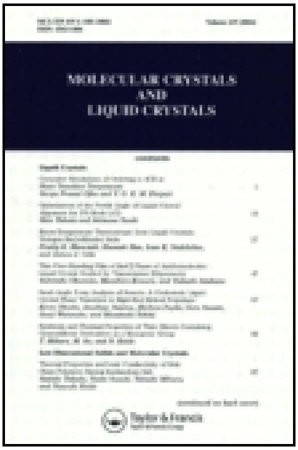

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics

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X-Ray Analysis of Liquid Crystalline Copolyesters and Copolyamides

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X-RAY ANALYSIS OF LIQUID CRYSTALLINE COPOLYESTERS AND COPOLYAMIDES

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Abstract The results of X-ray analyses are presented for two main chain liquid crystalline polymer systems: the copolyesters prepared from hydroxybenzoic acid (HBA), terephthalic acid (TPA) and biphenol (BP) (which is the basis of of XYDAR resins produced by Dartco) and the copolyamide prepared from TPA, p-phenylene diamine and 3,4'-diphenylene ether diamine (HM-50 fibers produced by Teijin). X-ray fiber diagrams of both copolymers contain a series of aperiodic intensity maxima along the meridian (fiber axis). These are predicted accurately by a nematic array of copolymer chains that have completely random monomer sequences and highly extended conformations. We have investigated these conformations based on the line profile of the meridional maximums at d = 2.1Å (2θ = 43°), which is seen for both copolymer systems. This width is a measure of the correlation length for the stiff chain conformation in the solid state. The continuous intensity distribution is predicted by treatment of the copolymer chain as a linear paracrystal with multimodal coordination statistics. An idealized linear chain with constant axial advance for each monomer type leads to a very sharp peak at 2.1Å; the width at half height predicted for an infinite chain of 50/25/25 copoly(HBA/TPA/BP) is 0.006° compared to the observed width of 1.4°. Significant nonlinearity is inherent in any real chain, and this is incorporated in the calculations in the form of histograms of the axial monomer lengths. The observed line widths are matched by relaxing the conditions for fully extended conformations by progressively increasing the allowed range of torsion angles and the diameter of the cylinder occupied by a single chain. Results for these copolymers are compared with those for other copolyesters in order to correlate chain extension with chemical structure.

Introduction

X-ray fiber diagrams of the thermotropic copolyester prepared from p-hydroxybenzoic acid (HBA) and 2-hydroxy-6-naphthoic acid (HNA) show a series of aperiodic meridional maxima, some of which shift in scattering angle (d-spacing) with the monomer ratio. Previous work in this laboratory[1,2] has shown that this behavior is predicted for a structure consisting of parallel chains with completely random comonomer sequence. The aperiodic meridional maxima arise due to correlations along the random sequences of monomer of different lengths. This effect has also been studied by Mitchell and Windle[3] and by Bonart and Mulzer.[4] A characteristic feature of the scattering by these copolymers is a sequence invariant meridional peak at d ≅ 2.1Å, and we have shown that the breadth of this peak can be used as a measure of the correlation length for the extended chain conformation in the solid state. In the present paper we show that this can also be done for two other wholly aromatic copolymers: the copolyester formed from HBA, teraphthalic acid (TPA) and biphenol (BP), which is the basis for the XYDAR family of resins produced by Dartco Mfg. (Augusta, GA), and the copolyamide formed from TPA, p-phenylene diamine (PDA) and 3,4'-diphenylene ether diamine (DPE), which is produced as HM-50 fibers by Teijin Co.(Osaka, Japan). Measurements of the observed line width at d=2.1Å are compared with those for stereochemically acceptable models. It will be shown that the results indicate that although the copolyesters have extended conformations, these are significantly less than fully extended.

In the case of copoly(HBA/HNA), the 1,4- and 2,6-aromatic linkages and the rigidity of the ester groups mean that the chain conformation will necessarily be extended as can be seen by figure 1. The intensity data on the meridian depends on the projection of the structure onto the fiber axis, and it can be seen that the advance per monomer along the fiber axis is approximately constant for each monomer type, and approximately equal to the residue lengths, which are 6.35Å and 8.37Å for HBA and HNA respectively. Homopolymers of HBA and HNA would both give rise to maxima at d ≅ 2.1Å, which corresponds to the third and fourth orders of the monomer repeats. As a consequence, this maximum is also predicted for the random copolymer at any monomer ratio.

If we calculate the theoretical meridional scattering for an array of infinite chains of random sequence, assuming that the advance per monomer is constant for each monomer type, then the predicted peak at d ≅ 2.1Å is extremely sharp, in contrast to the observed data, where this peak had a half width of 0.9-1.1°, depending on monomer ratio.[5] However, if we use a model consisting of chains of finite length, then the calculated peak is broadened, as is to be expected for a limited lattice. For 58/42 molar ratio copoly(HBA/HNA), the observed line width is reproduced using a chain length of ~11 monomers. This contrasts with a reported degree of polymerization of

~ 150($M_w \cong 25000$). A chain of 11 monomers would have a length of ~ 77Å. (Application of the Scherrer equation to the observed line width yields a "crystallite size" of ~ 79Å.) This length can be thought of as a solid state correlation length for the extended chain conformation. The calculations assume a perfectly straight chain where the advance per monomer is exactly equal to the monomer length. As can be seen in fig. 1, this is only approximately true: the correlation length corresponds to the distance along the chain beyond which the approximation of a completely straight chain breaks down.

The actual chain can be modeled more realistically[6] by allowing for the non-linearity by incorporating functions that describe the distributions of monomer lengths, i.e. the lengths of the projections on the fiber axis. These distributions can be derived in the form of histograms by surveying the atomic coordinates of models of random chains set up using standard bond lengths and angles. This was first done for copoly(HBA/HNA) where we observed that this broadened the 2.1Å peak without affecting the aperiodic peaks at higher d-spacings. However, until the present this was only a qualitative analysis. In the present paper we describe quantitative comparisons of observed and calculated peak widths for copoly(HBA/TPA/BP) and copoly(TPA/PDA/DPE).

EXPERIMENTAL

Specimens of copoly(HBA/TPA/BP), mole ratio 50/25/25, were obtained from Dr. N.D. Field at Dartco Manufacturing, Augusta, GA, U.S.A., in the form of melt spun fiber and molded plaques. Specimens of solution spun (HM-50) fiber of copoly(TPA/PDA/DPE) mole ratio 50/25/25, were obtained from Teijin Co., Osaka, Japan.

X-ray fiber diagrams of the oriented polymer specimens (parallel arrays of fibers on the center of the core regions of the molded plaque of copoly(HBA/TPA/BP) were obtained using Ni-filtered CuKα radiation and a Searle torroidal focusing camera. Data were recorded with the chain axis at 90° to the beam and when tilted at three different angles in order to record the meridional maxima in the regions of 6, 3 and 2Å. Peak profiles were obtained by scanning the data for tilted species using an Optronics rotating drum densitometer. Meridional intensity data were also obtained using a Phillips PN 3550/10 diffractometer in the transmission mode.

RESULTS AND DISCUSSION

Fig. 2, curve a shows the meridional intensity data for 50/25/25 copoly(HBA/TPA/BP) recorded on film for tilted specimens. The diffractometer data for the same specimen are shown as curve b. Equivalent data for 50/25/25 copoly(TPA/PDA/DPE) are shown in Fig. 3. The film and diffractometer data are similar: the peaks in the diffractometer data are a little broader due to instrumental effects. The d-spacings of the observed intensity maxima are shown above the peaks. Figures 4 and 5 show the calculated intensities for infinite straight chain models for the polyester and polyamide. The d-spacings of the predicted maxima as shown above the peaks and can be seen to be in good agreement with the observed data in figures 2 and 3. These data have been discussed more fully elsewhere.[7,8] The predicted intensities are for models constructed from standard bond lengths and angles. The phenyl-ester and phenyl-amide inclinations were set at 30°. For the polyester, the HBA, TPA and BP residues had lengths of 6.35, 7.15 and 9.86Å, respectively, measured across the terminal ester oxygens; for the polyamide, the TPA, PDA and DPE residues had lengths of 7.26, 5.64, and 10.02Å, respectively, measured across the amide nitrogens. Significant conformational variation is possible for the DPE unit, depending on the torsion angles at the amide linkage. The length of 10.02Å corresponds to the most extended conformation.

In this paper we are concerned with the widths of the peaks at $d \cong 2.1$Å. The calculated peaks are not symmetrical, but they are approximately so. The asymmetry of the observed peaks derives from a layer line streak, such that off-meridional intensity is arced over the meridian due to fiber disorientation, which leads to a broadening of the peak at higher angles. Hence we have determined the width at half height to be twice the half width at half height measured at the low angle side of the peak. Following correction for instrumental broadening, this give half widths of 1.4° and 1.5° for the polyester and polyamide, respectively. These figures compare to the calculated half widths of 0.006° and 0.010° from the data in figures 4 and 5, respectively.

When one constructs actual models of the chains, there must be some non-linearity due to the fact that the linkage bonds are not co-linear. The adoption of a liquid crystalline structure during processing will tend to lead to an extended structure, but some non-linearity is inherent even in the case of fully extended conformations.

Atomic coordinates were derived for chains of monomers using sequences derived using a random number generator. Phenyl-ester and phenyl amide torsion angles were set at random at ± 30° or ± 150°, with the requirement that there were equal numbers of | 30° | and | 150° | options. Chains in which any atom was more than 12Å from the chain axis were rejected (and replaced by chains meeting this requirement). The axial advances per monomer are plotted as histograms for the two copolymers in figures 6 and 7.

When these distributions are incorporated into the calculation of the meridional intensity (as described in ref. 9), the results obtained are shown as curve b in figures 4 and 5. It can be seen that the main effect is to increase the width of the peak at d≅2.1Å. The half widths are now 0.09° and 0.11° for the polyester and polyamide, respectively. These widths are an order of magnitude larger than those obtained using idealized straight chains, but they are still a further order of magnitude below those observed. The only way to broaden the peak still further is to broaden the length distributions, i.e. to use more sinuous or non-linear conformations. There are numerous ways of making the chains more non-linear via changes in the torsion and especially in the bond angles of the ester or amide groups. Curve c in figures 4 and 5 shows the calculated data obtained when the widths of the three histograms in figures 6 and 7 have been arbitrarily doubled, leaving the shapes of the distributions and their mid points unchanged. This broadens the 2.1Å peaks to 0.44 and 0.52°, which are roughly comparable to the observed data. The actual chain conformation is now being refined as part of our analyses of the three dimensional structure.

The main conclusion here is that we can broaden the calculated 2.1Å peak by taking a more realistic model of the copolymer chain which allows for the non-linearity that is inherent even in full extended conformations. However, it is clear that the chains must be significantly contracted from the fully extended conformation in order to match the observed x-ray intensity data. Liquid crystallinity during processing will inevitably lead to extended conformations, but it is likely that there will be some structural adjustment in the solid state so as to optimize the chain packing. An important requirement in the case of the polyamides will be optimize the entertain hydrogen bonding. In the analogous homopolymer, poly(p-phenylene teraphthalamide) the chains can form linear C=O...H-N intermolecular hydrogen bonds between every monomer. This cannot be the case in random copoly(TPA/PDA/DPE), where there must be some off-setting of, for example, a C=O on one chain and an N-H on a neighboring chain. It seems reasonable therefore that there could be some contraction of the chains so as to turn the amide groups and allow for the formation of more linear hydrogen bonds. It is possible that such non-linearity may also occur in the polyester so as to optimize the dipole-dipole interactions. For both copolymers, chain sinuosity may also occur so as to allow for better stacking of the aromatic units.

Acknowledgments

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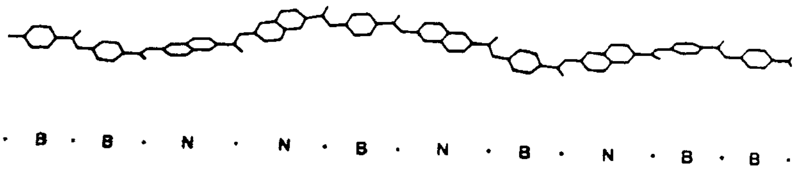

Fig. 1 Projection of a model of a typical random sequence of copoly(HBA/HNA).

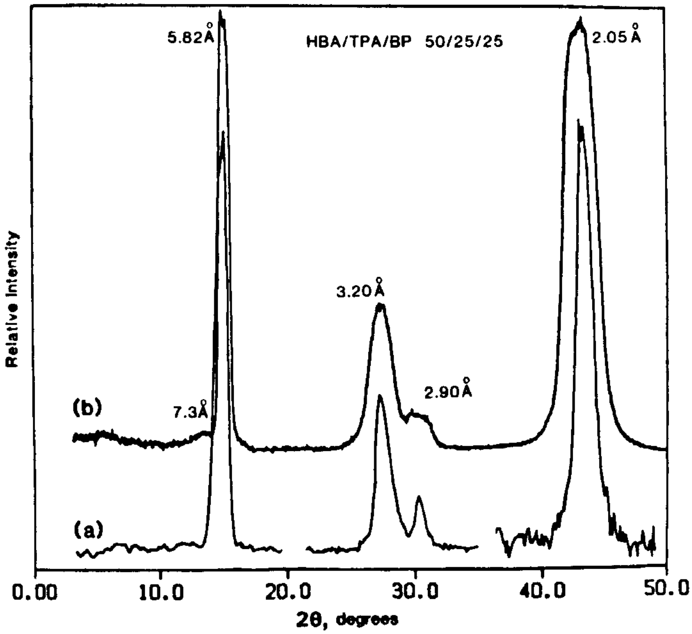

Fig. 2

(a) Intensity profiles of meridional maxima at the 6Å, 3Å and 2Å regions for the molded copoly(HBA/TPA/BP) plaque obtained by densitometer scans of the x-ray film data with the specimen tilted at the approximate Bragg angles.

(b) Observed data from a θ/2θ diffractometer scan of a molded plaque along the meridional direction.

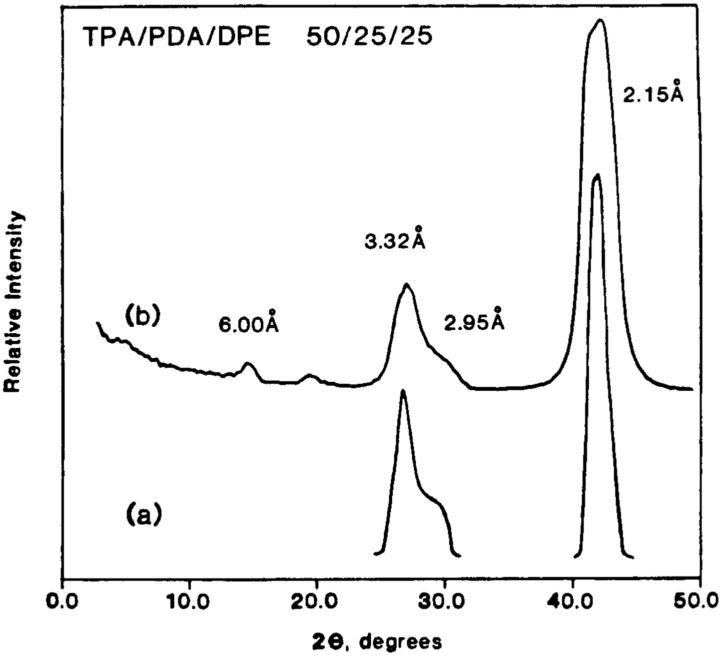

Fig. 3

(a) Intensity profiles of meridional maxima in the 3Å and 2Å regions for the copoly(TPA/PDA/DPE) fibers from densitometer scans of the x-ray film data with the specimen tilted at the approximate Bragg angles.

(b) Observed data from a θ/2θ diffractometer scan of the fibers along the meridional direction.

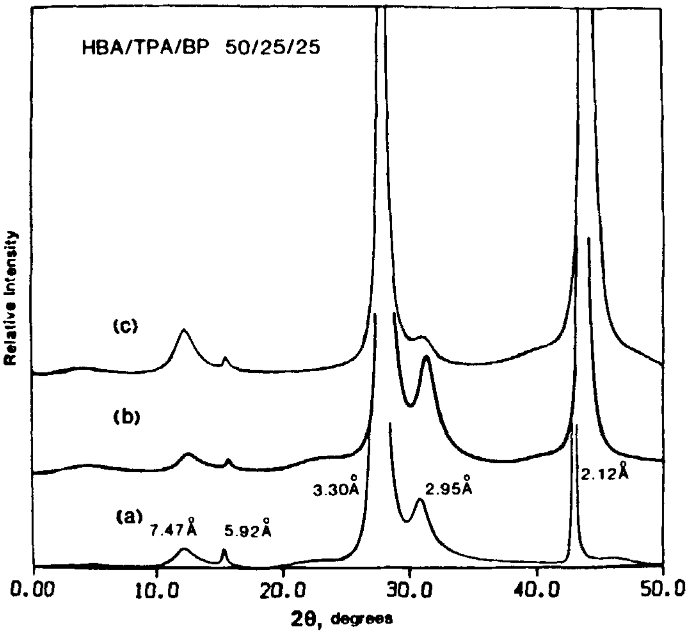

Fig. 4

(a) Calculated data of copoly(HBA/TDA/BP) with constant residue lengths;

(b) Calculated data using the distribution of residue lengths shown in figure 6;

(c) Calculated data obtained by arbitrarily doubling the distribution of figure 6.

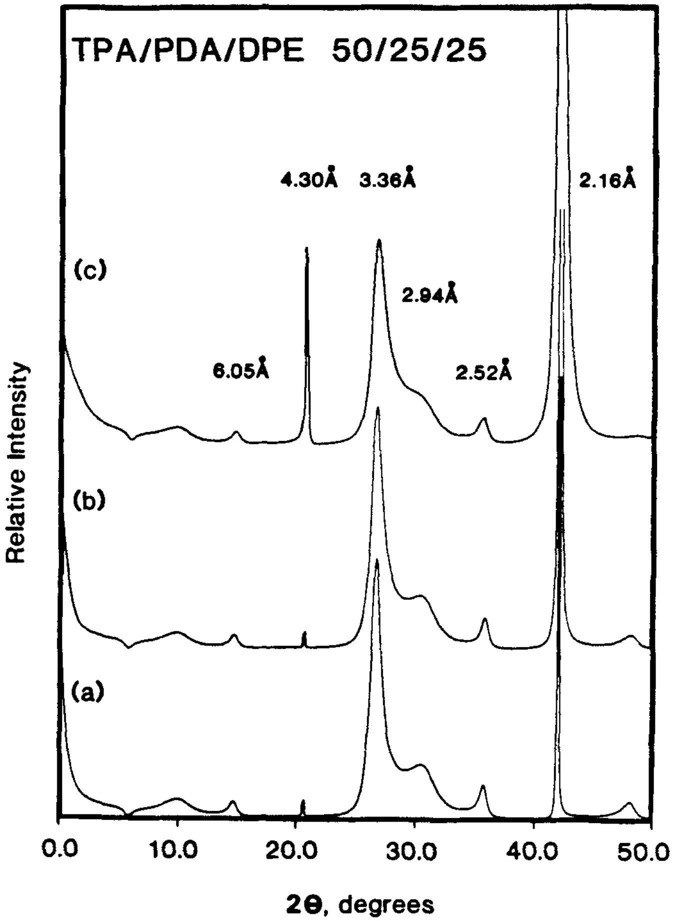

Fig. 5

(a) Calculated data of copoly(TPA/PDA/DPE) with constant residue lengths;

(b) Calculated data using the distribution of residue lengths shown in figure 7;

(c) Calculated data obtained by arbitrarily doubling the distribution of figure 7.

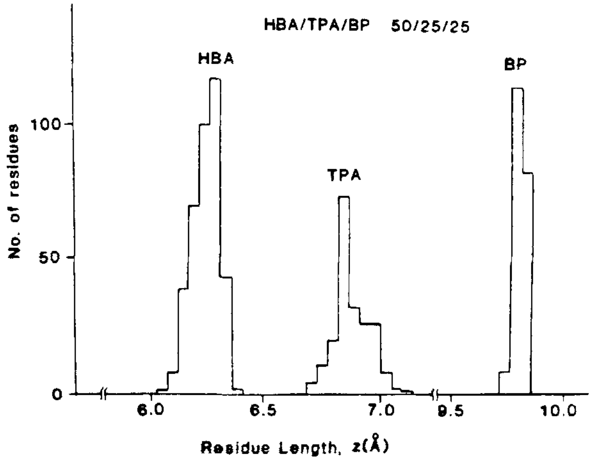

Fig. 6 Histograms of axially projected lengths of the comonomers in chains of copoly(HBA/TPA/BP). This distribution was generated by considering 50 chains of 16 comonomers each.

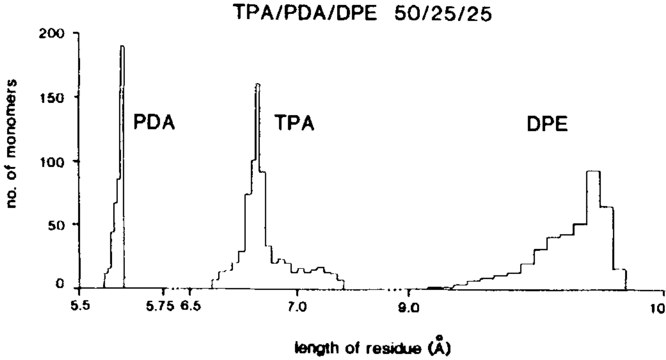

Fig. 7 Histograms of axially projected lengths of the comonomers in chains of copoly(TPA/PDA/DPE). The distribution was generated by considering 100 chains of 15 monomers each.