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Chain Conformation of the Technora Copolyamide

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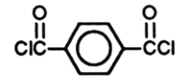
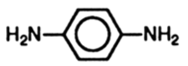
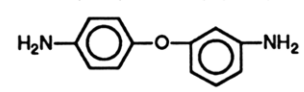
ABSTRACT: This paper describes further X-ray diffraction work on the structure of the copolyamide prepared from terephthaloyl chloride (TPA), phenylenediamine (PDA), and 3,4′-diaminodiphenyl ether (DPE). X-ray fiber diagrams of this material consist of a series of nonperiodic layer lines, and we have shown previously that these are consistent with a structure consisting of parallel chains of completely random comonomer sequence. The meridional peak positions are predicted accurately for a fully extended chain conformation, and the peak intensities are also in reasonably good agreement. However, there is a less than adequate match between the observed and calculated peak profiles, most notably that for the peak at $d \cong 2.15$ Å, which is predicted to be very much sharper than that observed. The latter peak has been shown to be a measure of the correlation or persistence length for the stiff chain conformation in the solid state and is predicted to be extremely sharp when the chain is modeled by a linear infinite chain of random monomer sequence. A better fit to the broader observed peak is achieved by using a model that incorporates nonlinearity of the chain conformation due to the presence of the ether and 1,3-phenylene linkages, as well as torsional variations. This has been done by defining the nonlinearity in terms of histograms of the axial advance per monomer for each monomer type, based on a survey of models of a large number of chains with sequences selected by Monte Carlo methods. It is clear that the requirements of chain packing imply highly extended conformations, and this probably involves some distortion of the bond and torsion angles in order to align the random sequences.

Introduction

A previous paper from this laboratory[1] described X-ray analysis of the structure of a copolyamide prepared from the following monomers in a 50/25/25 mole ratio:


terephthaloyl chloride (TPA)


p-phenylenediamine (PDA)


3,4′-diaminodiphenyl ether (DPE)

This polymer is processed from *N*-methyl-2-pyrolidone solution as a high-strength, high-modulus fiber by Teijin Ltd. (Osaka, Japan) under the trade name Technora (previously HM-50). The resultant fiber is reported to have mechanical properties comparable to Kevlar 49 (du Pont) but with improved hydrolytic stability.[2,3]

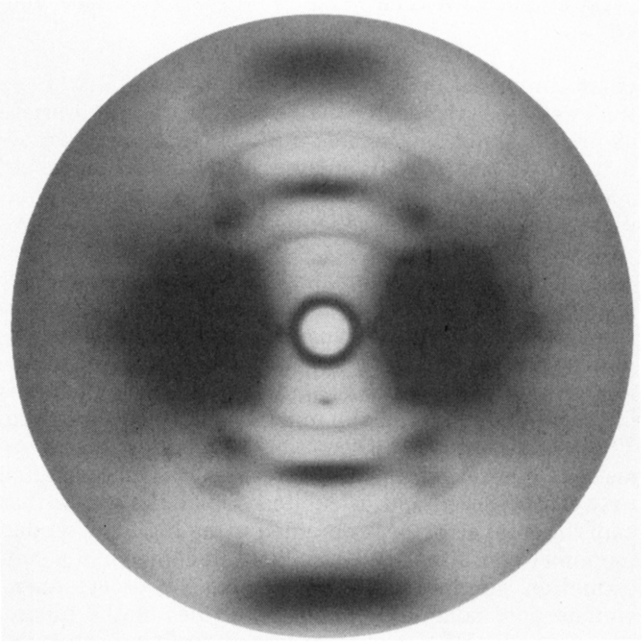


Figure 1. X-ray fiber diagram of the copolyamide Technora. The fiber axis is vertical.

The X-ray fiber diagram (Figure 1) of the copolyamide fibers shows a high degree of axial orientation of the molecules and also that there is some three-dimensional order. A most interesting feature of the data is the occurrence of a series of aperiodic layer lines. Meridional maxima are observed at *d*-spacings, which are not orders of simple repeat. These data are analogous to those for wholly aromatic copolyesters, such as those prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA).[4–9] In the latter systems, the observed aperiodic layer lines are predicted for a structure consisting of parallel chains of completely random monomer sequence. The copolyester chains have highly extended conformations in which the axial advance per monomer is approximately constant (but different) for each monomer type. The aperiodic meridional maxima arise due to the structural correlations that occur along such chains. For the copolyesters, the predicted X-ray data have been found to be sensitive to nonrandomness, which leads to changes in positions and also to splitting of the meridional maxima, such that all but minimal blockiness can be ruled out for melt-spun fibers. Recent NMR work on partially deuterated copoly(HBA–HNA) has confirmed the random comonomer sequence.[10]

Prediction of the conformation of the Technora copolyamide is more difficult than for copoly(HBA–HNA) and the other wholly aromatic copolyesters studied previously, because the 1,3-phenylene and ether linkages lead to "kinks" in the chain. However, an overall extended

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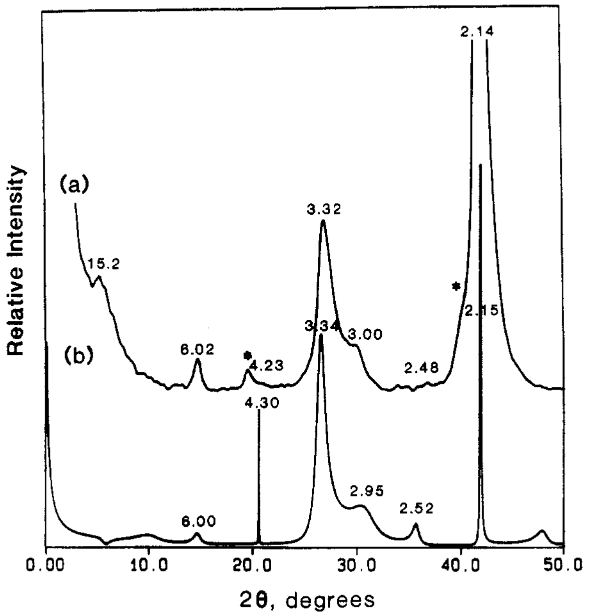

Figure 2. (a) $\theta/2\theta$ diffractometer scan of X-ray intensity scattered by Technora fibers along the meridional direction. The d-spacings are shown above the individual peaks. Peaks marked with an asterisk are off-meridional intensity arced over the meridian due to disorientation. The peak at d = 2.14 Å ($\theta \cong 42°$) is truncated to allow side expansion. (b) Calculated meridional intensity for idealized linear chains of random sequence. The peaks at d = 4.3 Å (21.5°) and 2.15 Å (42°) have been truncated.

chain conformation is possible, because the effect of one kink can be reversed by the next with the appropriate choice of torsion angles, i.e., if a "zig" is followed immediately by a "zag". NMR analyses of low molecular weight specimens of this copolymer[11] are consistent with a completely random monomer sequence.

In our initial calculations,[1] the structure was modeled as a nematic array of chains with random monomer sequences, constructed using standard bond lengths and angles. We considered a range of possible models encompassing the most contracted and fully extended conformations for each monomer and compared the positions of the predicted meridional maxima with those observed. The calculation led to prediction of aperiodic meridionals in each case, and the best agreement (when the match between observed and calculated d-spacings was within experimental error) was obtained using highly extended monomer conformations: the TPA monomer had a conformation similar to that reported for poly(p-phenyleneteraphthalamide),[12] and the planes of the phenyl groups in the DPE monomer were mutually perpendicular, as is seen in diphenylene ether model compounds.[13]

Figure 2 compares the calculated intensity reported in ref 1 with the observed data in the form of a $\theta/2\theta$ diffractometer scan along the meridional direction. The agreement of the positions and intensities of the observed and calculated peaks is apparent. The peaks at $d \cong 4.3$ Å ($2\theta \cong 21°$) and 2.15 Å (42°) in the calculated data are very sharp, and both have been truncated. The observed peak at 2.15 Å has also been truncated for convenience. The actual arcs under the observed and calculated peaks at 2.15 Å are approximately equal. However, the peaks do not match, the calculated peaks (both 4.3 and 2.15 Å) being much narrower than those observed. These peaks are invariant in that, unlike the other maxima, they do not shift with monomer ratio or with sequence distribution. They can be thought of as Bragg peaks that arise because 4.3 and 2.15 Å are, respectively, the 3rd and 6th order of the PDA–TPA repeat and the 4th and 8th order of the DPE–TPA repeat. The calculated data are for an infinite chain, and hence the predicted peaks are very sharp: their widths are increased when finite chains are considered. The same effect has been reported for copoly(HBA–HNA),[15] where it was shown that the width of the invariant peak at 2.1 Å could be reproduced using models consisting of short chains of 9–13 monomers. This led to the concept of a solid-state correlation length, which is 70–90 Å in the latter case, and is the length beyond which the approximation of a completely straight chain breaks down.

In the present paper we have extended our previous work in an effort to refine the conformation of the copolyamide. We have constructed stereochemically acceptable models for the chains and have surveyed these in order to determine the distribution of the axial advances for each monomer type. These have been incorporated into the calculations in order to match the observed peak profiles.

Tashiro et al.[14] have recently suggested that the observed X-ray data can in fact be explained by a blocky structure. Although they acknowledge that our predictions for a random sequence are consistent with the observed data, they question the sensitivity of the predictions to nonrandomness. They suggest that the nonperiodic peaks arise due to overlap of the periodic peaks predicted for poly(PDA–TPA) and poly(DPE–TPA), coupled with shifts due to the effect of the "Laue term for small crystallite size." These points are addressed below in the Results and Discussion.

Experimental Section

Fibers of Technora (HM-50) copolyamide prepared with a 50/25/25 mole ratio of TPA–PDA–DPE were supplied by Teijin Ltd. (Osaka, Japan). A linear $\theta/2\theta$ X-ray intensity scan for these fibers in the meridional (fiber axis) direction was obtained using a Phillips PN 3550/10 diffractometer with Ni-filtered Cu Kα radiation. Fibers were arranged parallel in bundles approximately 20 mm wide and 0.5 mm thick, and the data were recorded in the transmission mode with a constant slit width.

Theoretical Modeling. In the previous work on this copolyamide,[1] it was shown that the meridional intensity could be derived from the scattering of a single average chain, following the work of Biswas and Blackwell[16] on the analogous copolyester. For an infinite chain of point monomers the meridional intensity, $I(Z)$, is expressed as

$$I(Z) = 1 + 2\,\mathrm{Re}\left(\frac{H_1(Z)}{1 - H_1(Z)}\right) \qquad (1)$$

where $H_1(Z)$ is the Fourier transform of the first nearest-neighbor probability function and Re designates the real component. $H_1(Z)$ can be written as

$$H_1(Z) = \sum_A \sum_B H_{AB}(Z) \qquad (2)$$

where the summations are over all monomers and the $H_{AB}(Z)$ terms are the components for the AB nearest-neighbor pairs. Each $H_{AB}(Z)$ is the product of composition and phase terms, which define the monomer ratios, the allowable chemical combinations, and the monomer axial lengths. For the copolyamide studied here, TPA and PDA are chemically symmetrical, but the DPE monomer has a sense depending on whether the 1,4-phenylene precedes or follows the 1,3-phenylene unit. Thus, there are in effect four monomers: TPA, PDA, up-DPE, and down-DPE, which are further abbreviated to T, P, D, and B, respectively. Of the sixteen possible monomer pair combinations, only six are chemically allowed: none of the monomers may react with themselves, and a TPA must come between each diamine. $H_1(Z)$ can be conveniently written in matrix form with nonallowed pairs denoted by zeros:

$$H_1(Z) = \begin{bmatrix} 0 & H_{\mathrm{TP}}(Z) & H_{\mathrm{TD}}(Z) & H_{\mathrm{TB}}(Z) \\ H_{\mathrm{PT}}(Z) & 0 & 0 & 0 \\ H_{\mathrm{DT}}(Z) & 0 & 0 & 0 \\ H_{\mathrm{BT}}(Z) & 0 & 0 & 0 \end{bmatrix} \quad (3)$$

We can write $H_1(Z)$ as a product of three matrices

$$H_1(Z) = \mathbf{P}\cdot\mathbf{M}\cdot\mathbf{X}(Z) \quad (4)$$

where

$$\mathbf{P} = \begin{bmatrix} p_{\mathrm{T}} & 0 & 0 & 0 \\ 0 & p_{\mathrm{P}} & 0 & 0 \\ 0 & 0 & p_{\mathrm{D}} & 0 \\ 0 & 0 & 0 & p_{\mathrm{B}} \end{bmatrix} \qquad \mathbf{M} = \begin{bmatrix} 0 & M_{\mathrm{TP}} & M_{\mathrm{TD}} & M_{\mathrm{TB}} \\ M_{\mathrm{PT}} & 0 & 0 & 0 \\ M_{\mathrm{DT}} & 0 & 0 & 0 \\ M_{\mathrm{BT}} & 0 & 0 & 0 \end{bmatrix}$$

$$\mathbf{X}(Z) = \begin{bmatrix} X_{\mathrm{T}}(Z) & 0 & 0 & 0 \\ 0 & X_{\mathrm{P}}(Z) & 0 & 0 \\ 0 & 0 & X_{\mathrm{D}}(Z) & 0 \\ 0 & 0 & 0 & X_{\mathrm{B}}(Z) \end{bmatrix} \quad (5)$$

The terms in the **P** matrix are the monomer compositions, which in the present case are $p_{\mathrm{T}} = 0.5$, $p_{\mathrm{P}} = 0.25$, and $p_{\mathrm{D}} = p_{\mathrm{B}} = 0.125$. (We assume equal proportions of up- and down-DPE units.) The **X** matrix contains phase terms due to the separation of the first nearest neighbors: $X_A(Z) = \exp(2\pi i Z z_A)$, where z_A is the axial length of monomer A. The M_{AB} terms in the **M** matrix are the probabilities of the addition of monomer A to a chain ending in monomer B. For a random copolymer where all possible combinations can occur, $M_{AB} = p_A$. In the present case only 6 of the 16 combinations are possible: $M_{AB} = 2p_A$ for the allowed combinations and zero for the others. (In general, the M_{AB} terms are proportional to p_A and are normalized such that $\sum M_{AB} = 1$ for each row of the **M** matrix.) Note that with the above treatment it is only possible to consider a random sequence, because in this copolymer nonrandomness appears in the second nearest neighbors. Nonrandom structures can be treated by considering the copolymer to be a sequence of diamine–TPA units, i.e., dimers, as described in ref 1.

The meridional intensity, $I(Z)$, may now be written

$$I(Z) = 1 + \sum_A \sum_B 2p_A \,\mathrm{Re}\,[T_{AB}(Z)] \quad (6)$$

where $T_{AB}(Z)$ is an element of the matrix $\mathbf{T}(Z)$ corresponding to the pair AB and $\mathbf{T}(Z)$ is defined as

$$\mathbf{T}(Z) = \frac{\mathbf{M}\cdot\mathbf{X}(Z)}{\mathbf{I} - \mathbf{M}\cdot\mathbf{X}(Z)} \quad (7)$$

in which **I** is the unity matrix.

When we use atomic models for the monomers, the intraresidue interference effects are taken into account by multiplying each element $T_{AB}(Z)$ of the $\mathbf{T}(Z)$ matrix by the Fourier transform of the corresponding monomer pair cross convolution, $F_{AB}(Z)$. Equation 7 becomes

$$I(Z) = \sum_A p_A F_{AA}(Z) + \sum_A \sum_B 2p_A \,\mathrm{Re}\,[F_{AB}(Z) T_{AB}(Z)] \quad (8)$$

where

$$F_{AB}(Z) = \sum_j \sum_k f_{A,j} f_{B,k} \exp[2\pi i Z(z_{B,k} - z_{A,j})] \quad (9)$$

The subscript pairs A,j and B,k designate the jth atom in residue A and the kth atom in residue B when both residues have the same origin; f is the atomic scattering factor, and z is the axial atomic coordinate.

In the above model, the axial advance per monomer is assumed to be equal to the residue length from nitrogen to nitrogen, z_{B}, which can only occur if all the nitrogens are collinear. Any stereochemically acceptable model for the chain is significantly nonlinear, even in its fully extended conformation, due in large part to the ether and 1,3-phenylene linkages. As a result, the projected monomer lengths cannot be constant for each monomer type; rather there must be a distribution of such lengths. These distributions have been derived experimentally as histograms from a survey of stereochemically acceptable models of a large number of chains with random sequences selected by Monte Carlo methods. These data were then incorporated into the intensity calculations by replacing the terms in the $\mathbf{X}(Z)$ matrix by

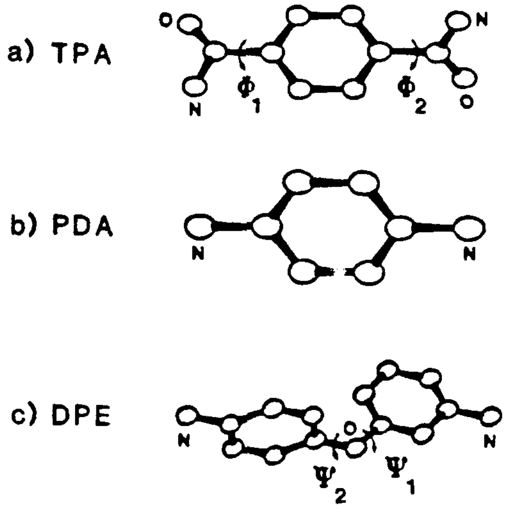

Figure 3. Projection of the monomer structure: (a) terephthalamide (TPA), (b) phenyldiamine (PDA), and (c) diphenyl ether (DPE).

$$X_A(Z) = \sum p_{i,A} \exp(2\pi i Z z_{i,A}) \quad (10)$$

where $p_{i,A}$ is the fraction of the total content of monomer A, which has axial length $z_{i,A}$. In principle, separate $F_{AB}(Z)$ terms need to be computed for each combination of axial lengths for monomers A and B in the atomic model. However, the $F_{AB}(Z)$ functions vary slowly with Z, and $F_{AB}(Z)$ calculated using coordinates for one particular axial projection of each monomer is an adequate approximation.

Model Building. Projections of monomer units in the copolymer chain are shown in Figure 3. Atomic coordinates for the three monomers were derived using standard bond lengths and bond angles, as described in ref 1. The PDA unit is conformationally invariant and is planar with a N···N length of 5.64 Å. The conformation and hence the N–N length of the TPA unit depends on the phenyl–amide torsion angles, ϕ_1 and ϕ_2. These angles were set at ±30° or ±150° (0° and 180° correspond to coplanarity), consistent with the amide–phenyl inclination determined for poly(*p*-phenyleneterephthalamide).[12] These torsion angles result in four possible N···N lengths for the TPA unit: 6.75, 6.86, 7.15, and 7.26 Å.

The greatest potential for conformational variability is found in the DPE unit where the ether bridge torsion angles, Ψ_1 and Ψ_2, define the conformation. The N···N length is independent of Ψ_2 since rotation of the 1,4-linked-phenylene does not affect the position of the 4′-nitrogen. Depending on Ψ_1, the N···N length ranges from 7.39 to 10.02 Å. Note that the repeat distance for poly(TPA–DPE) reported by Tashiro et al.[14] was 17.3 Å, which matches our value of 17.28 Å (7.26 + 10.02) obtained using the longest axial lengths for the two monomers from our model building.

Monomer Axial Length Distributions. Chains of 15 monomers were set up with sequences determined using a random number generator. The conformation of the DPE unit was fixed at its maximum length and the phenyl–amide torsion angles were selected at random from the four values ±30° and ±150°; the chains were required to fit to a cylinder of diameter 10 Å (based on the center of the atoms), which allows some degree of nonlinearity but eliminates severely bent or kinked chains. The maximum diameter of 10 Å was chosen arbitrarily: some perspective is given by the fact that the idealized linear chain would have a diameter of approximately 5 Å. Histograms of axial advance per monomer for each monomer type were derived from 100 such chains.

Results and Discussion

The calculated meridional intensity for an atomic model of an infinite idealized straight chain constructed from fully extended monomers is presented as curve b in Figure 2, where it is compared with the observed diffractometer scan (curve a). The observed and calculated *d*-spacings are shown above the peaks and are seen to be in good agreement. These calculated data have been reported previously: the observed *d*-spacings differ slightly from those in ref 1 and are more accurate. The peak at 15.2 ± 0.2 Å was not reported previously. There appears to be a peak in this position in the calculated data, which becomes more clearly resolved in the work presented below. The peaks marked with an asterisk on the observed data are seen in the fiber pattern to be due to nonmeridional intensity arced over the meridian as a result of fiber disorientation. The weak peak at $d = 2.48$ Å is seen only in the film data. After correction for instrumental broadening, the half-width of the observed peak at $d = 2.14$ Å was 0.9°, compared to 0.01° for the calculated peak. Figure 4a shows 7 typical chains of 15 monomers with random sequences, constructed as described above. Histograms of axial lengths derived from a survey of 100 chains of 15 monomers are presented in Figure 4b. Incorporation of this distribution into the intensity calculations (Figure 5a) has the effect of broadening the width of the invariant peak to 0.06°. However, this is still 1 order of magnitude less than the observed width of 0.9°. Furthermore, the predicted peaks shift to lower *d*-spacings as a result of the reduction in the average monomer lengths from the fully extended values.

It is clear that greater nonlinearity is necessary to increase the width of the invariant peak to match that observed. Some idea of the distortions necessary was obtained by arbitrarily increasing the widths of the histograms presented in Figure 4b. In this exercise, the average monomer lengths and the shapes of the histograms were retained, but the data were stretched to higher and lower limits; that is, the widths of all three histograms were doubled, tripled, and quadrupled. The calculated intensities for these three models are shown in Figure 5, curves b–d respectively. These data are very similar to Figure 5, curve a, except that the width of the invariant peak has increased to 0.24°, 0.51°, and 0.86°, respectively.

The agreement between the observed and calculated peak positions can be restored if the average monomer lengths are increased to the fully extended lengths used previously. The expanded histograms were shifted such that the average monomer lengths correspond to the fully extended lengths. The calculated intensity curve for the model based on shifted histograms, which had also been expanded x4 in width, is shown in Figure 6, curve b, where it is compared to the observed diffractometer scan, curve a. The observed and calculated *d*-spacings are shown above the peaks. It can be seen that there is now good agreement between the observed and calculated data in terms of peak position, intensity, and profile. Note the match between the observed and calculated peaks in the 15-Å region.

The above exercise is designed simply to show the type of distortions that are needed in order to fit the observed data. Expansion of the histograms while leaving the average N···N lengths equal to the "fully extended" lengths means that half the monomers are stretched beyond the normally accepted stereochemical limits. Relaxation of the constraints on the phenyl–amide and diphenyl ether torsion angles during modeling can lead to some extension of the conformation, but this does not result in anything like the extension required. We conclude, therefore, that the conformations of the chain are distorted in the solid-state structure and are more extended than those expected for fully extended isolated chains. This distortion probably arises due to the need to pack the copolymer chains, which are nonlinear due to the kinks at the 1,3-phenylene and ether linkages. In a repeating copolymer formed from these monomers, the kinks would be able to pack in phase. However, in a random copolymer, kinked monomers on one chain will inevitably occur alongside straight sections of neighboring chains, resulting in spaces between the chains if serious stereochemical overlap is to be avoided. These spaces can only be closed up if the chains are stretched or flattened, so that they have a more linear conformation. This requires small but significant distortion of the monomers. Some of the distortion probably results from small, cooperative changes in all the bond lengths and angles. The chain can also

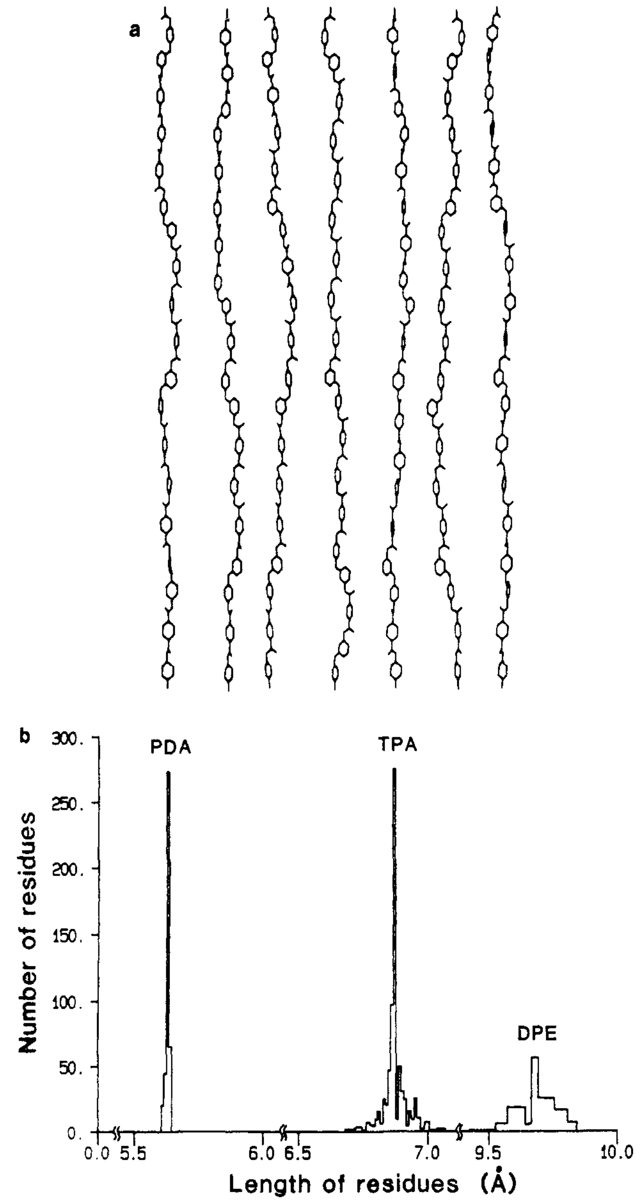

Figure 4. (a) Projections of models of five typical chains of 15 monomer units. (b) Histograms of axial advance for the three monomer types, derived from 100 chains of 15 monomers.

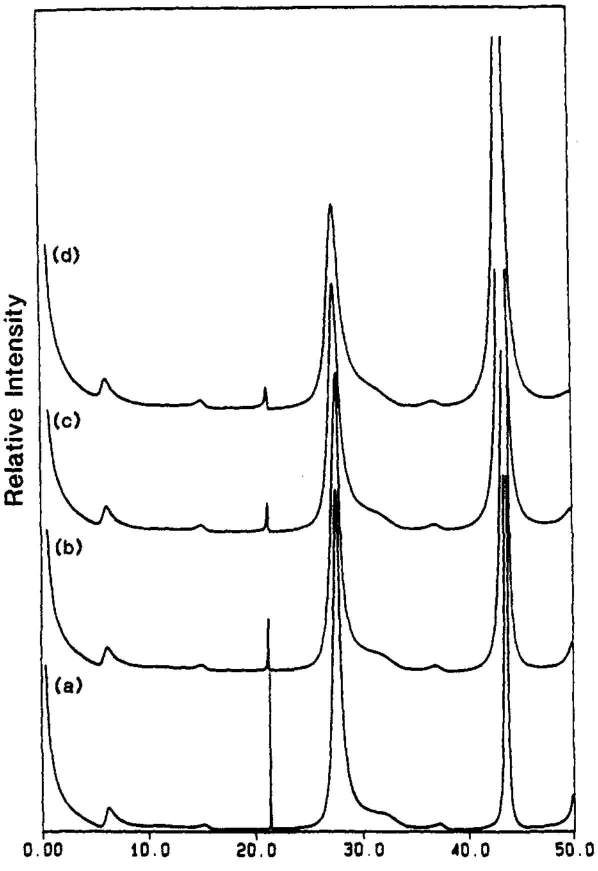

Figure 5. Calculated meridional intensity for (a) nonlinear chain models defined by the histograms in Figure 4b and after (b) doubling, (c) tripling, and (d) quadrupling the widths of those histograms.

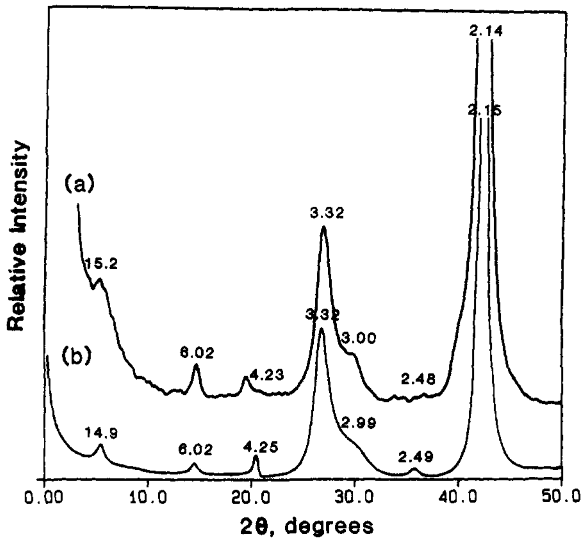

Figure 6. (a) Observed meridional intensity data (from Figure 2a). (b) Calculated meridional intensity for a model in which the widths of the histograms in Figure 4b were quadrupled and then shifted as described in the text. The *d*-spacings are indicated above the peaks.

be straightened significantly if we allow some deviation from planarity of the amide groups, and this seems a reasonable possibility based on our experience with a thermotropic random copolyester carbonate, where nonlinearity is restored by torsional deformation of the carbonate group.[17]

The above work is based on the possible structure of the isolated chain. A true picture of the actual chains can only emerge from a study of the packing of an array of chains, since the actual distortions will depend on the local sequences on adjacent chains. This problem is now under consideration using computer molecular modeling methods.

As mentioned earlier, Tashiro et al.[14] have suggested that the X-ray data is compatible with a blocky structure rather than the random copolymer structure proposed above. We have checked the sensitivity of our analysis to nonrandomness by modifying the nearest-neighbor statistics and find that the match between the observed and calculated meridional peak positions becomes unacceptable for all but minimal blockiness. Blockiness can be defined in terms of the probabilities for linkages of identical dimers, e.g., (PDA–TPA)–(PDA–TPA), and nonidentical dimers, e.g., (PDA–TPA)–(DPE–TPA). We find that when the ratio of the probability of identical dimers to that for nonidentical dimers is ≥ 1.4 times that for the random structure, the match between the observed and calculated data then becomes unacceptable. However, under these circumstances the predicted peaks are still aperiodic: the above ratio needs to be increased to about 4 before the calculated data contains approximately periodic peaks due to poly(PDA–TPA) and poly(DPE–TPA). These alternating copolymers would give rise to peaks that are at 12.9 and 17.3 Å, respectively. It is very significant that the first peak observed on the meridian is at $\cong 15.2$ Å, where it is expected for a random copolymer containing equal molar proportions of the two diamines, i.e., halfway between the two dimer repeats, which is the average axial advance per dimer.

Tashiro et al. suggest that the meridional maxima are composites of those predicted for the blocks. This suggestion is problematical especially in the 3-Å region, where it is hard to see how predicted peaks at 3.45 and 2.88 Å for poly(TPA–DPE) and at 3.22 Å for poly(TPA–PDA) can be combined to give the observed doublet at 3.32 and 3.00 Å. They also discuss the possibility that the peak at 6.45 Å for poly(TPA–PDA) is shifted to 6.02 Å due to the effects of small crystallite size. (In general, the scattered intensity for a periodic structure is the product of the Laue function for a point lattice and the structure factor for the repeat unit. Hence, a broad intensity maximum for a very limited lattice may be shifted from its position in the Laue function if it occurs in a region of rapid angular variation of the structure factor.) We considered this possibility in our calculations where we made predictions for both point and atomic monomers using eqs 6 and 8 below. Equation 6 is the equivalent of the Laue function; eq 8 contains $F_{AB}(Z)$ terms analogous to the structure factor (squared). These $F_{AB}(Z)$ terms are relatively flat in the region of the peak at 6.02 Å, and the *d*-spacing for chains of point monomers is unchanged by the introduction of the intramonomer interference effects. Furthermore, explanation of the data in terms of crystallinity of blocky sequences ignores the contribution of oriented random sequences to the overall diffraction pattern. It would be better to use our procedures with modification of the nearest-neighbor statistics to model a block structure.

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Registry No. (TPA)(PDA)(DPE) (copolymer), 60201-66-3.

Synthesis and Characterization of Carbon Atom Bridged Heterocyclic Polymers of Specified Conjugation Length. 1. Novel Polyterthiophenes

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ABSTRACT: New polymers containing α-(5,5″-terthiophenediyl) segments separated by an sp^3-carbon atom in the main chain were synthesized by acid-catalyzed polymerization of α-terthienyl with aldehydes and characterized. The polyterthiophenes (PTTs) containing CRH bridging groups are soluble in organic solvents. The methylene-bridged polymer, poly[α-(5,5″-terthienyl)methylene] (PTTM), is highly crystalline whereas the benzylidene-bridged and heptylidene-bridged polymers are largely amorphous. The sp^3-bridged polyterthiophenes exhibit solution optical absorption maxima from 362 to 379 nm, depending on the side group at the bridge carbon, as expected for the nonconjugated polymers. The new heterocyclic polymers represent the first example of main chain polymers containing conjugated segments of precisely defined π-electronic conjugation length. The polymers are useful precursors to multiblock conjugated copolymers, with alternating aromatic α-(5,5″-terthienyl) and α-(5,5″-terthienylquinodimethane) segments in the main chain. They are the first examples of organic semiconductor superlattices and also have excellent third-order nonlinear optical properties.

Introduction

One of the important contemporary problems in polymer science is the design, synthesis, characterization, and processing of new polymeric materials with interesting or useful linear optical, nonlinear optical, electrooptical, electronically conducting, magnetic, or superconducting properties for applications in electronic and photonic technologies. A related perennial problem is the fundamental understanding of the underlying structure–property relationships in the materials. Conjugated polymers, as a class, represent one of the most fertile areas of investigation relative to these problems. Research in the last decade has led to important progress in the experimental and theoretical understanding of electronic and electrical properties in conjugated polymers and achievement of semiconducting to metallic conductivities ($\sim 10^2$ to $10^5\ \Omega^{-1}\ \mathrm{cm}^{-1}$) in doped conjugated polymers.[1–4] More recently, the same conjugated polymers have become of wide interest because they exhibit ultrafast (picosecond or less) and large third-order nonlinear optical properties ($\chi^{(3)} \sim 10^{-12}$–10^{-8} esu).[5–8]

Aromatic heterocyclic conjugated polymers based on the five-membered thiophene, pyrrole, and furan rings (Figure 1, structure III) have been widely investigated by several research groups.[6,8–19] Initial interests on conjugated polypyrroles and polythiophenes stemmed from both the high conductivity ($\sim$10–1000 $\Omega^{-1}\ \mathrm{cm}^{-1}$) and exceptional stability in their doped state.[9,10,14] Recently, synthesis of poly(3-alkyl-2,5-thiophenediyl)[16–18] and poly(3-alkyl-2,5-pyrrolediyl)[19] has led to the solution characterization of properties of these conjugated polymers. An earlier chemical and electrochemical synthesis[20] of poly(1,3-benzo[c]thiophenediyl) or polyisothianaphthene (PITN), whose optical band gap is remarkably small (1.13 eV), demonstrated the significant effect of molecular structure on the intrinsic electronic and optical properties of heterocyclic polymers.

A central idea in the theoretical and experimental understanding of many properties of conjugated polymers[1–28] is the concept of "conjugation length" or "π-electronic delocalization length". Although there is no one universal measure of the π-electronic delocalization length,[21–29] L_{d}, of a conjugated system, the underlying chemical or physical notion of the extent of sp^2-carbon π-orbital overlap is often clear. Experimentally measurable parameters which have been used as measures of the electronic delocalization length of conjugated systems include the chain length or the number of repeating units in the chain, the number of conjugated double bonds, the wavelength

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