

# Rigid Rod Polyamides Based on 2,2',6,6'-Tetrasubstituted Biphenyls: Synthesis, Characterization, and Structures

C. HE,<sup>1,\*</sup> A. C. GRIFFIN,<sup>2</sup> and A. H. WINDLE<sup>1</sup>

<sup>1</sup>Department of Materials Science & Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom; <sup>2</sup>Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge CB2 3RA, United Kingdom

## SYNOPSIS

Polyamides based on 4,4'-diamino-2,2',6,6'-tetrasubstituted biphenyls and phenylterephthalic acid have been synthesized, and the structures and properties of this series of polymer have been studied. It is shown that the polymers have an amorphous structure although some degree of short-range order is present. This class of polymer, while consisting of comparatively stiff rodlike molecules, demonstrates high solubility and low glass transition temperatures. The behavior is due to the combination of the noncoplanar conformation of the twisted biphenyl and the fact that they have bulky side groups in the 2,2'- and 6,6'-positions that weaken the interchain interactions (like hydrogen bonding and van der Waals forces) and frustrate parallel packing of the polymer chains. © 1994 John Wiley & Sons, Inc.

## INTRODUCTION

The intrinsic tendency of rigid rod polymer chains to mutually align leads one to view them as the natural basis for creating high-tensile fibers, as indeed they are. It is because of the poor properties of fibers in the nonaxial direction, and especially in compression along the fiber axis,<sup>1-3</sup> that we have taken another approach. The objective has been to design and synthesize rigid rod molecules that are, nevertheless, prevented from aligning parallel and forming mesophases. The approach is based on the synthesis of monomer consisting of 4,4'-biphenyl units, which are 2,2',6,6'-tetrasubstituted. The bulky side groups combined with the noncoplanar conformation of the twisted biphenyl units effectively put lumps as "carbuncles" along the otherwise rodlike chain, with the objective of destabilizing parallel packing.

A detailed study by Gray et al.<sup>4</sup> on 2,2', 2,2',6,6', and 2,2',6,6'-substituted 4,4'-di-(*p-n*-alkoxybenzylideneamino)biphenyls revealed quantitatively

the effect of increasing interplanar angle on liquid crystallinity and established a guide to synthesis and predictivity of mesomorphism in this type of structure. Increasing *ortho* substitution results in decreasing stability of the mesophase, i.e., lower  $T_{M-I}$ .

In the field of polymeric liquid crystals, Gaudiana et al.<sup>5</sup> described the use of 2,2'- and 2,2',6,6'-substituted biphenyls to synthesize amorphous and soluble *para*-linked aromatic polyamides primarily using the trifluoromethyl group in the 2,2'-position. Similarly, polyesters<sup>6</sup> made from *para*-linked biphenyls substituted in the 2,2'-position were also amorphous and soluble and had a lower melting temperature than that of the unsubstituted analog. Related work<sup>7</sup> involved large lateral substituents such as phenyl and biphenyl in aromatic polyesters and polyamides, which resulted in reduced melting temperatures, decreased tendency to crystallize, and increased solubility. Schmidt<sup>8</sup> employed 2,2'-dimethylbiphenyls as key monomers to prepare soluble and low melting liquid crystalline polyesters. The use of long alkyl groups as lateral substituents (bound solvent concept) has also led to lower melting temperatures and to interesting new mesophases.<sup>9</sup>

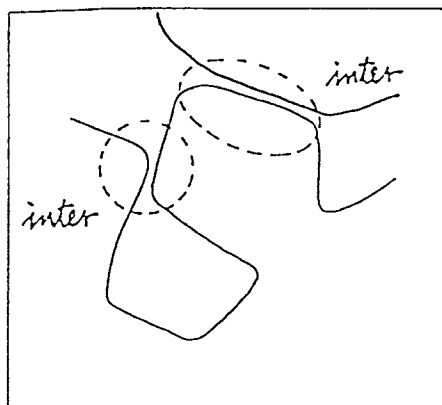
All the polymer work described above had, as its goal, improved processibility of liquid crystalline

\* To whom correspondence should be addressed.

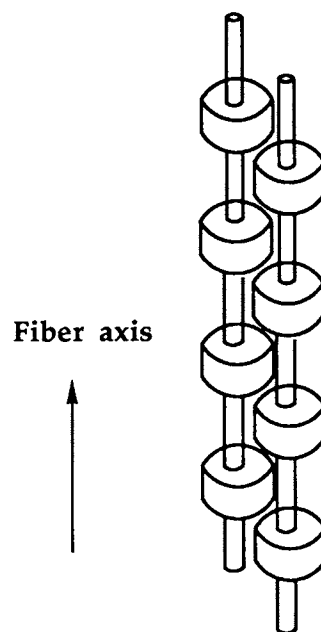
polymers by chemical modification rather than the elimination of the melt anisotropy. The aim of this work was to use tetra-substituted biphenyls to eliminate anisotropy in the melt or solution while retaining chain linearity and stiffness through 4,4-chain connectivity. A further aim of the work was to employ substituents, which, in addition to filling space and stabilizing nonparallel chain packing, are also, in principle, capable of further reaction, i.e., network formation.

The chemical structures chosen centered on 2,2',6,6'-tetracarboxybiphenyl and its esters. This tetra acid, through its methyl and ethyl esters, can be synthesized from simple and available precursors. Crucial to this synthetic approach is the Ullmann coupling reaction that can form the biphenyl molecules with the requisite tetra-*ortho* substitution pattern. The pendant esters can not only be exchanged for larger esters groups, but also can serve as possible cross-linking sites.

In this study, wide-angle X-ray diffraction (WAXS) and computer simulation have been applied to study the conformation and packing of rigid rod polyamides synthesized using 2,2',6,6'-tetra-substituted biphenyls. WAXS is an appropriate technique to study interchain and intrachain correlation in amorphous polymers and thus to determine both chain conformation and packing. Studies<sup>10-15</sup> of PMMA and PS polymers demonstrated how the interpretation of the WAXS could be significantly enhanced if the polymer glass was oriented. Above all, it becomes possible to distinguish between inter- and intrachain correlations, of which the latter can be modeled by Monte Carlo representation of individual chains. It was also ap-



**Figure 1** Diagram to illustrate how intersegmental interaction can occur between parts of the same as well as different molecules.



**Figure 2** Interdigitation of side groups for the example of parallel chains.

parent that at the orientation level available ( $P_2 < 0.33$ ), the molecular conformation was essentially the same as that in the unoriented polymer.

From the diffraction standpoint, "interchain" is used to imply intersegmental, in the sense that two neighboring segments may or may not belong to the same molecule,<sup>16</sup> a distinction that nevertheless will not generally affect their relative position and thus diffraction signature (e.g., Fig. 1). Another *caveat*, which may be much more relevant to a liquid crystalline phase in which the molecules tend to lie parallel, is that the relative intensity of the meridional reflections may be affected by longitudinal correlations with the position of neighboring chains. For example, the first meridional repeat from one of the chains depicted in Figure 2 would be much reduced in intensity if the adjacent molecule were to interlock as illustrated.

It has been shown that the position of the first intermolecular diffuse peak can, for an unoriented specimen, be used to give an estimate of mean spacing of the neighboring chains using the approximate relationship<sup>17,18</sup>

$$\delta = 1.22(\lambda/2 \sin \theta)$$

Similar arguments lead to an equivalent expression that is applicable to the principal equatorial peaks of a well-oriented noncrystalline sample<sup>19,20</sup>:

$$\delta = 1.11(\lambda/2 \sin \theta)$$

These relations are useful in this initial study where the aim was to follow the influence of chemical chain variables on simple packing parameters. In terms of structural analysis, this approach is but a first step, and further studies will involve full quantitative modeling of the scattering.

## MONOMER SYNTHESIS

The synthetic schemes for the monomers is shown in Figure 3. The monomers of 2-bromoisophthalic acid, dimethyl-2-bromoisophthalate, and tetramethylbiphenyl-2,2',6,6'-tetracarboxylate were synthesized according to Coulson,<sup>21</sup> whereas phenylterephthalic acid was synthesized according to the procedures of Preston et al.<sup>22</sup> and Weisburger and Weisburger.<sup>23</sup> The synthesis of other monomers is original work.

### 2-Bromoisophthalic Acid (1)

To a 1 L flask equipped with magnetic stirring was added 30 g (162 mmol) 2-bromo-*m*-xylene (from Aldrich) along with 600 mL of water. Potassium permanganate 105 g (665 mmol) (20% excess) was added in three portions during the reaction once every 3 h. The solution was refluxed in an oil bath for about 12 h until the purple color had almost disappeared. A small amount of methanol was carefully added to destroy unreacted potassium permanganate and the solution was filtered hot. The precipitated manganese dioxide was washed with 50 mL hot water. The filtrate was then cooled and extracted with ether to remove unreacted 2-bromo-*m*-xylene. Then, the aqueous filtrate was concentrated to about 200 mL under vacuum and then acidified with concentrated hydrochloric acid until strongly acidic. The white precipitate of 2-bromoisophthalic acid was extracted with ether (50 mL  $\times$  3), the ether layer was dried over anhydrous MgSO<sub>4</sub>, and the solvent was removed to give white solid 2-bromoisophthalic acid: 24.5 g, yield 60.4%. This acid may be slightly contaminated with some 2-hydroxyisophthalic acid. Mp 212°C (lit.<sup>21</sup> 212°C); IR in KBr COOH: 1684 cm<sup>-1</sup>, 2499–3082 cm<sup>-1</sup>.

### Dimethyl 2-Bromoisophthalate (2)

To 20 g (82 mmol) 2-bromoisophthalic acid (1) was added 300 mL methanol and 2 mL concentrated sulfuric acid. The mixture was then brought to reflux

in an oil bath for about 40 h, after which the solution was concentrated to 60 mL under vacuum. Then, 50 mL of 5% KOH solution was added (to render the solution basic). At this point, any unreacted 2-bromoisophthalic acid and hydroxyisophthalic acid can be completely removed. The solution was extracted with ether (60 mL  $\times$  3). The ether layer was washed with water and dried over MgSO<sub>4</sub>. The solvent was removed and the dimethyl-2-bromoisophthalate was obtained as a colorless liquid: 16.8 g, yield 75.4%. IR COOCH<sub>3</sub>: 1736 cm<sup>-1</sup>, 2954 cm<sup>-1</sup>. NMR in CD<sub>3</sub>OD ( $\delta$ ) Ar—H: 7.65d, 2H; 7.39t, 1H; COOCH<sub>3</sub> 3.89s, 6H.

### Tetramethylbiphenyl-2,2',6,6'-Tetracarboxylate (3)

Dimethyl-2-bromoisophthalate (2) 16.8 g (61.5 mmol) and 10 g (158 mmol) copper bronze (Aldrich) were added in a 250 mL flask that was placed in an oil bath. The mixture was heated and a vigorous reaction began at 180°C; after being kept at 200–210°C for 15 min, the reaction mixture was cooled and extracted with acetone (40 mL  $\times$  4). The acetone solutions were combined and the solvent was removed to give a solid product that was a light green in color. After recrystallization from acetone/hexane, 9 g of white cubic of tetramethylbiphenyl-2,2',6,6'-tetracarboxylate was obtained: yield 75.4%. Mp 124–125°C (lit.<sup>21</sup> 124°C): IR in KBr COOCH<sub>3</sub>: 1721 cm<sup>-1</sup>, 2957 cm<sup>-1</sup>. NMR in CDCl<sub>3</sub>: ( $\delta$ ) Ar—H 8.14d, 4H; 7.48t, 2H; COOCH<sub>3</sub> 3.57s, 12H.

### Tetramethyl-4,4'-Dinitrobiphenyl-2,2',6,6'-tetracarboxylate (4)

To 9 g (23.3 mmol) of tetramethylbiphenyl-2,2',6,6'-tetracarboxylate (3) was added 100 mL of a 1 : 1 HNO<sub>3</sub>/H<sub>2</sub>SO<sub>4</sub> solution in an ice bath. The reaction mixture was then heated to 40°C and kept at room temperature for about 10 h. When thin-layer chromatography (TLC) showed no starting materials or a mononitro compound, the reaction solution was cooled and then poured into 200 mL of ice water with vigorous stirring. The precipitated product was filtered and washed with a large amount of water and then dried in a vacuum oven; 9.9 g of crude product tetramethyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate was obtained. This solid was then recrystallized from CHCl<sub>3</sub>/CH<sub>3</sub>OH to give a white needle product. Mp 231–232°C. IR (KBr) CO<sub>2</sub>CH<sub>3</sub> 1744 cm<sup>-1</sup>, 2958 cm<sup>-1</sup>; NO<sub>2</sub> 1354 cm<sup>-1</sup>, 1534 cm<sup>-1</sup>. NMR in CDCl<sub>3</sub> ( $\delta$ ) Ar—H 9.08s, 4H; COOCH<sub>3</sub> 3.72s, 12H.

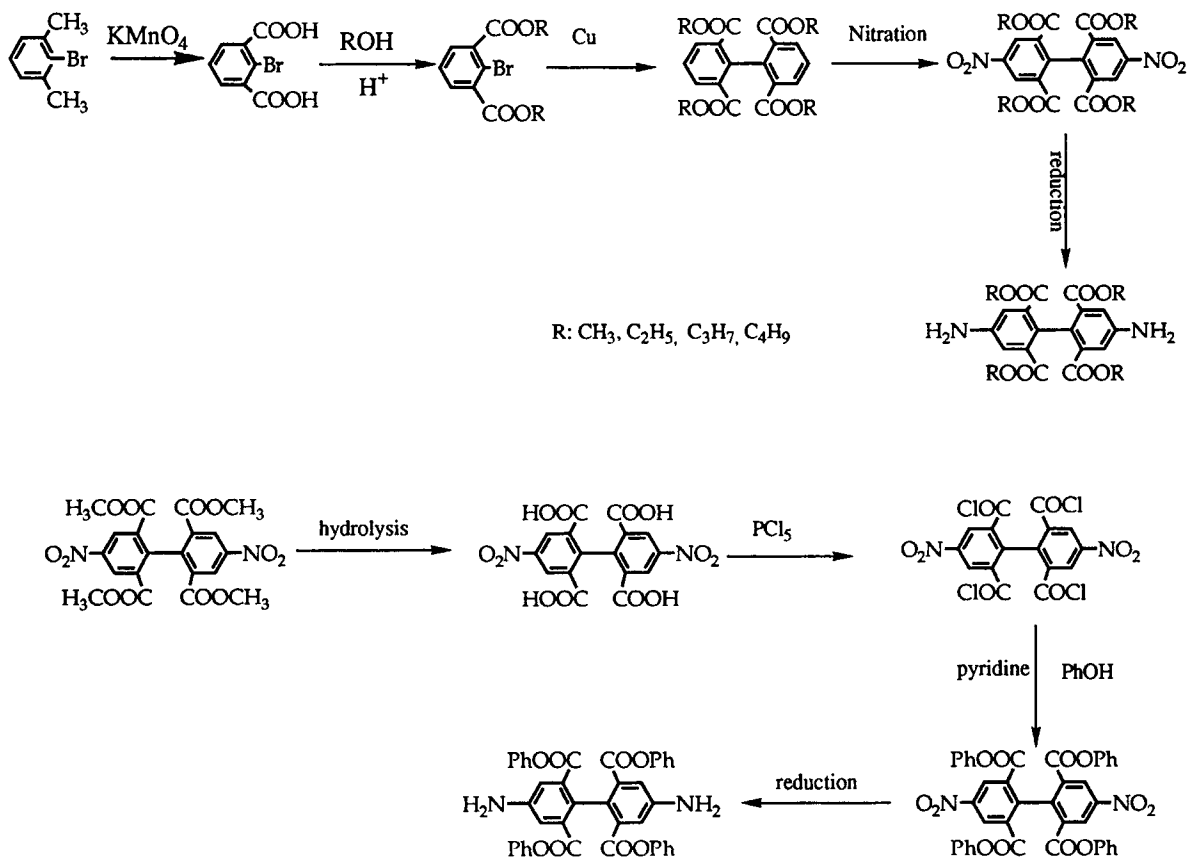


Figure 3 Molecule synthesis scheme.

ANAL: Calcd: C, 50.43%; H, 3.39%; N, 5.88%.  
Found: C, 49.82%; H, 3.14%; N, 5.73%.

#### Tetramethyl-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate (5)

Into a 25 mL flask was placed 1 g (2.1 mmol) of tetramethyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate (**4**). To this was added 10 mL of concentrated hydrochloric acid and 2 g (16.8 mmol) of tin powder (Aldrich). The reaction was kept at room temperature for 1 h with stirring. Then, 4 mL of methanol was added and the mixture was brought to reflux on a water bath. (The purpose of addition of methanol is to prevent hydrolysis of the ester groups.) The reaction mixture was refluxed for about 3–4 h until a perfectly clear solution resulted when a few drops of the reaction solution was diluted. Following this, the reaction mixture was cooled to room temperature. Gradually, a solution of 7.5 g of potassium hydroxide in 15 mL ice-water was added, the hydroxide of tin that at first precipitated all dissolved, and the solution was then strongly alkaline. A white precipitate was collected by using a centri-

fuge (6000 rpm, 20 min). The precipitated product was recrystallized from acetone/water to give the colorless needles of tetramethyl-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate: 0.24 g, yield 40%. Mp 240°C. IR in KBr CO<sub>2</sub>CH<sub>3</sub> 1721 cm<sup>-1</sup>, 2956 cm<sup>-1</sup>; NH<sub>2</sub> 3372 cm<sup>-1</sup>, 3464 cm<sup>-1</sup>. NMR in CDCl<sub>3</sub> (δ) Ar—H 7.31s, 4H; NH<sub>2</sub> 5.01s, 4H; COOCH<sub>3</sub> 3.47s, 12H.

ANAL: Calcd: C, 57.69%; H, 4.84%; N, 6.73%.  
Found: C, 57.54%; H, 4.83%; N, 6.60%.

#### Diethyl-2-Bromoisophthalate (6)

Diethyl-2-bromoisophthalate was prepared from 2-bromoisophthalic acid and ethanol according to the procedure of (**2**) to give a colorless liquid product: yield 71.5%. IR COOC<sub>2</sub>H<sub>5</sub> 1737 cm<sup>-1</sup>, 2875 cm<sup>-1</sup>, 2939 cm<sup>-1</sup>, 2985 cm<sup>-1</sup>.

#### Tetraethylbiphenyl-2,2',6,6'-tetracarboxylate (7)

Tetraethylbiphenyl-2,2',6,6'-tetracarboxylate was prepared from diethyl-2-bromoisophthalate according to the procedure given for (**3**) to give a yellow

oil product. After cooling at room temperature, it solidified. Recrystallization from hexane yielded colorless needles of tetraethylbiphenyl-2,2',6,6'-tetracarboxylate: yield (73%). Mp 68°C. IR in KBr  $\text{CO}_2\text{C}_2\text{H}_5$  1731  $\text{cm}^{-1}$ , 2981  $\text{cm}^{-1}$ , 2930  $\text{cm}^{-1}$ , 2873  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ar—H 8.11d, 4H; 7.47t, 2H;  $\text{CO}_2\text{CH}_2\text{CH}_3$  3.95q, 8H; 0.95t, 12H.

#### Tetraethyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate (8)

Tetraethyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate was synthesized from tetraethylbiphenyl-2,2',6,6'-tetracarboxylate according to the procedure given for (4) to give a white needle product: yield 90%. Mp 150°C. IR (KBr)  $\text{CO}_2\text{C}_2\text{H}_5$  1744  $\text{cm}^{-1}$ , 2958  $\text{cm}^{-1}$ ;  $\text{NO}_2$  1358  $\text{cm}^{-1}$ , 1534  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ar—H 9.01s, 4H;  $\text{CO}_2\text{CH}_2\text{CH}_3$  4.09q, 8H; 1.15t, 12H.

ANAL: Calcd: C, 54.14%; H, 4.54; N, 5.26.  
Found: C, 54.01%; H, 4.44%; N, 5.21%.

#### Tetraethyl-4,4'-Diaminobiphenyl-2,2',6,6'-tetracarboxylate (9)

Tetraethyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate 1 g (1.88 mmol) was placed in a 100 mL flask in a water bath. To the flask was added 10 mL of methanol and 30 mL of ethyl acetate. When the nitro compound was totally dissolved, 0.24 g of Pd/C (10%) and 0.9 g (14.3 mmol in two portions during the reaction) of ammonium formate was added to the solution; the reaction was under nitrogen at 40°C. When t.l.c showed no evidence of the nitro compound, the reaction solution was filtered. The filtrate was washed with water, dried over anhydrous  $\text{MgSO}_4$ , and the solvent was removed. The crude product was recrystallized from ethyl acetate/hexane to give 0.65 g of white needles of tetraethyl-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate: yield 74%. Mp 200°C. IR in KBr  $\text{COOC}_2\text{H}_5$  1700  $\text{cm}^{-1}$ , 2985  $\text{cm}^{-1}$ , 2937  $\text{cm}^{-1}$ , 2903  $\text{cm}^{-1}$ ;  $\text{NH}_2$  3365  $\text{cm}^{-1}$ , 3454  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ar—H 7.36s, 4H;  $\text{NH}_2$  3.84, 4H;  $\text{CO}_2\text{CH}_2\text{CH}_3$  3.95q, 8H; 0.98t, 12H;

ANAL: Calcd: C, 61.01%; H, 5.97%; N, 5.93.  
Found: C, 60.90%; H, 5.97%; N, 5.93%.

#### 4,4'-Dinitrobiphenyl-2,2',6,6'-tetracarboxylic Acid (10)

Tetramethyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate 2 g (4.2 mmol) and 25 mL of 20% potassium hydroxide solution were heated to 80°C with stirring for 4 h. The reaction solution was then filtered hot.

The filtrate was cooled (when cooling the light, golden potassium salt precipitates), and the acid salt was collected and then acidified in water with hydrochloric acid until strongly acidic. The very fine precipitated product was collected and dried in a vacuum oven; 1.56 g of 4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylic acid was obtained. This product was used for further reaction without recrystallization. IR in KBr  $\text{COOH}$  1728  $\text{cm}^{-1}$ , 2513–3110  $\text{cm}^{-1}$ ;  $\text{NO}_2$  1316  $\text{cm}^{-1}$ , 1546  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  only shows Ph—H absorption; there is no  $\text{CO}_2\text{CH}_3$  absorption.

#### Tetraphenyl-4,4'-Dinitrobiphenyl-2,2',6,6'-tetracarboxylate (11)

A mixture of 1.5 g (3.6 mmol) of 4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylic acid and 3 g (14 mmol) of phosphorous pentachloride,  $\text{PCl}_5$ , was refluxed on an oil bath until the mixture become a homogeneous solution.  $\text{POCl}_3$  in the mixture was removed by vacuum distillation, and the acid chloride product (yellow in color) was used further without purification.

To this acid chloride, 1.5 g (16 mmol) phenol in 20 mL of dried pyridine was added in one portion with stirring. A vigorous reaction started at once and the reaction solution became warm. The reaction (guarded with an anhydrous calcium chloride tube) was carried out at room temperature with stirring for about 20 h. Then, the reaction solution was poured into dilute hydrochloric acid solution ( $\text{HCl}:\text{H}_2\text{O} = 1 : 4$ ), followed by extraction with ethyl acetate. The ethyl acetate layer was washed with cold potassium hydroxide solution (3%) to remove unreacted phenol and acid, then washed with water, followed by drying over anhydrous  $\text{MgSO}_4$ . The solvent was removed and the crude product was recrystallized from  $\text{CHCl}_3/\text{MeOH}$  to yield 1.45 g of tetraphenyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate: yield 56%. Mp 209°C. IR in KBr  $\text{COOPh}$  1737  $\text{cm}^{-1}$ , 3089  $\text{cm}^{-1}$ ;  $\text{NO}_2$  1354  $\text{cm}^{-1}$ , 1536  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ar—H 9.29s, 4H;  $\text{COOPh}$ —H 7.36t, 8H; 7.25t, 4H; 7.00d, 8H

ANAL: Calcd: C, 66.30%; H, 3.34%; N, 3.87%.  
Found: C, 66.49%; H, 3.19%; N, 3.87%.

#### Tetraphenyl-4,4'-Diaminobiphenyl-2,2',6,6'-tetracarboxylate (12)

Tetraphenyl-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate was synthesized from tetraphenyl-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate according to the procedure given for (9) to give a white needle product: yield 76%. Mp 227°C. IR in KBr  $\text{COOPh}$

1750  $\text{cm}^{-1}$ , 1725  $\text{cm}^{-1}$ , 3066  $\text{cm}^{-1}$ ;  $\text{NH}_2$  3357  $\text{cm}^{-1}$ , 3380  $\text{cm}^{-1}$ , 3434  $\text{cm}^{-1}$ , 3492  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ar—H 7.59s, 4H;  $\text{NH}_2$  3.93s, 4H;  $\text{COOAr}$ —H 7.27t, 8H; 7.13t, 4H, 6.91d 8H.

ANAL: Calcd: C, 72.28%; H, 4.25%; N, 4.21%.  
Found: C, 72.12%; H, 4.18%; N, 4.14%.

#### Di(*n*-propyl)-2-Bromoisophthalate (13)

Di(*n*-propyl)-2-bromoisophthalate was synthesized from 2-bromoisophthalic acid and 1-propanol according to the procedure given for (2) to give a colorless liquid: yield 76.3%.

#### Tetra(*n*-propyl)biphenyl-2,2',6,6'-tetracarboxylate (14)

Tetra(*n*-propyl) biphenyl-2,2',6,6'-tetracarboxylate was synthesized from di(*n*-propyl)-2-bromoisophthalate and copper bronze according to the procedure given for (3) to give an oil product, which, when kept in an ice bath, becomes a solid: yield 80.6%. The tetra(*n*-propyl)biphenyl-2,2',6,6'-tetracarboxylate was used for further reaction without crystallization (TLC shows only one product that is different from the starting materials). IR  $\text{CO}_2\text{C}_3\text{H}_7$  1723  $\text{cm}^{-1}$ , 2961  $\text{cm}^{-1}$ .

#### Tetra(*n*-propyl)-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate (15)

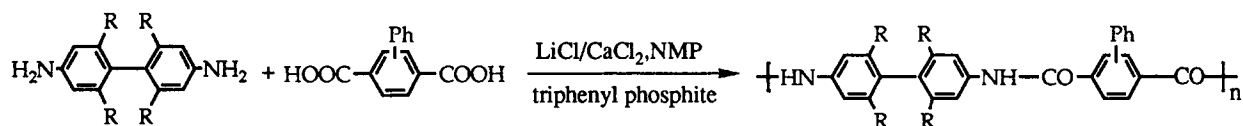
Tetra(*n*-propyl)-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate was synthesized from tetra(*n*-propyl)biphenyl-2,2',6,6'-tetracarboxylate according to the procedure for (4), except that the reaction was prolonged to 40 h. A white needle product was obtained: yield 80%. Mp 155°C. IR (KBr)  $\text{COOC}_3\text{H}_7$  1737  $\text{cm}^{-1}$ , 2961  $\text{cm}^{-1}$ ;  $\text{NO}_2$  1346  $\text{cm}^{-1}$ , 1531  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ph—H 9.03s, 4H;  $\text{CO}_2\text{C}_3\text{H}_7$ : 4.05t, 8H; 1.59q, 12H; 0.87t, 12H.

ANAL: Calcd: C, 57.14%; H, 5.48%; N, 4.76%.  
Found: C, 56.94%; H, 5.37%; N, 4.65%.

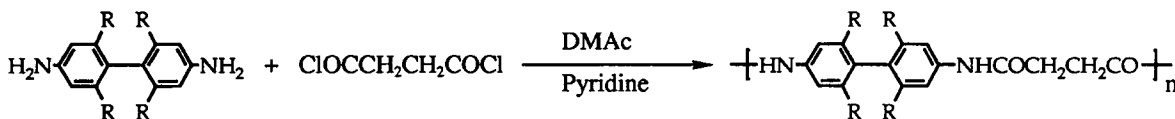
#### Tetra(*n*-propyl)-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate (16)

Tetra(*n*-propyl)-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate was synthesized from tetra(*n*-propyl)-4,4'-dinitrobiphenyl-2,2',6,6'-tetracarboxylate according to the procedure for (9) to give a white needle product: yield 70%. Mp 194°C. IR in KBr  $\text{COOC}_3\text{H}_7$  1687  $\text{cm}^{-1}$ , 2961  $\text{cm}^{-1}$ ;  $\text{NH}_2$  3367  $\text{cm}^{-1}$ , 3452  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ph—H 7.38s, 4H;  $\text{CO}_2\text{C}_3\text{H}_7$  3.89t, 8H; 1.36q, 8H; 0.86t, 12H.

ANAL: Calcd: C, 63.62%; H, 6.86%; N, 5.30%.  
Found: C, 63.53%; H, 6.93%; N, 5.22%.

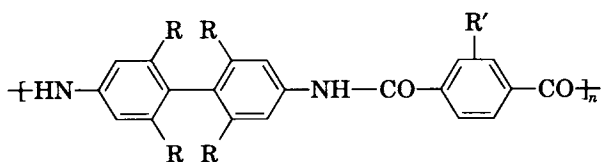


R:  $\text{CO}_2\text{CH}_3$ ,  $\text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{CO}_2\text{C}_3\text{H}_7$ ,  $\text{CO}_2\text{C}_4\text{H}_9$ ,  $\text{CO}_2\text{Ph}$



R:  $\text{CO}_2\text{CH}_3$ ,  $\text{CO}_2\text{C}_2\text{H}_5$ ,  $\text{CO}_2\text{C}_3\text{H}_7$ ,  $\text{CO}_2\text{C}_4\text{H}_9$ ,  $\text{CO}_2\text{Ph}$

Figure 4 Polymer synthesis scheme.

**Table I Molecular Weight of Polymers**

Polymer	R	R'	Intrinsic Viscosity (g/dL)	$M_n$	$M_w$
PBPA	CO <sub>2</sub> CH <sub>3</sub>	Ph	0.64		
PBPB	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Ph	0.61		
PBPC	CO <sub>2</sub> C <sub>3</sub> H <sub>7</sub>	Ph	0.66	23,400	50,000
PBPD	CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	Ph	1.06	20,900	28,600
PBPE	CO <sub>2</sub> Ph	Ph	0.81	19,100	31,400

Molecular weights of polymers were measured by the GPC method in THF solvent at 30°C using polystyrenes as standard. The intrinsic viscosities were determined in DMF at 25°C.

#### Di(*n*-butyl)-2-bromoisophthalate (17)

Di(*n*-butyl)-2-bromoisophthalate was synthesised from 2-bromoisophthalic acid and 1-butanol according to the procedure given for (2) to give a colorless liquid product: yield 70% (TLC showed only one spot different from the starting materials).

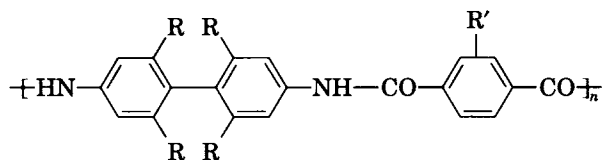
#### Tetra(*n*-butyl)biphenyl-2,2',6,6'-tetracarboxylate (18)

Tetra(*n*-butyl)biphenyl-2,2',6,6'-tetracarboxylate was synthesized from di(*n*-butyl)-2-bromoisophthalate and copper bronze according to the procedure

given for (3) to give an oil product: yield 78% (TLC shows only one spot different from the starting materials). The product was used for further reaction without recrystallization. IR CO<sub>2</sub>C<sub>4</sub>H<sub>9</sub> 1723 cm<sup>-1</sup>, 2954 cm<sup>-1</sup>.

#### Tetra(*n*-butyl)-4,4'-dinitrophenyl-2,2',6,6'-tetracarboxylate (19)

To 6 g (10.9 mmol) of tetra(*n*-butyl)biphenyl-2,2',6,6'-tetracarboxylate was added 50 mL of a mixture of HNO<sub>3</sub> and H<sub>2</sub>SO<sub>4</sub> (1 : 1). The reaction was kept at 40°C in a water bath for about 36 h. When the t.l.c. showed no starting materials or mononitro

**Table II Solubilities of Polymers**

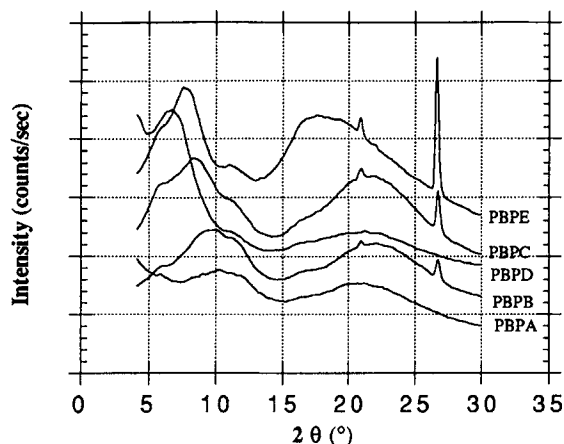
Polymer	R	R'	DMAc	DMF	THF
PBPA	CO <sub>2</sub> CH <sub>3</sub>	Ph	yes	modest < 5%	no
PBPB	CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	Ph	gel	gel	no
PBPC	CO <sub>2</sub> C <sub>3</sub> H <sub>7</sub>	Ph	yes	yes	modest
PBPD	CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	Ph	yes	yes	yes
PBPE	CO <sub>2</sub> Ph	Ph	yes	yes	yes

**Table III** Glass Transition Temperatures of Polymers

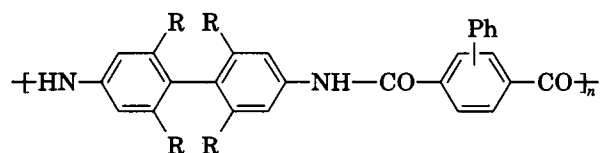
Polymer	PBPA	PBPB	PBPC	PBPD	PBPE
$T_g$ , °C	215	210	175	200	160

Glass transition temperatures of polymers were determined by DSC.

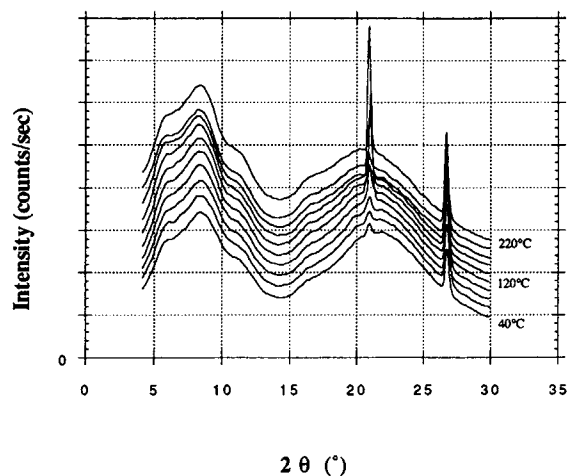
compound, the reaction solution was cooled and then poured into 200 mL of ice water with vigorous stirring. The precipitated product was filtered and washed with a large amount of water and then dried in a vacuum oven. This crude product was then recrystallized from ethanol to give a white crystal product—5.3 g of tetra(*n*-butyl)-4,4'-dinitrophenyl-2,2',6,6'-tetracarboxylate: yield 76%. Mp 78°C. IR (KBr)  $\text{COOC}_4\text{H}_9$  1736  $\text{cm}^{-1}$ , 2960  $\text{cm}^{-1}$ ;  $\text{NO}_2$  1350  $\text{cm}^{-1}$ , 1532  $\text{cm}^{-1}$ . NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ph—H 9.03s, 4H;  $\text{CO}_2\text{C}_4\text{H}_9$ : 4.07t, 8H; 1.51t, 8H; 1.30q, 8H; 0.87t, 12H.



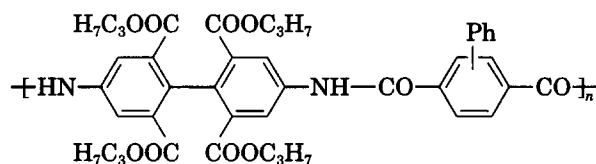
**Figure 5** X-ray powder diffraction of polymers defined below. The radiation  $\text{K}\alpha$  with a quartz internal standard giving the sharp peaks at  $2\theta$ : 26.66° and 20.88°. The scan temperature was 40°C. Five diffuse peaks and identification as listed in Table IV:



R:	Polymer
$\text{CO}_2\text{CH}_3$	PBPA
$\text{CO}_2\text{C}_2\text{H}_5$	PBPB
$\text{CO}_2\text{C}_3\text{H}_7$	PBPC
$\text{CO}_2\text{C}_4\text{H}_9$	PBPD
$\text{CO}_2\text{Ph}$	PBPE



**Figure 6** Powder scan of polymer PBPC made at increasing temperature during a stepped sequence of annealing. Peaks 2 and 5 ( $\sim 8^\circ$  and  $\sim 20^\circ$   $2\theta$ ) shift slightly to lower angles as the polymer expands on heating. The glass transition temperature of PBPC is 175°C:



ANAL: Calcd: C, 59.62%; H, 6.25%; N, 4.35%.  
Found: C, 59.49%; H, 6.17%; N, 4.20%.

#### Tetra(*n*-butyl)-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate (20)

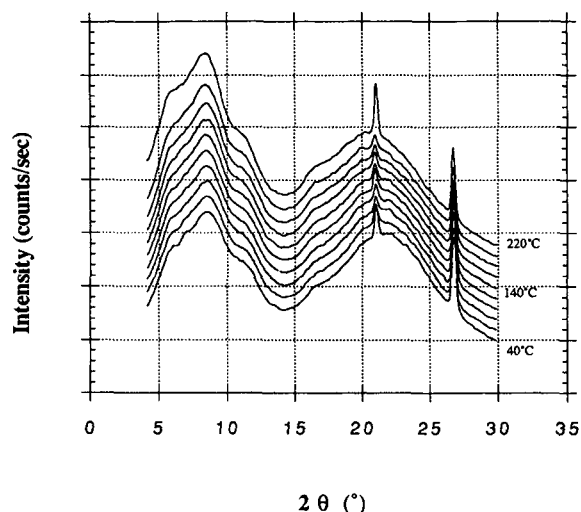
Tetra(*n*-butyl)-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate was synthesized from tetra(*n*-butyl)-4,4'-dinitrophenyl-2,2',6,6'-tetracarboxylate according to the procedure for (9) to give a white needle product: yield 74%. NMR in  $\text{CDCl}_3$  ( $\delta$ ) Ph—H 7.37s, 4H;  $\text{CO}_2\text{C}_4\text{H}_9$  3.96t, 8H; 1.33q, 8H; 1.20t, 8H; 0.89t, 12H.

ANAL: Calcd: C, 65.80%; H, 7.53%; N, 4.79%.  
Found: C, 65.89%; H, 7.71%; N, 4.71%.

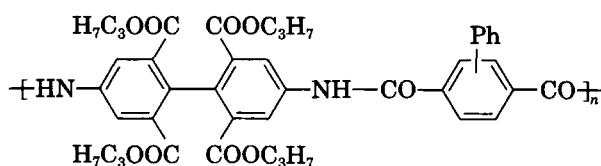
#### POLYMER SYNTHESIS

The direct polycondensation<sup>24</sup> of diamine and diacid was used for the preparation of the polyamides. The preparation procedure for the poly(2,2',6,6'-tetracarboxymethyl-4,4'-biphenylene-2,5-biphenyldicarboxamide) (PBPA) is given below and is representative of that used for all the other polymers in this





**Figure 7** As in Figure 6, except that the scans were made at decreasing temperature. These plots show that there is no clear evidence of crystallinity induced by the heat treatment:

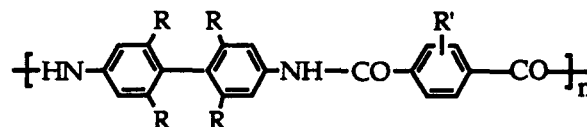


series. The polymerization schemes are shown in Figure 4.

#### Poly(2,2',6,6'-tetracarboxymethyl-4,4'-biphenylene-2,5-biphenyldicarboxamide)

A 100 mL dried round-bottom flask was equipped with magnetic stirrer and a calcium chloride drying

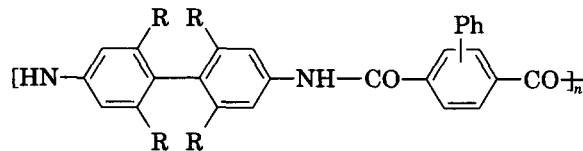
tube. One gram (2.4 mmol) of tetramethyl-4,4'-diaminobiphenyl-2,2',6,6'-tetracarboxylate and 0.581 g (2.4 mmol) phenylterephthalic acid were added. Then, 40 mL of a mixture solvent (NMP/pyridine 5 : 1;  $\text{CaCl}_2/\text{LiCl}$  3 : 1;  $\text{LiCl}$  1 g/60 mL solvent mixture) and 1.3 mL (5 mmol) dried triphenylphosphite were added. All solvents and solids were anhydrous. The reaction flask was put into an oil bath, the reaction solution kept at  $100^\circ\text{C}$  with stirring, and the reaction carried out overnight (about 18 h). After that time, the reaction solution was poured into 200 mL ice water; the resulting fibrous solid was collected and washed with copious volumes of water and the product was dried in a vacuum oven at  $80^\circ\text{C}$  for 18 h. The polyamide biphenyls (PBP) that have been synthesized by this method are summarized in following:



R	R'	Polymer Codes
$\text{CO}_2\text{CH}_3$	Ph	PBPA
$\text{CO}_2\text{C}_2\text{H}_5$	Ph	PBPB
$\text{CO}_2\text{C}_3\text{H}_7$	Ph	PBPC
$\text{CO}_2\text{C}_4\text{H}_9$	Ph	PBPD
$\text{CO}_2\text{Ph}$	Ph	PBPE

The succinic acid-based polyamides that were synthesized from 2,2',6,6'-tetrasubstituted-4,4'-diaminobiphenyls and succinoyl chloride are included for structural comparison with the terephthalic acid-

**Table IV** Peak Positions of Polymers in X-ray Powder Diffraction



Polymer	R	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5
PBPA	$\text{CO}_2\text{CH}_3$	$6.0^\circ$	$10.3^\circ$	$11.0^\circ$	$17.5^\circ$	$22.0^\circ$
PBPB	$\text{CO}_2\text{C}_2\text{H}_5$	$6.0^\circ$	$9.6^\circ$	$11.0^\circ$	$17.5^\circ$	$22.2^\circ$
PBPC	$\text{CO}_2\text{C}_3\text{H}_7$	$5.8^\circ$	$8.4^\circ$	$11.0^\circ$	$17.5^\circ$	$21.9^\circ$
PBPD	$\text{CO}_2\text{C}_4\text{H}_9$	Overlap <sup>a</sup>	$6.8^\circ$	$11.0^\circ$	$17.5^\circ$	$22.0^\circ$
PBPE	$\text{CO}_2\text{Ph}$	$5.8^\circ$	$7.7^\circ$	$11.0^\circ$	$17.5^\circ$	

<sup>a</sup> Peak 1 in this polymer overlaps with peak 2.

based polyamides, but their detailed polymer characterization will be described in a separate report.

## CHARACTERIZATION

### Molecular Weight

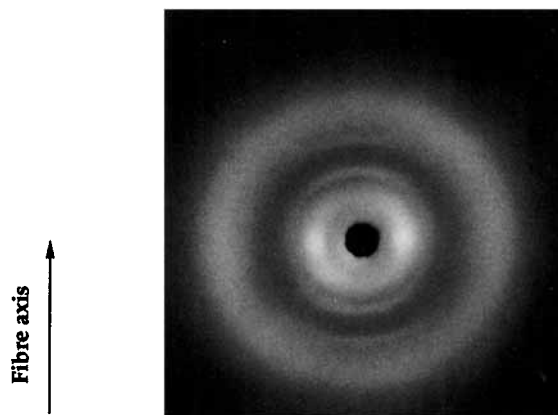
Molecular weights of the polymers listed in Table I were measured by GPC in THF solvent using polystyrenes as standards. The intrinsic viscosities were determined in DMF at 25°C.

Although the polymer synthesis was performed on a 1 g scale, the molecular weight is still reasonably high. The degree of polymerization (DP) of these polymers is around 20–50, which corresponds to lengths of molecular chains of 280–700 Å.

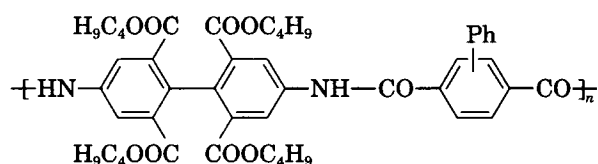
### Solubilities

High solubility is one of the features of all the 2,2',6,6'-tetrasubstituted polymers, unlike typical unsubstituted aromatic polyamides that are only soluble in very strong solvents such as concentrated sulfuric acid. As shown in Table II, these polymers exhibit high solubility in typical amide solvents (DMAc and DMF) without added salt, whereas some of the polymers are even soluble in THF. From Table II, it can be seen that the solubility increases with the number of carbon atoms in the side groups.

The increase in bulk of the side groups will tend to force the chains apart and thus weaken, if not



**Figure 8** X-ray fiber pattern of PBPD drawn in an oil bath at 180°C to a draw ratio of 2. There are two strong meridional maxima at 11° and 17.5° 2θ. These two peaks correspond to the second and the third orders of the polymer repeat unit. The first order of meridional diffraction is very difficult to distinguish. The maximum at 6.8° 2θ concentrates strongly on the equator and that at 22° more weakly:



eliminate, interchain hydrogen bonding between the amide groups, irrespective of whether the parallel packing of the chain is also disrupted. In any case,

**Table V** Comparison of Powder Diffractions and Fiber Diffractions

Polymer	R	Powder Diffraction	Fiber Diffraction	
			Meridian	Equator
PBPD	CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	6.8°		7.4°
		11.0°	11.0°	
		17.5°	17.5°	
		22.0°		22.0°
PBPE	CO <sub>2</sub> Ph	5.8°		7.7°
		7.7°		
		11.0°	11.0°	
		17.5°	17.5°	

the twisted conformation of the tetrasubstituted biphenyl will make it more difficult for its amide groups to be positioned properly to achieve hydrogen bonding<sup>25</sup> or translational mobility.

In addition to the contribution to solubility, the flexibility inherent in the side groups can contribute to the entropy and, thus, to the free energy of solution. None of the polymers of this series showed any crystallinity, and, thus, this is not a factor in affecting the solubility here.

### Glass Transition Temperatures

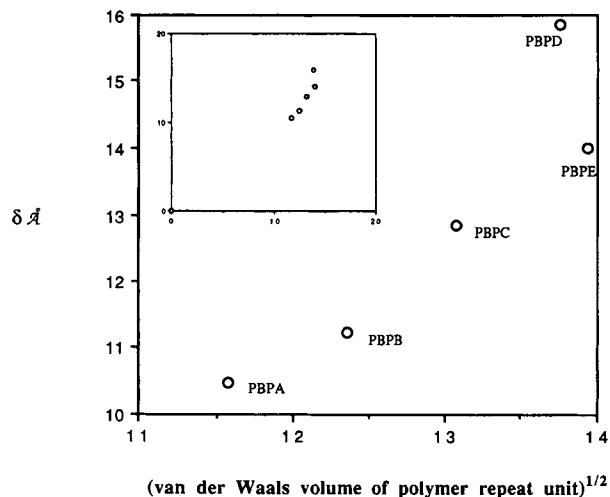
The glass transition temperatures listed in Table III were determined by DSC (Perkin-Elmer 7 Series thermal analysis system); the heating rate was 10°C/min. It can be seen that with an increase of the number of carbons in the side groups the glass transition temperature decreases. Again, this indicates a weakening of the interchain bonding due to the bulky side groups. It is also likely that the long alkyl side groups, while acting as a plasticizer, will facilitate the cooperative motion of the polymer chains or segments. All the polymers exhibit amorphous structure. There were no evidence of liquid crystallinity or crystallinity.

### DETERMINATION OF PHYSICAL STRUCTURE

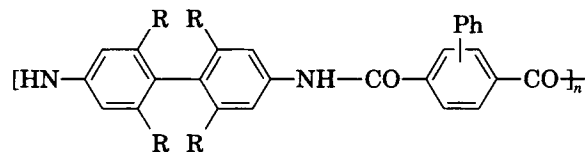
Wide-angle X-ray diffraction (WAXS) was used in studying polymer structures. Polymer samples were prepared for diffraction by dissolving the polymer in a solvent, DMAc, and subsequently precipitating in water. The samples were then washed in water several times and dried in vacuum at 60°C overnight. Prior to the diffraction scan, the polymer powder samples were put on a silicon crystal plate, heated to their softening temperature, and then cooled to room temperature. X-ray diffraction was carried on a Siemens diffractometer D500TT, using CuK $\alpha$  radiation 1.5418 Å and a Ni filter. Scan speed was 0.2°/min. Quartz ( $2\theta$ : 26.66°, 20.88°) was used as an internal standard for calibration.

For computer modeling, the Cerius program (Cerius molecular modeling software for materials research from Molecular Simulation of Burlington, MA, and Cambridge, UK) was used to simulate the X-ray scattering from a single-chain model. The DP of the model was 30, and the resultant pattern was the average of scattering of 1000 chains in different conformations.

Figure 5 shows diffraction scans from samples of unoriented polymers synthesized with different



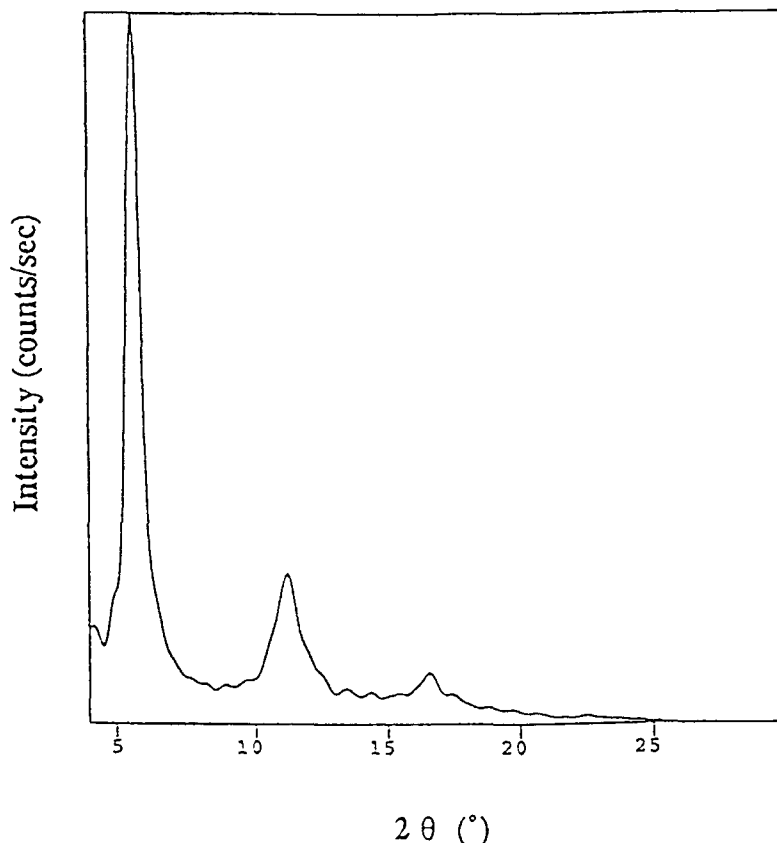
**Figure 9** Relation between interchain distances and the square root of van der Waals volumes of polymer repeat units for the series of polymers. The van der Waals volumes of the molecule were calculated by using the van der Waals radii for hydrogen, nitrogen, and oxygen as 1.20, 1.50, and 1.40 Å, respectively, according to Ref. 26, and 1.65 Å for carbon. The interchain distances  $d$  were calculated according to the equation  $\delta = 1.22(\lambda/2 \sin \theta)$ :



R:	Polymer
CO <sub>2</sub> CH <sub>3</sub>	PBPA
CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub>	PBPB
CO <sub>2</sub> C <sub>3</sub> H <sub>7</sub>	PBPC
CO <sub>2</sub> C <sub>4</sub> H <sub>9</sub>	PBPD
CO <sub>2</sub> Ph	PBPE

tetra-substituted groups. Each of the polymers had been annealed with the temperature stepped at 20°C intervals up to 220°C, followed by the same cooling protocol. Using the C<sub>3</sub>H<sub>7</sub>-tetra-substituted polymer as an example, Figures 6 and 7 show diffraction scans made during the heating and cooling, respectively. Despite this thermal treatment, there is no evidence of crystallinity in any of the samples (the sharp peaks at 20.88° and 26.66° $2\theta$  are due to quartz added as an internal standard). The positions of the diffuse maxima as measured at 40°C are summarized in Table IV, the peaks having been numbered in order of increasing  $2\theta$ .

The fiber diagrams prepared from samples PBPC, PBPD, and PBPE (fibers could not be drawn from the two molecules with smaller substituents owing



**Figure 10** Simulation of meridional diffraction from PBPD based on a single-chain model with  $DP = 30$ . The diffraction calculated is the average from 1000 chains built in random conformations appropriate to the temperature  $20^{\circ}\text{C}$ . The pattern shows three orders at  $5.8^{\circ}$ ,  $11.0^{\circ}$ , and  $17.0^{\circ} 2\theta$ .

to their brittleness) set the trend that peaks 1, 3, and 4 are meridional maxima, which are in the same position for all samples. Peak 2 concentrates on the equator, whereas peak 5 shows very little orientation, although it is marginally equatorial in PBPD. Here, the oriented fiber diagram of PBPD is shown in Figure 8 as an example; the results are summarized in Table V.

Peak 2 changes its position systematically with the change in side groups; it represents an interchain distance that increases as the size of the side group increases. Figure 9 is a plot of the apparent spacing of the chains, determined from the peak position using the relation for unoriented chains discussed above, against the square root of the van der Waals volume of the polymer repeat unit.

Although the plot may appear reasonably linear over the range of chain spacings obtained, it will not extrapolate to zero. So, whereas it might be expected that the chain spacings may be proportional to the square root of the van der Waals volume, the relationship here is distinctly different (see Fig. 9).

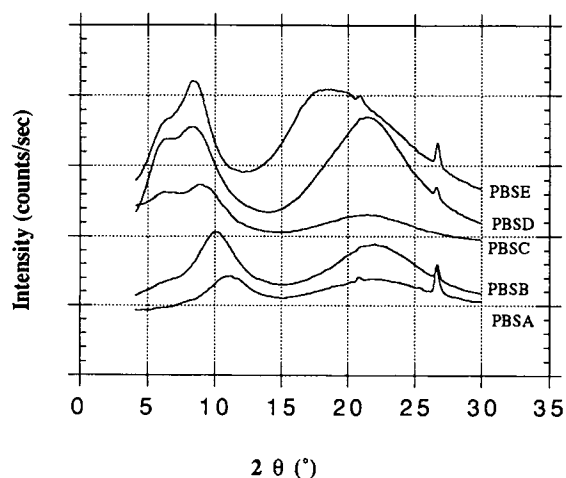
A further confirmation of the distinction between meridional and equatorial maxima comes from the WAXS plots made as a function of temperature shown for PBPC in Figures 6 and 7. As far as could be ascertained, the position of the three meridional maxima were independent of temperature, whereas peak 2 moved slowly to lower angles as the temperature increased. The observed shift over the temperature range  $40\text{--}220^{\circ}\text{C}$  would correspond to a mean thermal expansion coefficient of  $9 \times 10^{-5}/\text{K}$ , which is quite typical of the intrinsic value obtained normal to the chain axis in oriented thermotropic polymers.<sup>27</sup>

The three meridional peaks correspond to the first, second, and third orders of diffraction from the chain repeat. Figure 10 shows the calculated unoriented scattering from a single chain in the extended, rigid conformation. The peak positions correspond exactly to those observed experimentally, as shown in the right-hand column of Table V.

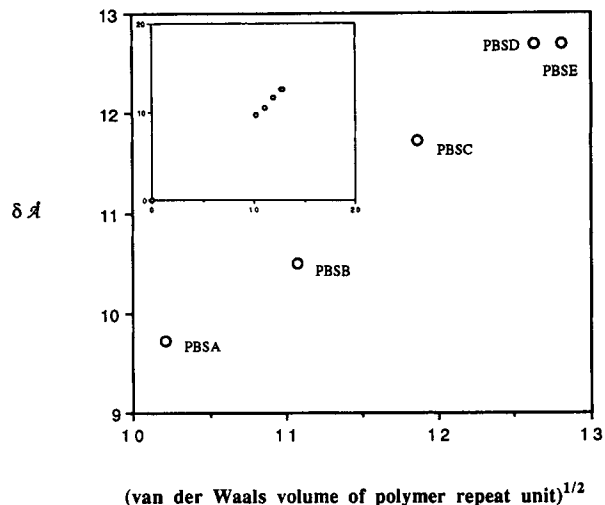
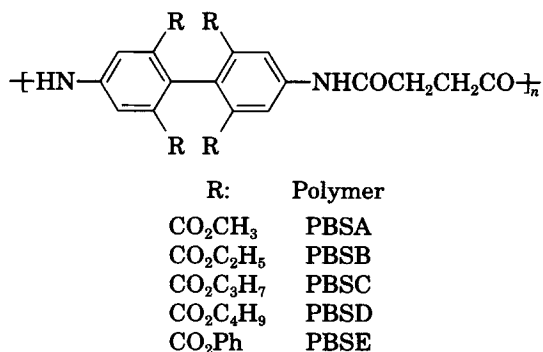
There is, however, a significant discrepancy between the predicted intensities of the meridional dif-

fraction and those seen experimentally. Whereas the predicted intensity of the first peak is much stronger (in relative terms) than that seen experimentally; the predicted intensity of the third order peak appears weaker than that seen experimentally. Indeed, in the fiber pictures, it was difficult to see the first order at all but the third-order peak is relatively strong. Although it is difficult to be sure at this stage, we would suggest that the weak first order and the strong third order are due to the interdigitation of the side groups on neighboring molecules, as illustrated schematically in Figure 2.

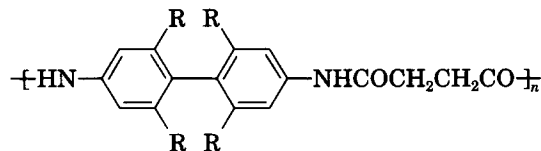
X-ray powder diffraction of similar chains containing a flexible unit based on succinic acid was also studied. Figure 11 shows the powder scan of an equivalent series in which the phenylterephthalic acid is replaced by succinic acid that contains a  $(\text{CH}_2)_2$  unit between acid functionalities. The curves are different in one major respect in that only the first-order diffraction of the polymer repeat unit is



**Figure 11** A series of X-ray diffraction scans as in Figure 5, with polymers based on the tetra-substituted biphenyl unit combined with succinic acid rather than phenylterephthalic acid. Again, the sharp peaks represent the internal quartz standard:



**Figure 12** The relation between interchain distances and the square root of van der Waals volumes of polymer repeat unit for the succinic acid polymers.



R:	Polymer
$\text{CO}_2\text{CH}_3$	PBSA
$\text{CO}_2\text{C}_2\text{H}_5$	PBSB
$\text{CO}_2\text{C}_3\text{H}_7$	PBSC
$\text{CO}_2\text{C}_4\text{H}_9$	PBSD
$\text{CO}_2\text{Ph}$	PBSE

apparent, although higher orders can be seen in patterns from drawn fibers. This difference represents the greater flexibility of the molecule, which means that the axial periodicity is imperfect.

The similarities in the case of the interchain interaction maxima are also notable. Peak 2 shifts continually to lower angles as the side group mass is increased, as shown in Figures 11 and 12. Note also the development of the maximum at  $22^\circ$  that appears to be characteristic of the interalkane peak as seen in molten polyethylene. It is intriguing that in the case of tetraphenyl substituents (for both backbones), this peak shifts to about  $18.5^\circ 2\theta$ , which is characteristic of the interphenyl peak in polystyrene and also in liquid benzene.

## CONCLUSIONS

Polyamides based on 4,4'-diamino-2,2',6,6'-tetra-substituted biphenyls and phenylterephthalic acid

have been synthesized. This class of polymer demonstrates high solubility and low glass transition temperatures due to the noncoplanar conformation of the twisted biphenyl and the bulky side groups in the 2,2',6-, and 6' positions that weaken the interchain interactions (like hydrogen bonding and van der Waals forces) and frustrate parallel packing of the polymer chains.

The polymers of this series have an amorphous structure in both the melt and the glass, despite the semirigid nature of the backbone. It is apparent that the addition of bulky yet discrete side groups to a rigid rod backbone to give "carbuncles" is sufficient to prevent not only crystallinity but also liquid crystallinity. The observations that the rod spacing increases more rapidly with increasing side group size than might be expected on the basis of volume arguments suggests that the interchain packing becomes less efficient as the "carbuncles" are made larger.

C. H. would like to thank The ORS and Cambridge Overseas Trust for providing a scholarship.

## REFERENCES

1. A. J. Kinloch, *Fracture Behaviour of Polymer* p. 127, Applied Science, 1983.
2. F. J. McGarry and J. E. Moalli, *Polymer*, **32**, 1811 (1991).
3. F. J. McGarry and J. E. Moalli, *Polymer*, **32**, 1817 (1991).
4. D. J. Byron, G. W. Gray, and B. M. Worrall, *J. Chem. Soc.*, 3706 (1965).
5. R. A. Gaudiana, R. A. Minns, R. Sinta, N. Weeks, and H. G. Rogers, *Prog. Polym. Sci.*, **14**, 47 (1989).
6. R. Sinta, R. A. Gaudiana, R. A. Minns, and H. G. Rogers, *Macromolecules*, **20**, 2374 (1989).
7. W. Hatke, H.-L. Land, H.-W. Schmidt, and W. Heitz, *Makromol Chem. Rapid. Commun.*, **12**, 235 (1991).
8. H.-W. Schmidt, *Makromol Chem. Makromol. Symp.*, **26**, 47 (1989).
9. M. Ballauff and G. F. Schmidt, *Mol. Cryst. Liq. Cryst.*, **147**, 163 (1987).
10. A. Colebrooke and A. H. Windle, *J. Macromol. Sci.-Phys.*, **B12**(3), 373 (1976).
11. R. Lovell and A. H. Windle, *Polymer*, **22**, 125 (1981).
12. J. R. Waring, J. R. Lovell, G. R. Mitchell, and A. H. Windle, *J. Mater. Sci.*, **17**, 1171 (1982).
13. R. Lovell, G. R. Mitchell, and A. H. Windle, *Discuss. Faraday Soc.*, **68**, 48 (1979).
14. R. Lovell and A. H. Windle, *Polymer*, **17**, 488 (1976).
15. G. R. Michell, R. Lovell, and A. H. Windle, *Polymer*, **21**, 981 (1980).
16. G. R. Michell, in *Order in the Amorphous 'State' of Polymers*, S. E. Keinath, Ed., 1985, p. 8.
17. H. P. Klug and L. E. Alexander, *X-ray Diffraction Procedures*, Wiley, New York, 1954, pp. 631-633.
18. W. O. Statton, in *Handbook of X-ray in Research and Analysis*, McGraw-Hill, New York, 1967, Chap. 21, p. 14.
19. G. Oster and D. P. Riley, *Acta Crystallogr.*, **5**, 272 (1952).
20. L. E. Alexander and E. R. Michalik, *Acta Crystallogr.*, **12**, 105 (1959).
21. E. A. Coulson, *J. Chem. Soc.*, 1298 (1937).
22. J. Y. Jadhav, J. Preston, and W. R. Krigbaum, *J. Polym. Sci. Part A Polym. Chem.*, **27**, 1175 (1989).
23. E. K. Weisburger and J. H. Weisburger, *J. Org. Chem.*, **23**, 1193 (1958).
24. F. Higashi, S.-I. Ogata, and Y. Aoki, *J. Polym. Sci. Polym. Chem.*, **20**, 2081 (1982).
25. R. A. Gaudiana, K. A. Minns, H. G. Rogers, R. Sinta, L. D. Taylor, D. Kalyanaraman, and C. McGowan, *J. Polym. Sci. Part A Polym. Chem.*, **25**, 1249 (1987).
26. P. W. Atkins, *Physical Chemistry*, 2nd ed., Oxford University Press, Oxford, 1982, p. 751.
27. Y. Takeuchi, F. Yamamoto, and Y. Shuto, *Macromolecules*, **19**, 2059 (1986).

Received August 30, 1993

Accepted January 27, 1994