# Structure of Semirigid Polyamides with Bulky Groups in Backbone 

CHAOBIN HE, ${ }^{1 *}$ ANSELM C. GRIFFIN, ${ }^{2,+}$ ALAN H. WINDLE ${ }^{1}$<br>${ }^{1}$ Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge CB2 3QZ, United Kingdom<br>${ }^{2}$ Melville Laboratory for Polymer Synthesis, University of Cambridge, Pembroke Street, Cambridge, CB2 3RA, United Kingdom

Received 3 October 1996; accepted 18 April 1998


#### Abstract

The structure of a range of systematically synthesized polyamides, as well as some corresponding component molecular fragments, were studied using wide angle X-ray scattering and computer modeling methods. The molecules all contained tetrasubstituted biphenyls within the amide components, while the aliphatic acid components contained different lengths of the alkyl sequence. A model representing the molecular packing in fiber samples is proposed. It indicates that the polymer backbones are organized in a distorted hexagonal lattice while the intervening pendant side groups still remain randomly packed. © 1999 John Wiley \& Sons, Inc. J Appl Polym Sci 72: 309-319, 1999


Key words: biphenyls; polymers; X-ray scattering; crystallization; modeling

## INTRODUCTION

The interest in polymers containing substituted biphenyls has largely been driven by the possibility of liquid crystallinity in some molecules. ${ }^{1-5}$ Many studies have demonstrated how effective the alkyl side groups are in reducing the melting temperatures and thus enhancing the temperature range over which liquid crystallinity might be observed. In the case of poly( 1,4 phenylene 2,5-dialkoxyterephthalate), for example, nematic mesophases have been observed in the polymers with short side chains containing between two

[^0]and six carbon atoms. The polymers with longer side chains ( $n \geq 10$ ) exhibit a layer type mesophase that has also been observed for the analogous polyamides, ${ }^{6,7}$ polyimides, ${ }^{6,8}$ and other polyesters ${ }^{9}$ where the flexible chains are attached to one or both rings. In some cases the substituted biphenyls, particularly the tetrasubstituted biphenyls, have been used to try to destabilize the liquid crystallinity rather than to promote it. This is based on the argument that if rigid chain polymers have bulky groups at intervals along them as with tetrasubstituted biphenyls, they can only display parallel packing of the rodlike molecules at the expense of considerable internal voids with the consequent energy penalty. Hence, the packing should assume nonparallel (random) form. ${ }^{10}$ A potential application of rigid chain non-liquidcrystalline polymers is in the area of molecular composites.

This article focuses on the physical structure of a specially synthesized series of polyamides containing tetrasubstituted biphenyls within the
amide portion of the chain. The key questions were whether such molecules would show liquid crystallinity and whether their particular form would preclude parallel packing. The structural assessment is based on a systematic wide angle X-ray diffraction analysis on the unoriented and fiber specimens of the chain molecules, as well as on the small molecule fragments. The interpretation of the patterns is supported by molecular modeling.

## EXPERIMENTAL

## Synthesis of Monomers and Polymers

Small molecules and monomers were synthesized according to the procedure described in the literature. ${ }^{10}$ Biphenyl, succinoyl chloride, adipoyl chloride, sebacoyl chloride, and dodecanedioyl dichloride were obtained from Aldrich. The polyamides were synthesized using diacid chloride and diamide monomers. The preparation procedure for the poly( $2,2^{\prime} 6,6^{\prime}$-tetracarboxymethyl $4,4^{\prime}$-biphenylenesuccinicamide) (PBSB) is given below and is representative of that used for all the other polymers in this study:


Tetramethyl-4,4'-diamino-biphenyl-2, $2^{\prime}, 6,6^{\prime}-$ tetracarboxylate ( $1000 \mathrm{mg}, 2.4 \mathrm{mmol}$ ) was introduced into a $100-\mathrm{mL}$ dried reaction flask equipped with a magnetic stirrer and calcium chloride drying tube, and 10 mL of dried $N, N$-dimethylacetamide (DMAc) added to dissolve the diamino compound followed by a few drops of pyridine. Then a $372-\mathrm{mg}$ ( 2.4 mmol ) solution of succinoyl chloride in 20 mL dried DMAc was added quickly; an additional 26 mL of dried DMAc was used to complete the transfer. The reaction solution was kept at $0-5^{\circ} \mathrm{C}$ for 3 h with stirring and then at room temperature overnight. At completion the solution was poured into 400 mL of water, and the resulting fibrous solid was collected and washed with a copious amount of water. The product was dried in a vacuum oven for 18 h .

Monomers representing polymer repeat units were synthesized using corresponding monoacid chlorides and diamides. The preparation procedure is similar to that for polymerization.

NMR analysis showed that there was no sign of hydrolysis of the side groups, confirming the chemical structure of the polymers.

## Sample Preparation

Polymer samples for diffraction were made by dissolving the synthesized materials in DMAc and reprecipitating in water, washing with water, and drying in a vacuum at $80^{\circ} \mathrm{C}$ overnight. Prior to the diffraction scan, the polymer powders were put on an irrationally cut silicon single crystal plate, heated to their softening temperature, and then cooled to room temperature. This procedure ensured a full density sample with a flat surface for accurate diffraction measurement in the reflection geometry. Fiber was first spun by drawing from the melt on a hot stage at about $140^{\circ} \mathrm{C}$ and then drawn in an oil bath at a temperature close to the glass transition temperature. All the small molecule samples were examined in their molten states.

## X-Ray Diffraction

X-ray diffraction measurements were made using a Siemens D500TT diffractometer with nickel filtered $\mathrm{CuK} \alpha$ radiation. Quartz was used as an internal standard for calibration. The hot stage was mounted on the Siemens diffractometer, and the actual temperature of the sample was calibrated by measuring the lattice parameter of copper powder. The oriented fiber patterns of the polymers were recorded photographically using a flat plate transmission camera.

## Computer Modeling

For computer modeling, the CERIUS molecular modeling software for materials research, program (Molecular Simulation Inc., Cambridge, U.K.) and an SG Indigo computer were used to simulate the X-ray scattering from various lattice models.

## SMALL MOLECULES TO POLYMERS

A study of X-ray scattering from a class of small molecules illustrates how the X-ray signatures change systematically with a change of the chem-

$A$ (1)




Figure 1 Wide angle X-ray scattering scans of the polymer PBSE and its corresponding component fragments. The scans were made at temperatures above the crystalline melting point of each of the small molecule components.
ical structures of molecules, especially with the size of the molecules. Figure 1 shows a series of wide angle X-ray scattering curves from a series of molecules based on the biphenyl group. It progressively illustrates the effect of adding $2,2^{\prime}, 6,6^{\prime}$ substituted groups to the biphenyl molecules, then the addition of $4,4^{\prime}$ functional groups, and finally the polymerization through these latter
groups to form a linear, comparatively rigid polyamide chain. The scan from the simple biphenyl molecule (Fig. 1, curve A) shows an intermolecular peak at $19^{\circ} 2 \theta(\mathrm{CuK} \alpha)$ with a substantial tail toward lower angles (larger spacings); such peaks are typical of the packing of aromatic groups that have a significantly anisotropic shape. It is possible to identify the main peak with packing correlations of the "side by side" type while the low angle tail is associated with correlations involving the long axes of one or both molecules of a neighboring pair. The addition of $\mathrm{CO}_{2} \mathrm{C}_{4} \mathrm{H}_{9}$ side chains, which make the molecules wider and thus less anisotropic in shape, leads to two peaks (Fig. 1, scan B). The lower angle of the two at $9.5^{\circ}$ corresponds to the intermolecular distances of the enlarged molecule that will now be much more spherical in shape than in the unsubstituted form. The peak at $21^{\circ}(2 \theta)$ is assigned to the packing between the saturated hydrocarbon side chains entangled in the region between neighboring biphenyl cores. It is similar in position and form to the interchain peak in molten alkanes or, indeed, polyethylene. The addition of the methyl amide groups in the $4,4^{\prime}$ positions predictably moves the intermolecular peak (Fig. 1, curve C) to a still smaller angle ( $8.3^{\circ}$ ) because of the increased bulk of the molecule. This peak is also somewhat sharper, possibly indicating that the molecules are even more spherical in form. On the other hand the inter-side-chain peak is also changed. It is little less sharp than for the case without the $4,4^{\prime}$ substituents and shifted to a slightly lower angle. A possible interpretation is that the addition of the short amide chains into the aliphatic "phase" compromises the quality of packing. The polymerization of the molecule through the amide groups has a distinct influence on the scattering (scan D). First there is an additional peak at $6.3^{\circ}$ that at $14.5 \AA$ corresponds to the chemical repeat along the straight chain molecule with $\mathrm{CH}_{2}$ groups in the backbone in the trans conformation. The appearance of a "polymerization peak" was first noted by Catz ${ }^{11}$ in his study of polystyrene in 1936, although the peak in that case has subsequently been identified as interchain correlation. ${ }^{12}$ The other component of the intermolecular peak at $8.3^{\circ}$ is unchanged in position with respect to that of scan C, whereas the inter-side-chain peak is now sharper again and positioned exactly as the interhydrocarbon peak in scan B. It appears that the scattering between the side chain no longer involves the amide linking groups that are now linking the


| monomer: | $\mathrm{R}:$ |
| :--- | :--- |
| A | H |
| B | $\mathrm{CO}_{2} \mathrm{CH}_{3}$ |
| C | $\mathrm{CO}_{2} \mathrm{C}_{2} \mathrm{H}_{5}$ |
| D | $\mathrm{CO}_{2} \mathrm{C}_{4} \mathrm{H}_{9}$ |

Figure 2 X-ray scans of the biphenyl molecule with various $2,2^{\prime}, 6,6^{\prime}$ substituents. The scans were made at temperatures above the crystalline melting temperature of each of the small molecule components.
units and that the level of the order in the packing is correspondingly enhanced. While intriguing in its own right, this diffraction series of the chain and some of its component fragments underpins the interpretation of origin of each of the three peaks in the polymer scan.

Figure 2 is a related series illustrating the effect on the diffraction of having smaller $2,2^{\prime}, 6,6^{\prime}$ side chains substituted on the simple biphenyl molecule (Fig. 2, curve A). Note that scan D is the same as scan B in Figure 1. The two smaller side groups show intermolecular peak positions at appropriately intermediate positions, while the positions of the inter-side-chain peak at $22^{\circ}$ is little
affected. A surprising aspect is that its intensity does not seem to increase as the proportion of side chain material increases. Nevertheless, the scans of Figure 2 serve to reinforce confidence in the interpretation of the two major peaks in terms of intermolecular and inter-side-chain correlations.

The three scans of Figure 3 parallel scans A, C, and D of Figure 1, except that the side chains are replaced by phenyl groups connected through the single ester link. As before, it is possible to iden-



Figure 3 X-ray scan of the polymer and its corresponding component fragments with phenyl $2,2^{\prime}, 6,6^{\prime}$ substituents. The scans were made at temperatures above the crystalline melting point of each of the small molecule components.
tify both intermolecular and inter-side-chain groups in scan B and, additionally, the polymerization peak in scan C. Again the "equivalent Bragg spacing" of this peak is $14.5 \AA$, confirming the significant extension of the molecule. The packing between the phenyl groups is not as close as for the hydrocarbon chains, however.

## POLYMER SERIES WITH DIFFERENT SIDE GROUPS AND CHAIN REPEATS

On the basis of the studies above, it is possible to identify the features of the scattering curves of the polymer series with some confidence. Figure 4 shows the effect of different $2,2^{\prime}, 6,6^{\prime}$ substituents on the polymeric scattering for a chain backbone of fixed composition. The intermolecular peak (peak 2) changes smoothly in position with the increasing bulk of the side groups (reading from bottom to top) whereas the position of the in-


Figure 4 A series of X-ray diffraction scans from the polymers based on the tetrasubstituted biphenyl unit combined with succinic acid. Polymer PBSA is a crystalline polymer and is not included in this diagram. The sharp peaks at $20.9^{\circ}$ and $26.7^{\circ} 2 \theta$ are the internal quartz standard.


| H | PBSA |
| :---: | :---: |
| $\mathrm{CO}_{2} \mathrm{CH}_{3}$ | PBSB |
| $\mathrm{CO}_{2} \mathrm{C}_{2} \mathrm{H}_{5}$ | PBSC |
| $\mathrm{CO}_{2} \mathrm{C}_{3} \mathrm{H}_{7}$ | PBSD |
| $\mathrm{CO}_{2} \mathrm{C}_{4} \mathrm{H}_{9}$ | PBSE |
| $\mathrm{CO}_{2} \mathrm{Ph}$ | PBSG |



Figure 5 The effect of temperature on the positions of the three main peaks of polymer PBSE. The glass transition temperature of this polymer is $135^{\circ} \mathrm{C}$.

tramolecular polymerization peak (peak 1) is unaffected by the nature of the side groups, at least for those scans in which it can be detected. The position of the inter-side-group peak (peak 3) is constant for the aliphatic side chains but shifts to a lower angle where the side group is a benzene ring. Further confirmation of the identity of the peaks is provided by Figure 5, which is a series of scattering curves for one molecule as a function of temperature. The position of the intramolecular polymerization peak (1) is unchanged with temperature whereas the intermolecular and the in-


Figure 6 X-ray scans of a series of polymers in which the repeat length of the backbone was systematically changed through the addition of further $\left(\mathrm{CH}_{2}\right)_{2}$ units to the acid monomer.


| $m$ | Polymer |
| ---: | :--- |
| 2 | A or PBSG |
| 4 | B |
| 8 | C |
| 10 | D |

ter-side group peaks move to lower angles with increasing temperature, a consequence of thermal expansion and in accord with their identification with nonbonded interactions.

## Polymerization Peak

The fact that the polymerization peak was difficult to detect when the biphenyl substituents were smaller than the ethyl group (Fig. 4) bears closer scrutiny. Figure 6 shows the X-ray scattering of a series of polymers that were designed with different lengths of the flexible $\left(\mathrm{CH}_{2}\right)_{n}$ spacer within the acid portion of the chain to follow the drift of the polymerization peak with a different length of the polymer repeat unit. In this series the polymerization peak only appears in the polymer with two $\mathrm{CH}_{2}$ groups (in fact, polymer PBSG of Fig. 4). The peak is not present in any polymer with more than two $\mathrm{CH}_{2}$ groups. It is
worth noting that the calculated persistence lengths for polymers A (PBSG), B, C, and D, according to the method described in other articles, ${ }^{13,14}$ are $40,20,15$, and $10 \AA$, respectively. The absence of the polymerization peak can thus be attributed to the increasing flexibility of the molecules associated with the longer flexible sequence; this means that an underlying chain repeat of $14.5 \AA$ cannot assert itself because the molecule is not sufficiently straight.

## Interchain Peak

The polymers studied here were synthesized by linking tetrasubstituted biphenyls. As in the case of the component fragments (Figs. 1-3), the position of the interchain peak (2) depends on the size of the pendant side groups; the bigger these groups, the lower the scattering angle, indicating a larger spacing. Indeed, the plot of the interchain distance against the square root of the van der Waals volume of the bulky, tetrasubstituted biphenyl groups is linear. ${ }^{13}$ It should be emphasized, however, that the position of this peak also changed systematically with the length of the polymer backbone. Figure 6 shows that the longer the backbone repeat, the lower the diffraction angle. This result underlines the fact that peak 2 does not represent the packing arrangement of interside groups alone, but the packing arrangements of side groups and the backbone as a whole.

It is interesting to compare our finding with the reports of similar diffraction studies ${ }^{15}$ on poly( $n$-alkyl acrylate) and poly( $n$-alkyl methylacrylate). The scattering curves from these two classes of polymer were dominated by two broad peaks: an intermolecular interaction peak and an inter-side-chain interaction peak. The position of the intermolecular peak, equivalent to our interchain peak (2), depends on the size of the pendant side group. It was suggested that, although this intermolecular interaction peak corresponded to the intersegmental correction, it represented the "local order" in the polymers and was thus a property of the macromolecular state. In contrast, our study shows that this interchain correlation peak in the polymer system examined here is also a main feature of the scattering from the monomer and component biphenyl fragments.

## Inter-Side-Chain Peak

Figure 4 also shows that the polymers display a significant peak (peak 3) at a higher angle. As
indicated above for the polymers with the alkyl side groups, the position of peak 3 at $22^{\circ} 2 \theta$ is consistent with scattering from correlations arising from van der Waals contacts of nonbonded atoms among the side groups. It is also independent of the lengths of the side groups. For the polymer with phenyl substituents, peak 3 is at $17.5^{\circ} 2 \theta$. It is also much less symmetrical. Separation of this peak by using standard curve fitting routing (assuming that all peaks have a normal distribution) resolves it into two components, one at $17.5^{\circ} 2 \theta$ and the other at $25^{\circ} 2 \theta$, as illustrated in Figure 7. These two peaks are consistent with the correlations between the aromatic rings and the one at a higher angle corresponding to face to face correlations of the rings.

## X-RAY FIBER DIFFRACTION PATTERNS

Although the analysis of the wide angle X-ray scattering from unoriented specimens, particularly that coupled with the analyses of monomers and component fragments of the molecules, enabled the secure identification of the origins of the various peaks, 2 -dimensional diffraction information from oriented samples would provide ideal confirmatory evidence and also show whether orientation as fiber drawing produced any additional level of positional order within the structure. ${ }^{16}$ We were successful in obtaining fiber only from polymers PBSD and PBSE, which were those


Figure 7 Decomposition of the scan from PBSG (phenyl ester substituents) into component peaks. The Gaussian method was used in separation of the board halos while the Lorentz method was used to fit the quartz calibration peak at $26.7^{\circ} 2 \theta$.

(a)

(b)

Figure 8 Flat film fiber pattern of polymer PBSD drawn in an oil bath at $130^{\circ} \mathrm{C}$ to a draw ratio of 3 . There are two meridional peaks at $6.1^{\circ}$ and $12.2^{\circ}$. Both pictures are from the same negative but with different exposure times to enhance the contrast of the fourpoint scattering.

with smaller side groups or phenyl side groups proving too brittle to draw. The fiber patterns obtained are shown in Figures 8 and 9. The orientation achieved is quite good with a $P_{2}$, esti-


Figure 9 X-ray fiber pattern of polymer PBSE drawn in an oil bath at $115^{\circ} \mathrm{C}$ to a draw ratio of 2.5 . Both pictures are from the same negative but with different exposure times as in Figure 8.

mated from the azimuthal width of the second meridional peak, in the range of $0.8-0.85$.

## Fiber Pattern of PBSD $\left(\mathrm{CO}_{2} \mathrm{C}_{3} \mathrm{H}_{7}\right.$ Side Group)

This pattern is shown in Figure 8. Three orders of meridional peaks, corresponding to the chain re-
peat of $14.5 \AA$, can be detected. Of these, the second order is by far the clearest and the best oriented. The first order shows comparatively poor orientation, while the third is largely masked by the intense ring at $22^{\circ} 2 \theta$. The fact that the second-order meridional peak is the strongest in the fiber pattern while the diffractometer scan of the unoriented samples shows only the first order is worthy of comment. Before one moves to an interpretation based on the introduction of additional order by the fiber drawing operation, it should be noted that the appearance of the second-order maximum in the fiber pattern can often be accounted for by the comparatively more efficient sampling of meridional rather than equatorial intensity in reciprocal space, because the latter is spread out around a ring. The apparently poor level of orientation shown by the first-order maximum may be associated with the staggered disposition of neighboring molecules along the chain axis. This issue is further discussed below. The most intense maximum in Figure 8 (PBSD) is at $9^{\circ}(2 \theta)$ and it corresponds to an interchain distance of $9.8 \AA$, which is at the same position as peak 2 in the powder diffraction. It does show some concentration of intensity on the equator [Fig. 8(b)], which is consistent with its interchain identity. However, this ring also bears a clear "four-point pattern" of off-equatorial maxima, the peaks actually being at $9.7^{\circ} 2 \theta$. The presence of such maxima indicates that the chains are correlated on a lattice of some type, and it may also be read as signs of crystallinity. The scattering halo at about $22^{\circ}$ $2 \theta$, which was identified from the scans of unoriented samples (peak 3) as representing side chain

Table I Peak Positions for Powder Scattering of Polymers


| Polymer | R | Peak 1 | Peak 2 | Peak 3 |
| :---: | :---: | :---: | :---: | :---: |
| PBSA | H |  |  |  |
| PBSB | $\mathrm{CO}_{2} \mathrm{CH}_{3}$ | $6.1^{\circ}$ | $11.1^{\circ}$ | $22.0^{\circ}$ |
| PBSC | $\mathrm{CO}_{2} \mathrm{C}_{2} \mathrm{H}_{5}$ | $6.1^{\circ}$ | $10.1^{\circ}$ | $22.0^{\circ}$ |
| PBSD | $\mathrm{CO}_{2} \mathrm{C}_{3} \mathrm{H}_{7}$ | $6.1^{\circ}$ | $9.0^{\circ}$ | $22.0^{\circ}$ |
| PBSE | $\mathrm{CO}_{2} \mathrm{C}_{4} \mathrm{H}_{9}$ | $6.1^{\circ}$ | $8.4^{\circ}$ | $22.0^{\circ}$ |
| PBSG | $\mathrm{CO}_{2} \mathrm{Ph}$ | $6.1^{\circ}$ | $8.4^{\circ}$ | $17.5^{\circ}$ |

[^1]Table II Comparison of Powder and Fiber Diffractions


| Polymer | R | Diffraction |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | Equatorial | Meridional | Four-Point Off-Equatorial | Powder |
| PBSD | $\mathrm{CO}_{2} \mathrm{C}_{3} \mathrm{H}_{7}$ | $9.0^{\circ}$ | $6.1^{\circ}$ | $9.7^{\circ}$ | $6.1^{\circ}$ |
|  |  | $22.0^{\circ}$ | $12.2^{\circ}$ |  |  |
|  |  |  | $17.6^{\circ}$ |  | $22.0^{\circ}$ |
| PBSE | $\mathrm{CO}_{2} \mathrm{C}_{4} \mathrm{H}_{9}$ | $6.2^{\circ}$ | $6.0^{\circ}$ | $8.8^{\circ}$ | $6.1^{\circ}$ |
|  |  | $8.8{ }^{\circ}$ | $12.2^{\circ}$ |  |  |
|  |  | $22.0^{\circ}$ | $17.6^{\circ}$ |  | $22.0{ }^{\circ}$ |

correlations, is also marginally concentrated on the equator, suggesting that the side chains in this case had a slight tendency to align with the molecular backbones.

## Fiber Pattern of Polymer PBSE $\left(\mathrm{CO}_{2} \mathrm{C}_{4} \mathrm{H}_{9}\right.$ Side Group)

The fiber pattern of polymer PBSE as shown in Figure $9(a, b)$ is similar to that of polymer PBSD


Figure 10 Computer simulation of X-ray scattering for polymer PBSE. The X-ray pattern was calculated from a distorted hexagonal close packed structure with packing motifs of $(0,0,0)$ and $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$. The simulated pattern has a fair agreement with the experimental data of Figure 9.
$\left(\mathrm{CO}_{2} \mathrm{C}_{3} \mathrm{H}_{7}\right.$ side group) because both of them have a strong second-order meridional scattering and a four-point off-equatorial scattering. On the equator there are three equatorial scattering maxima of which the two low angle scattering peaks are overlapping.

Table II is the summary of the results of the fiber patterns. From the above observations it can be confirmed that peak 1 in powder diffraction is the intrachain correlation peak while peak 2 and peak 3 are the interchain interaction peaks.

## RESULTS AND DISCUSSION

The polymers discussed in this article show no optical textures or multiple transitions in DSC, which would indicate that they are liquid crystalline. They are in fact transparent glasses and there is no evidence of crystallinity. Yet, the sharp meridional reflections are evidence of comparatively straight molecules, at least with the least flexible of the acid monomer [only one $\left(\mathrm{CH}_{2}\right)_{2}$ group]. Set against these general observations is the evidence for 3 -dimensional order in the fiber patterns, especially the appearance of four-point patterns on the main interchain ring as in Figures 8(b) and 9(b). In addition, the fact that it is only the second-order meridional maximum and not the first, which is well oriented and sharply defined, is also an indication of interchain order. It is not difficult to envision chain packing regimes that can rise to a strong second-order meridional scattering and a four-point off-equatorial scattering. Body centered orthorhombic and hexagonal close packings are such examples.

A more detailed interpretation of the fiber pattern was pursued in the case of polymer PBSE and its fiber pattern (Fig. 9). Scattering was calculated for a variety of packing regimes using CERIUS software and compared with the experimental data. A satisfactory fit with the fiber patterns of Figure 9 was obtained for a sheared hexagonal close packed structure ( $\gamma=100^{\circ}$ ) with the packing motif of $(0,0,0)$ and $\left(\frac{1}{3}, \frac{2}{3}, \frac{1}{2}\right)$ and cell parameters of $a=b=14 \AA$ and $c \stackrel{{ }^{3}}{=} 14.5 \AA$. The best fit with respect to peak widths corresponded to a model size of $40 \times 40 \times 300 \AA$, although the significant widths could equally well be the consequence of paracrystalline distortion. In the simulation methyl esters were used as the side groups instead of butyl esters to avoid the difficulty in assigning the position of butyl side groups, because the side groups are still randomly packed under orientation. The calculated scattering pattern in Figure 10 shows that the significant features of the experimental pattern are reproduced. Note the weakness of the oriented first-order meridional diffraction, the double equatorial maxima, and the clear four-point pattern. The most significant feature of the pattern is the indication that the chains are longitudinally interdigitated (the $c=\frac{1}{2}$ positioning of the second chain in the motif).

Although one can take the evidence above as suggesting some measure of crystalline order, it must be kept in mind that the bulky side chains are definitely not crystalline, although the broad halo corresponding to the inter-side-chain correlations is slightly concentrated on the equator in the fiber patterns. A model representing this packing structure is shown in Figure 11. While the polymer backbones are located at the fixed positions of a distorted hexagonal lattice, the pendant side groups, although accommodated into the lattice, are noncrystalline. It should be noted that it is the flexible side groups acting as a form of bound solvent that by diluting the concentration of rigid molecules enables the comparatively rigid chain to be melted or dissolved at all, and there is little chain entropy to be gained when comparatively rigid molecules are melted or dissolved.

It has been possible to describe the 3 -dimensional order in one example of a semirigid polyamide with significant $2,2^{\prime}, 6,6^{\prime}$ substitution. However, the classification of this order does present something of a puzzle. There is evidence of a 3 -dimensional lattice, although a significant proportion of the contents of the unit cell are not


Figure 11 An illustration of the proposed model of chain packing showing the interdigitation of the substituted biphenyl groups and the absence of crystallization in the side chains.
definable in position. Such an arrangement is not unusual, because noncrystalline units can have well-defined shapes, such as in the case of colloidal silica particles that are organized on a lattice to produce the crystal type order of the mineral opal. There is also the analogy of lyotropic liquid crystals in which the presence of noncrystalline solvent enables rather than prevents the formation of (admittedly limited) levels of packing order.

Chaobin He would like to thank the Cambridge Overseas Trust and ORS for providing a scholarship.

## REFERENCES

1. Byron, D. J.; Gray, G. W.; Worrall, B. M. J Chem Soc 1965, 3706.
2. Gaudiana, R. A.; Minns, R. A.; Sinta, R.; Weeks, N.; Rogers, H. G. Prog Polym Sci 1989, 14, 47.
3. Sinta, R.; Gaudiana, R. A.; Minns, R. A.; Rogers, H. G. Macromolecules 1989, 22, 2374.
4. Hatke, W.; Land, H.-L.; Schmidt, H.-W.; Heitz, W. Makromol Chem Rapid Commun 1991, 12, 235.
5. Schmidt, H.-W. Makromol Chem Makromol Symp 1989, 26, 47.
6. Ballauff, M. Angew Chem Int Ed Eng 1989, 28, 1130.
7. Ebert, M.; Hermanschonherr, O.; Wendorff, J. H.; Ringsdorf, H.; Tschirner, P. Makromol Chem Rapid Commun 1988, 9, 445.
8. Duran, R.; Ballauff, M.; Wenzel, M.; Wegner, W. Macromolecules 1988, 21, 2897.
9. Rodriguezparada, J. M.; Duran, R.; Wegner, G. Macromolecules 1989, 22, 2507.
10. He, C.; Griffin, A. C.; Windle, A. H. J Appl Polym Sci 1994, 53, 561.
11. Latz, J. R. Trans Faraday Soc 1936, 32, 77.
12. Mitchell, G. R.; Windle, A. H. Polymer 1984, 25, 920.
13. He, C.; Windle, A. H. Macromol Theory Simul 1995, 4, 289.
14. He, C. Ph.D. dissertation, University of Cambridge 1994.
15. Miller, R. L.; Royer, R. F. J Polym Sci Poly Phys Ed 1984, 22, 2021.
16. Colebrooke, A.; Windle, A. H. J Macromol Sci Phys 1976, B12, 373.

[^0]:    * Present address: Polymer \& Colloids Group, Cavendish Laboratory, University of Cambridge, Department of Physics, Madingley Road, Cambridge CB3 0HE, U.K.
    ${ }^{\dagger}$ Present address: Department of Chemistry \& Biochemistry, University of Southern Mississippi, Hattiesburg, MS 39406

    Correspondence to: A. C. Griffin.
    Journal of Applied Polymer Science, Vol. 72, 309-319 (1999)
    © 1999 John Wiley \& Sons, Inc.
    CCC 0021-8995/99/030309-11

[^1]:    ${ }^{\text {a }}$ This peak can be separated into two peaks: one at $17.5^{\circ}$ and the other at $25^{\circ}(2 \theta)$.

