9. 3,3″-Di(4-chlorocarbonylphenyl)-5,5″,6,6″-tetraphenyl-p-terphenyl (**9b**)*

Compound **9b** was prepared as a pale yellow solid in 62% yield (1.03 g) from the reaction of **8b** (1.59 g, 2.05 mmol) with thionyl chloride (15 ml) in the presence of DMF (0.5 ml) according to the procedure described for **9a**. It was recrystallized from a mixture of chloroform/petroleum ether (1:1 v/v) (m.p. > 280°C). Anal. Calcd for $C_{56}H_{36}Cl_2O_2$: C, 82.85%; H, 4.47%. Found: C, 81.97%; H, 4.50%. IR (KBr, cm^{-1}): 1774, 1734 (C=O); 1604, 1488 (aromatic); 1208, 1176 (–C–C=O stretching). ^{1}H-NMR (DMSO-d_6): 8.03 (m, 4H, aromatic *ortho* to C=O); 7.74–6.90 (m, 28H, other aromatic).



^{13}C-NMR (DMSO-d_6): 166.75 (21); 144.94 (4); 142.30 (13, 17); 139.83, 138.26, 138.10, 136.95 (5, 7, 8, 9, 11); 134.45 (1); 131.98 (2); 129.26, 129.18, 128.91 (12, 15, 19); 128.38, 127.49 (3, 6, 14, 16, 18, 20); 125.35 (10).

2.4. Preparation of polymers

*2.4.1. Polyamides **PA1**, **PA2, PA3,** and **PA4** (Chart 1)*

As a typical procedure for the preparation of polyamides the synthesis of **PA1** is given. A flask was charged with a solution of **4a** (0.60 g, 0.48 mmol) in DMAc (15 ml) containing 5 wt% LiCl. Triethylamine (0.17 g, 1.68 mmol) was

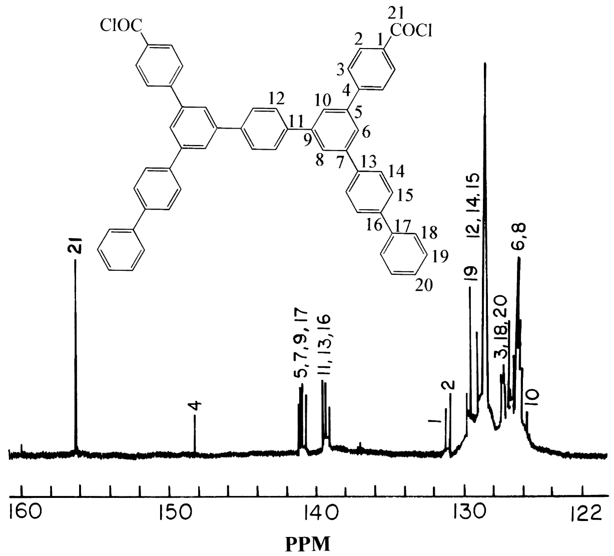


Fig. 2. ^{13}C-NMR spectrum of **9a** in DMSO-d$_6$ solution.

added to the solution. Terephthaloyl chloride (0.17 g, 0.84 mmol), dissolved in DMAc (5 ml), was added dropwise to the stirred solution at −10°C. Stirring of the mixture was continued at this temperature for 5 h and then at room temperature overnight in a stream of N$_2$. The mixture was poured into water, and the pale yellow-brown precipitate was filtered, washed with hot ethanol (95%) and then with hot acetone, and dried to afford **PA1** (0.69 g, 97%).

2.5. Polyimides *PIP* and *PIB* (Chart 2)

As a typical procedure for the preparation of polyimides, the synthesis of **PIP** is given. PMDA (0.12 g, 0.56 mmol) was added to a stirred solution of **4b** (0.40 g, 0.56 mmol) in DMAc (20 ml). The solution became viscous, and stirring was continued at room temperature for 6 h under N$_2$. Acetic anhydride (5 ml) and pyridine (2 ml) were added to the solution, and it was heated at 100°C overnight. It was subsequently poured into water, and the brown precipitate was filtered, washed with water and then with hot acetone, and dried to afford **PIP** (0.49 g, 98%).

The reaction yields, the inherent viscosities, and the elemental analyses for all polymers are given in Table 1.

3. Results and discussion

Two new aromatic diamines **4a** and **4b** were prepared according to the reaction sequence of Scheme 1. More particularly, 1,4-benzenedicarboxaldehyde was condensed with a double molar amount of 4-nitroacetophenone in boiling acetic anhydride to afford chalcone **1**. The latter reacted with 4-phenylacetophenone or deoxybenzoin in the presence of BF$_3$·Et$_2$O to yield substituted pyrylium salts **2**. They reacted subsequently with sodium acetate in acetic anhydride to afford compounds **3**. It has been reported that refluxing 2,4,6-triarylpyrylium salts with excess carboxylic acid anhydrides (RCH$_2$CO)$_2$O (R = H or Me) in the presence of condensing agents like sodium acetate results in 1,3,5-triarylbenzenes [17]. Finally, compounds **3** were catalytically hydrogenated to the corresponding diamines **4** by means of hydrazine hydrate.

An analogous synthetic route was used to synthesize the corresponding dicarboxylic acids **8** starting from 4-methylacetophenone (Scheme 2). The intermediate dimethyl compounds **7** were oxidized utilizing KMnO$_4$.

The structures of the monomers were identified by elemental analyses as well as IR and NMR spectroscopy. Figs 1 and 2 present the ^{13}C-NMR spectra of compounds **4a** and **9a** in DMSO-d$_6$ solution. Assignments of peaks are given in the figures. The –COCl moiety of **9b** gave a characteristic upfield peak at 156 ppm. Most of the aromatic carbon nuclei had comparable shifts and appeared in the region of 130–125 ppm in both spectra.

Table 1
Yield, inherent viscosities and elemental analyses of polymers

Polymer	Yield (%)	n_{inh} (dl/g)	Empirical formula	Elemental analysis			
					C (%)	H (%)	N (%)
PA1	97	1.04[a]	$(C_{62}H_{42}N_2O_2)_n$	Calcd	87.92	5.00	3.31
				Found	87.06	4.92	3.28
PA2	97	0.98[a]	$(C_{62}H_{42}N_2O_2)_n$	Calcd	87.92	5.00	3.31
				Found	86.98	5.07	3.36
PA3	87	0.86[b]	$(C_{62}H_{42}N_2O_2)_n$	Calcd	87.92	5.00	3.31
				Found	86.95	4.96	3.37
PA4	83	0.92[a]	$(C_{62}H_{42}N_2O_2)_n$	Calcd	87.92	5.00	3.31
				Found	87.15	4.93	3.25
PIP	98	1.35[b]	$(C_{64}H_{38}N_2O_4)_n$	Calcd	85.50	4.26	3.12
				Found	84.87	4.15	3.07
PIB	97	1.27[b]	$(C_{71}H_{42}N_2O_5)_n$	Calcd	85.01	4.22	2.79
				Found	84.73	4.17	2.86

[a] Inherent viscosity in CCl$_3$COOH (0.5 g/dl) at 30°C.

[b] Inherent viscosity in DMAc (0.5 g/dl) at 30°C.

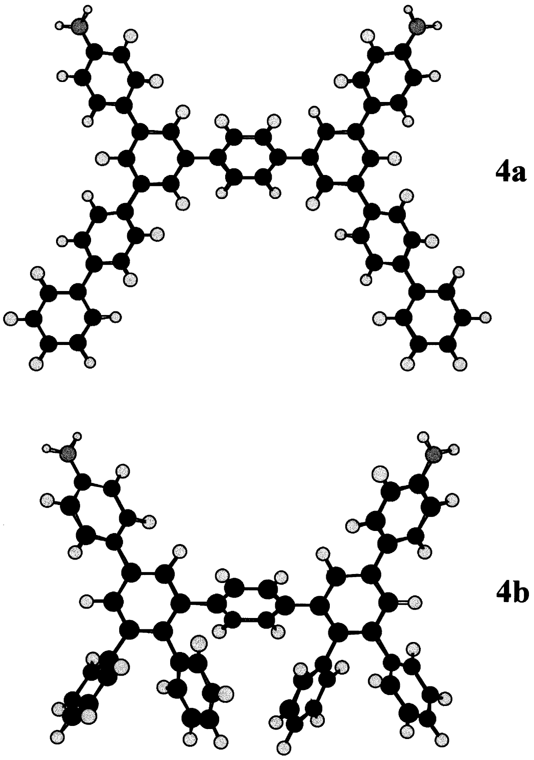


Fig. 3. Optimized geometries of **4a** (top) and **4b** (bottom) (CS Chem3D pro Molecular Modeling System, Version 3.5, 1995; CambridgeSoft Corporation, 1995).

To obtain fundamental information about the structural characteristics of diamines **4a** and **4b**, their optimized geometries were calculated by means of the CS Chem3D Pro (version 3.5) modelling system (Fig. 3). Obviously, **4a** is more coplanar than **4b** because the factor of deviation from plane (FDP) is 0.668 and 0.932, respectively. Note that the value of FDP is zero for an absolutely planar structure. In the case of **4b**, it seems that the phenyls at positions 5, 5″, 6, and 6″ are almost perpendicular to the two terminal phenyl rings of *p*-terphenyl. In addition, the middle ring of the *p*-terphenyl segment is more twisted in **4b** than in **4a**.

Wholly aromatic polyamides and polyimides were prepared, the structures of which are shown in Charts 1 and 2. Polyamides **PA1** and **PA2** were synthesized by reacting diamines **4a** and **4b**, respectively, with terephthaloyl chloride. Polyamides **PA3** and **PA4** were prepared from the reactions of acid chlorides **9a** and **9b**, respectively, with 1,4-diaminobenzene. Finally, polyimides **PIP** and **PIB** were synthesized from the reactions of **4b** with PMDA or BTDA. The yields of the preparation reactions were 83–98%, and their inherent viscosities ranged from 0.86 to 1.35 dl/g.

Fig. 4 presents typical FTIR spectra of polymers **PA1** and **PIB**. Polyamide **PA1** showed absorptions at 3270 (N–H stretching), 1668 (C=O), 1596 (aromatic), 1510 (N–H deformation and aromatic), and 1316 cm^{-1} (C–N stretching). Polyimide **PIB** displayed absorptions at 1780, 1724, 1368, and 1094 cm^{-1} associated with the imide structure.

The ^{1}H-NMR spectrum of polyamide **PA3** in DMSO-d_6 solution showed the following peaks (ppm): 10.05 (br, 2H, NHCO); 8.23 (m, 4H, aromatic *ortho* to C=O); 8.03–7.49 (m, 32H, other aromatic of dicarboxylic acid segment) and 6.55 (m, 4H, aromatic of diamine segment). On the other hand, the ^{13}C-NMR spectrum of **PA3** displayed a characteristic peak at 164 ppm assigned to the –NHCO– moiety.

The crystallinity of polymers was evaluated by means of X-ray diffractograms (Fig. 5). All polymers were generally amorphous with some low-level ordering. This feature was attributed to the phenyl or 4-biphenylyl side groups of *p*-terphenyl, which increased significantly the disorder in the chains. Upon comparing polyamides **PA1** and **PA2** it seems that the latter displayed a stronger and sharper reflection peak at about $2\Theta = 20°$, indicating a slightly

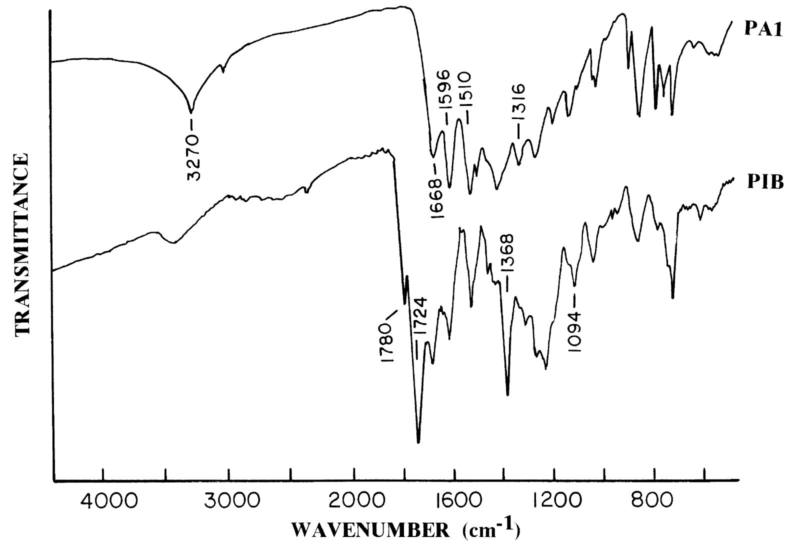


Fig. 4. FTIR spectra of **PA1** and **PIB**.

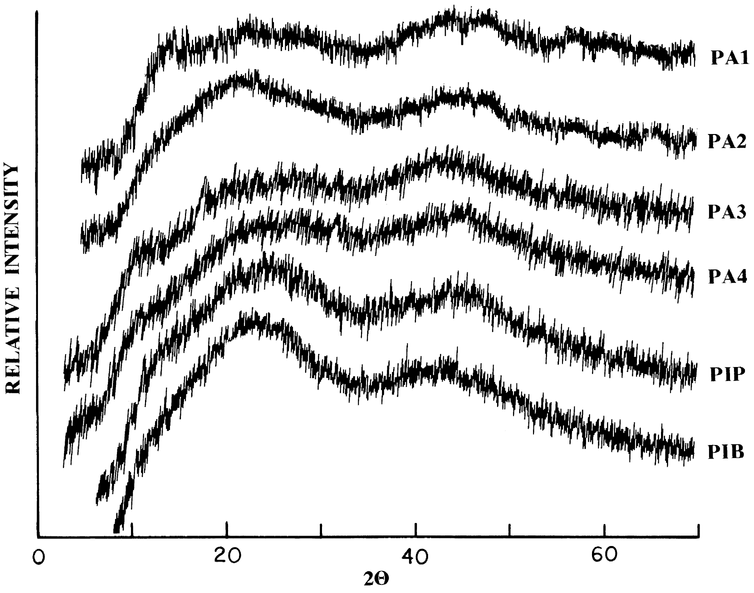


Fig. 5. X-ray diffraction patterns of polymers.

higher packing density [18]. This behaviour is reasonable because the longer 4-biphenylyl groups of **PA1** caused much disorder in chains, although the diamine segment of this polyamide is more coplanar (see above). Polyamides **PA3** and **PA4** as well as polyimides **PIP** and **PIB**, as compared in pairs, showed nearly identical diffraction patterns.

The isothermal water absorption of the polyamides was determined and correlated with their hydrophilicity. Polyamides **PA1**, **PA2**, **PA3**, and **PA4** showed water uptake of 3.91, 4.30, 2.21, and 4.44%, respectively, after 50 h exposure time. The corresponding numbers of moles of absorbed water per amide equivalent weight were 0.92, 1.01, 0.52, and 1.04. It seems that the polyamides containing 4-biphenylyl side groups on the *p*-terphenyl segment displayed lower hydrophilicity than the corresponding ones bearing pendent phenyls. The relatively lower hydrophilicity of polyamides with 4-biphenylyl side groups has also been observed in our previous work [13,15]. Interestingly, polyamide **PA1** exhibited significantly higher hydrophilicity than **PA3**, although they possess the same structure with different orientation of the amide groups. However, such a behaviour was not observed for polyamides **PA2** and **PA4**. Note that the model diamides of **PA1** and **PA2** had almost the same FDP values (0.91 versus 0.94), as they were calculated by means of the CS Chem3D modelling system. Therefore, the difference of hydrophilicity should not be attributed to stereochemical reasons.

One of the aims of the present investigation was the enhancement of the polymer solubility by introducing voluminous pendent groups along the polymer backbone. Table 2 outlines the solubilities of the polymers. All polyamides, apart from **PA3**, as well as all polyimides dissolved in polar aprotic solvents (DMF, NMP, DMAc) and CCl_3COOH upon heating. The solutions of these polyamides did not form gels or precipitate on cooling. Polyamide **PA3** showed higher solubility, being soluble in these solvents at room temperature. In addition, it dissolved in heated, less efficient solvents such as 1,1,2,2-tetrachloroethane, 1,2-dichlorobenzene and cyclohexanone. The polymers of the present investigation as compared

Table 2
Solubilities of polymers[a]

Polymer	Solvent[b]							
	DMF	NMP	DMAc	CCl_3COOH	TCE	DCB	CH	1,4-Dioxane
PA1	+[c]	+[c]	+[c]	+	−	−	−	−
PA2	+[c]	+[c]	+[c]	+	−	−	−	−
PA3	++	++	++	++	+	+	+	+−
PA4	+[c]	+[c]	+[c]	+	−	−	−	−
PIP	+	+	+	+	+−	+−	+−	+−
PIB	+	+	+	+	+	+−	+	+

[a] Solubility: ++, soluble at room temperature; +, soluble in hot solvent; +− partially soluble; −, insoluble.

[b] DMF, *N*,*N*-dimethylformamide; NMP, *N*-methylpyrrolidone; DMAc, dimethylacetamide; TCE, 1,1,2,2-tetrachloroethane; DCB, 1,2-diclorobenzene; CH, cyclohexanone.

[c] Solvent containing 5% w/w LiCl.

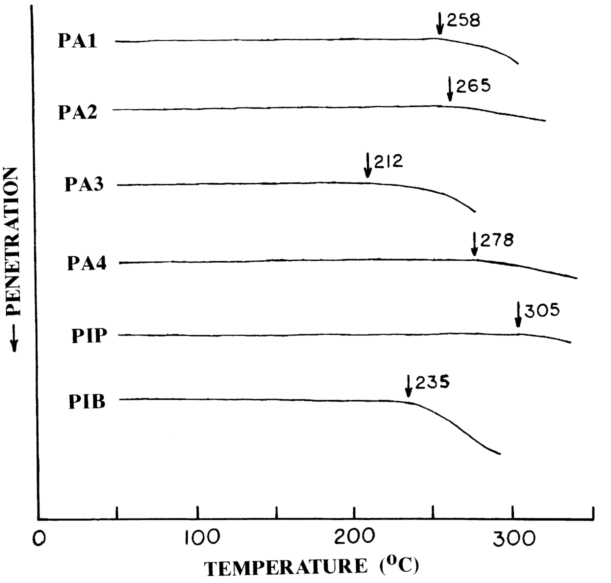


Fig. 6. TMA thermograms of all polymers. Conditions: N_2 flow, 60 cm^3/min; heating rate, 20°C/min.

with our previously synthesized analogous polymers containing *p*-terphenyl units in the main chain showed somewhat lower solubility [12,13].

The UV–vis spectra of polyamides **PA1**, **PA2**, **PA3** and **PA4** in DMF solution showed absorption maxima at 299, 285, 280 and 274 nm, respectively, and had a short tail into the visible region. It seems that the absorption maxima of polyamides followed the order **PA1** > **PA2** and **PA3** > **PA4**. This suggests that the polyamides derived from the less coplanar diamine **4b** possessed a shorter chromophore length. When the solutions of polyamides in DMF were exposed to a UV lamp, they were not fluorescent. It has been reported that other analogous polyamides prepared from 4,4″-diamino-3,5,3″,5″-tetraphenyl-*p*-terphenyl [15] and 4-amino-4″-carboxy-2′,6′-diphenyl-*p*-terphenyl [13] showed blue fluorescence. However, the polyamides of the present investigation were not fluorescent probably because the amide linkages lie on the side phenyls instead of being in a *para* position on the two terminal rings of *p*-terphenyl. The non-fluorescence could be caused by ion separation during the excitation procedure [13].

The DSC traces (second heating) of polymers did not show any distinct and reproducible transition up to 300°C. The glass transition temperatures (T_g) of polymers were determined by the TMA method using a loaded penetration probe. They were obtained from the onset temperatures of these transitions recorded at the second heating (Fig. 6). Polymers **PA1**, **PA2**, **PA3**, **PA4** and **PIP** displayed T_g transitions at 258, 265, 212, 278 and 305°C, respectively. Polyimide **PIB** showed a gradual relaxation starting at about 235°C attributable to a gradual weakening of intermolecular forces as the temperature increased [19]. The T_g values of polyamides was in the order **PA1** < **PA2** and **PA3** < **PA4**. It is obvious that the polyamides bearing 4-biphenylyl pendent groups displayed lower T_g values than the corresponding ones with phenyl pendent groups. The longer 4-biphenylyl side groups along the polymer backbone increased the polymer free volume, thus resulting in a reduction in T_g. No melting of all polymers was detected by both DSC and TMA.

The thermal stability of polymers was evaluated by TGA and IGA. Fig. 7 presents typical TGA traces for polymers **PA2**, **PA3** and **PIB** in N_2 and air. The initial decomposition temperature (IDT), the polymer decomposition temperature (PDT), and the maximum polymer decomposition temperature (PDT_{max}) in both N_2 and air as well as the anaerobic char yield (Y_c) at 800°C for all polymers are listed in Table 3. IDT and PDT were determined for the temperature at which 0.5 and 10% weight losses were observed, respectively. PDT_{max} corresponds to the temperature at which the maximum rate of weight loss occurred. The polymers were stable up to 365–394°C in N_2 and 357–386°C in air and afforded anaerobic char yields of 61–75% at 800°C. They displayed weight losses of 11.2–16.2%, following 20 h isothermal aging at 300°C in static air (Table 3).

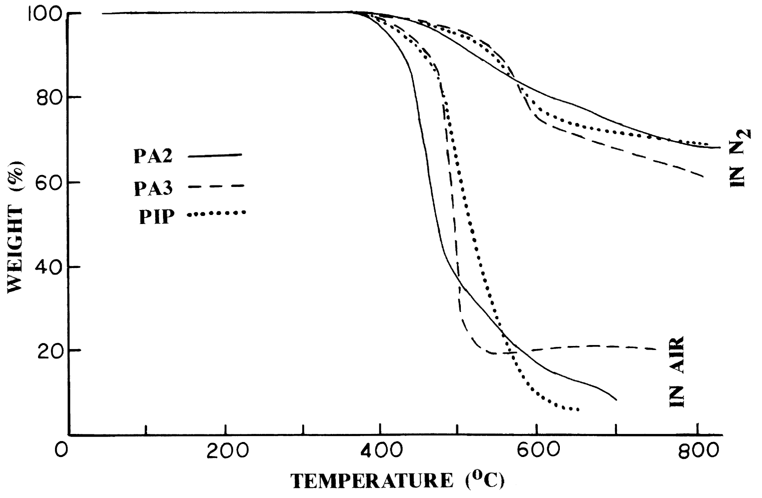


Fig. 7. TGA thermograms in N_2 and air of polymers **PA2, PA3** and **PIP**. Conditions: gas flow, 60 cm^3/min; heating rate, 20°C/min.

Table 3
Thermal stabilities of polymers

Polymer	In N_2				In air			
	IDT[a] (°C)	PDT[b] (°C)	PDT^c_{max} (°C)	Y^d_c (%)	IDT (°C)	PDT (°C)	PDT_{max} (°C)	Weight loss[e] (%)
PA1	365	482	533	62	357	419	467	16.2
PA2	389	512	508	68	373	417	456	12.3
PA3	392	542	578	61	375	456	489	15.1
PA4	377	537	552	75	370	433	512	11.9
PIP	394	548	563	69	386	444	489	11.2
PIB	387	543	578	64	375	436	482	11.7

[a] Inital decomposition temperature.
[b] Polymer decomposition temperature.
[c] Maximum polymer decomposition temperature.
[d] Char yield at 800°C.
[e] Weight loss after 20 h isothermal ageing at 300°C in static air.

4. Conclusions

Two new aromatic diamines **4a** and **4b**, which are derivatives of *p*-terphenyl, and the corresponding acid chlorides **9a** and **9b** were synthesized through pyrylium salts by a convenient method. They were used for the preparation of wholly aromatic polyamides and polyimides. The polymers were amorphous and dissolved in polar aprotic solvents and CCl_3COOH at room temperature or on heating. The solutions of polyamides in DMF were not fluorescent and showed absorption maxima at 274–299 nm. The polyamides **PA1** and **PA3** containing 4-biphenylyl side groups on the *p*-terphenyl segment displayed lower hydrophilicity as well as lower T_g values than the corresponding polyamides **PA2** and **PA4** bearing pendent phenyls. All polymers did not show melting and their T_g values ranged from 212 to 305°C.

References

[1] Duran R, Ballauff M, Wenzel M, Wegner G. Macromolecules 1988;21:2897.
[2] Jadhav JY, Krigbaum WR, Preston J. Macromolecules 1988;21: 538.
[3] Jadhav JY, Preston J, Krigbaum WR. J Polym Sci Part A Polym Chem 1989;27:1175.
[4] Kricheldorf HR, Burger R. J Polym Sci Part A Polym Chem 1994; 32:355.
[5] Kricheldorf HR, Schmidt B. Macromolecules 1992;25:5471.
[6] Kricheldorf HR, Schmidt B, Burger R. Macromolecules 1992;25:5465.
[7] Hatke W, Schmidt H-W, Heitz W. J Polym Sci Part A Polym Chem 1991;29:1387.
[8] Cheng SZD, Lee SK, Barley JS, Hsu SLC, Harris FW. Macromolecules 1991;24:1882.
[9] Harris FW, Feld W, Lanier LH. Appl Polym Symp 1975;26:421.
[10] Schmitz L, Rehahn M, Ballauff M. Polymer 1993;34:646.
[11] Schmitz L, Rehahn M. Macromolecules 1993;26:4413.
[12] Spiliopoulos IK, Mikroyannidis JA. Macromolecules 1996;29:5313.
[13] Spiliopoulos IK, Mikroyannidis JA. Macromolecules 1998;31:522.
[14] Spiliopoulos IK, Mikroyannidis JA. Polymer 1997;38:2733.
[15] Spiliopoulos IK, Mikroyannidis JA. Macromolecules 1998;31:515.
[16] Spiliopoulos IK, Mikroyannidis JA. Macromolecules 1998;31:1236.
[17] Zimmerman T, Fischer GW. J Prakt Chem 1987;329(6):975; Chem Abstr 1988;109:169929q.
[18] Hsiao SH, Yang CP, Chu KY. Macromolecules 1997;30:165.
[19] Rogers HG, Gaudiana RA, Hollinsed WC, Kalyanaraman PS, Manello JS, McGowan C, Minns RA, Sahatjian S. Macromolecules 1985;18:1058.