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X-ray Diffraction by Liquid-Crystalline Polymers

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X-ray Diffraction by Liquid-Crystalline Polymers

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Following a brief introduction to how acicular molecules form liquid-crystalline (LC) arrays in polymers, relevant elements of x-ray diffraction theory are discussed. It is shown that meaningful structural information can be obtained only when molecular arrays aligned by external forces are examined, a condition that is frequently easier to achieve in polymer than in monomer arrays. The published results of x-ray studies are reviewed critically and the interpretations of recorded intensity distributions are discussed in terms of model calculations and cylindrical distribution functions. Examples cited include side-group and main-chain LC homopolymers and main-chain copolymers.

Keywords: liquid-crystalline polymers, x-ray diffraction

INTRODUCTION

Although most liquids are optically isotropic, it has been known for nearly one century that aggregates of anisometric molecules can form stable liquid-like phases that exhibit uniaxial or biaxial anisotropies. In fact, such molecular aggregates can undergo several phase changes between the isotropic liquid and the crystalline solid phase as a function of temperature, in which case they are said to be thermotropic, or as a function of their concentration in a solvent, in which case they are said to be lyotropic. Friedel, who was the first to employ x-ray diffraction to categorize such aggregates, proposed the term mesomorphism[1] to describe this state of aggregation. He was preempted

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by a co-discoverer of the anisotropic liquids,[2] however, who called them liquid crystals and this term has gained widespread acceptance. This is unfortunate only because it emphasizes the noun 'crystal' whereas the characteristic of mesomorphic aggregates is that they are liquids having anisotropic properties. (Only a very small group of mesomorphic phases consist of molecular arrays approaching the three-dimensionally periodic order characteristic of crystals.)

The present discussion will be limited to thermotropic mesophases which can be subdivided into two broad classes[3,4] called nematic, if the aggregate has only one degree of order (molecular alignment parallel to a single director), or smectic, if there is a second (rarely a third) degree of order. Nematic mesophases can be further subdivided to include cholesteric ordering in which the molecules align by spiraling about a single direction while smectic mesophases form several distinct arrays[4] composed of uniaxially or biaxially aligned molecules frequently referred to as two-dimensional liquids. The diffraction of x rays by such arrays has been reviewed by several authors.[5–8]

It is not surprising that the polymerization of mesomorphic monomers should lead to polymers that exhibit similar structural arrays as a function of temperature.[9] The early attempts to synthesize such liquid-crystalline (LC) polymers were made by simulating the comb-like (paraffinic) polymers[10,11] and sometimes produced LC ordering in solid polymers, i.e., they did not exhibit an anisotropic liquid-like phase before melting into an isotropic liquid.[12] In the past ten years, however, the structures and properties of such side-group LC polymers have been explored more systematically to discern the roles played by the polymer backbone, the anisometric molecule attached to it, and a flexible spacer group frequently interposed between them.[10,11]

In an extension of Flory's seminal analysis[13] of the ordering of rigid molecules in solution, Di Marzio concluded[14] that the ordered alignments induced would be maintained even if the liquid was totally replaced by a flexible polymer. The first successful attempts to synthesize an array in which the anisometric monomers constituted the thermotropic main-chain polymer were not announced, however, until 1975.[15,16] Since then considerably more effort has gone into developing a variety of main-chain LC polymers.[17]

In monomer liquid crystals, the possible arrays can be described in terms of orientational, positional and, more rarely, conformational correlations between molecules. The way that such ordering affects their thermodynamic properties has been thoroughly discussed by

Wunderlich[18] who also enumerates the possible phases that can coexist in LC polymers. As is well known, solid polymers can be glassy (disordered) or crystalline (partially or, more rarely, fully ordered). When such polymers undergo a mesomorphic phase change upon heating, the LC arrays produced cause them to become anisotropic liquids which, upon further heating, undergo a transition to isotropic (disordered) liquids or decompose. Upon cooling from the mesomorphic state, the LC array can be frozen-in thereby forming an anisotropic glass or, alternatively, a polycrystalline array exhibiting preferred orientation.

The present review is concerned with the diffraction of x rays by LC polymers so that the basic diffraction theory is discussed first. It is not unlike the theory of electron or neutron diffraction but the significantly different samle geometries (thin films or bulky samples) required by these particle beams impose certain limitations (or advantages) on their use. Similarly, microscopic examinations of LC polymers often have proven to be less helpful in following their phase changes,[19] although, under optimal conditions, much can be learned.[20] As will be stressed below repeatedly, reliable characterization of molecular arrays by x-ray diffraction is possible only in aligned samples. This is equally true for monomer liquid crystals.[5] The much greater tendency of polymers to form glasses upon cooling, moreover, makes it considerably easier to quench the LC arrays so that they can be examined at room temperature without the encumberence of external magnets to maintain the molecular alignments. Thus, although polymerization complicates the analysis by introducing such additional parameters as the role of molecular-weight distributions, high viscosity, and possible coexistence of crystalline regions, it also can yield samples eminently suited for analysis by x-ray diffraction.

DIFFRACTION THEORY

Within one year of the discovery of x-ray diffraction,[21] C. G. Darwin published two comprehensive papers[22] describing the complete kinematical theory of x-ray diffraction by crystals that has lasted to the present with only modest expansions to include special aspects of the crystalline state. Eight years later, he examined the dynamical interactions between the diffracted and incident x-ray beams[24] and concluded that all that could be said about this topic had been and turned his scientific curiosity to the field of medicine. Independently, Debye[24] and Ehrenfest[25] were analyzing the intensity of x rays scat-

tered by gases and concluded that constructive interferences (intensity maxima) were produced by the positional order within a molecule, called the internal interference effect by Debye, as well as by possible correlations between molecules, called the external interference effect.

The intensity of x-ray scattering by any atomic array can be expressed in terms of the atomic scattering factors f, in electron units, by[26]

$$I = \Sigma_m \Sigma_n f_m f_n \exp (2\pi i/\lambda)(S - S_0) \cdot (R_m - R_n) \tag{1}$$

where S_0 and S are, respectively, unit vectors denoting the directions of the incident and scattered x-ray beams of wavelength λ, R_m is a vector from an atom arbitrarily placed at the origin to the mth atom in the array, and the two summations are carried out over all the irradiated atoms.† Realizing that diffracted intensities are measured during time intervals that are much longer than those associated with atomic motions, Debye derived the time-averaged intensity scattered by a random atomic (molecular) array

$$\bar{I} = \Sigma_m \Sigma_n f_m f_n \frac{\sin kr_{mn}}{kr_m} \tag{2}$$

where $k = (4\pi/\lambda)\sin\theta$, $r_{mn} = R_m - R_n$, and θ is one half of the angle between S and S_0.

When a three-dimensionally ordered array (crystal) is considered, the interatomic vector in (1) can be expressed in terms of the three unit-cell vectors a, b, and c of the lattice and a vector to the nth atom within each cell r_n

$$R_m^n = m_1 a + m_2 b + m_3 c + r_n \tag{3}$$

Substituting (3) in (1) and combining like terms, it can be shown[27] that the summation over the n atoms within the unit cell, called the structure factor $F = \Sigma_n f_n \exp (2\pi i/\lambda)(S - S_0) \cdot r_n$, represents the internal interference effect, while the three sums over m_1, m_2, and m_3 determine the external interference effect. For a triply periodic lattice array, these sums become delta functions[27] which have nonzero values

†An intensity expressed in electron units can be readily converted to an intensity measured in the laboratory by multiplying it by appropriate geometrical and physical factors.[21]

only when the three Laue conditions

$$(S-S_0)\cdot a = h\lambda,\ (S-S_0)\cdot b = k\lambda, \text{ and } (S-S_0)\cdot c = l\lambda \qquad (4)$$

are simultaneously satisfied for integer values of h, k, and l (including zero). For a crystal composed of M unit cells, the intensity in electron units then reduces to

$$I = FF^*M^2 = |F|^2M^2 \qquad (5)$$

where F^* is the complex conjugate of F. It is also easy to show that the intensity maxima (5) constitute a regular lattice array in reciprocal space defined by a^*, b^*, c^* in terms of which the diffraction vector

$$\sigma \equiv (S-S_0)/\lambda = (ha^* + kb^* + lc^*) \equiv \sigma_{hkl} \qquad (6)$$

Equation (5) illustrates an important constraint placed on the interpretation of measured intensities, viz., that only the magnitude of the generally complex F is determined experimentally. Thus the electron density distribution that Bragg[28] defined in terms of a position vector in the crystal cell $r = xa + yb + zc$ by

$$\rho(xyz) = (1/V)\Sigma_h\Sigma_k\Sigma_l F_{hkl} \exp 2\pi i(\sigma\cdot r) \qquad (7)$$

cannot be determined directly. As shown by Patterson,[29] a Fourier series based on the measured F^2 values

$$P(XYZ) = (1/V^2)\ \Sigma_h\Sigma_k\Sigma_l F^2_{hkl} \cos 2\pi(hX+kY+lZ) \qquad (8)$$

yields maxima at the terminals of interatomic vectors drawn from a common origin of the unit cell which now contains N^2 peaks for a crystal of N atoms per unit cell.

Since the electron density distribution in (7) is a continuous function of x, y, and z, it is possible to express the structure factor as a Fourier integral[30] with the integration carried out over one unit-cell volume

$$F_{hkl} = \int\int\int \rho(xyz) \exp[2\pi i(hx+ky+lz)]\, dxdydz \qquad (9)$$

The Patterson function (8) now can be derived by means of a faltung or convolution operation

$$P(XYZ) = \int\int\int \rho(xyz)\ \rho(x+X, y+Y, z+Z)\, dXdYdZ \qquad (10)$$

which reduces to (8) by direct substitution of (7) in (10).

Finally, it follows[37] that the diffracted intensity (1) is the Fourier transform of the Patterson function (10)

$$I(\sigma) = \int\int\int P(XYZ) \exp[-2\pi i(\sigma \cdot R)]\, dX\, dY\, dZ \qquad (11)$$

and that $P(XYZ)$ can be obtained directly from the inverse transform of (11). Here σ is any vector from the origin in reciprocal space (equal to σ_{hkl} when the Laue conditions are satisfied).

When dealing with the less ordered molecular arrays encountered in mesophase materials, it is frequently more convenient to employ the Fourier integrals[31] although the same results can be obtained using the Fourier series formulations.[32] Thus the Fourier transform of a line is a plane (orthogonal to the line) and of a periodic (linear) array of points spaced d apart, a stack of parallel planes spaced $1/d$ apart. Conversely, the transform of a plane is a line and of a stack of parallel planes spaced d apart, a linear array of points (orthogonal to the planes) spaced $1/d$ apart. Alternatively, it can be shown[27] that (1) can be manipulated to give

$$I = F^2 \frac{\sin^2\pi(\sigma \cdot M_1 a)}{\sin^2\pi(\sigma \cdot a)} \frac{\sin^2\pi(\sigma \cdot M_2 b)}{\sin^2\pi(\sigma \cdot b)} \frac{\sin^2\pi(\sigma \cdot M_3 c)}{\sin^2\pi(\sigma \cdot c)} \qquad (12)$$

where M_1, M_2 and M_3 are the numbers of unit cells in a crystal along the three unit-cell vector directions. For a 'one-dimensional' crystal, let $M_1 = M_2 = 1$. Equation (12) will have nonzero values only when the Laue conditions (4) are satisfied, i.e., when $\sigma \cdot c = 1$. In this case $\sigma = \sigma_{001}$ and the only nonzero values of I occur at the 00l nodes of the reciprocal lattice.

For an isotropic liquid, the electron density $\rho(r)$ depends on r only so that a straightforward Fourier inversion of the radially symmetric intensity distribution in (2) yields a radial distribution function[33] that describes the 'average' number of atoms surrounding an 'origin' atom. In the case of liquid crystals, much more information can be gained by using aligned samples having at least uniaxial symmetry,[5] a condition that is fairly easily induced in LC polymers by mechanical or magnetic means. In this case it is more informative to use a cylindrical distribution function[34] instead of an isotropic one. It should be noted, however, that molecular alignments induced by the walls of a capillary containing the liquid crystal can combine with those produced by an external magnetic field to yield biaxial samples.[35] (Similarly, the biaxiality of smectic mesophases can be retained by careful melting of smectogenic single crystals.[36,37]) It is important, therefore, to ascer-

tain that the expected cylindrical symmetry is actually present in a sample since even nematic liquid crystals may exhibit biaxiality.[38]

The general form of the cylindrical distribution function (cylindrically-symmetric Patterson function) was first derived by Wrinch[39] and in greater detail by Norman,[40] who showed that a centrosymmetric cylindrical distribution D can be expanded in a series of Legendre polynomials P_{2n} of even order.

$$D(R,\alpha) = \sum_{n=0}^{\infty} D_{2n}(R)\, P_{2n}(\cos\alpha) \tag{13}$$

where

$$D_{2n}(R) = (-1)^n\, 4\pi \int_0^{\infty} \sigma^2\, I_{2n}(\sigma)\, J_{2n}(2\pi\sigma R)\, d\sigma \tag{14a}$$

and

$$I_{2n}(\sigma) = 1/2\ (4n+1) \int_0^{\pi} I(\sigma,\phi)\, P_{2n}(\cos\phi)\, \sin\phi\, d\phi \tag{14b}$$

while α is the angle that the radius vector R forms with the unique (cylinder) axis in real space and ϕ is the angle the diffraction vector σ forms with the unique axis in reciprocal space.

Milberg has pointed out[41] that the zeroth term in (13) represents the radial distribution function $D_0(R)$ obtained by transforming the isotropic or radially symmetric intensity distribution in reciprocal space. Subtracting $D_0(R)$ from $D(R,\alpha)$ then yields a difference-distribution function that contains all of the anisotropic distribution features albeit on a relative scale. It can be calculated directly from the anisotropic intensity distribution, i.e., by substracting the isotropic $I_0(S)$ from $I(S,\phi)$ in (14b), so that such contributions to the isotropic x-ray scattering as Compton scattering, etc., do not have to be evaluated separately.

The above equations highlight the theoretical bases for intepreting the diffraction of x rays by various LC aggregations. Cylindrical Patterson functions have been widely used in the structure analyses of synthetic and natural polymer fibers for many years and, as recently demonstrated by Mitchell and Windle,[40] are equally useful in deducing structural information for extruded polystyrene glasses. These authors have also applied such analyses to the study of thermotropic

LC polymers,[41,42] specifically, copolyesters of poly(ethylene terepthalate) and *p*-acetoxy benzoic acid.

A different application of the above relations was demonstrated by Gudkov[45] who observed that the 002 reflection was more intense than the 001 reflection in the smectic mesophase of poly-p-n-hexyloxybenzoyl-p-oxyphenyl-N-methacryloyl-ω-aminolaurate. Note that, when $h = k = 0$, the one-dimensional Fourier series in (7) and (8) require only F_{00l} coefficients but the resulting density distributions represent projections of the entire three-dimensional array onto a single line (the z axis). Thus their interpretation in terms of a bilayer structure owes much to the author's chemical intuition. This example does illustrate the importance of considering all aspects of x-ray diffraction intensities such as their relative magnitudes (including $I \approx 0$), shapes (sharp vs. diffuse), and their extent throughout reciprocal space if cyndrindrical (radial) symmetry is absent. Further details can be found in the texts cited among the references to this review.

SIDE-GROUP LC POLYMERS

The interest in LC polymers has been growing steadily as testified by the number of symposia that have been recorded in their proceedings volumes.[46–48] Only a limited number of review papers, however, have discussed x-ray diffraction results in any detail.[10,11,49,50] This is due, in part, to the need to combine experimental results from several complementary techniques to gain a fuller understanding. It is also due to the very limited information that can be deduced when unaligned samples only are examined. In what follows, some of the more extensive structural analyses based primarily on x-ray diffraction intensities will be reviewed, beginning with side-group LC polymers. This name, incidentally, reflects the fact that the LC ordering in these polymers, Figure 1, results from cooperative interactions between pendant LC units which are usually attached to the polymer 'backbone' by flexible spacer groups like methylene.[51] In the mesophase region, x-ray diffraction by such polymers resembles that by comb-like polymers which have been previously studied extensively in the solid state.[52] Concurrently, their diffraction photographs (Usually recorded by passing a pinhole-collimated filtered x-ray beam through a cylindrical or planar sample normal to the beam which, in turn, is normal to a flat photographic plate.) also resemble those of monomer liquid crystals. It is to be hoped, therefore, that the name LC polymers

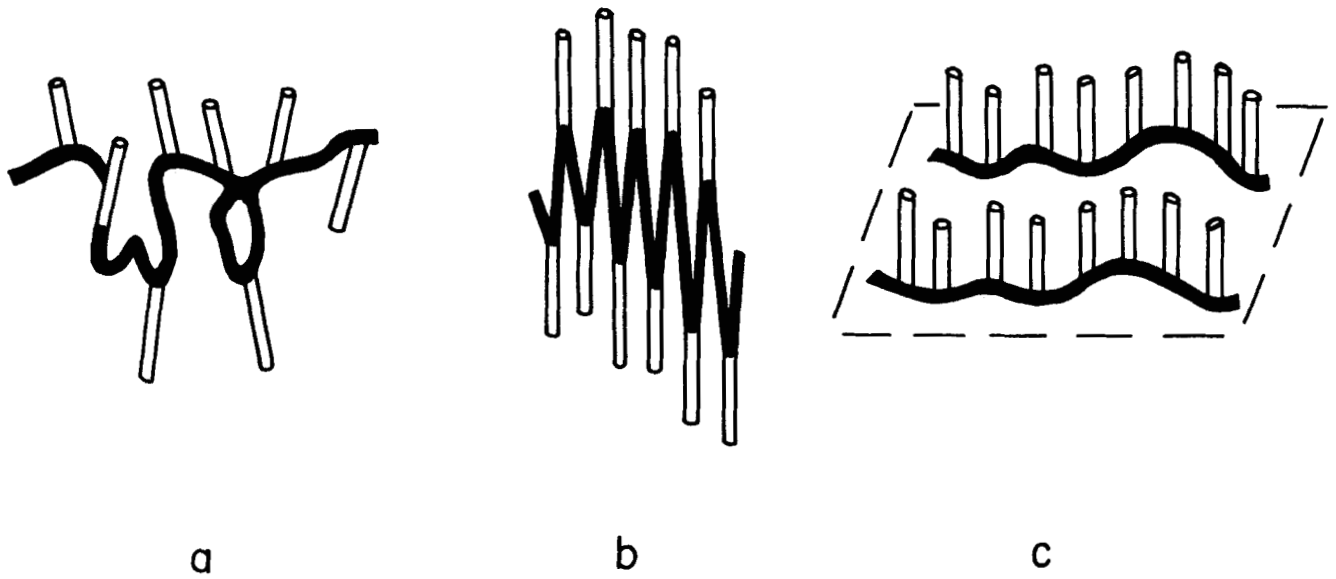

FIGURE 1 Schematic presentation of ordering in side-group LC polymers. (After Vasilenko, *et al.*[58])
a. weakly interacting side groups (nematic).
b. strongly interacting side groups (nematic).
c. smectic ordering of side groups.

will be applied only to those compounds that exhibit a liquid-like viscosity in a mesomorphic range confirmed by DSC, microscopy, or x-ray diffraction.

In their examination of several polymers derived from LC monomers and exhibiting mesomorphic order, Clough, Blumstein, and de Vries[12] carefully stressed that the polymers were hard and brittle and "not liquid crystals in the usual sense of that term." They examined six polymers whose x-ray photographs showed at least one sharp inner reflection ($2\theta \sim 4$–$5°$) so that they were classified as smectic, three nematic polymers whose inner ring was weak and diffuse, and two whose inner rings were broader than the usual smectic reflections so that they were classified as intermediate in order between nematic and smectic. It is interesting to note that the polymerizations took place from the nematic melts of the monomers and, in two cases, it proved possible to produce aligned samples, respectively, by casting a film and by conducting the polymerization in a 10 T magnetic field. In addition to a very large and broad arc at the equator, the magnetically aligned polymer yielded several sharp meridional arcs representing orders 1,2,3,5,6,7,9,10,11, and 13—more suggestive of the packing of helical polymer molecules[53] than of smectic layers in monomer liquid crystals. (Note the systematic absence of the 004, 008, and 0012 reflections.)

A similar result had been obtained in the polymerization of a Schiff base monomer on a methacrylic backbone from its nematic range in a 7 T magnetic field.[54] Again a smectic ordering was assigned on the basis of four relatively sharp meridional arcs and one broad and diffuse equatorial arc. It is interesting but not surprising to note that, when the polymerization was carried out under identical conditions except in the isotropic temperature range of the monomer, the magnetic field caused no molecular alignment. The unaligned LC polymer yielded four 'sharp' Debye-Scherrer rings and one diffuse halo whose d values matched those of the aligned sample. The authors proposed[54] that the LC ordering is smectic with a high degree of long-range order normal to the layers but only limited short-range order within the layers. In an extension of this work, Wendorff *et al.*[55] demonstrated that the formation of smectic and nematic LC polymers can be related to the length of the side group. Their results did not allow them to draw any direct conclusions about the disposition of the backbone polymer chain, however.

The general but unstated assumption has been that the polymer backbone meanders throughout the sample, contributing only background scattering of x-rays. As clearly evident in pictorial

models[56–58] and in Figure 1c, it probably lies in planes between smectic layers formed by the side groups but otherwise remains unrestricted. For smectic ordering, Wendorff[49] has suggested that packing considerations favor a planar 'bundle' of more or less aligned chains over a random coil configuration. Recall from the introductory discussion of x-ray diffraction that a stack of parallel planes produces periodically spaced intensity maxima along a row in reciprocal space that is normal to these planes. No requirements on the distribution of scattering centers (electron density) within these planes was stipulated. Thus x-ray scattering by a smectic array of parallel side groups (Figure 1c) wil be intensified by the presence of polymer backbones in equally spaced parallel layers. In fact, the higher orders of diffraction by smectic layers reported for the LC polymers (only one or two are typically observed in monomer liquid crystals) are probably due to a stricter coplanarity imposed by the main chains so that a careful examination of diffraction data should reveal considerable information about how planar the disposition of the backbone polymers actually is. In this connection, it should be noted that Zugenmaier and Müggе[59] succeeded in obtaining a highly crystalline fiber of polymethylisiloxane with mesogenic side groups by annealing it in the LC state in a 2.3 T magnetic field and then slowly cooling the fiber to room temperature. The well ordered main-chain conformation deduced for this crystalline fiber closely resembled that in an extruded and quenched fiber, exhibiting predominantly smectic ordering, as deduced from the many similarities of their respective x-ray diffraction diagrams.

The way that the chemical nature of the backbone polymer, the side-group mesogen, and the spacer used to couple them affects the possible LC structures can be monitored by x-ray diffraction. Such studies,[11,60,61] however, use x-ray diffraction as fingerprints (frequently Debye-Scherrer photographs with their inherent ambiguities) so that they are not further discussed here. Suffice it to note that shorter mesogenic units lead to nematic and longer units to smectic arrays.[60] Similarly, there is a minimum length that the flexible spacer must have[61] to assure liquid crystallinity in the side-group polymer.

As already pointed out,[11] LC polymers differ from monomer mesomorphs in that the anisotropic (mesomorphic) melt may pass through a glass transition temperature upon cooling rather than the sharper melting point characteristic of a transition to the crystalline state. According to Shibaev and Platé,[11] side-group LC polymers tend to be glass forming so that their anisotropic electrical, mechanical, and optical properties can be retained in the solid state. These authors

present numerous examples of x-ray studies through 1982, including those published in journals or dissertations not easily accessible outside their country of origin.

Pursuing the observation that there is a definite relationship between the alignment of LC polymers in electric fields and their mesophase structure,[62] Shibaev and his collaborators examined the smectic arrays of LC polyacrylates,[63] aligned electrostatically and by shear deformation between two glass plates. This work was extended to include polymethacrylates[64] and shorter side groups that led to the formation of nematic mesophases. Although it is surprising that their polymer 2, containing 5 CH_2 units in the side group, is a highly ordered nematic in the glassy state (two very sharp and a third weaker meridional reflections suggest a smectic layering of considerable extent) their polymer with 11 CH_2 units forms both Sm_A and Sm_C phases.[63] Their normal-beam photographs and proposed smectic layerings are depicted in Figure 2. Figure 2a shows the smectic-A mesophase for which the three meriodional reflections yield interplanar spacing values of 44.0 ± 1.0, 29.0 ± 0.5, and 16.1 ± 0.5 Å, respectively. (This photograph closely resembles that of their polymer 2, imputed to be nematic.) The corresponding three d values for the smectic-C phase shown in Figure 2b are 39.0 ± 1.0, 19.7 ± 0.5, and 16.6 ± 0.5 Å, respectively. Although d_{001} and d_{002} have declined in the tighter packing of the smectic-C phase while d_{003} did not, it seems unlikely that there are two kinds of Sm_C layers being formed as the authors suggest (Ref. 64, p. 378). Alternatively, the side groups in the Sm_A layers may be more loosely packed than suggested at the bottom of Figure 2a and a careful examination of the intensity distribution (especially of the 003 meridional arc) might disclose the nature of the slight disordering in the layer sequences.

Because of the sluggish nature of certain thermal transitions in LC polymers, x-ray diffraction provides a more reliable means of characterization than DSC or optical microscopy—so successfully used in the study of monomer liquid crystals. Thus a smectic-A phase formed on cooling a nematic polymethacrylate rod failed to appear optically but was clearly shown to exist in the parallel x-ray study.[65] Similarly, x-ray diffraction was necessary to identify the formation of Sm_A and Sm_C phases, respectively, by structurally similar chloroacrylates and methacrylates. Since diffraction intensities are related to molecular arrays in a truly unique way, an x-ray diffraction photograph obtained with the incident beam directed along the plane of a cast LC azomethyne polymer film[67] clearly demonstrated that the uniaxial optic axis (normal to the film plane) was produced by a

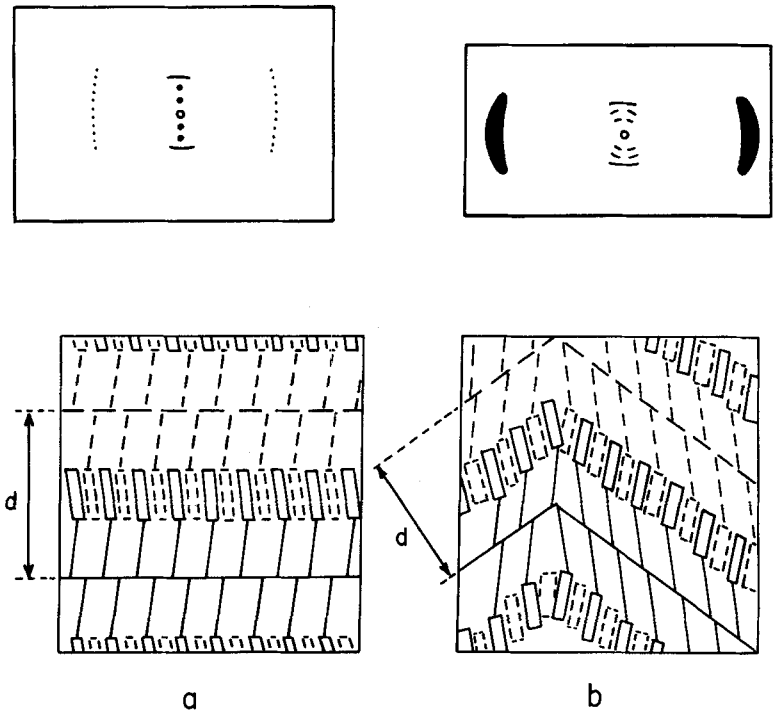

FIGURE 2 Schematic of normal-beam x-ray photographs and proposed smectic layering. (After Kostromin *et al.*[63,64])
a. smectic—A mesophase.
b. smectic—C mesophase.
The texture axis is vertical for both photographs.

smectic-A layering forming a single oriented domain within the film. Similarly, x-ray diffraction of aligned (by drawing fibers from the mesophase melt) LC polymers having phenyl benzoate side groups that differed in the length of the spacer molecule[68] confirmed that smectic phases were favored by the longer spacers. Such separation of the interactions of the side groups with each other from the influence of the polymer backbone led to crystallization when the spacer groups were longer than 12 Å. Upon heating, the crystalline polymer transformed to the highly ordered Sm_B phase. A monitoring of the relative intensities of two meridional reflections as a function of temperature in the smectic phase suggested that LC ordering increases (larger ordered domains from) for the more tightly linked side groups,[68] i.e., those having shorter spacer groups.

A study of four LC polymers having phenyl benzoate side groups[69]

yielded normal-beam photographs ranging from those typical of nematic ordering to several kinds of smectic ordering. The authors attribtue four off-meridian reflections for one polymer to the formation of 'blocks' of mesogenic units and the appearance of two off-meridian reflections to tilted smectic layers in a chevron array[69] (like Figure 2b). Unlike the case of smectic-C-type ordering depicted in Figure 2b, both photographs clearly show several 00l reflections along the meridian which, by themselves, would suggest smectic-A-type layering for both polymers. By comparison, the occurrence of four off-meridian reflections were interpreted by Davidson *et al.*[65] to be caused by fluctuations in the lattice spacings. Neither group of investigators considered the possible contribution of the polymer backbone to the diffraction intensities. If moving-film methods capable of exploring the intensity distribution throughout reciprocal space had been used in place of the normal-beam (Laue) photographs, it is likely that more definitive structural information could have been deduced.

X-ray diffractometers are even more limited in that they can 'see' the intensity distribution only along the line of the scan in reciprocal space. They yield, however, quantitative data that are extremely useful when intensity changes or peak shifts caused by temperature in, say, the smectic range are to be studied. Since, frequently, only two 00l reflections are available for such studies,[70,71] it is difficult to assess the significance of the order parameters that can be deduced thereby. This is especially true since the direct applicability of the paracrystal model[72] or the mean-field approximation[73] to the ordering of smectic LC polymers has yet to be demonstrated. In such studies it is also important to bear in mind that not only is the peak intensity diminished exponentially as a function of temperature (Debye-Waller effect), but also that temperature-diffuse scattering produces maxima in reciprocal space[74] at the same sites specified by the Laue conditions (4).

MAIN-CHAIN POLYMERS

In addition to the general review of main-chain LC polymers,[17] the factors affecting the relative rigidity of long-chain molecules composed of anisometric monomers have been considered by Ciferri.[75] Typically, the more rigid the molecular chain, the greater its tensile strength—an obviously desirable mechanical property. Tight binding leading to rigidity, however, raises the melting oint of the polymer

so that it becomes more difficult to process. The melting point (and the clearing point for LC polymers) can be reduced by decreasing the molecular weight (chain length) or by introducing flexible spacers within the chain making it less rigid (weaker) thereby.[51,76–78] Making the flexible spacer too long, however, 'frees' the rigid monomers to such an extent that they form isotropic liquids that may be in equilibrium with the nematic mesophase formed by the same polymer.[77] Thus a range of properties can be induced in homopolymers and to an even larger extent in copolymers and blends. This is the principal reason for the growing interest in main-chain LC polymers since their introduction a decade ago.[15]

Although conceptually related to monomer mesophases, the molecular arrays formed by main-chain polymers can be expected to differ more pronouncedly than those of side-group polymers because the anisometric units are bonded at both ends to the molecular chain. Whereas mesogenic side groups can interact with each other quite freely, particularly if they are joined to the backbone polymer by flexible spacers, any interaction between mesogenic units in the main-chain polymer requires a cooperative involvement of the entire polymer chain. If the polymer chains are fairly rigid, therefore, they are most likely to favor a parallel alignment (nematic) without any chain-to-chain (side-to-side) correlation. Flexible spacers 'free' the mesogenic units so that more chain-to-chain interactions are possible, particularly under the action of external mechanical, magnetic, or electrostatic forces. Thus Maret and Bloomstein[79] found that polymers forming a 'true' nematic phase over an extended temperature range could be aligned quite readily in a strong magnetic field (~16 T) and cooled to room temperature (glassy solid) retaining the nematic alignment. By comparison, polymers containing chiral (cholesteric) molecules could not be aligned while polymers that produced only segmental chain alignments (narrow nematic range) also could not be aligned magnetically but tended to crystallize on cooling.

A representative x-ray diffraction diagram of a fairly rigid polymer in nematic alignment is reproduced in Figure 3. The nematic melt of this polymer yields a single halo in the diffraction diagram characteristic of the side-to-side separation distance. If it is aligned in the nematic range, magnetically or by drawing (extruding) a fiber, then the parallel but uncorrelated alignment of the periodic chains produces a set of 00l planes (disks) in reciprocal space in addition to the broader equatorial arcs. Such alignments have been observed previously and allow the repeat distance along the chain and the number of parallel chains forming a 'correlated' bundle to be estimated.[80]

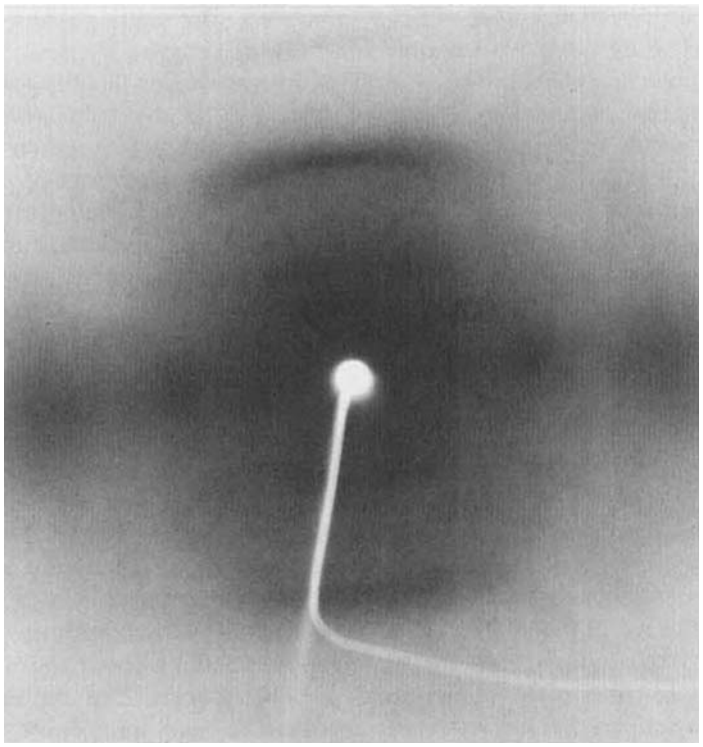

FIGURE 3 Normal-beam photograph of a fiber drawn from the nematic melt. (Recorded by H. Chin using filtered Fe Kα radiation.)

Because a more extensive interaction between neighboring chains (requiring systematic displacements of the individual chains along their lengths as well as conformational alignments of neighboring units) is difficult to achieve, such polymers do not crystallize readily and prefer to retain their LC arrays in the glassy (solid) state.

The diffraction photograph produced by a main-chain LC polymer containing flexible spacers is shown in Figure 4. The constituent chains were aligned by drawing a fiber from the nematic melt as in the case above. Comparison with Figure 3 shows that there is considerably more interaction between the mesogenic groups in neighboring chains. In fact, the formation of four intense off-meridional maxima suggests a fairly extended alignment. By introducing more (or less) interactive side groups in a polymer, the degree of such cooperative alignment can be altered significantly.[81] It is also possible to extend the molecular alignment by annealing a fiber for a few hours at a temperature

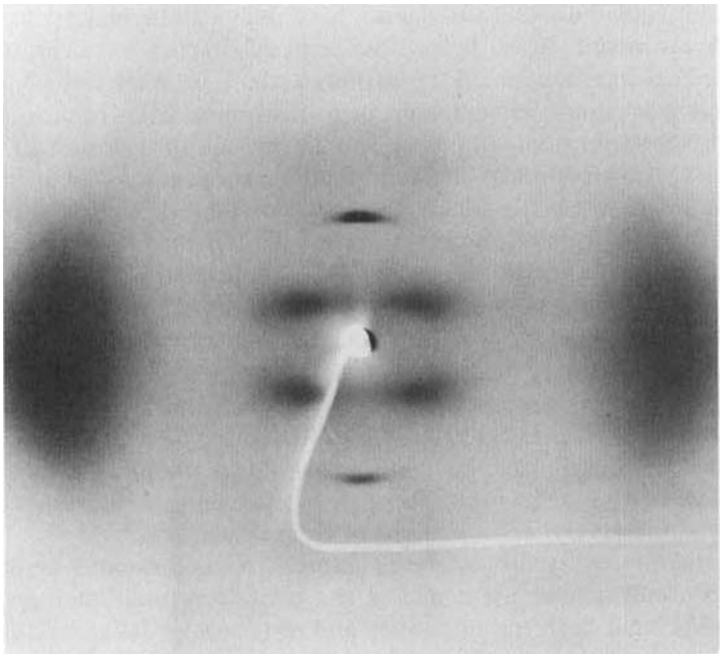

FIGURE 4 Normal-beam photograph of a fiber drawn from the nematic melt. (Recorded by H. Chin using filtered Fe Kα radiation.)

below the nematic melting point. Prolonged annealing of the solid fiber however, may destroy the 'nematic' array by abetting three-dimensional crystallization.

It should be noted that four off-meridional diffraction maxima have been observed quite frequently in x-ray diffraction photographs of LC polymers and monomers and even earlier in nonmesogenic polymers like nylon and polyethylene whose molecules had been aligned by mechanical means.[82] (For example, Figure 2b shows the off-meridional maxima that are 'typical' of a chevron-like Sm_C structure.) Similar diffraction diagrams were first observed in nematic mesophases of the monomers *p*-azoxybenzene[83] and BOCP.[84] de Vries attributed the four maxima to individual smectic-C-like layers formed in the nematic phase[84] and called them "skewed cybotactics." Subsequently Azároff showed that a quite different molecular model also could be postulated to explain their origin.[85] More recent x-ray diffraction studies using moving-film methods to explore the reciprocal space showed that these four maxima were cross sections of biaxial

intensity distributions[35] and did not have the unixial symmetry of the de Vries model. Nevertheless, the term cybotactic† has been used somewhat indiscriminately by various authors whether referring to actual four-point x-ray diagrams or to faint inner halos occurring in Debye-Scherrer photographs of nematic mesomorphs. Note that the intensity distribution of the four maxima in Figure 4 has uniaxial (cylindrical) symmetry about the fiber axis (as expected in a fiber diagram). Four-point arrays also have been recorded by Bloomstein *et al.*[86] for thermotropic polyesters composed of azoxybenzene mesogenic moieties joined by a alkanedioyl spacers. Atkins *et al.*[87] recorded similar four-point diffraction from a shear-induced alignment in a lyotropic mesophase of hydroxypropyl cellulose. In this case the authors were able to relate it to helicoidal chains packed parallel to each other but without lateral ordering among neighboring chains. They were able to confirm this model, despite the limited number of x-ray reflections recorded, by examining the intensity distribution in several cross sections of reciprocal space.

Generally, x-ray diffraction diagrams of aligned samples provide an informative tool for deducing the underlying molecular arrays provided that both the intensities and distributions (shapes) of the diffraction maxima are taken into account. Gudkov *et al.*[88] examined two aromatic polyimids formed into well oriented films by stretching and annealing. PMB yielded a normal-beam photograph with five (sharp) 00l reflections and three (broader) equatorial reflections while the x-ray photograph of DPO-PP was similar except that all reflections were more diffuse. By forming optical transforms of the diffraction photographs (analogs of Patterson distributions) the authors were able to confirm the packing of proposed molecular models. Thus Gudkov *et al.*[88] demonstrated that the presence of hinge groups along the DPO-PP chains was the probable reason why they failed to improve their relative alignment even after extended annealing.

By comparison, Roviello and Sigiru[89] recorded diffraction diagrams of two aligned nematic polyesters that are very similar to what one obtains from 'normal' nematic monomers. When these fibers were annealed for about twenty hours at temperatures below the nematic melting point, the diffraction diagrams became typical of well crystallized fibers. In fact, it was possible to demonstrate that different crystalline polymorphs could be formed by altering the thermal his-

†Cybotaxis is defined in Webster's 3rd International Dictionary (1981) as "a transient orientation of molecules in a liquid revealed by x-ray diffraction effects analogous to those produced by crystals."

tory of the fiber. When one observes a 'typical' nematic x-ray photograph showing a pair of broad crescents at the equator and no meridional reflections, little can be gleaned about the molecular alignment other than that there is very little alignment taking place. In such a case it may be possible to learn about any supramolecular alignments (ordering) by measuring the small-angle scattering.† This has been done with some success for nematic monomers.[90]

Relatively few x-ray studies of smectic main-chain polymers have been published. Bosio *et al.*[77] observed that increasing the length of the flexible spacer between rigid aromatic moieties in a polymer chain leads to the formation of smectic rather than nematic mesophases. These authors show two x-ray photographs that have two sharp meridional reflections and one pair of wide arcs on the equator which they attribute to Sm_A ordering.[77] A careful examination of their Figure 18, Plate 2 shows that each equatorial arc is split into two more intense portions lying above and below the equator which suggests a smectic-C-type ordering with interchangeable tilt directions for the molecules comprising the layers. This also appears to be the case in the polyester (TO-11) studied by Noel *et al.*[92] (their Figure 14) and would explain the 4–5% drop in the 'layer spacing' on going from the crystalline to the smectic region. Since the authors also have microscopic evidence indicative of Sm_C formation, the smooting out of the intensity distribution in the equatorial arcs, at an elevated temperature in the smectic range, can be attributed to thermal (statistical) fluctuations in molecular tilts more plausibly than to a possible Sm_C to Sm_A transition.

Considerably more information about the molecular arrays in LC polymers can be obtained by utilizing the entire intensity distribution recorded in reciprocal space to calculate the corresponding cylindrical (Patterson) distribution function (13). A straightforward experimental procedure for doing this has been evolved by Mitchell and Windle.[41,43] A transmission diffractometer arrangement is used to record the diffracted intensities which are subsequently smoothed, corrected for physical and geometrical factors, and suitably normalized to give a 'reduced' intensity function like (14b). Figure 5a reproduces such a reduced intensity distribution[43] for a nematic LC polymer in the form of an extruded pellet while Figure 5b shows the intensity var-

†Small-angle x-ray scattering (SAX) is the measurement of the intensity scattered at $\theta \leqslant 2°$, i.e., in the direction of the incident beam.[91] When speaking of wide-angle x-ray diffraction (WAX) at relatively small scattering angles ($2° < \theta < 6°$ for Cu Kα) one should use adjectives other than "small-angle" so as not to confuse SAX with WAX.

iations along the meridian (extrusion direction) and equator, respectively. By assuming suitable models, it is possible to calculate both the intrachain and interchain scattering intensities as well as the overall scattering recorded in Figure 5a. The results of such calculations by Mitchell and Windle[43] are reproduced in Figure 6. The good agreement of Figures 6b and 5b underscores the relative ease with which intrachain scattering from a model can be 'fitted' to the measured distribution. The interchain scattering depends on the degree of alignment and on the assumptions underlying the calculational procedures employed, as carefully pointed out by these authors.[43]

COPOLYMERS AND POLYMER BLENDS

The competing properties of rigidity and low melting points for main-chain LC polymers can be accomodated, in part, by combining two or more dissimilar monomers to form a copolymer. How this affects the x-ray diffraction diagram has been illustrated most graphically by Stamatoff[94] who compared the diffraction by three spun fibers displaying well oriented fiber (uniaxial) texture. A relatively rigid lyotropic homopolymer yields meridional disks (like Figure 3) while a random copolymer shows a slight tendency and an ordered (alternating) copolymer shows a strong tendency for lateral ordering. Upon annealing all three fibers, the nematic homopolymer shows an increased parallelism of the rigid chains without any "match up" of neighboring monomer segments whereas the alternating copolymer becomes three-dimensionally ordered (crystalline). Other x-ray characterizations have also been reported for nematic copolymers[95,97] and smectic copolymers.[99] Watanabe and Kirgbaum[99] examined a series of mesogenic polymer mixtures and random copolymers and found that they could form nematic or smectic copolymers depending on various factors including the odd-even character of their flexible spacers. As noted above, randomness in a copolymer chain prevents three-dimensional ordering (crystallinity) from occurring.

A most systematic approach to studying the ordering sequences along copolymer chains has been carried out by Blackwell, Chivers, and Gutierrez and their associates.[100–108] Focussing their attention on the meridional reflections, the early analyses were limited to reproducing their aperiodic spacing values (σ_{001} values in reciprocal space) by calculating the Fourier transform of random copolymer models generated by a random-number (Monte-Carlo) generator.[108] The underlying reason for the success of this approach was demonstrated

recently by Davies and Lakeways[109] who reduced the problem to calculating two phase factors, each as a function of the two monomer lengths and their respective probability of occurrence. Based on their simple analytical treatment, these authors were able to reproduce quite well the spacings measured by Blackwell *et al.*[105] but not the intensity profiles. The more recent calculations of Blackwell, Chivers, and Guiterrez include intraresidue (atomic) scattering interactions[100–103] which enable them to carry out a more exact comparison with their measured intensities (Figure 7). It also helps them to estimate the stiff-chain persistence length from the reflection widths.[100] It is hoped that extensions of these studies will make use of the off-meridional reflections, clearly evident in Figure 7, to provide further information regarding the lateral packing of the copolymer chains.

Still another way to modify the mechanical and other properties of polymers is to form blends (mixtures) of two polymers or of a polymer with a monomer. A 50–50 blend of poly(butylene terephthalate) (PBT) with a polyarylate, a noncrystallizable copolyester, suggest a nematic ordering for PBT in the blend.[110] (Regrettably, no attempt was made to align the molecules because the PBT tended to crystallize in the quenched films.) In another study,[111] two thermotropic LC polymers were blended with monomer liquid crystals and x-ray diffraction (Debye-Scherrer method) was used with optical microscopy and DSC to establish the resulting phase diagrams. The authors observed a transesterification reaction taking place in the solid state which suggests itself as a potentially new processing technique for polymers[112] leading to a main-chain polyester having a more rigid (stable) polymer backbone.

CONCLUSION

The systematic investigation of the 'structures' of LC polymers by x-ray diffraction holds out considerable promise provided it is recognized that they are polymers first and foremost. Instead of seeking to explain their x-ray diffraction by means of analogies to monomer liquid crystals, they should be examined by analogy to procedures described in the extensive literature on polymer (fiber) texture studies. Whenever possible, fiber diagrams should be recorded using well aligned samples. (Chung *et al.*[112] have shown how LC polymers can be aligned also by epitaxy.) In doing this it is preferrable to use Fe Kα radiation which yields comparable exposures (intensities) to Cu Kα but increases the diffraction angles (resolution) and lessens the

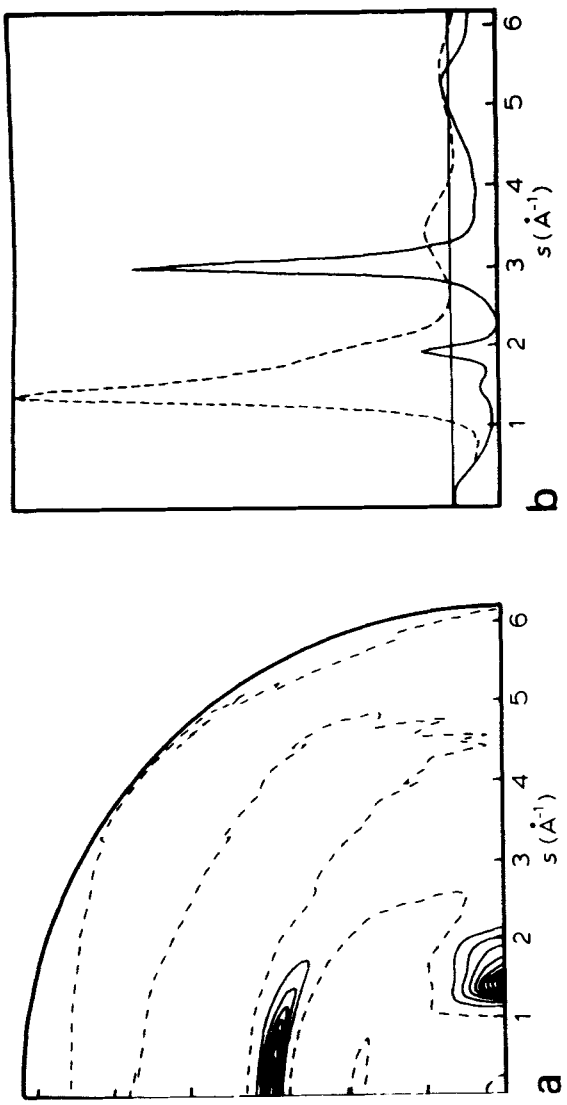

FIGURE 5 Reduced intensity of a thermotropic LC copolymer.[43] (Reproduced by permission.)
a. Normalized intensity distribution.
b. Meridional (solid) and equatorial (dashed) sections of scattering intensity in a.

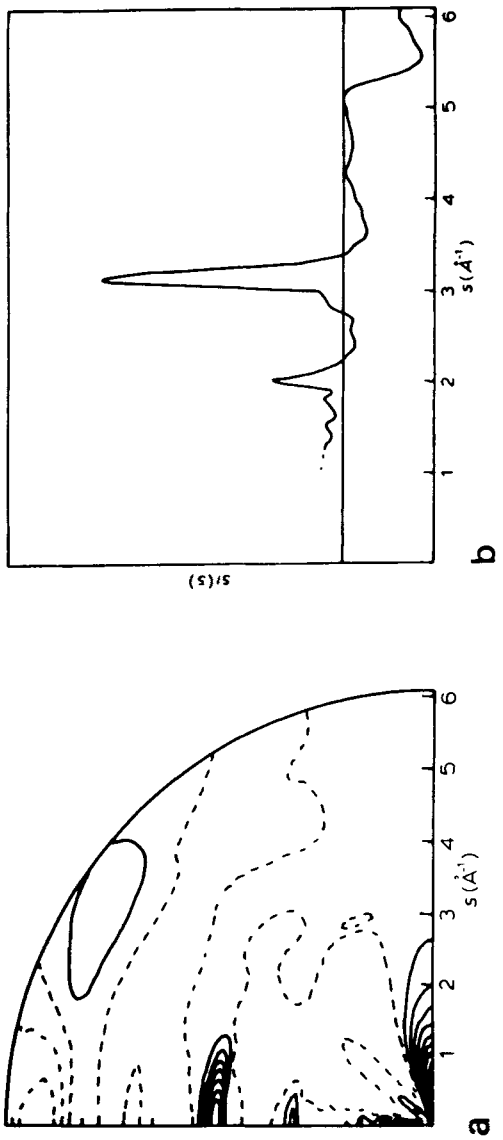

FIGURE 6 Calculated intensity for thermotropic LC copolymer.[43] (Reproduced by permission.)
a. Normalized intensity distribution.
b. Meridional section of scattering in a. (Compare this to solid curve in Figure 5b.)

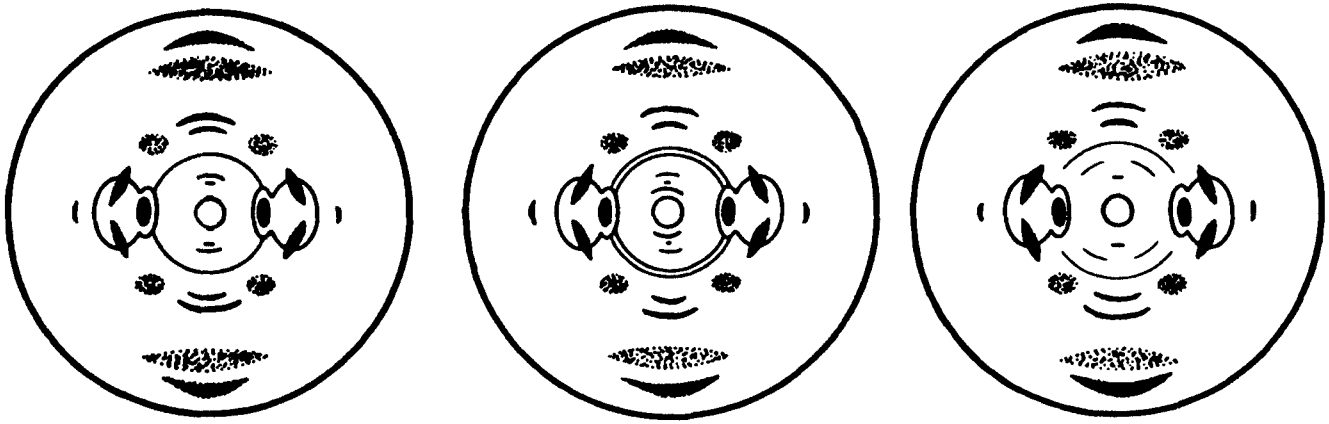

FIGURE 7 Schematics of x-ray diagrams[101] of copoly(HBA/DHN/TPA) in the monomer ratios: (a) 60/20/20, (b) 50/25/25, (c) 40/30/30. (Reproduced by permission.)

geometrical dependence (Lorentz factor) of the intensities of inner reflections. Use of a crystal monochromator to eliminate the diffraction of noncharacteristic radiation is also highly desirable. Care should be exercised to record all intensities without overexposing the stronger reflections since this distorts their true shapes. A simple way to do this is to use a multiple-film pack in which successive films act as attenuation filters. Finally, all aspects of the recorded intensities should be used to derive appropriate structural models and the scattering by all components of the LC polymer (backbone, mesogenic units, spacers) should be considered.

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