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Comparison of the Axial Correlation Lengths and Paracrystalline Distortion for Technora and Kevlar Aromatic Polyamide Fibers

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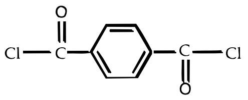
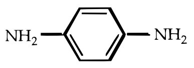
ABSTRACT: X-ray fiber diagrams of the aromatic copolyamide Technora, prepared from terephthaloyl chloride and equimolar proportions of *p*-phenylenediamine and 3,4′-diaminodiphenyl ether, contain a series of nonperiodic layer lines that point to a structure consisting of parallel chains of random comonomer sequence. The meridional peak positions are predicted accurately for fully extended, infinite chains, and the observed and calculated peak intensities are also in reasonably good agreement. However, there is a less adequate match between the observed and calculated peak profiles, which are predicted to be very much sharper than those observed. The latter agreement is improved by using a model consisting of finite chain segments with a slightly nonlinear (sinuous) conformation. The best agreement for unannealed Technora is obtained with an ordered segment length of 300 ± 15 Å and sinuosity of $g = 1.52 \pm 0.05\%$, where g is analogous to the index of paracrystalline distortion in a homopolymer structure. Very similar results are obtained for fibers that have been thermally annealed. These data are strikingly similar to those for Kevlar fibers (poly(*p*-phenylene terephthalamide)), for which the crystallite size along the fiber axis direction is 350 ± 10 Å with a paracrystalline distortion of 2.32 ± 0.08% for Kevlar 29, increasing to 400 ± 12 Å with a paracrystalline distortion of 1.71 ± 0.06% for Kevlar 149. Consequently, although Technora is a random copolymer and the presence of the random diaminodiphenyl ether leads to a more distorted lateral packing of the chains than occurs in Kevlar, the fibers produced by the dry-jet wet-spinning process have extended conformations that are very similar in linearity to those for Kevlar, which probably account for the analogous high tensile strengths and moduli.

Introduction

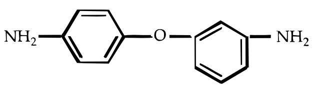
X-ray methods have been used to compare the structures of Technora and Kevlar fibers. Technora is based on the aromatic copolyamide prepared from terephthaloyl chloride (TPA), *p*-phenylenediamine (PPD), and 3,4′-diaminodiphenyl ether (DPE) in a 50/25/25 mole ratio.[1−6] Kevlar is the alternating copolymer of TPA and PPD, i.e. poly(*p*-phenylene terephthalamide). The chemical structures of these monomers are shown below:



terephthaloyl chloride
(**TPA**)



p-phenylene diamine
(**PPD**)



3,4′-diaminodiphenylether
(**DPE**)

Technora is processed from *N*-methyl-2-pyrrolidone solution as a high-strength, high-modulus fiber by Teijin Ltd. (Osaka, Japan) and is reported to have mechanical properties comparable to those of Kevlar (DuPont), but with improved hydrolytic stability.[5,6] NMR analyses of low molecular weight specimens of this copolymer are consistent with a completely random monomer sequence.[7]

The X-ray fiber diagrams of Technora and Kevlar 29, 49, and 149 fibers are shown in Figure 1. All show a high degree of axial orientation of the molecules, but it is clear that the three-dimensional order is not as extensive in Technora as it is in the three Kevlar preparations. A most interesting feature of the data for the Technora copolyamide is the occurrence of nonperiodic layer lines, analogous to those observed for wholly aromatic copolyesters and copolyimides.[8−13] The most frequently studied of the latter polymers are the copolyesters prepared from *p*-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA). The X-ray fiber diagrams of copoly(HBA/HNA) contain nonperiodic layer lines that shift progressively along the fiber axis direction with changes in comonomer ratio. These effects are predicted by considering scattering of a single extended chain averaged over all possible sequences of a completely random copolymer. The *p*-phenylene and 2,6-naphthylene units are linked by planar ester groups, with the result that the conformation is highly extended, and the advance along the chain goes in steps that correspond approximately to the lengths of the HBA and HNA moieties. The nonperiodic meridional maxima arise due to the structural correlations that occur along such chains. Excellent agreement is obtained between the observed and calculated meridional *d*-spacings for the different comonomer ratios using a completely random comonomer sequence. Modification of the combination statistics to consider nonrandom sequences rapidly destroys this agreement, and all but marginal deviation from randomness can be ruled out. NMR analysis on partially deuterated copoly(HBA/HNA) has confirmed the random comonomer sequence.[14]

Prediction of the conformation of the Technora copolyamide is more difficult than for copoly(HBA/HNA), because the 1,3-phenylene and ether linkages of the DPE unit can potentially lead to "kinks" in the chain. Nevertheless, an overall extended conformation is possible, because the effect of one kink can be reversed by

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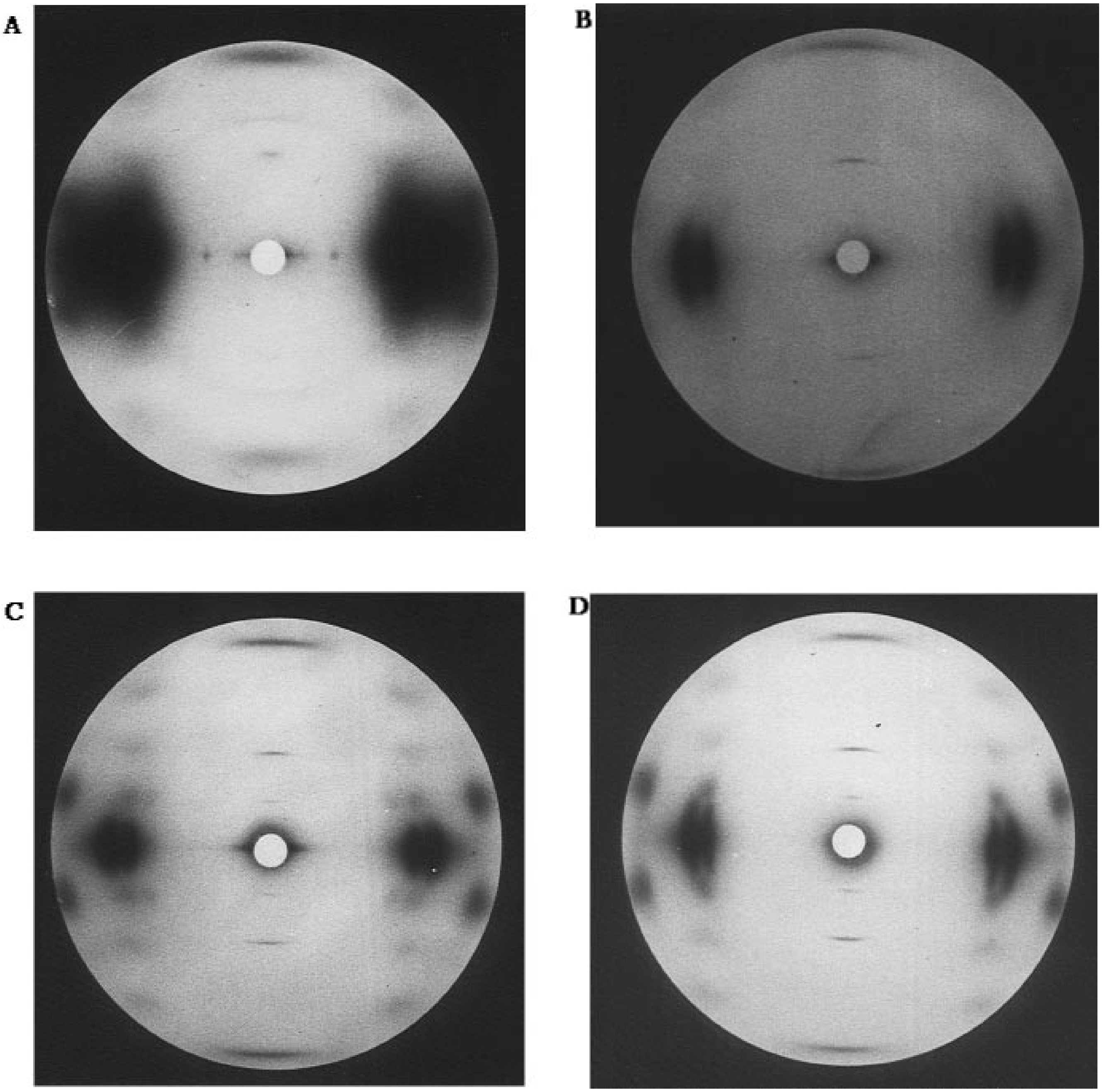

Figure 1. X-ray fiber diagrams of (A) Technora, (B) Kevlar 29, (C) Kevlar 49, and (D) Kevlar 149. The fiber axis is vertical in each case.

rotation about the next rotatable bond, i.e., a “zig” can be followed immediately by a “zag”. In a previous paper from this laboratory, Blackwell *et al.*[6] considered a range of possible models for the DPE unit and compared the positions of predicted meridional maxima with those observed. Nonperiodic layer lines were predicted for all models, but the best agreement between the observed and calculated *d*-spacings was obtained using the most highly extended DPE conformation, in which the planes of the phenyl groups were mutually perpendicular, as occurs in diphenylene ether model compounds.[15]

Figure 2 compares the observed X-ray intensity along the chain axis direction with that predicted for the model of the isolated chain described in ref 5. There is good agreement between the positions of the observed and calculated peaks and an approximate match of the intensities. However, the peak profiles do not match: some of the calculated peaks are much narrower than those observed. This arises because the calculated data are for an idealized linear infinite chain, with constant axial advance for each monomer type. In a later report, Cageao *et al.*[6] considered a more realistic model for the chains that allowed for nonlinearity even in the most extended conformation, such that the advance along the fiber axis for each monomer is not constant but falls into a relative narrow distribution about an average value. The distribution functions for each monomer advance were estimated from a survey of models of fully extended chains of different sequences. Incorporation of these data into the prediction of the scattering patterns led to some broadening of the maxima. The strong maximum at $d \approx 2.15$ Å ($2\theta \approx 43°$), which was essentially a δ function for the idealized straight infinite chain, now had a half-width of 0.06°. However, this was still very much narrower than the observed peak half-width of 0.9° for this peak.

The peak widths in the nonperiodic diffraction patterns for this type of copolymer have been investigated

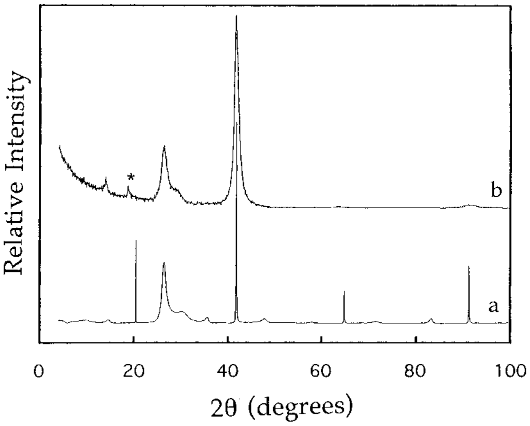

Figure 2. (a) Calculated meridional intensity plotted against 2θ for infinite idealized linear chains of the Technora copolyimide with random comonomer sequence. (b) X-ray diffractometer scan (intensity versus 2θ) of Technora fibers along the fiber axis direction. The peak marked with an asterisk is an off-meridional maximum arced over the meridian due to disorientation.

in detail by Wu *et al.*[16] for aromatic copolyimides, where it was shown that line widths can be reproduced in models in which the scattering units are nonlinear chains of finite length. These parameters can be separated because successive orders of the invarient peaks have different widths. Wu *et al.* refined the chain lengths and nonlinearity in order to obtain the best match between observed and calculated half-widths for three meridional maxima. In the present paper, we have applied the same techniques to determine the lengths and nonlinearity of the chain segments in the ordered regions of Technora copolyamide fibers, by matching the half-widths of the meridional peak at $d \approx 2.15$ and its second order at $d \approx 1.08$ Å. The results for Technora are compared with axial crystallite sizes and paracrystallinity data determined for Kevlar fibers. The effect on the structures of thermal annealing the fibers for different lengths of time will also be discussed.

Experimental Section

Materials. Fibers of the Technora (HM-50) copolyamide, which contain a 50/25/25 mole ratio of TPA/PPD/DPE units, were supplied by Teijin Ltd. (Osaka, Japan). Fibers of Kevlar 29, 49, and 149, which are preparations of poly(*p*-phenylene terephthalamide) with progressively higher tensile stengths and moduli, were supplied by DuPont (Wilmington, DE).

Thermal Annealing. Thermal annealing of Kevlar 29 and Technora fibers at constant length was performed in a vacuum oven at 300 °C for 2, 4, 8, 16, 48, and 72 h. Kevlar 49 and 149 fibers were annealed under the same conditions for 48 h.

X-ray Diffraction. Specimens for X-ray diffraction were prepared as bundles of about 40−60 parallel fibers. X-ray fiber diagrams were recorded on Kodak Direct Exposure X-ray film (DEF 5) using a Searle torroidal camera with Cu Kα radiation. Linear $\theta/2\theta$ X-ray intensity scans of the fibers along the fiber axis (meridional) direction were recorded using Cu Kα radiation and a Philips PN 3550/10 diffractometer equipped with a diffracted beam monochromator. The instrument was used in the transmission mode with a constant slit width of 0.033°. Axial profiles of the meridional maxima were obtained by measuring the intensity at 0.05° increments of 2θ with constant collection time, such that ~2000 counts were recorded at the maximum intensity. The apparent crystallite sizes were calculated from the integral half-widths of the meridional maxima, using the Scherrer equation. Silicon powder with a 325 mesh size was used as standard sample to evaluate the instrumental broadening, for which we assumed Gaussian profiles. The silicon peak at $2\theta = 28.46°$ had an integral half-width of 0.058°.

The longitudinal crystallite sizes and paracrystalline distortion parameters g for Kevlar fibers were derived from the integral half-widths of several orders of 00l reflections, using the Hosemann equation:[17]

$$\delta^2 = 1/L^2_{hkl} + (\pi g n)^4/d^2_{hkl} \qquad (1)$$

where δ is the integral half-width, L_{hkl} is the mean dimension of the crystallite perpendicular to the hkl plane, d_{hkl} is the mean interplanar spacing, n is the order of the reflection, and g is the parameter of paracrystallinity: $g = \Delta d_{hkl}/d_{hkl}$, where Δd_{hkl} is the standard deviation for the distribution of interplanar spacings. The lengths and nonlinearity of the ordered chain segments for Technora were derived by trial and error matching of the observed and calculated intensity data using the analysis for the scattering by nonperiodic copolymer chains described in ref 16. These procedures are summarized in the next section.

The degree of orientation, f_c, was determined using the Hermans equation from the azimuthal intensity distribution for the meridional reflection on the second layer line. These data were recorded on film for single Technora or Kevlar fibers tilted at the appropriate Bragg angle and scanned using an Optronics P-1000 digital microdensitometer. The aperture and stepping raster were set at 100 μm; the detector range was 0−2.0 optical density.

Molecular Models. Atomic models of the monomer residues were constructed using bond lengths, bond angles, and torsion angles derived from standard databases, as described in ref 3. Models for the copolymer chains were constructed using the SYBYL software package (Tripos Inc.). For the predictions of the scattering of the random copolyamides along the fiber axis direction, we used models in which the lengths of the monomer units between their terminal nitrogen atoms were 7.26 Å for TPA, 5.64 Å for PPD, and 10.02 Å for DPE.

Theoretical Scattering by Nonperiodic Chains. Prediction of the scattering by random copolymers with extended chain conformation[8−12] uses concepts that are similar to those in the treatment of paracrystallinity in homopolymers. $I(Z)$, the intensity of scattering along the chain axis direction, is calculated from $H_1(Z)$, the Fourier transform of the first nearest-neighbor terms in the autocorrelation function $Q(z)$ of an extended chain. For the Technora copolyamide, TPA and PPD 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, the copolyamide can be thought of as a sequence of four monomers: TPA, PPD, 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 can react with themselves, and a TPA must react with one or the other of the two diamines. $H_1(Z)$ can be conveniently written as the product of the Fourier transform of three components: the monomer ratio, the combinatorial probabilities, and the phase terms arising from atomic projections of a given monomer along the chain axis. These components are presented in matrix form:

$$H_1(Z) = \mathbf{P{\cdot}M{\cdot}X} \qquad (2)$$

where

$$\mathbf{P} = \begin{bmatrix} p_T & 0 & 0 & 0 \\ 0 & p_P & 0 & 0 \\ 0 & 0 & p_D & 0 \\ 0 & 0 & 0 & p_B \end{bmatrix} \qquad \mathbf{M} = \begin{bmatrix} 0 & M_{TP} & M_{TD} & M_{TB} \\ M_{PT} & 0 & 0 & 0 \\ M_{DT} & 0 & 0 & 0 \\ M_{BT} & 0 & 0 & 0 \end{bmatrix}$$

$$X(Z) = \begin{bmatrix} X_T(Z) & 0 & 0 & 0 \\ 0 & X_P(Z) & 0 & 0 \\ 0 & 0 & X_D(Z) & 0 \\ 0 & 0 & 0 & X_B(Z) \end{bmatrix} \qquad (3)$$

p_A is the molar proportion of monomer A; for Technora, $p_T = 0.5$, $p_P = 0.25$, and $p_D = p_B = 0.125$. (We assume equal proportions of up- and down-DPE units.) The M_{AB} terms in the **M** matrix are the probabilities of the addition of monomer B to a chain ending in monomer A. $X_A(Z)$ is the phase term for monomer A:

$$X_A = \exp(2\pi i Z z_A) \tag{4}$$

where z_A is the length of monomer A projected along the chain axis.

To consider an atomic model, we multiply each component of $H_1(Z)$ by $F_{AB}(Z)$, the Fourier transform of the cross convolution of monomer A with monomer B, which is given by

$$F_{AB}(Z) = \sum_{j=1}^{N_A} \sum_{k=1}^{N_B} f_{A,j} f_{B,k} \exp(2\pi i Z(z_{B,k} - z_{A,j})) \tag{5}$$

Here, f is the atomic scattering factor and z is the atomic coordinate along the chain axis direction. The subscripts A,j and B,k designate the jth of N_A atoms of monomer A and the kth of N_B atoms of monomer B, respectively. If the chain is sinuous, such that the monomer axial advances are only approximately constant, it is necessary to replace X_A by a distribution function. If this distribution is assumed to be Gaussian with standard deviation σ, eq 6 becomes

$$X_A = \exp(-2\sigma^2\pi^2 Z^2) \exp(2\pi i Z z_A) \tag{6}$$

σ is more conveniently expressed as g, the percentage of the average monomer axial advance. $I(Z)$ is given by

$$I(Z) = \mathrm{Re}\left(\frac{1 + H_1(Z)}{1 - H_1(Z)}\right) \tag{7}$$

where Re designates the real components. For a finite chain of N monomers, this becomes

$$I(Z) = \mathrm{Re}\left(\left(\frac{1 + H_1(Z)}{1 - H_1(Z)}\right) - \left(\frac{H_1(Z)(1 - H_1^N(Z))}{N(1 - H_1(Z))^2}\right)\right) \tag{8}$$

For an infinite chain model with constant axial advances for the different monomers, the peaks in $I(Z)$ are nonperiodic and in general have finite width. The only exceptions are some of the peaks predicted for chains in which z_A, z_B, ... are simple multiples of a common length factor, a; for example, $z_A = 3a$ and $z_B = 4a$ in a two-component copolymer. In such a case, we predict periodic δ-functions at $Z = 1/a$, $2/a$, $3/a$, ..., with broader, aperiodic peaks between them. The periodic peaks are invariant; i.e. their positions are independent of monomer ratio. For a finite and/or sinuous chain, these sharp maxima are broadened, and hence their widths in the observed data can be used to evaluate the length and sinuosity of the scattering units, in the same way as we derive the crystallite size and paracrystallinity index for a homopolymer. From eqs 2−8, the calculated peak profiles depend on chemical composition through p_A, p_B ,..., on the chain length through N, and on the distribution of axial projection lengths through σ.

The widths of the predicted peaks in $I(Z)$ were determined by the same method as used for the observed data. The calculated intensity was plotted against 2θ, and the integral half-widths were determined by fitting Gaussian functions to the peaks at $d \approx 2.15$ and 1.08 Å. For the peak at $d \approx 2.15$ Å, the calculated intensity falls to essentially zero on either side of the peak. However, this is not the case for the peak at $d \approx$ 1.08 Å and a linear background drawn between the minima on either side of the peak was subtracted before fitting a Gaussian function.

Results and Discussion

Technora. The calculated meridional intensity for an idealized infinite straight chain of random sequence is presented in Figure 2 (curve a), where it is compared with the observed diffractometer scan along the chain axis direction (curve b). It can be seen that there is good agreement between the positions of the observed and calculated peaks (see ref 6) and that there is also an approximate match between their intensities. However, the peak profiles do not match: although the predicted peaks at $d \approx 2.15$ and 1.08 Å have finite widths, they are much narrower than those observed. These peaks arise because of the approximate coincidence of the sixth order of the TPA + DPE advance (12.90 Å) and eighth order of the PPD + DPE advance (17.28 Å). Thus there is an invariant maximum at $d \approx 2.15$ Å, and that at d $\approx$ 1.08 Å is the second order.

In our previous work on analogous wholly aromatic copolyimides,[16] we refined the structure to match the peak widths for three orders of the invariant diffraction maxima. The width of the first maximum could be matched by modification of either the chain length or the sinuosity, but to obtain a match also for the higher orders, it was necessary to refine both of these parameters simultaneously. We used the same procedure to refine the structure of the Technora copolyamide.

Examples of plots of intensity versus 2θ for models of idealized straight copolyamide chains of different segment lengths are shown in Figure 3A, together with the observed diffractometer scan. It can be seen that the peak positions are the same for all models, but the peaks at $d \approx 2.15$ and 1.08 Å ($2\theta \approx 43$ and 91°) broaden as the chain length decreases. These peaks are shown on an expanded 2θ scale in Figure 3B. We see that the observed peak width for the first-order peak is matched approximately for a chain length of 166 Å, but for this model, the predicted second-order peak is much sharper than that observed. Figure 3C shows data analogous to those in Figure 3B but for models of infinite chains with different degrees of nonlinearity. Here we see that width of the first-order peak is matched at g = 1.84% ($\sigma = 0.14$ Å), but the predicted second-order peak is now much broader than that observed.

The segment length and linearity were then refined simultaneously by trial and error in order to obtain the best match between the observed and calculated half-widths. Figure 4A compares the observed intensity data with the calculated intensities for the model giving the best agreement, for which we used a chain length of 300 ± 15 Å and a sinuosity of $g = 1.52 \pm 0.05\%$ ($\sigma = 0.116$ $\pm$ 0.005 Å). The observed and calculated data for the two peaks are presented on an expanded scale in Figure 4B, which shows the good fit obtained. Estimates of the limits of experimental error in the fit of the predicted curve allow for the noise in the diffractometer data. The chain length of 300 ± 15 Å corresponds to a degree of polymerization of 40 ± 2, considerably less than the length of the fully extended chain. We envisage a morphology in which the extended copolymer chain passes though successive ordered regions along the fiber axis direction, which are separated by discontinuities or disordered regions. Within the ordered regions the chains are almost, but not completely, straight, with the extent of nonlinearity being defined by the distribution of $g = 1.52 \pm 0.05\%$ about the ideal monomer advances.

Diffractometer data along the fiber axis direction for Technora fibers that had been annealed for 24 and 48 h were very similar to those for the untreated sample and could be fitted by a model with a chain segment length of 310 ± 15 Å, i.e. DP = 41 ± 2, and a sinuosity of $\sigma = 0.112 \pm 0.005$ Å ($g = 1.48 \pm 0.05\%$). The latter parameters are within experimental error of those for the untreated specimen, indicating that heat treatment

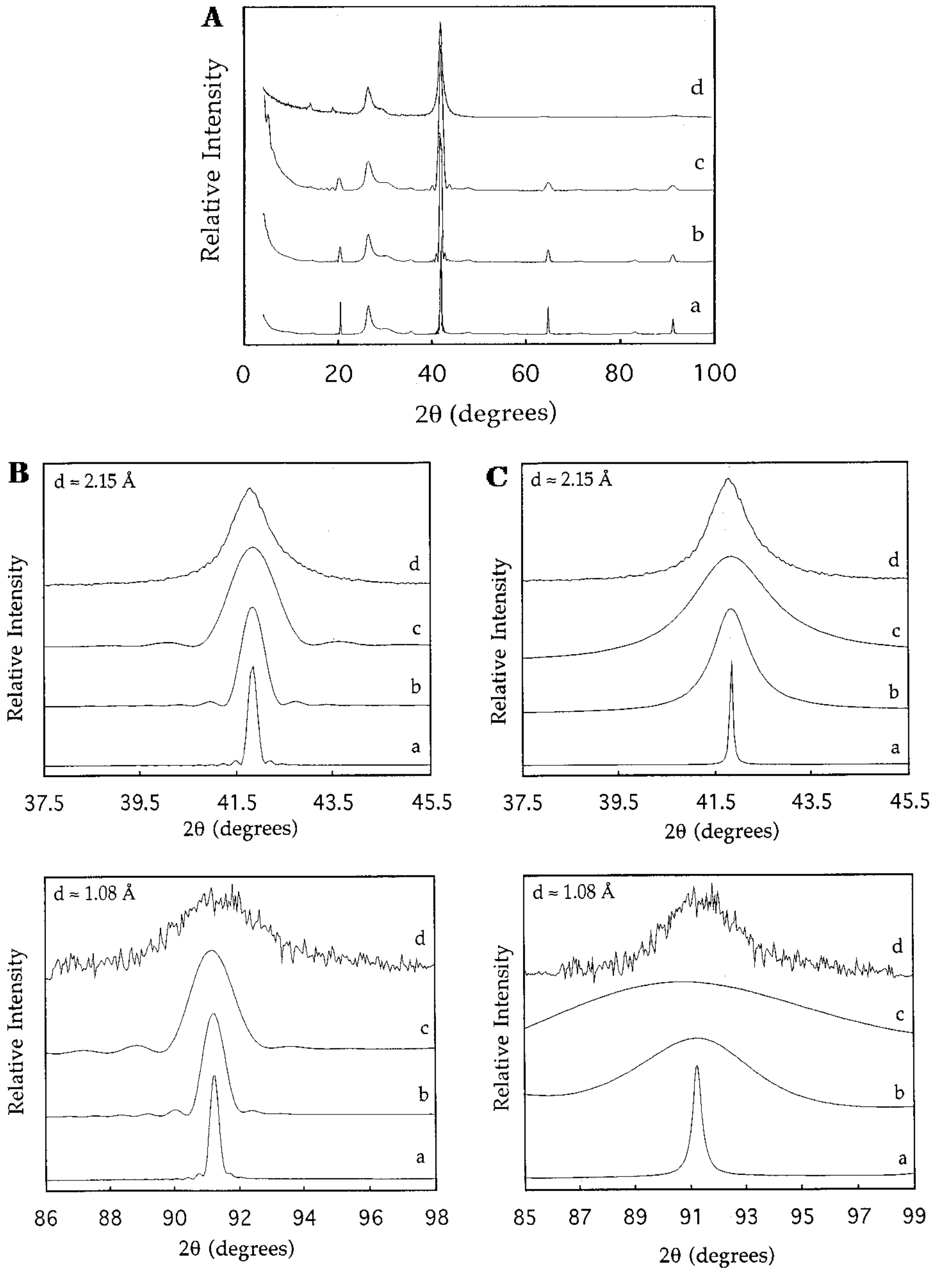

Figure 3. (A) Calculated meridional intensity for the Technora copolyamide plotted against 2θ for finite linear chain models with different degrees of polymerization (N): (a) $N = 50$, (b) $N = 25$, (c) $N = 15$, (d) observed data. (B) Peaks at $d \cong 2.15$ and 1.08 Å from (A) plotted on an expanded 2θ scale: (a) $N = 50$, (b) $N = 25$, (c) $N = 15$, (d) observed data. (C) Equivalent data to (B) for infinite chain models with different degrees of nonlinearity (σ): (a) $\sigma = 0.08$ Å, (b) $\sigma = 0.14$ Å, (c) $\sigma = 0.20$ Å, (d) observed data.

leads to very little improvement in the order along the chain axis direction. Figure 5 shows diffractometer scans along the equatorial direction recorded in the transmission mode for untreated and thermally annealed Technora fibers. The data are dominated by a single broad peak at $2\theta \approx 22°$, which becomes sharper after annealing for 24 h, suggesting an improvement of lateral order. This order is not extensive, but after subtraction of an amorphous background and insertion of the peak widths into the Scherrer equation, we obtained *apparent* lateral crystallite sizes of 22 ± 1 Å for untreated fibers to 30 ± 1 Å for those annealed for 24 h. These parameters have no absolute meaning, because the peak a $2\theta \approx 22°$ is probably a composite of several maxima, but they are useful for comparison purposes. We can conclude that although thermal treatment has little effect on the perfection of the chain conformation, it does result in some improvement of the lateral order. The degree of orientation was $f_c = 0.978 \pm 0.003$ before and 0.985 ± 0.002 after annealing; i.e. the improvement is on the fringe of experimental error.

Kevlar. The Scherrer crystallite size along the chain axis derived from the integral breadth of the first peak (002) is 300 ± 10 Å for Kevlar 29 and increases to 330 ± 10 Å for Kevlar 49 and 370 ± 12 Å for Kevlar 149. Figure 6 shows plots of δ^2 against n^4 for the 002, 004, and 006 reflections for all three preparations, which yield corrected axial sizes and paracrystallinity indices of $L_{00l} = 350 \pm 10$ Å, $g = 2.32 \pm 0.08\%$ for Kevlar 29, $L_{00l} = 360 \pm 10$ Å, $g = 1.92 \pm 0.07\%$ for Kevlar 49, and $L_{00l} = 400 \pm 12$ Å, $g = 1.71 \pm 0.06\%$ for Kevlar 149. These data are compared with those for Technora in Table 1. The corrected axial crystallite size for Kevlar 49 is lower than the value of ~900 Å reported by Barton.[18] However, this difference probably arises from the differences in the corrections for experimental broadening. Our observed 002 half-width of 0.26° was actually lower than the value of 0.31° reported by

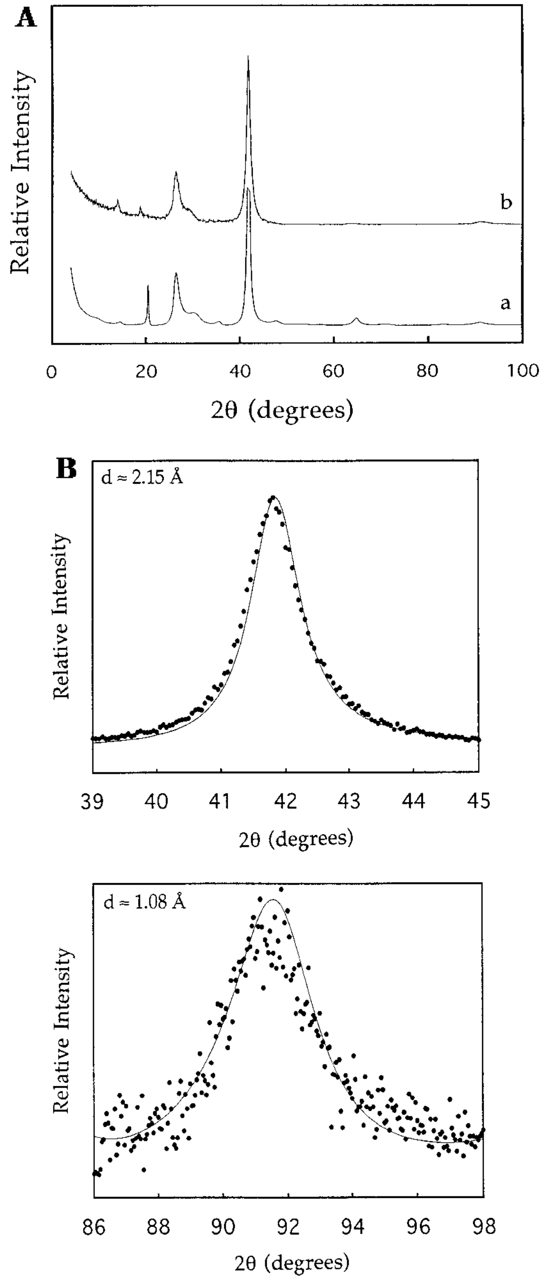

Figure 4. (A) Bottom trace: Calculated meridional intensity plotted against 2θ for a finite, sinuous chain with $N = 40$ (length = 301.8 Å), $\sigma = 0.116$ Å, and $g = 1.52\%$. The peak at $d \cong 2.15$ Å is truncated to facilitate scale expansion. Top trace: Observed data. (B) Observed (●) and calculated (solid line) peaks at $d \cong 2.15$ and 1.08 Å from (A) plotted on an expanded 2θ scale.

Barton, but the measured width of the silicon peak at $2\theta = 28.46°$ used for instrumental broadening was considerably lower: 0.058° compared to 0.175° in Barton's data, due to our use of smaller diffractometer slits (0.033 versus 0.1°).

Figure 7 presents the corrected axial crystallite size and paracrystallinity index for Kevlar 29 plotted against time of annealing at 300 °C at constant length. It is seen that L_{00l} increases with annealing time until it levels out at 410 ± 10 Å after 24 h. g decreases over the same time range and levels out at 2.05 ± 0.06%. We examined only Kevlar 49 and 149 that had been annealed for 48 h, when a similar increases occurred in these parameters: for Kevlar 49 we obtained $L_{00l} = 438 \pm 8$ Å, $g = 1.75 \pm 0.06\%$; for Kevlar 149 we obtained $L_{00l} = 430 \pm 10$ Å, $g = 1.69 \pm 0.06\%$.

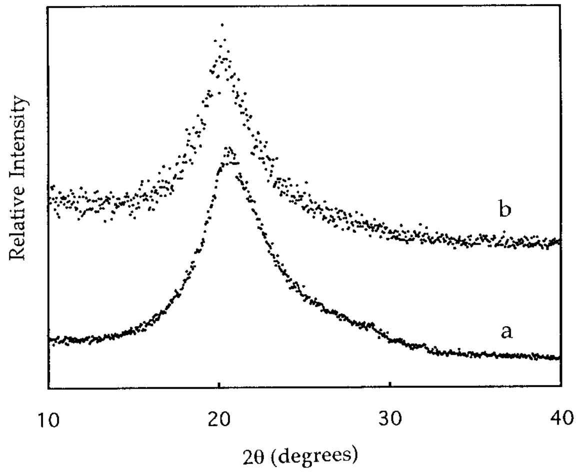

Figure 5. X-ray diffractometer scans for Technora fibers along the equatorial direction: (a) annealed; (b) unannealed.

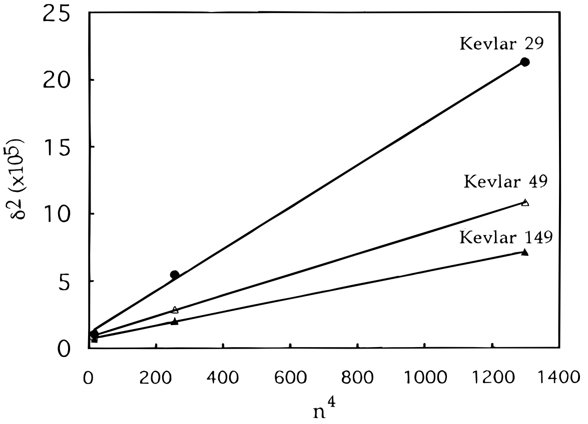

Figure 6. Plots of observed integral half-width δ^2 against order n^4 for the 002, 004, and 006 reflections for Kevlar 29, 49, and 149 fibers.

Table 1. Structural Parameters Determined for Unannealed and Annealed Kevlar and Technora Fibers

	longitudinal crystallite size (L, Å)	paracrystalline distortion (g,%)	degree of orientation (f_c)
Kevlar 29			
unannealed	350 ± 10	2.32 ± 0.08	0.961 ± 0.005
annealed	410 ± 10	2.05 ± 0.06	0.967 ± 0.004
Kevlar 49			
unannealed	360 ± 10	1.92 ± 0.07	0.982 ± 0.003
annealed	438 ± 8	1.75 ± 0.06	0.985 ± 0.002
Kevlar 149			
unannealed	400 ± 12	1.71 ± 0.06	0.991 ± 0.002
annealed	430 ± 10	1.69 ± 0.06	0.993 ± 0.002
Technora			
unannealed	300 ± 15	1.52 ± 0.05	0.978 ± 0.003
annealed	310 ± 15	1.48 ± 0.05	0.985 ± 0.003

Lateral crystallite sizes were determined from the integral widths of the 110 peaks in the diffractometer scans recorded along the equatorial direction in the transmission mode. The values obtained were 72 ± 6, 87 ± 7, and 108 ± 8 Å for unannealed Kevlar 29, 49, and 149, respectively, increasing to 88 ± 8, 104 ± 10, and 130 ± 10 Å, respectively, after annealing for 48 h at 300 °C at constant length. Thus there is an appreciable improvement in the lateral registration of the chains as a result of annealing. That this ordering is more extensive than in Technora is not surprising given that the later is a random copolymer.

Table 1 also shows the degree of orientation obtained from the azimuthal arcing of the second layer line of

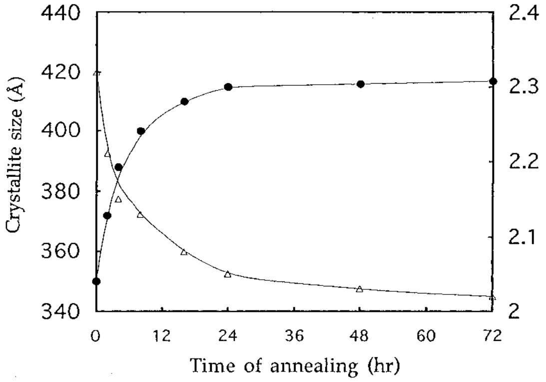

Figure 7. Axial correlation lengths and parameters of paracrystalline distortion for Kevlar 29 fibers derived from integral half-widths of three orders of the meridional reflection plotted as functions of annealing time.

meridional reflections. The values determined are consistently higher after annealing, but the differences are still within experimental error. The difference in the degrees of orientation for Kevlar 149 ($f_c \cong 0.991 \pm 0.002$) and Kevlar 49 ($f_c \cong 0.982 \pm 0.003$) probably accounts for the dramatic change in tensile modulus from 120 GPa for Kevlar 49 to 180 GPa for Kevlar 149.[19,20] Using the Northolt model[21] to predict the effect of misorientation on modulus, deviation of the average chain orientations of 2° ($f_c \cong 0.99$) and 3° ($f_c \cong 0.98$) from the fiber axis result in 20 and 50% decreases in the tensile modulus from the theoretical value. The better linear chain perfection and crystalline orientation in Kevlar 149 are consistent with scanning electron microscopy by Krause *et al.*,[20] who observed a periodic, pleated sheet structure along the axial direction on the surface of Kevlar 49 fibers, but not on the surface of Kevlar 149 fibers.

Conclusions

The nonperiodic layer lines observed for Technora are definitive for a random microstructure and a highly extended chain conformation. Even so, the diffraction data indicate the existence of significant three-dimensional order. Not surprisingly, the main difference between Technora and Kevlar is in the lateral packing, which is much more disordered in Technora due to the random comonomer sequences. However, the striking feature of our results is that Technora and Kevlar have similar degrees of perfection in the linearity of the chain conformation. Following correction for the effect of distortion, we obtain an ordered segment length of $L = 300 \pm 15$ Å and a paracrystalline distortion of $g = 1.52 \pm 0.05\%$ for unannealed Technora compared to $L = 350 \pm 10$ Å and $g = 2.32 \pm 0.08\%$ for unannealed Kevlar 29. Although Technora is a random copolymer, the analysis of the crystallite size and distortion along the fiber direction can be made in the same way as that for a homopolymer based on the line widths of the invariant meridional maxima. The latter arise because the axial advances for the TPA–DPE and PPD–DPE units are almost in the ratio 3:4. Note that if the model were to be adjusted so that these lengths are exactly in the ratio 3:4 (they are presently within approximately 0.2%), then the differences in the L and g values determined would be minuscule compared to the experimental error for the fit with the experimental data. Conversely, if models were chosen with axial advances that deviate further from the ratio of 3:4, this would lead to a broadening of the invariant peaks predicted for the straight infinite chain. A match with the observed data could still be obtained for reasonable stereochemical models, but only if we utilized larger values of L and smaller values g. Consequently, the present values for L and g are at the lower limit for L and the higher limit for g and are for the most likely models of the monomers based on standard stereochemistry.

Thus the values of L and g derived for Technora are directly comparable to those for Kevlar, such that the Technora chain contains ordered segments with length 300 ± 15 Å, approaching the value of 350 ± 10 Å for unannealed Kevlar 29, whereas the value of $g = 1.52 \pm 0.05\%$ indicates a more linear structure than is seen even for annealed Kevlar 149, for which $g = 1.69 \pm 0.06\%$. Kevlar represents one of the most crystalline of all fibrous polymer preparations, but it appears that this is not the critical factor determining the chain linearity. Rather, we can conclude that the dry-jet wet-spinning process produces a highly extended chain conformation for Technora that is at least as linear as that in Kevlar, correlating with the similar tensile properties.

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