Polymer Vol. 39 No. 23, pp. 5799–5807, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00085-8

Rigid-rod benzobisthiazole polymer with reactive 2,6-dimethylphenoxy pendent groups

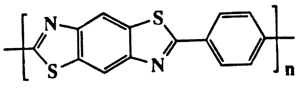
M. Dotrong[a], M.H. Dotrong[a], H.H. Song[b], U. Santhosh[c], C.Y-C. Lee[d] and R.C. Evers[d],*
[a]*Nonmetallic Materials Division, University of Dayton Research Institute, Dayton, OH 45469, USA*
[b]*Department of Macromolecular Science, Hannam University, Taejon, South Korea*
[c]*AdTech System Research, Inc., Dayton, OH 45424, USA*
[d]*Materials Directorate, Wright Laboratory, Wright-Patterson Air Force Base, OH 45433-7750, USA*
(Received 30 December 1997; revised 13 January 1998; accepted 21 January 1998)

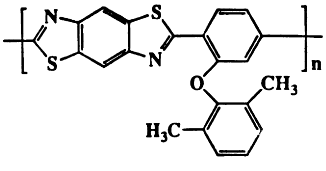
Polycondensation in polyphosphoric acid of 2,5-diamino-1,4-benzenedithiol dihydrochioride with 2-(2,6-dimethylphenoxy)terephthaloyl chloride led to rigid-rod benzobisthiazole polymers with thermally reactive dimethylphenoxy pendants. Soluble polymers with intrinsic viscosities as high as 15.5 dl/g (methanesulphonic acid, 30°C) were obtained. The polymers became insoluble after heat-treatment at approximately 400°C, possibly indicative of a crosslinking reaction between the polymer chains at the pendant sites. Fibres spun from a lyotropic polyphosphoric acid solution and heat treated at 425°C exhibited a tensile modulus of 91 GPa, a tensile strength of 1.10 GPa, and a compressive strength of 400 MPa. Wide-angle X-ray scattering patterns of the polymer fibres indicated that the bulky pendants significantly enhanced the axial registration between the neighbouring rigid-rod polymer backbones. © 1998 Published by Elsevier Science Ltd. All rights reserved.

(Keywords: rigid-rod polymers; compressive strength; axial registration)

INTRODUCTION

Poly[benzo(1, 2-*d*:4,5-*d'*)bisthiazole-2, 6-diyl]-1, 4-phenylene (PBT)[1] can be prepared in high molecular weight in a polyphosphoric acid (PPA) solution and fabricated from its lyotropic reaction medium into fibres and films with exceptional tensile strength and modulus[2]. Because of its high thermooxidative stability coupled with its outstanding specific tensile properties, this rigid-rod aromatic–heterocyclic polymer has been considered for various applications in severe aerospace environments. However, a serious obstacle to its use in these applications is the low compressive strength of these fibres compared to that of carbon fibres derived from polyacrylonitrile[3]. Consequently, efforts have been directed toward the improvement of the compressive strength of PBT fibre through chemical modification of polymer structure[4] and/or changes in fibre processing procedures for fibres or films[5]. Under the present effort, PBT with 2,6-dimethylphenoxy pendent groups (PPBT) was prepared and subjected to thermal treatment to give a crosslinked system that was expected to be less prone to the buckling behaviour previously observed within the highly fibrillar PBT fibres[6].


PBT


PPBT

The mechanism and the site for the crosslinking of PPBT is not yet known. However, it is expected that loss of the entire pendent group through cleavage of the carbon–oxygen bonds (path A) would be less favoured compared to the loss of the relatively extended methyl groups (path B) through cleavage of carbon–carbon bonds or the loss of hydrogen atoms (path C) from the methyl groups through cleavage of benzylic carbon–hydrogen bonds (*Figure 1*). Path C is probably the preferred cleavage mode due to the lower bond dissociation energy for a benzylic carbon–hydrogen bond compared to other potential bond cleavages[7]. In the latter two cases, the reactive crosslink sites are generated outside of the rigid-rod polymer backbone, with a radical charge being localized in the phenoxy pendant, thus leaving the highly conjugated π-electron system of the polymer backbone intact.

In this paper, the synthesis of PPBT through the

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* To whom correspondence should be addressed

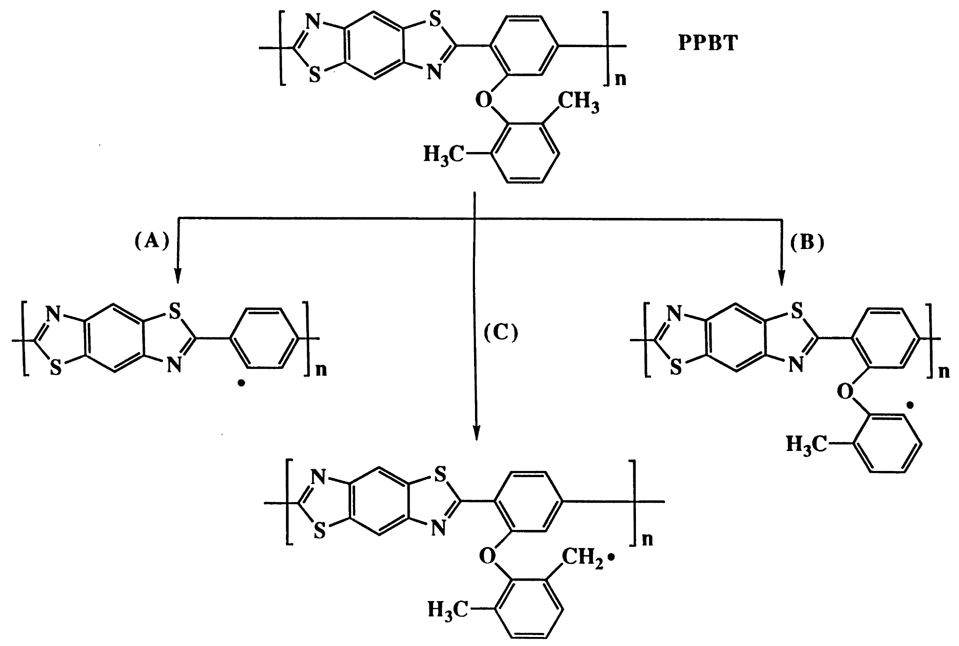


Figure 1 Possible crosslink sites

polycondensation of 2,5-diamino-1,4-benzenedithiol dihydrochloride (DABDT) with 2- (2,6-dimethylphenoxy)terephthaloyl chloride is reported along with the processing of PPBT into fibres and the mechanical characterization and morphology of the resultant fibres.

EXPERIMENTAL

Synthesis

All reagents were purified prior to use. Solvents were ACS grade and were used without further purification. 2,5-Diamino-1,4-benzenedithiol dihydrochloride was prepared according to the procedure of Wolfe *et al.*[1].

Dimethyl-2-(2,6-dimethylphenoxy)terephthalate

Potassium *t*-butoxide (90.6 g, 0.80 mol) was added to a stirred solution of 97.6 g of 2,6-dimethylphenol (0.80 mol) in 320 ml of dry toluene and 800 ml of dry *N,N*-dimethylformamide (DMF) under a nitrogen atmosphere. The reaction mixture was heated until a volume of 300 ml of toluene was removed by distillation, and was then cooled to room temperature. Dimethyl-2-nitroterephthalate (191.2 g, 0.80 mol) was added and the reaction was stirred at 100°C overnight. After the reaction was allowed to cool to room temperature. approximately 600 ml of DMF was removed on a rotary evaporator at 80°C/50 mmHg. The remaining mixture was chilled and poured with stirring into ice-water. Following several extractions with ethyl acetate, the combined extracts were washed with saturated NaCl solution and then dried over anhydrous sodium sulphate. Removal of solvent from the dried solution yielded 88.4 g of dark brown liquid. Distillation of the brown material using a short-path apparatus at 150-153°C/0.1 mmHg yielded a yellowish solid. Recrystallization from ethanol followed by recrystallization from hexane gave 58 g (28% yield) of white solid (m.p. 82–84°C).

^1H n.m.r. ($CDCl_3$): 2.16 ppm (s, CH_3), 3.90 ppm (s, $COOCH_3$), 4.03 ppm (s, $COOCH_3$), 7.21–8.10 ppm (m, aromatic H). I.r. (KBr): 1734 cm^{-1}, 1727 cm^{-1} (C=O), 1228 cm^{-1} (Ph–O–Ph). MS (EI): 314 m/e (M^+). Elemental analysis: calculated for $C_{18}H_{18}O_5$, C 68.78, H 5.77; found, C 68.65, H 5.79.

2-(2,6-Dimethylphenoxy)terephthalic acid

To a stirred solution of 17 g (0.425 mol) of NaOH in 25 ml of water were added 26.79 g (0.085 mol) of dimethyl-2-(2,6-dimethylphenoxy)terephthalate and 50 ml of ethanol. The reaction mixture was stirred at reflux overnight. After cooling to room temperature, the reaction mixture was acidified with concentrated HCl to yield a precipitate, which was collected on a filter and suction dried to yield 24.45 g of white solid. Recrystallization from ethanol/water (3:1) yielded 22.6 g (93%) of white crystals, m.p. 315–317°C.

^1H n.m.r. (d_6-acetone): 2.16 ppm (s, CH_3), 7.20–8.20 ppm (m, aromatic H). I.r. (KBr): 3057 cm^{-1} (OH), 1697 cm^{-1} (C=O), 1289 cm^{-1} (Ph–O–Ph). MS. (EI): 286 m/e (M^+). Elemental analysis: calculated for $C_{16}H_{14}O_5$, C 67.12, H 4.93; found, C 67.11, H 5.05.

2-(2,6-Dimethylphenoxy)terephthaloyl chloride

2-(2,6-Dimethylphenoxy)terephthalic acid (20.0 g, 0.069 mol), 100 ml of thionyl chloride and a few drops of DMF were stirred at reflux overnight. After removing excess thionyl chloride by distillation, 100 ml of toluene were added to the solution and then distilled to remove residual thionyl chloride. The remaining yellow material was distilled at 140–143°C/0.07 mmHg and the resultant solid was recrystallized twice from hexane to yield 14.7 g (65% yield) of white crystals, m.p. 65–67°C.

^1H n.m.r. ($CDCl_3$): 2.10 ppm (s, CH_3), 7.20–8.30 ppm (m, aromatic H). I.r. (KBr): 1776 cm^{-1}, 1758 cm^{-1} (COCl). MS (EI): 323 m/e (M^+). Elemental analysis: calculated for $C_{16}H_{12}O_3Cl_2$, C 59.46, H 3.74, Cl 21.94; found, C 59.70, H 3.91 Cl 21.69.

1,4-Bis(2-benzothiazoyl)-2-(2,6-dimethylphenoxy)benzene

2-(2,6-Dimethylphenoxy)terephthaloyl chloride (1.000 g, 3.094 mmol) and *o*-aminothiophenol (0.923 g, 7.425 mmol) were stirred under a nitrogen atmosphere in 15 g of 83% PPA at 165°C for 24 h. The homogenous yellow solution was poured into ice-water and the precipitated yellow crude product was isolated by filtration. Following air drying, recrystallization in toluene (charcoal) gave 1.35 g (95% yield) of white crystalline product, m.p. 252°C.

^{1}H n.m.r. ($CDCl_3$): 2.24 ppm (S, CH_3); 7.23–8.82 ppm (m, aromatic H); ^{13}C n.m.r. ($CDCl_3$, ppm): 166.50, 161.8, 155.6, 154.4, 150, 136.7, 136.5, 135.3, 131.3, 130.5, 129.5, 126.4, 126.2, 126.0, 125.5, 125.0, 123.9, 123.5, 123.1, 121.6, 121.3, 121.1, 111.7, 16.4. I.r. (KBr): 1605 cm^{-1}, 1561 cm^{-1} (C=C, C=N), 1188 cm^{-1} (Ph–O–Ph); MS (EI): 464 m/e (M^+64.2%). Elemental analysis: calculated for $C_{28}H_{20}N_25_2O$, C 72.38, H 4.33, N 6.00, S 12.80; found, C 72.41, H 4.54, N 5.98, S 13.28.

PPBT polymer (Table 1, Trial 4)

2,5-Diamino-1,4-benzenethiol dihydrochloride (1.9586 g, 7.988 mmol) and 2-(2,6-dimethylphenoxy)terephthaloyl chloride (2.581 g, 7.988 mmol) were stirred in 19.28 g of 77% PPA under a stream of nitrogen at room temperature for 1 h. Then the temperature was raised slowly to 40°C for 2 h, 60°C for 18 h, and 100°C for 2 h. After the dehydration was complete, the yellow solution was cooled down to room temperature and 8.45 g of phosphorus pentoxide was added to bring the final phosphorus pentoxide content of the PPA up to 83.0%. After the mixture was stirred at 100°C for 3 h, the temperature was quickly raised to 165°C. The homogeneous mixture became dark red and stir opalescence appeared after 3 h. The mixture was stirred at this temperature for 24 h and subsequently at 180°C for 10 h. The extremely viscous mixture was then poured into water. The precipitated polymer was stirred very vigorously in a blender until it was broken up into a fine, fibrous form. It was washed with dilute ammonium hydroxide and extracted with water in a continuous extraction apparatus for 24 h. Upon drying at 100°C in vacuo for 24 h, orange–red fibrous polymer (3.07 g, 98% yield)) was obtained. An intrinsic viscosity of 11.6 dl/g in methanesulphonic acid at 30°C was recorded.

^{13}C CPMAS n.m.r.: 16.9 ppm (CH_3), 256.9–185.9 (aromatic C), I.r. (KBr): 1607 cm^{-1}, 1563 cm^{-1} (C=C, C=N), 1193 cm^{-1} (Ph–O–Ph). Elemental analysis: calculated for $(C_{22}H_{12}S_2N_2O)n$: C 68.72, H 3.74, N 7.28, found C 67.25, H 3.75, N 7.24.

Fibre spinning

PPBT polymer with an intrinsic viscosity of 11.6 dl/g (*Table 1*, Trial 4) was selected for processing into fibre by a dry-jet wet-spin process[5]. The spinning conditions are shown in *Table 2*. The dynamic viscosities were measured in a capillary rheometer at the spinning temperature and corresponded to the same shear rate as encountered during spinning. The fibres were spun at 100°C through a 0.25 mm spinneret and coagulated in deionized water and subsequently washed in a 3% solution of ammonium hydroxide. After further washing in distilled water, the fibres were dried, first at room temperature in air, then at 50°C in vacuum. The fibres were then heat-treated under tension in a nitrogen atmosphere for 40 s at 300, 350, 395, 425 and 460°C, respectively, for mechanical and morphological characterization.

Table 1 Synthesis of PPBT

Trial no.	Polymer conc. (%) (w/w)	Temp. (°C)	Time (h)	$[\eta]^a$ (dl/g)
1	10	165	24	6.7
2	14	165	24	11.0
3	14	165/185	24/10	15.5
4	10	165/185	24/10	11.6

^{a}Methanesulphonic acid, 30°C

Table 2 Processing conditions of PPBT fibre

Pressure (psi)	Viscosity (poise)	Spin–draw ratio
1215	7500	9.5
1375	8000	12

Mechanical and morphological characterizations

The tensile and compressive properties of the as-spun and heat-treated fibres were measured with an Instron-1130 instrument. Tensile modulus was determined according to ASTM standard D3379-75 test procedure[8] using 1, 3, and 5 inch gauge length specimens, while the compressive strength was determined by the recoil test method[9] on 1 inch samples. A JEOL-840 scanning electron microscope (SEM) operated at 20 keV was used to image the fracture of fibres. Wide-angle X-ray scattering patterns of fibres were obtained by using a Rigaku RU-200 rotating anode generator (operating at 45 kV and 70 mA) along with a Picker diffractometer and a Statton flat film camera. The X-ray beam was collimated by the two-pin hole and monochromated by a Ni filter.

RESULTS AND DISCUSSIONS

Synthesis

The requisite monomer, 2(2,6-dimethylphenoxy)terephthaloyl chloride, was prepared via a multi-step procedure in which dimethyl-2-nitroterephthalate underwent nucleophilic attack by potassium(2,6-dimethylphenoxide) to yield dimethyl-2-(2,6-dimethylphenoxy)terephthalate. Saponification with sodium hydroxide yielded the free diacid which, upon treatment with thionyl chloride, provided the required diacid chloride.

The feasibility of the polycondensation reactions were demonstrated by a model reaction (*Figure 2*). Model compound 1,4-bis(2-benzothiazoyl(-2-(2,6-dimethylphenoxy)benzene was synthesized in quantitative yield by reaction of 2-(2,6-dimethylphenoxy)terephthaloyl chloride with *o*-aminothiophenol in PPA at 165°C for 24 h. The model compound structure was confirmed by spectroscopic and elemental analysis. A molecular peak at 464 m/e (64.2%) was observed during mass spectroscopy. The presence of the methyl groups was indicated by a singlet at 2.23 ppm in the ^{1}H n.m.r. spectrum and by a peak at 16.44 ppm in the ^{13}C n.m.r. spectrum. The infrared spectrum displayed two strong absorptions at 1588 and 1519 cm^{-1}, and a very strong absorption at 1188 cm^{-1} attributable to the benzothiazole and phenoxy structures, respectively.

The PPBT polymer was synthesized by polycondensation of 2-(2,6-dimethyl-phenoxy)terephthaloyl chloride with DABDT in 83% PPA according the 'adjustable P_2O_5 method' of Wolfe and Sybert[10] (*Figure 2*). The conditions and results of the polymerization reactions are shown in *Table 1*. The reaction carried out at 165°C and 10% (w/w) polymer concentration for 24 h provided a polymer with an intrinsic viscosity of 6.7 dl/g (Trial 1). Attempts to optimize the polymer molecular weight were conducted through changes in reaction concentration and temperature.

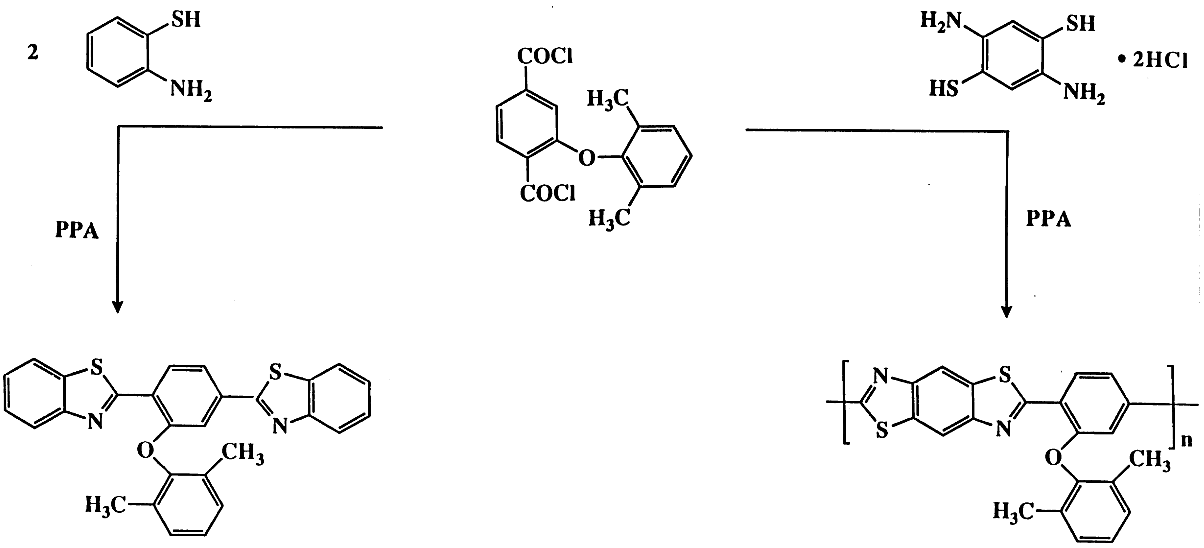


Figure 2 Synthesis of model compound and PPBT

Table 3 Mechanical properties of PPBT fibre

Sample	Fibre diameter (μm)	Tensile modulus (GPa)	Tensile strength (GPa)	Tensile strain (%)	Compressive strength (MPa)
As-spun SDR = 9.5	49.3 ± 10	48	0.90 ± 0.03	3.3	400 ± 30[a]
As-spun SDR = 12	45.2 ± 1.1	48	0.90 ± 0.05	2.8	400 ± 30[a]
300°C HT SDR = 12	48.5 ± 1.3	84	1.10 ± 0.07	1.2	300 ± 30
350°C HT SDR = 12	48.2 ± 0.9	87	1.20 ± 0.06	1.3	300 ± 30
395°C HT SDR = 12	48.1 ± 0.5	94	1.20 ± 0.06	1.2	300 ± 50
425°C HT SDR = 12	46.3 ± 1.3	91	1.10 ± 0.08	1.2	400 ± 50
460°C HT SDR = 12	47.2 ± 0.7	97	1.10 ± 0.10	1.4	300 ± 30

SDR, spin–draw ratio; HT, heat treatment temperature
[a] Cold-drawn fibre

A somewhat higher intrinsic viscosity of 11.0 dl/g was obtained when the polymer concentration was increased to 14% (w/w) (Trial 2). When the polymerization reaction was carried out at 165°C for 24 h and subsequently at 185°C for 10 h, higher intrinsic viscosities were obtained. The highest intrinsic viscosity of 15.5 dl/g was recorded when the polymer concentration was 14% (w/w) (Trial 3). A lower polymer concentration of 10% (w/w) led to a lower intrinsic viscosity of 11.6 dl/g (Trial 4). Stir opalescence, indicative of the lyotropic nature of the polymer solutions, was observed during all polymerization trials. The polymer solutions exhibited birefringence under a polarized microscope.

Polymer characterization

The PPBT polymer was obtained as a highly fibrous, golden-orange coloured material upon isolation from the reaction mixture by precipitation in water, extensive washing with ammonium hydroxide and water, and drying at 100°C in vacuo. The polymer was soluble in methanesulphonic acid and sulphuric acid. The chemical structure of the polymer was substantiated by elemental analysis and by comparison of its ^{13}C CPMAS n.m.r. and infrared spectra with the ^{13}C n.m.r. and infrared spectra of the model compound. A peak displayed at 16.88 ppm on the ^{13}C CPMAS n.m.r. spectra of the polymer was indicative of the methyl groups (*Figure 3*). The presence of the benzothiazole and phenoxy structures was verified by two absorptions in the infrared spectra at 1562 and 1521 cm^{-1}, and an absorption at 1183 cm^{-1}. respectively. The thermal behaviour of the polymer was studied by thermogravimetric analysis (t.g.a.) in air, thermogravimetric-mass spectral analysis (TG/MS), and differential scanning calorimetry (d.s.c.). Breakdown in t.g.a. in air occurred in two steps with onsets of degradation being observed at 412°C (6% weight loss) and 528°C (90% weight loss) (*Figure 4*). D.s.c. in a nitrogen atmosphere gave no indication of a glass transition temperature. However, it exhibited an exotherm starting at 425°C which could be associated with the first onset of degradation at 412°C under t.g.a. In TG/MS, two major degradation processes occurred at 470 and 680°C. The typical degradation products of the benzobisthiazole moiety such as H_2S, NH_3, HCN, C_6H_5CN, $C_6H_4(CN)_2$ and CS_2 were observed. Among the degradation products from the pendent groups which could be thermally released were methane, dimethylphenol, xylene and hydrogen. While the release of methane, dimethylphenol and xylene occurred at 470, 460 and 445°C, respectively, no conclusive evidence of hydrogen evolution was observed (*Figure 5*). The polymer became insoluble in methanesulphonic acid upon heat treatment at 400°C for 1 h in a nitrogen atmosphere, possibly attributable to crosslinking of the rigid-rod polymer through the reactive pendent groups. However, comparison of the infrared and ^{13}C CPMAS n.m.r. spectra of the polymer before and after the heat treatment offered no conclusive evidence of crosslinking.

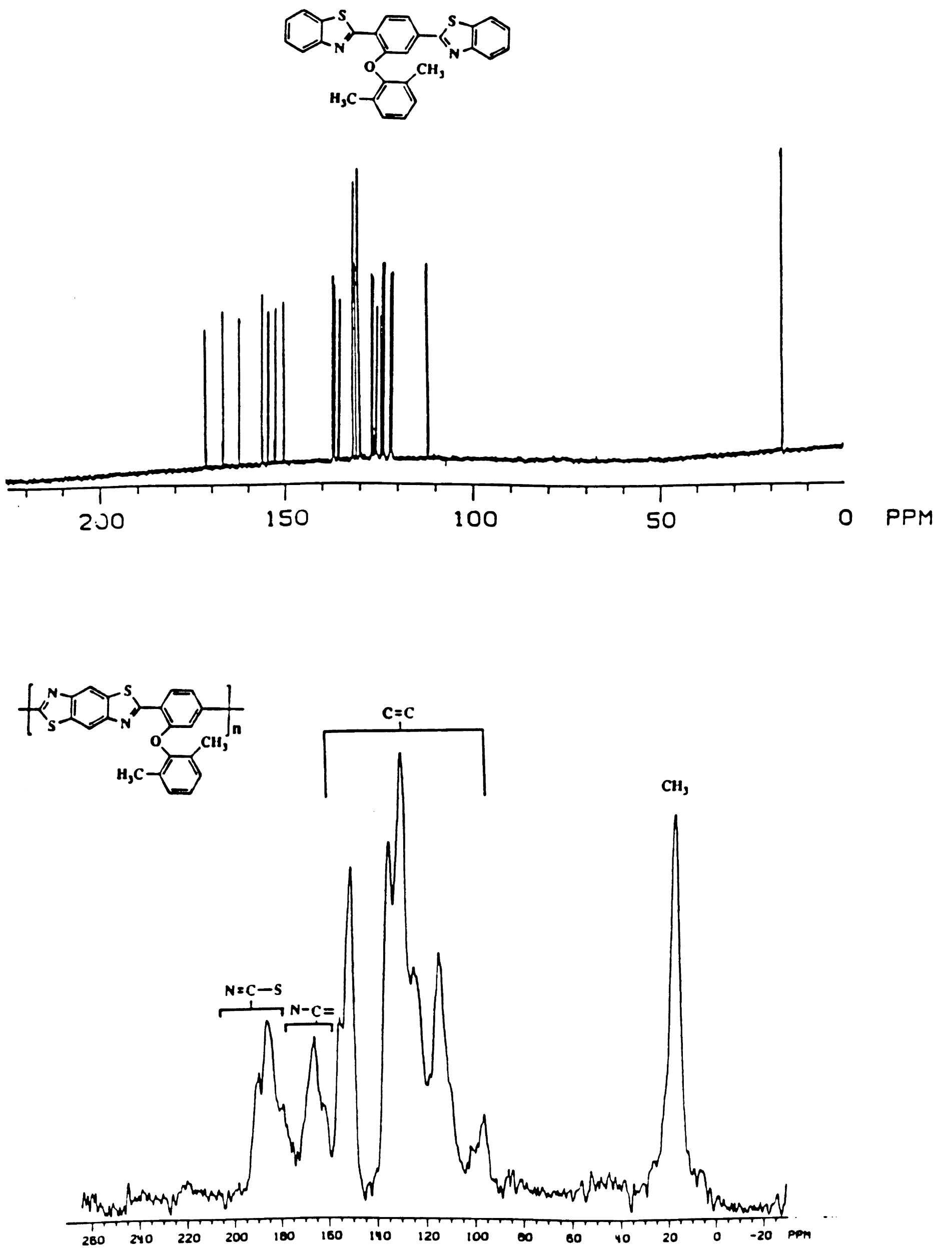


Figure 3 ^{13}C n.m.r. of model compound and PPBT

Mechanical properties and morphology of fibres

The tensile and compressive properties of heat-treated PPBT fibres are listed in *Table 3*. While the tensile modulus doubled from the as-spun state to the heat-treated state, its maximum value of 97 GPa is somewhat lower than that of heat-treated PBT fibre. The low tensile strength can be explained due to the fact that the bulky dimethylphenoxy pendants may have caused a disruptive packing order of polymer molecules leading to a low degree of orientation of the polymer chains. Furthermore, heat-treated PPBT fibres have a lower tensile strength than that of the heat-treated PBT fibres, and the PPBT polymers started to degrade at around 400°C.

The tensile fracture mode in PPBT fibres showed a marked change from the as-spun to the 460°C heat-treated state. It was found that the as-spun fibres as well as the fibres heat-treated at a temperature lower than 400°C all fibrillated on fracture. They also kinked near the tab ends. This behaviour is similar to that of PBT fibres. At even higher heat-treatment temperatures, the fibres became so brittle that the recoil compressive stress corresponding to the tensile failure broke the fibres at the tab ends. In all cases, fibrillation and axial splitting in PPBT fibres were more severe than in PBT fibres.

After heat-treatment for 40 s in a nitrogen atmosphere at 300°C and above, all PPBT fibres swelled but were no longer soluble at room temperature in methanesulphonic acid, probably due to crosslinking between the polymer chains. The fibres deepened slightly in colour to a darker golden yellow and were also not soluble at room temperature in other acidic solvents such as sulphuric acid or trifluoromethane sulphonic acid. However, their recoil compressive strength, shown in *Table 3*, was similar to that of PBT fibres (0.30 GPa). Even though the PPBT fibres did not fibrillate with ease as compared to the PBT fibres, their brittle fracture ends and the peeled fibres showed a fibrillar morphology (*Figure 6*). The diameter of the fibrils (~100–500 nm) and the aspect ratio of the buckling units (~5–6) were both similar to that seen in PBT. SEM also showed a

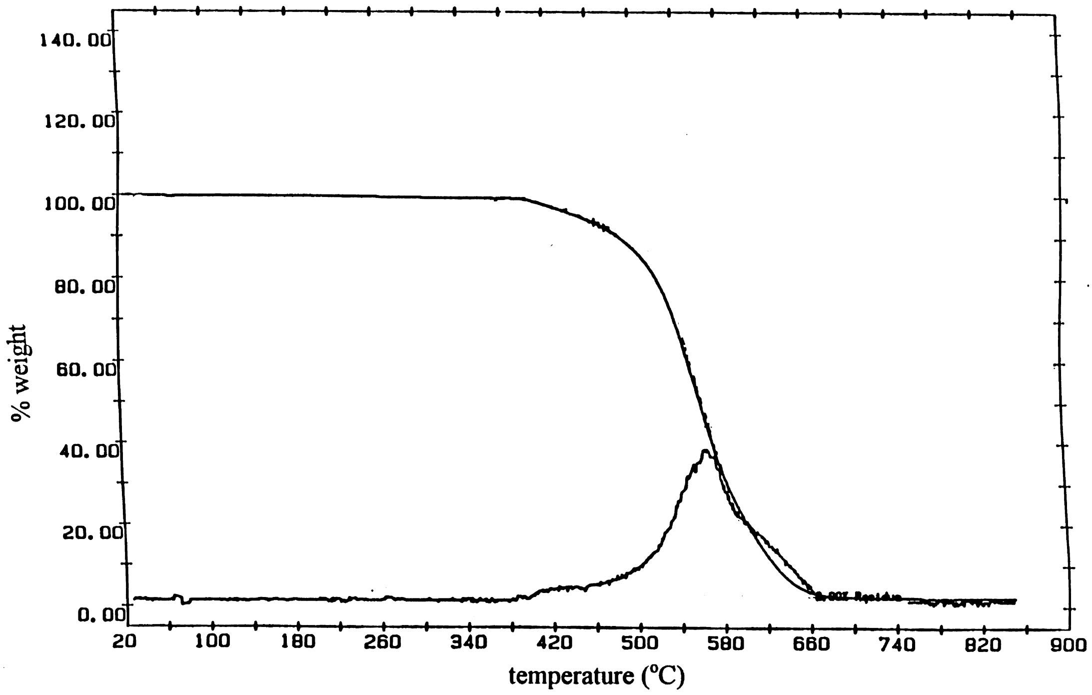


Figure 4 T.g.a. of PPBT in air

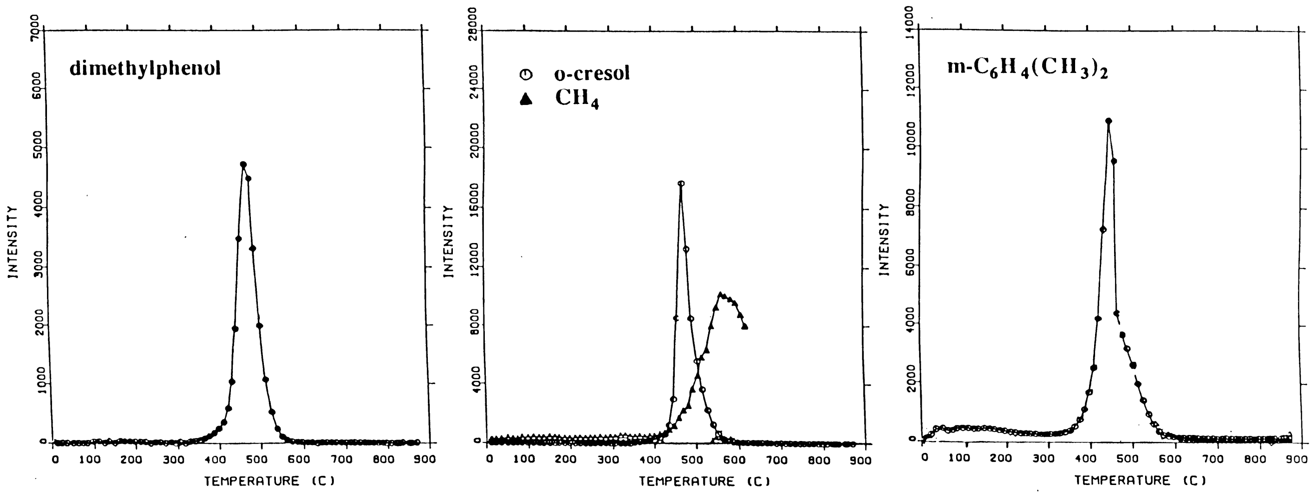


Figure 5 T.g.a./MS analysis of PPBT showing release of degradation products of dimethylphenoxy pendant

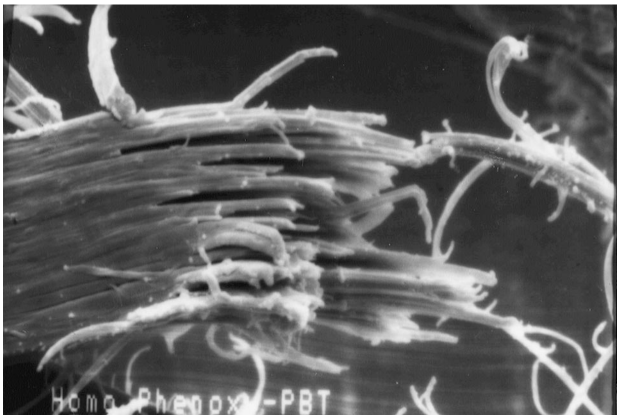


Figure 6 Fibrillar morphology of PPBT fibre after heat treatment at 300°C

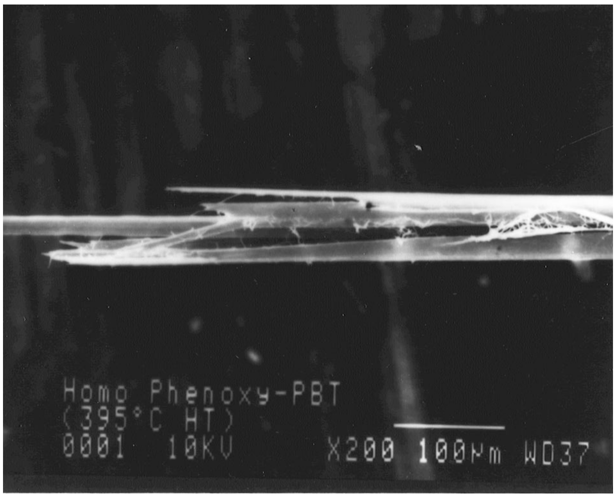
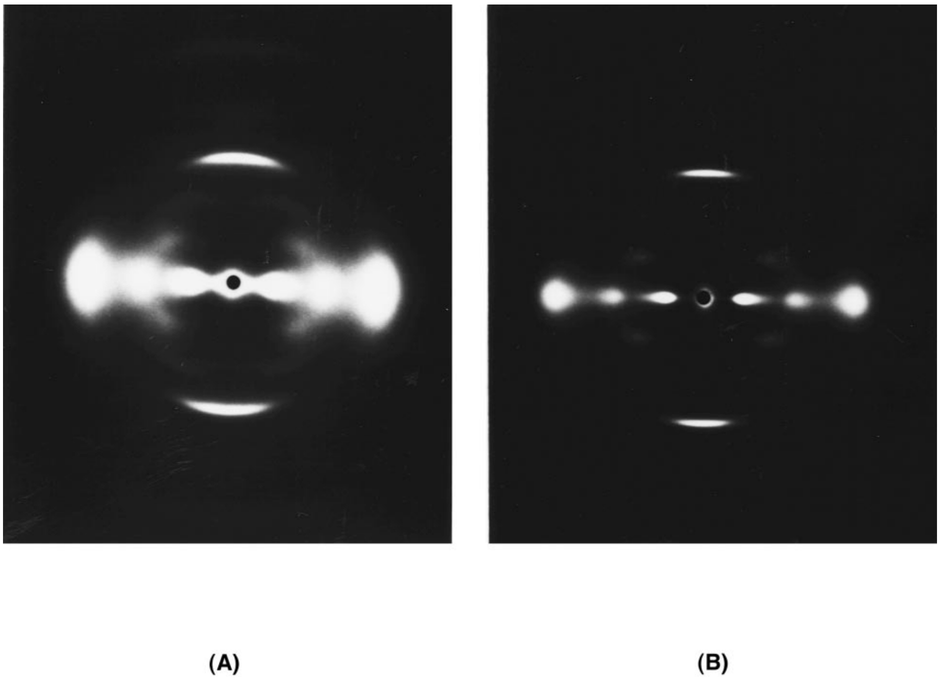


Figure 7 Skin–core structure of PPBT fibre after heat treatment at 395°C



(A) (B)

Figure 8 Flat film X-ray of PPBT fibre: (A) before heat treatment and (B) after heat treatment at 460°C

Table 4 *d*-spacing (Å) of PPBT and PBT fibre

PPBT		PBT
As-spun	Heat treated (460°C)	Heat treated (600°C)
12.48	13.35	—
5.55	5.42	5.83
3.52	3.50	3.51

distinct skin–core structure in all the fibres (*Figure 7*). During fracture, the 2 μm thick skin readily cracked and peeled off to reveal a cylindrical core in the centre. Examination of the skin–core interface showed a very weak interface which gave the appearance of the skin just lying on the surface of the core.

Flat film X-ray patterns of PPBT fibres are shown in *Figure 8*. Pattern A was measured from the as-spun fibre and pattern B was from the fibre heat-treated at 460°C. Improved packing order due to thermal treatment was clearly seen in the X-ray patterns. Three main diffraction peaks were noted along the equator. Layer streaks, the typical characteristics of rigid-rod polymers in a nematic state, were absent. Instead, a strong peak at the third layer position was observed. The bulky pendants may have played a role in enhancing the axial registration of the neighbouring PPBT backbones. The intensity profiles along the equator from the Picker diffractometer are shown in *Figure 9*. The peak positions and corresponding *d*-spacings were summarized and compared with those of PBT fibres in *Table 4*. The first peak at $2\theta = 6.620$ (13.35 Å) was not observed in the X-ray patterns of PBT. The second peak at $2\theta = 16.340$ (5.42 Å) was somewhat shorter than that of the side-to-side inter-chain packing distance of PBT. The 5.42 Å spacing was, in fact, the distance between the pendant and PBT backbone. The peak at $2\theta = 25.410$ (3.50 Å) matched exactly with the peak of PBT, assigned to the face-to-face inter-chain distance. The first peak of 13.35 Å apparently arose from the layer structure, where the side-by-side packing distances were further increased by the bulky pendants. Such layer structures were observed in the case of other rigid-rod polymers with aliphatic pendants[11,12]. As illustrated in *Figure 10*, two possible chain packings can be expected to accommodate the bulky pendant leading to a backbone separation of 13.35 Å.

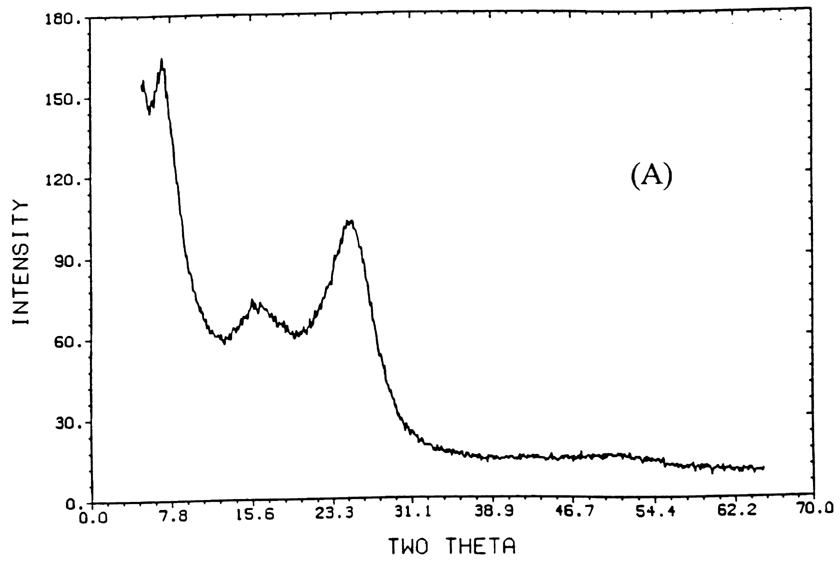
Packing A seems to be the case with PPBT. Since the probability of having the pendant at the 2 and 6 or 3 and 5 positions is equal against the 1–5 axis rotation of phenylene case B initially appears to be more plausible. However, case B was rejected since this packing would not yield the two peaks at 5.4 Å. In case A, on the other hand, all the pendants in the polymer chain are facing in the same direction in which appears to be an unrealistic situation. Nevertheless, similar packing structures have been reported[12] and case A clearly exhibited a more densely packed state

CONCLUSION

Rigid-rod polymer PPBT having a reactive dimethylphenoxy pendant was successfully prepared in high molecular weight and spun into fibres which exhibited a skin–core morphology with a fibrillar substructure and a large side-by-side molecular packing. The polymer became no longer soluble in methanesulphonic acid after heat treatment at 300°C, possibly indicative of a thermally induced cross-linking between the polymer chains. However, crosslinking did not seem to have a significant effect on the compressive strength of PPBT fibre.

ACKNOWLEDGEMENTS

We are grateful to E. Soloski of the University of Dayton Research Institute for thermal analysis and Dr. E. Grant Jones of System Research Laboratory, Inc., for TG/MS. The n.m.r. spectra were obtained from Spectra Data Services, Inc.



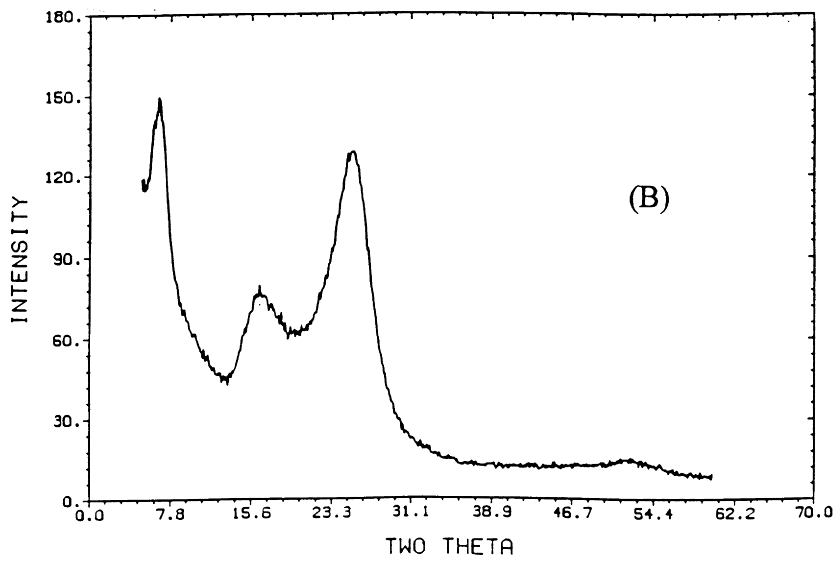


Figure 9 X-ray intensity of PPBT fibres from equatorial scan: (A) before heat treatment and (B) after heat treatment at 460°C

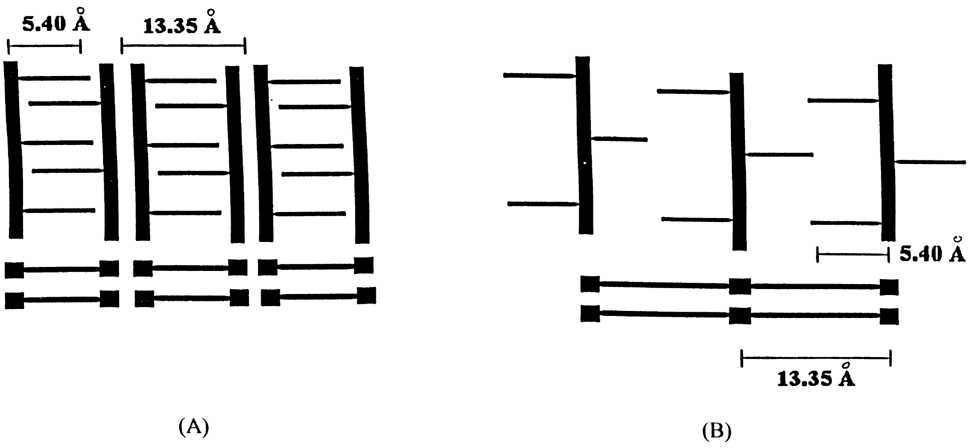


Figure 10 Schematic describing the packing of PPBT

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