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X-ray Analysis of the Structure of HM-50 Copolyamide Fibers

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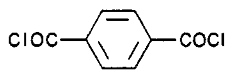
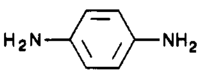
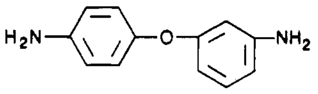
ABSTRACT: Initial X-ray work is described toward determination of the structure of high-strength copolyamide fibers prepared from terephthaloyl chloride (TPA), *p*-phenylenediamine (PDA), and 3,4′-diaminodiphenyl ether (DPE), with a TPA/PDA/DPE monomer mole ratio of 50/25/25. The X-ray fiber diagrams indicate a high degree of axial orientation of the molecules, and there is some three-dimensional order, although this is not as extensive as for the 50/50/0 copolymer, poly(*p*-phenyleneterephthalamide). A very interesting feature of the data for the 50/25/25 copolymer is the occurrence of a series of aperiodic meridional maxima. These are reminiscent of those reported previously (Blackwell, J.; Gutierre, G. A. *Polymer* **1982,** *23,* 671. Gutierrez, G. A.; Chivers, R. A.; Blackwell, J.; Stamatoff, J. B.; Yoon, H. *Polymer* **1983,** *24,* 937) in fiber diagrams of wholly aromatic copolyesters, where they arise due to structural correlations along chains of completely random sequence. We have applied a similar analysis to the copolyamide structure: the copolymer chains are modeled first as an array of points separated by the appropriate monomer lengths, and the predicted X-ray scattering is averaged over all possible monomer sequences in a nematic structure. The lengths of the DPE and TPA units depend on the torsion angles at the phenyl-ether and phenyl-amide linkages, and hence a variety of models need to be considered. We find that the best agreement between the positions of the observed maxima and those calculated for a completely random sequence is obtained when the chains have highly extended conformations. Conversion from point to atomic models for the monomers leads to good agreement for both positions and intensities of the meridional maxima. These results point to the effect of intermolecular interactions in enhancing the extended conformation in liquid crystalline polymers.

Introduction

A new high-strength copolyamide fiber prepared from a 50/25/25 mole ratio of the following monomers has recently been reported.[3,4]


terephthaloyl chloride (TPA)


p-phenylenediamine (PDA)


3,4′-diaminodiphenyl ether (DPE)

This fiber is designated HM-50 by Teijin Ltd. (Japan) and is processed by dry jet-wet spinning from *N*-methyl-2-pyrrolidone solution. HM-50 is reported to have mechanical properties comparable to those of Kevlar 49 (Du Pont) and to have excellent resistance to hydrolytic degradation.

We are using X-ray methods to investigate the structure of this copolyamide, which is analogous to the wholly aromatic copolyesters we have studied previously.[1,2,5-8] As will be described below, inspection of the X-ray fiber diagrams of HM-50 reveals the presence of a series of aperiodic meridional maxima, similar to those seen for the copolyesters. For the latter systems we have shown that this effect is predicted for a structure consisting of parallel copolymer chains of completely random monomer sequence. For example, in a copolymer prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA), the 1,4- and 2,6-aromatic linkages inevitably lead to an extended conformation in which the axial advance per monomer is approximately equal to the monomer length. Hence, in projection onto the fiber axis, the polymer chain is seen as a random sequence of units of two different but constant lengths, and the aperiodic meridional maxima arise from the monomer-monomer correlations inherent in such a structure.

In the case of the HM-50 copolymer, however, the situation is complicated by the possible conformational variability of the DPE unit, due to the presence of the ether linkage and the 1,3-phenylene moiety. Thus a range of monomer lengths is possible, and this could also lead to distinct nonlinearity of the chain. We have compared the X-ray data for HM-50 with those predicted for random copolymer chains with a variety of monomer conformations, and the results are presented below.

Experimental Section

HM-50 fibers (Teijin) were arranged in a parallel bundle, and X-ray fiber diagrams were recorded on Kodak No-Screen film by using Ni-filtered Cu Kα radiation and a Searle toroidal focusing camera. X-ray scattering in the direction corresponding to the meridian of the fiber diagram, i.e., in the plane containing the fiber axis, was also recorded by using a Phillips PN 3550/10 diffractometer. Fibers were arranged parallel in a sheet, approximately 20 mm wide and 0.5 mm thick, and the data were recorded as a $\theta/2\theta$ scan in the transmission mode. The *d* spacings were calibrated with calcium fluoride.

Model Building

A. Monomer Units. Atomic models for the three monomer units were constructed by using standard bond lengths:[9] C—C (phenyl ring), 1.38 Å; N—C (amide), 1.35 Å; C—C (amide), 1.49 Å; N—C (phenyl), 1.41 Å; C═O, 1.18 Å; C—O (ether), 1.36 Å. All of the bond angles in the phenyl and amide groups were set at 120°. The C—O—C bridge angle in DPE was also set at 120°, consistent with values of 117-123° reported for phenyl ethers in the solid state. A bridge angle of 118° is reported for the most relevant model compound, 4,4′-bis(phthalimido)diphenyl ether.[10]

For convenience the monomer units in the copolymer chain are defined from nitrogen to nitrogen, as shown in Figure 1. The PDA unit is conformationally invariant and is planar, with a N-N length of 5.64 Å. The structure of the TPA unit depends on the phenyl-amide torsion angles, ϕ_1 and ϕ_2. In the structures proposed for poly(*p*-phenyleneterephthalamide),[11] the phenyl-amide inclinations are $\sim$30°, which is supported by studies of model compounds and conformational analysis.[9] This inclination is achieved by torsion angles of 30° and 150° (0° and 180° correspond to coplanarity) and leads to four possible N-N lengths for the TPA unit: 6.75, 6.87, 7.15, and 7.26 Å.

The largest potential for conformational variability comes from the DPE unit (Figure 1c), where the conformation is defined by the bridge torsion angles ψ_1 and ψ_2. The N-N length depends only on the value of ψ_1, since

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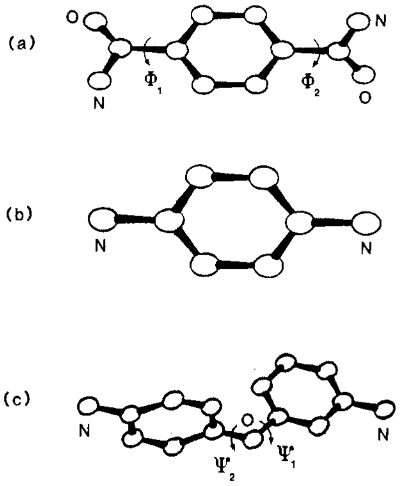

Figure 1. Structures of the HM-50 monomer residues: (a) terephthalamide (TPA); (b) phenylenediamine (PDA); (c) 3,4′-diaminodiphenyl ether (DPE). The residues are defined from nitrogen to nitrogen (see text).

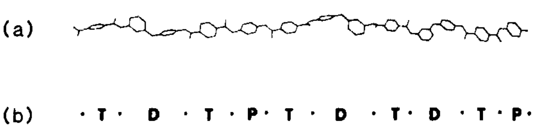

Figure 2. (a) Structure of a typical random sequence of the HM-50 copolymer. (b) Point model for the same chain.

variation of ψ_2 does not affect the position of the 4′ nitrogen, and this length varies from 10.02 to 7.39 Å, depending on the value of ψ_1. To construct an atomic model, we assumed that the planes of the phenyl groups are mutually perpendicular, as occurs (approximately) in model compounds such as 4,4′-bis(phthalimido)diphenyl ether,[10] diphenylene thioether,[12] and diphenylmethane.[13] Hence in constructing an atomic model of DPE, the N–N length was fixed by selecting ψ_1, after which ψ_2 was set so as to achieve perpendicular orientation of the two phenyl groups.

B. Polymer Chains. Figure 2 shows a typical random sequence of the HM-50 copolymer, constructed of TPA and DPE units with N–N lengths of 7.26 and 10.02 Å, respectively. Note that even with these restrictions the chain has considerable potential for nonlinearity, depending on the phenyl–amide torsion angles, and Figure 2 shows a relatively linear example. We anticipate, nevertheless, that the influence of neighboring chains will constrain the chain to be relatively straight (see discussion below). If this is the case, then the N–N vectors are approximately parallel to the overall chain axis, and hence the axial advance for each monomer type is approximately constant. In the idealized chain the axial advance for each monomer should be equal to its N–N length, but because of nonlinearity there will be a distribution of lengths and the averages will be somewhat lower. In the present work we have used constant values for the axial lengths: a later paper will consider the effect of a distribution of lengths.

For the initial calculations, the monomers were approximated as points positioned at the nitrogen atoms: this led to a model for the chain consisting of a linear array of points separated by the (constant) monomer lengths. We also worked with a model in which the copolymer is treated as a random sequence of DPE–TPA and PDA–TPA dimers, in which case each dimer was approximated as a point at the initial nitrogen. Conversion to an atomic model was achieved by adding the appropriate monomer or dimer to each point. Note that in an atomic model we need to consider the sense of the DPE unit, i.e., whether the 1,3-phenylene comes before or after the 1,4-phenylene. We have assumed that the chains contain equal proportions of "up" and "down" DPE units, and these are treated as though they are two different monomers.

Intensity Calculations

The meridional intensity $I(Z)$ was calculated for point and atomic models by using the procedure developed in our work on the copolyesters. (These are summarized below and described in more detail by Biswas and Blackwell.[14]) For a point model, $I(Z)$ is derived as the Fourier transform ($\mathcal{F}$) of the autocorrelation function $Q(z)$, which describes the probability of the separation of point monomers or dimers.

$$I(Z) = \mathcal{F}[Q(z)] \tag{1}$$

The most convenient way to evaluate $\mathcal{F}[Q(z)]$ is to treat the chain as a one-dimensional paracrystal with specific coordination statistics. In the case of a point model made up of an array of three different dimers, each of which can combine with the other two, the intensity is given by

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

where Re designates the real component and $H_1(Z)$ is given by

$$H_1(Z) = \sum_{\mathrm{A}}\sum_{\mathrm{B}} H_{\mathrm{AB}}(Z) \tag{3}$$

where

$$H_{\mathrm{AB}}(Z) = \sum_{\mathrm{A}}\sum_{\mathrm{B}} M_{\mathrm{AB}} \exp(2\pi i Z z_{\mathrm{B}}) \tag{4}$$

Here the M_{AB} terms are components in a matrix defining the probabilities of dimer nearest neighbors. If we further abbreviate the dimer pairs PDA–TPA, DPE(up)–TPA, and DPE(down)–TPA as J, K, and L, then the dimer probability matrix, M_{D}, is third order and is as follows for the 50/25/25 copolymer.

$$M_{\mathrm{D}} = \begin{bmatrix} M_{\mathrm{JJ}} & M_{\mathrm{KJ}} & M_{\mathrm{LJ}} \\ M_{\mathrm{JK}} & M_{\mathrm{KK}} & M_{\mathrm{LK}} \\ M_{\mathrm{JL}} & M_{\mathrm{KL}} & M_{\mathrm{LL}} \end{bmatrix} = \begin{bmatrix} 0.2500 & 0.1250 & 0.1250 \\ 0.1250 & 0.0625 & 0.0625 \\ 0.1250 & 0.0625 & 0.0625 \end{bmatrix} \tag{5}$$

The z_{B} terms in eq 4 are the dimer lengths, z_{J} and $z_{\mathrm{K}} = z_{\mathrm{L}}$. Alternatively we can work with the model consisting of point monomers rather than dimers. We have four monomers: TPA, PDA, DPE(up), and DPE(down), which are further abbreviated to T, P, D, and B. The M_{AB} terms in eq 4 are now the components of the monomer neighbor probability matrix, M_{M}, which is fourth order and has the following form for the 50/25/25 copolymer.

$$M_{\mathrm{M}} = \begin{bmatrix} 0 & M_{\mathrm{PT}} & M_{\mathrm{DT}} & M_{\mathrm{BT}} \\ M_{\mathrm{TP}} & 0 & 0 & 0 \\ M_{\mathrm{TD}} & 0 & 0 & 0 \\ M_{\mathrm{TB}} & 0 & 0 & 0 \end{bmatrix} = \begin{bmatrix} 0 & 0.250 & 0.125 & 0.125 \\ 0.250 & 0 & 0 & 0 \\ 0.125 & 0 & 0 & 0 \\ 0.125 & 0 & 0 & 0 \end{bmatrix} \tag{6}$$

Here the zeros arise because only certain combinations are allowed: the monomers cannot react with themselves and a diamine must be followed by TPA. The z_{B} terms in eq 4 are the monomer lengths, z_{T}, z_{P}, and $z_{\mathrm{D}} = z_{\mathrm{B}}$.

Designation of a sense to the DPE unit is necessary only when the point model is converted to the atomic model, where we essentially "hang" monomer units on the indi-

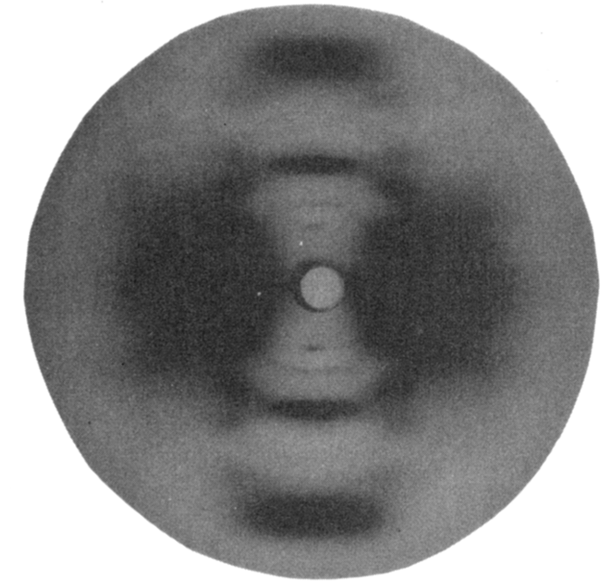

Figure 3. X-ray fiber diagram of HM-50. The fiber axis is vertical.

Table I
***d* Spacings (Å) of Meridional Reflections for HM-50 and Kevlar 49 [Poly(*p*-phenyleneterephthalamide)]**

HM-50	Kevlar 49	HM-50	Kevlar 49
	12.9	2.6	
6.00	6.45	2.6	
~4.4		2.12	2.15
3.26	3.22		

vidual points. Such conversion is achieved by multiplying each H_{AB} term by $F_{AB}(Z)$, the Fourier transform of the cross convolution of moiety A with moiety B (be they dimers or monomers). Equation 2 becomes

$$I(Z) = \sum_{A} p_A F_{AA}(z) + \sum_{A}\sum_{B} 2 \operatorname{Re} \frac{F_{AB}(Z) H_{AB}(Z)}{1 - H_1(Z)} \qquad (7)$$

in which

$$F_{AB}(Z) = \sum_{j}\sum_{k} f_{j,A} f_{k,B} \exp(-2\pi i Z(z_{k,B} - z_{j,A})) \qquad (8)$$

In eq 8, f and z are the atomic scattering factor and axial coordinate and the subscripts designate the jth atom of monomer A and the kth atom of monomer B, respectively.

Results and Discussion

Figure 3 shows the X-ray fiber diagram of HM-50 fibers. The Z-axis (meridional) $\theta/2\theta$ diffractometer scan is shown in Figure 4 (curve a). As is to be expected, the bulk of the scattering is in the equatorial plane centered on d = 4–5 Å. The scattering along the meridian direction is much weaker, but a series of maxima are detected, with d spacings as listed in Table I. The d spacings obtained by using the diffractometer are considered more accurate, but note that the two weakest maxima are detected only in the film data. There is a sharp maximum at 6.00 Å, followed by a doublet at 3.26 and 2.9 Å, and a broad strong maximum at d = 2.12 Å. In addition, there is a hint of meridional intensity in the film data just outside the ring at d = 4.5 Å. The latter ring, which is responsible for the weak peak in the diffractometer scan, derives from the strong equatorial reflection at this d spacing and points to the existence of a small fraction of the polymer with no axial orientation. We are reporting d ~4.4 Å for the meridional maximum outside the ring, although it is very weak, and it is difficult to be certain whether the intensity occurs on or just off the meridian. The film data also show a weak meridional at d = 2.6 Å.

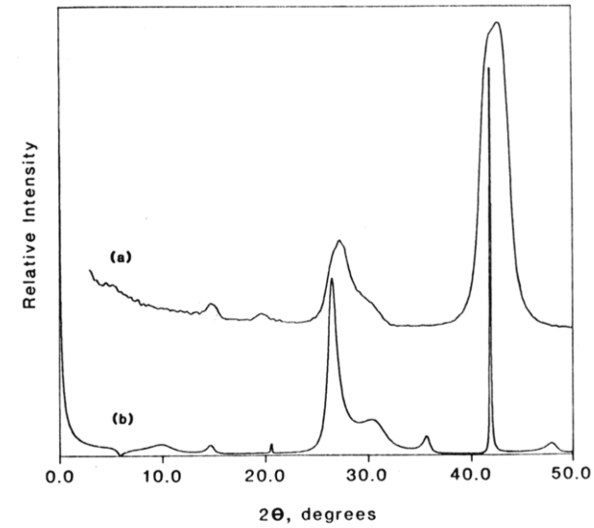

Figure 4. (a) X-ray diffractometer scan along meridional direction for HM-50 fibers. (b) Calculated meridional intensity for an atomic model.

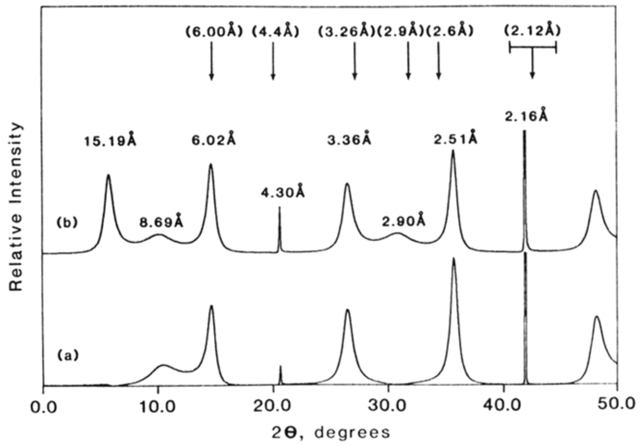

Figure 5. Calculated meridional intensities for point models of HM-50 (a) using point monomers and (b) using point dimers. The d spacings for the predicted peaks are the same for both models and are shown above the peaks in curve b, while the observed peaks are indicated by arrows, which have the d spacings shown in parentheses.

These meridional maxima are clearly aperiodic. For comparison Table I gives the meridional (00l) d spacings for poly(p-phenyleneterephthalamide),[15] which are the first, second, fourth, and sixth orders of the PDA–TPA repeat of c = 12.9 Å. Superficially, the X-ray patterns of HM-50 and poly(p-phenyleneterephthalamide) are very similar, except that HM-50 is much less crystalline. The most obvious characteristic difference between the two X-ray patterns is in the appearance of the sharp maximum at d = 6.00 Å for HM-50, which is readily distinguished from the d = 6.45 Å maximum for poly(p-phenyleneterephthalamide) and the splitting in the 3-Å region.

NMR analysis of this polymer indicates a random monomer sequence.[16] Our aim in this work has been to see if the aperiodic data can be explained in terms of a random copolymer, and, if so, what can be said with regard to the chain conformation. Our initial structural calculations were done for nematic arrays of chains of point monomers. These define the interresidue interference effects and allow for prediction of the positions of the meridional maxima. Extension of the calculations to an atomic model incorporates the intraresidue interferences and allows for comparison of both the positions and intensities of the maxima.

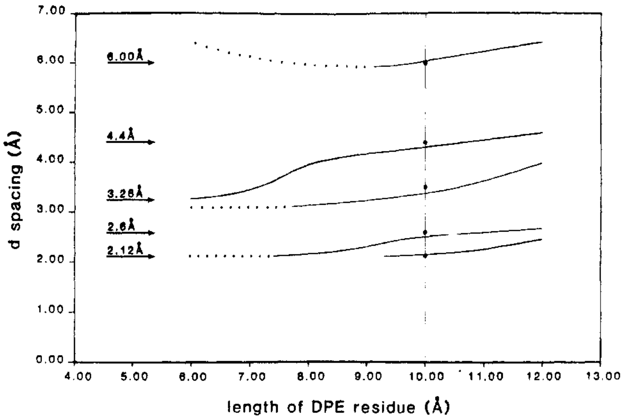

Figure 6. Plots of the variation in *d* spacing for five predicted meridional peaks with length of the DPE residue, while lengths of the TPA and DPE residues were held constant at 5.64 and 7.27 Å, respectively. The observed *d* spacings are indicated with arrows at the left-hand side. Best agreement is obtained at 10.0 Å, as indicated by the vertical line and the points for the observed positions.

Figure 5 shows the calculated intensity for chains of point monomers (curve a) and point dimers (curve b). In each case the constituent monomers had their most extended conformations corresponding to monomer lengths of 5.64, 7.26, and 10.02 Å for PDA, TPA, and DPE, respectively. Both point models lead to a set of aperiodic peaks: the *d* spacings are given above each peak and are the same for both models, but the predicted peaks have different intensities due to the absence of alternate points in the dimer model, which changes the interference effects. The observed *d* spacings are shown by the arrows at the top of the figure, and it can be seen that the agreement between observed and calculated *d* spacings is within about 0.1 Å, which is excellent considering the simplicity of the model.

Point model calculations were done for a range of monomer lengths: z_D = 12.0–6.0 Å, z_T = 8.0–6.5 Å, and z_P = 5.64 Å. Note that at the high end these ranges exceed the lengths possible for the DPE and TPA monomers and also that the lower values are unlikely due to the probable extended conformation of the chains. Figure 6 shows a plot of *d* for certain maxima (those to be matched with the observed data) for models with z_D = 12.0–6.0 Å, z_T = 7.26 Å, and z_P = 5.64 Å. Note that at $z_D < 9.0$ Å extra peaks begin to be generated. Some of the peaks of interest become shoulders on these extra peaks in the regions indicated by the dotted lines in Figure 6. It can be seen that the best agreement is obtained with z_D in the range 9.5–10.0 Å. For models with z_D = 10.02 Å, z_T = 7.5–6.0 Å, and z_P = 5.64 Å, the agreement is best at about z_T = 7.4–6.9 Å and deteriorates as z_T is reduced. In general, monomer lengths other than those corresponding to extended conformation lead to poor agreement between observed and calculated *d* spacings.

These results point to extended conformation for the DPE and TPA units and for the chain as a whole. The copolymer is processed from liquid crystalline solutions in *N*-methylpyrrolidone, in which the chains form nematic arrays. It appears that the intermolecular forces in the liquid crystal and/or in the final solid state lead to the chains adopting highly extended conformations, rather than the other options that are possible, given the nonlinearity of the ether linkage. This is consistent with theoretical calculations by Yoon et al.[17] and by Flory and Matheson,[18] which show that liquid crystallinity favors extended conformations in semiflexible polymers.

Finally we calculated the intensity for atomic models, at which stage the monomer and dimer point models converge and give the same results. Figure 4 (curve b) shows the calculated intensity for an atomic model consisting of fully extended monomers (z_T = 7.26 Å, z_P = 5.64 Å, and z_D = 10.02 Å). The calculated intensity has been corrected for the Lorentz effect for the geometry of a $\theta/2\theta$ scan. Introduction of the intramonomer interferences leads to prediction of the same set of peaks as seen for the point model, but the intensities can now be usefully compared with the observed data (curve a). We are only making visual qualitative comparisons at present, but the match is reasonable. The most obvious discrepancies are in the sharpness of the predicted peaks at d = 4.30 Å (21°) and 2.16 Å (42°) and the higher intensity predicted at d = 2.51 Å (35°). The calculated peak at d = 2.16 Å (42°) has been truncated and only ~6% of the peak height is shown. Hence the match with the observed (integrated) intensity is more reasonable than it appears in Figure 4. The sharpness of the calculated peaks at d = 4.30 and 2.16 Å arises from the definition of the model: these *d* spacings are the fourth and eighth orders of the length of the TPA–DPE dimer (17.28 Å) and also the third and sixth orders of the length of the TPA–PDA dimer (12.9 Å). This coincidence leads to sharp (Bragg) peaks at these *d* spacings. We have seen this effect previously for the liquid crystalline polyesters, and it was first commented on by Hendricks and Teller in studies of aperiodic layer structures.[19] Our model assumes a chain in which the N–N vectors have a constant axial projection for each monomer type. Inspection of Figure 2 shows this is only approximately the case, and even in the extended chain there will be some nonlinearity, leading to a distribution of axial lengths for each monomer. Incorporation of this distribution into the calculations will lead to a broadening (and a reduction in the peak intensity) for the maxima at 4.30 and 2.16 Å. A measure of the nonlinearity can be obtained from the observed width of the maximum at d = 2.12 Å, which yields a correlation length for the straight chain conformation. The high predicted intensity at d = 2.51 Å may also result from the assumed linearity of the chain. As we saw in calculations for the polyesters,[20] the relative intensities can be refined by modification of the atomic coordinates to take into account tilting of the monomers and averaging over different conformations. Further work is in progress in this area and will be described shortly.

Conclusions

The X-ray pattern of HM-50 copolyaramid fibers points to high orientation along the fiber axis as well as some lateral order. The existence of a series of aperiodic diffraction maxima along the meridian is consistent with a structure consisting of oriented chains of completely random monomer sequence. Best agreement is obtained for a model in which the chains have highly extended conformations. The greatest potential for nonlinearity is in the diphenyl ether diamine unit, but the right combination of torsion angles leads to an extended conformation.

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

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A Statistical Test of the Proposition That Intrahelix Salt Bridges Constitute a Significant Stabilizing Feature of the Tropomyosin Coiled-Coil Structure

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ABSTRACT: A statistical analysis is made of the correlation of the charge state of residue i in the amino acid sequence of α-tropomyosin with that of residues $i \pm 3$ and $i \pm 4$. Since the chains in this protein are essentially completely α-helical (3.6 residues/turn), the side chains of such pairs of residues are brought into juxtaposition by the secondary structure. It has therefore been proposed (Sundaralingam, M., et al. *Proc. Natl. Acad. Sci. U.S.A.* **1985,** *82,* 7944–7947) that such salt linkages are a major principle in stabilizing the structure in highly α-helical, two-chain, coiled-coil proteins. The statistical analysis, however, shows that the distribution of charged residues in α-tropomyosin with respect to these interactions is essentially random. The statistical property χ^2 is used to measure deviations from expectations based on the hypothesis of randomness. It is found that the value of χ^2 obtained for both the $i\cdot(i+4)$ and $i\cdot(i+3)$ interactions in tropomyosin is no larger than it would be for about 50% of the chains in a huge collection in which each chain has the same amino acid composition and length as tropomyosin, but in which the sequences are random. Thus, there is no reason to believe that the $i \pm 3$ and $i \pm 4$ positions near a given charged group at position i in tropomyosin are biased in favor of opposite charges. This analysis therefore does not support the idea that such intrahelical salt bridges are a major factor in stabilizing the coiled-coil structure. In contrast, it is also shown that a similar statistical test indicates a highly significant deviation from randomness for the interhelical salt bridges that have long been supposed to be a significant feature of the structure. An examination of other existing evidence also does not encourage assigning a significant role to intrahelical salt bridges in coiled-coil proteins.

The proteins tropomyosin and paramyosin and the large tail of the protein myosin have a common molecular structure, called the two-chain coiled coil.[1] In each case, the molecule comprises two poly(amino acid) chains that are essentially completely α-helical. The two constituent helices are arranged in parallel and in register with a slight supertwist. Because of its simplicity, the structure represents an opportunity for development of ideas concerning protein structure in general. In spite of its simplicity, however, the structure is a sharp challenge to our present understanding.

To date, very few general principles have become apparent that serve to define a given poly(amino acid) chain as one in which the two-stranded, coiled coil could be safely predicted to be the preferred conformation. Only four such principles, none quantitatively predictive, seem to have gained general acceptance. First, there must be an absence of α-helix-disruptive residues. That no coiled-coil poly(amino acid) can contain proline residues seems axiomatic. Not quite so understandably, but probably for similar reasons, tryptophan is absent as well and residues of low intrinsic helix-forming potential are few.[2] Second, it was noticed in even the earliest determinations of amino acid composition that such proteins have a greater fraction of charged residues than do most globular proteins.[3] This seemed understandable, since a molecule of extended form has a greater surface/volume ratio and therefore requires a greater fraction of hydrophilic residues in order to destabilize more compact conformations.

Third, hydrophobic residues must appear in a definite pattern in the sequence.[4–7] The sequence, as first reported for tropomyosin, is demonstrably based on a pseudorepeating heptet of residues. Position within each heptet is designated by letters a–g.[7] Positions a and d are ordinarily hydrophobic. This results in an extremely amphipathic helix, providing a hydrophobic streak to which another such helix can adhere. The a and d side chains of each helix readily articulate by "knobs-into-holes" packing.[8] It is generally agreed that this interhelix, hydrophobic interaction is a major factor in holding the chains together and probably also in maintaining the helical state in each.

Fourth, the sequence shows that residues in heptet positions e and g tend to be oppositely charged; in tropomyosin, those in e tend to be negatively charged, and those in g positively charged.[5–7] In the double-helical molecule this leads to salt links, predominantly between residue e in the nth heptet of one helix and residue g' of

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