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X-Ray Diffraction by Thermotropic Main-Chain Polymers Having Side Groups: Part A. Diffraction Theory

by

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X-ray Diffraction by Thermotropic Main-chain Polymers Having Side Groups: Part A. Diffraction Theory

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Synopsis

The diffraction of x rays by parallel extended chain molecules is examined first by considering the nematic packing of rigid-rod-like chains. Typically, such arrays produce disk-shaped intensity distributions about $00\underline{\ell}$ points along the meridian in reciprocal space and $\underline{h}\underline{k}0$ reflections along the equator corresponding to a hexagonal net. The introduction of periodic flexible spacers tends to diminish the long-range order along the chains so that only one or two $00\underline{\ell}$ reflections remain. Concurrently, the packing of the parallel chains becomes less regular, thereby broadening and weakening the equatorial reflections while permitting increased interchain interactions. This can lead to short-range ordering at right angles to the chains as well as smectic layering of the mesogenic units. The latter resembles small-molecule smectic ordering while the former is unique to mesomorphic polymer chains and is characterized by the appearance of off-axis intensity maxima in reciprocal space.

INTRODUCTION

A recent review of the literature on x-ray diffraction by liquid-crystalline polymers (LCPs) pointed out that unambiguous interpretations are possible only when the polymers have been aligned either by magnetic or mechanical means[1] so that a monodomain-like texture has been achieved. Depending on the stereochemistry and whether a homopolymer or a copolymer is being examined, the resulting texture can range from partly crystalline[2,3] to highly aligned monodomains.[4] Comparisons of the textures of homopolymers aligned by annealing for several hours at 5-10° above the nematic (melting) temperature in a very strong magnetic field (15 tesla) with those obtained by drawing a fiber directly from the nematic melt (air quenched) showed that a well aligned monodomain-like texture was produced by both means although some variations attributable to the substituents in the side groups were noted.[4] It should be realized that the high degree of alignment induced in such thermotropic polymers is not characteristic of their normal state, i.e., any order parameter deduced from such artificially aligned samples is not representative of the degree of alignment achieved by a bulk polymer in the mesomorphic state. Such alignement is essential, however, for the determination of the molecular 'structure' of the mesomorphic state. It is also indicative of the kind of texture that can be produced by suitable processing for subsequent applications .

The present discussion focuses on thermotropic main-chain polymers (with or without side groups). It is possible to distinguish rigid or rod-like chain molecules from semiflexible chain molecules because their structural and dynamical properties are different.[5-9] Rigid chains tend to pack like cylindrical rods even if their structure along the chain is quasiperiodic, as is the case in random copolymers,[10] whereas semiflexible chains pack more like extended necklaces made up of different sized beads.

In the isotropic liquid and mesomorphic states, the chains have several degrees of positional freedom, including rotational, so that when they are quenched to the room-temperature (glassy) state from a uniaxial stress field (magnetic or mechanical) they tend to form parallel extended monodomains collectively exhibiting uniaxial (rotational) symmmetry.

The attainability of such well-aligned monodomains (often without any trace of accompanying unaligned regions) suggests that their x-ray diffraction effects can be interpreted most effectively by utilizing the rigorous and extensive diffraction techniques developed for single crystals (c.f. Ref. 11). In what follows, the basic relationships predicting the expected (and often observed) x-ray diffraction effects from rigid and from semiflexible main-chain LCPs are developed. Two companion papers will illustrate actual structural models that can be deduced from recorded diffraction intensities by making use of the insights provided.

RIGID ROD-LIKE CHAINS

External Interference Effects

The packing of rigid chains having a periodic structure along the chain most nearly resembles that found in crystals. If these rigid chains have full rotational freedom about their chain axes, i.e., when there is no bonding or steric interference between neighboring parallel chains, then they can be expected to pack in a hexagonal closest packing at right angles to the chains. This is the reason for the higher density of rigid-rod-like LCPs than that found in comparable flexible ones.[10] Along the chain, each homopolymer has an identical array of periodically repeated monomers (except for their possible relative rotation about the chain axis) but, in the absence of chain-to-chain correlations, the relative displacements of the chains along their axes is quite random. It is convenient, therefore, to separate the diffraction effects of the monomer units comprising the chains from those produced by their array (packing) in the irradiated sample. The former depends on the scattering power f of the atoms comprising it and is expressed by the structure factor of the monomer molecule $F = \sum_n f_n \exp(2\pi i/\lambda)(S-S_0)\cdot r_n$. To determine the latter, named the external interference effect by Debye, use is made of a position vector

$$R_m = m_1 a + m_2 b + m_3 c + \delta_{m_1 m_2} c \qquad (1)$$

where a and b are translation vectors defining the $m_1 m_2$ lattice points through which the chains pass, c is the translation vector along the chain, and $\delta_{m_1 m_2}$ is the fractional displacement along c of the chain passing through the $m_1 m_2$ lattice point.

The diffraction intensity, expressed in electron units, then can be represented[†] by

$$I_{e.u.} = F^2 \sum_{m_1} \sum \sum \sum \sum \sum_{m_3'} \exp(2\pi i/\lambda)(S-S_0)\cdot(R_m - R_{m'}) \qquad (2)$$

where λ is the wavelength of the monochromatic incident beam, S and S_0 are unit vectors in the diffracted and incident beam directions, respectively, and F^2 represents the product of the structure factor with its complex conjugate.

When the diffracting sample forms the proper Bragg angle with the incident beam, i.e., when the third Laue condition $(S-S_0)\cdot c = \lambda \ell$ is satisfied by the M_3 monomers in each chain

$$I = F^2 M_3^2 \sum_{m_1} \sum \sum \sum_{m_2'} \exp(2\pi i/\lambda)(S-S_0)\cdot(X_m - X_{m'}) \exp 2\pi i \ell(\delta_m - \delta_{m'}) \qquad (3)$$

[†] Readers not already familiar with diffraction theory may want to consult Ref. 1.

where $X_m = m_1a+m_2b$ is the translation vector in the ab plane perpendicular to the chain axis c and m is shorthand for m_1m_2.

It is now possible to deduce what the diffraction effects produced by an array of parallel but randomly displaced periodic chains will be. When $\ell = 0$, i.e., in a plane perpendicular to the chain axis c, equation (3) shows that the diffraction intensity is identical to that for a triply periodic crystal. (This is physically understandable because the x-ray scattering in this plane is identical to that of the electron density of the periodically spaced chains projected onto that plane.) Thus, at appropriate angles formed by S and S_0, the first two Laue conditions $(S-S_0)\cdot a = \lambda h$ and $(S-S_0)\cdot b=\lambda k$ can be satisfied to yield sharp reflections in the $hk0$ net of the reciprocal lattice. Their locations are determined by $\sigma_{hk} = ha^*+kb^*$ where the reciprocal-lattice vectors $a^*=b^*$ for the hexagonal case.

When $\ell \neq 0$, the summations in (3) cannot be performed without specifying the values of the chain displacements δ_m. This has the effect of constraining the reciprocal-lattice vector

$$\sigma = [1/\lambda(S-S_0)\cdot X_m]\xi + \ell c^* \qquad (4)$$

where ξ is the vector component of σ in the a^*b^* plane.

The meaning of (4) is that the diffracted intensity is distributed in reciprocal space along planes perpendicular to the chain axes c and spaced $c^*=1/c$ apart. For an ideal set of rigid chains this distribution will appear as shown in Fig. 1. Keeping in mind that real LCP samples are made up of parallel bundles of extended monodomains, the equatorial dots in Fig. 1 actually represent intersections of concentric circles having radii equal to the magnitudes of

$$\sigma_{hk0} = (h^2 + hk + k^2)^{1/2}\, a^* \qquad (5)$$

for a hexagonal closest packing and $a^* = 1.155/a$ while h and k can assume all interger values including zero.

Effect of Packing Imperfections

Because the incident x-ray beam, even when properly monochromatized by prior reflection from a monochromator crystal, has a finite cross section and contains a certain amount of crossfire (divergence), the intensity distributions depicted in Fig. 1 have finite widths. If, moreover, the packing of the parallel chains in an aligned monodomain deviates from a perfect lattice array in the ab plane, an additional displacement correction must be made to R_m in (1). Provided that such deviations are small or directionally random (Gaussian) it is easy to show that the effect produced is quite similar to that of isotropic temperature-diffuse scattering[12] which produces broad maxima about the same reciprocal-lattice sites as those given by equation (4). The appearance of the intensity distribution in reciprocal space should then be more like that shown in Fig. 2.

If the chains (or chain segments) within each domain are not truly parallel (splay), then the resulting diffracted intensity distribution resembles a superposition of distributions like Fig. 2 oscillated about its center (direct-beam trace). In actual x-ray diffraction photographs, the presence (or absence) of arcing in the equatorial ($hk0$) reflections is the best indication of the amount of splay present.

Still other factors can contribute to the broadening of x-ray diffraction maxima. For present purposes, the finiteness of coherent regions, i.e., the maximum values that m_1, m_2, or m_3 attain in equation (2), may be relevant. As is well known, decreasing the coherently diffracting domain size along a, b, or c has the effect of broadening the otherwise sharp intensity distribution along a^*, b^*, or c^*, respectively. It is possible, using theoretical analyses developed for triply-periodic crystals, to estimate the magnitudes of these and possibly other contributions to the broadening of x-ray reflections[†]. For the case of liquid crystalline aggregations, however, the many degrees of positional freedom and the ever present temperature diffuse scattering render such analyses of questionable value. It may be possible to track *relative* changes in one or more parameters under highly controlled conditions. In most cases, however, one has to be satisfied with concluding that a sample is highly crystalline (truly periodic), if the reflections are sharp (Fig. 1), or mesomorphic, if they are broad (Fig. 2).

A final note about the lateral extent of the 00ℓ intensity distributions (Fig. 1). According to equation (4), the values of σ can range from plus to minus infinity. The diffracted intensity, however, is limited by the decline in F^2 which, in turn, falls off with increasing scattering angle because the scattering power of individual atoms declines sharply as $(S-S_0)\cdot(R_m-R_{m'})$ increases. The exponentially declining Debye-Waller (temperature) effect further attenuates the intensity in equation (2) with increasing scattering angle so that one typically observes finite "disks" of intensity passing through the 00ℓ points in reciprocal space.

Internal Interference Effect

The specific effect that the structure factor magnitudes may have on the intensity distribution in reciprocal space can be seen by considering the structure factor expression

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[†] In a related analysis of what effect the coherent domain size may have on the diffraction angle[13] (line position), it turned out that, for polymer molecules $m>4$ was sufficient to eliminate any observable line shifts.

$$\begin{aligned} F &= \sum_n f_n \exp\, (2\pi i/\lambda)(S-S_0)\cdot r_n \\ &= \sum_n f_n \exp\, 2\pi i(hx_n + ky_n + \ell z_n) \end{aligned} \qquad (6)$$

when the three Laue conditions are satisfied. Equation (6) shows that F assumes different values as a function of location in reciprocal space (given by h, k, and ℓ). Recalling that the electron density distribution $\rho(xyz)$ of the molecule is a continuous function of the position vector $r = xa + yb + zc$, the structure factor can be expressed alternatively as a Fourier integral over one unit cell (repeat unit)

$$\begin{aligned} F &= \int\int\int \rho(xyz) \exp\, (2\pi i/\lambda)(S-S_0)\cdot r(xyz)\, dxdydz \\ &= \int\int\int \rho(xyz) \exp\, [2\pi i(hx + ky + \ell z)]\, dxdydz \end{aligned} \qquad (7)$$

when the three Laue conditions are satisfied. This way of expressing $\underset{\sim}{F}$ is more convenient when its value at locations other than the reciprocal-lattice points $hk\ell$ is sought.

As already demonstrated by Mitchell and Windle[14], it is possible to make use of the carefully measured intensity distribution throughout reciprocal space to deduce the molecular 'structure' of a nematic LCP even when the number of x-ray reflections observed is limited. This is done by utilizing the Fourier integral relations between equations (7) and (1) (c.f. Ref. 1). When the external interference effect is more pronounced, as is typical of the relatively ordered packings of rigid-rod chains, then the intensity distribution within the extended meridional 00ℓ reflections is modulated by F^2 but, due to the broadening effects discussed above, it is unlikely that even very careful measurements would permit resolution of individual atomic locations $\underset{\sim}{r}_n$ within a monomer molecule. Nevertheless, as is further illustrated in the two companion papers (Parts B and C of this series), it is possible to make use of the relative intensities of the observed reflections to deduce reasonable molecular packing models. Such attempts have been made for homopolymers[15] and copolymers[14] by others.

Direct Calculations

The above analysis is similar to earlier ones of simple models representative of fibrous materials.[16] Thus Bear and Bolduan[17] considered the scattering of x rays by cylindrical bodies of various shapes having a periodic structure along the cylinder axis c. In reciprocal space, this produced a periodic array of parallel disks spaced 1/c apart whose lateral extent was relatable to the width and shape of the cylinder in direct space. Subsequently, Oster and Riley[18] considered the scattering by a parallel array of infinitely long solid and hollow cylinders. More recently, Adams et al.[19] extended these approaches to the nematic array of polybenzothiazole fibers and showed how it is possible to calculate the equatorial intensity distribution by averaging equation (3) and fitting the calculated values to those measured experimentally. Such curve fitting enables reasonable estimates of the number of individual parallel chains comprising a monodomain but its physical validity is often limited by uncertainties in the magnitudes of F^2 and the ubiquitous temperature effect.

Semiflexible LCP Chains

The introduction of flexible spacers between the rigid (aromatic) units along a polymer chain increases the interaction possibilities between neighboring chains while, concurrently, 'relaxing' the periodicity along a chain axis. Decreasing the long-range periodicity along a chain has the effect of broadening the reflections along c^* in recirprocal space and diminishing the intensity of higher-order reflections as ℓ increases. An immediate consequence of this is that, typically, only one or two diffuse meridional reflections are observed in practice. On the other hand, the observation of similar meridional reflections also in the case of loosely coupled dimer mesomorphs[3] indicates how pronounced the constructive interference effects in equation (2) can be even for the case of relatively short-range order. It should be noted here that aperiodic copolymer chains can yield relatively prominent aperiodically spaced meridional reflections[10,20]. This is so because the trigonometric functions comprising (2) are themselves periodic so that random linear arrays of two (or more) kinds of monomer molecules still produce clearly discernable maxima[21].

The increased relative splay of successive monomer units along a semiflexible LCP chain and their significantly higher degree of rotational freedom, as compared to rigid-rod-like chains, means that their packing should be less regular as well. Thus, typically, only one broad equatorial reflection is observed. This intensity maximum along the equator reflects the fact that the electron densities of the aligned chains, projected onto the xy plane of the irradiated sample, do not conform to a lattice array but do retain a certain interchain separation. The fact that these reflections can be quite broad means that this chain-to-chain separation varies over a range of values so that little physical meaning can be attached to their 'average' value which, moreover, is difficult to measure reliatly. Instead it is proposed that the practice of reporting *the observed range of values as determined by the diffraction angles corresponding to the limits of the peak width at half-maximum intensity* be adopted. This is most probably the true range of actual interchain separations after allowing for thermal and related line broadening effects.

When lateral interactions between the parallel LCP chains are considered, at least two kinds of possible interactions should be distinguished. One is a thermo-chemical interaction between the mesogenic monomer units which, because of the periodic flexible spacers joining them, are more likely to interact with each other than in the absence of such flexibility. As expected, increasing the length of the flexible spacers increases the probability that a smectic layering of the monomers will develop[22]. As is known from x-ray studies of small-molecule liquid crystals[23], the side-to-side ordering in smectic layers can range from lattice-like arrays, giving rise to several sharp equatorial reflections, to a complete absence of such long-range correlations so that only one broad equatorial reflection is observed. Since the electron density distribution within each xy layer does not affect the diffraction intensity (2) when $h=k=0$, as long as it is periodically repeated at right angles to the smectic layers, sharp (crystal-like) reflections will be produced whenever $(S-S_0)\cdot c=\lambda\ell$. Consequently, the intensity distribution should resemble that depicted in Fig. 3. Detailed variations in this distribution for different kinds of smectic arrays have been discussed by several authors already[23].

Another kind of interchain interaction is possible in aligned polymers (but not in small molecules) because their respective monomers are periodically joined along the chain length. When the chains are aligned parallel to each other in monodomains, steric constraints may be imposed by the conformation of individual molecules[24]. For example, when the monomers have attached to them a side group, these side groups may cause a "layering" by limiting the displacements δ along the chain directions [in equation (3)] to specific values only. Alternatively, polar or bonding interactions between certain components of the periodically repeated monomers may similarly cause an effective layering at right angles to the chain axes. Because the chains at right angles to these layers are periodic, the diffraction effects produced by such an array resemble more nearly those typical of 'crystalline' polymers than those of small-molecule mesomorphs. Specifically, in addition to relatively sharp meridional reflections, and broad (or sharp) equatorial reflections like Fig. 3, a number of off-axis reflections appear indicative of three-dimensional correlations (periodicities). The more pronounced such long-range order, the more the intensity distribution resembles that of a rotating single crystal. Interpretation of such fiber diagrams is discussed in a number of texts dealing with x-ray diffraction by polymers[25-27]. When only one or two sets of off-axis reflections are oberved, the order extends over relatively short distances (number of repetitions m) and these reflections in reciprocal space become extended in directions parallel to the foreshortened repetition directions in direct space. When comparing the relative amount (or linear extent) of such short-range ordering, it is recommended that the term *liquid crystallinity* be used to distinguish it from the degree of crystallinity of polymers, by which one means the proportion that is not amorphous. The absence of continuous broad halos in most diffraction photographs of aligned LCPs indicates that considerably less than 10% of the irradiated samples is truly amorphous (isotropic).

CONCLUSIONS

The diffraction of x-rays by thermotropic main-chain polymers differs from that by small-molecule liquid crystals in subtle but characteristic ways. These differences become clearly visible when the chain molecules are aligned in parallel monodomains by external (magnetic or mechanical) stresses. It is possible to recognize the nematic packing of rigid-rod-like chains by the disk-like intensity distributions at periodically spaced 00ℓ reflections along the meridian and by several more or less diffuse reflections along the equator. The spacing of the equatorial reflections corresponds to the two-dimensional packing periodicities of the rigid rods and is most likely to be that of a hexagonal closest packing. As previously shown,[19] it is possible to estimate the approximate size of the coherently scattering monodomains.

Semiflexible thermotropic polymer chains, formed by interposing periodic flexible spacers between the rigid monomers, pack in a looser, less ordered way so that the ordering along the chain and at right angles to it, typically, is of much shorter range. The shorter the range of this order along the chain axes in a nematic array, the broader and less intense the 00ℓ reflections become so that only the first one or two reflections may be readily apparent. Similarly, departures from periodicity in the interchain packings leads to a broadening of the equatorial reflections and a relative diminution of their intensities as well.

It is possible for the monomer units comprising the semiflexible LCP chains to order at right angles to the chain axis. When the flexible spacers allow it, a smectic layering results whose x-ray diffraction effects resemble those of small-molecule mesophases. Alternatively, interchain interactions can produce a short-range ordering unique to LCPs that is manifest by the appearance of off-axial reflections whose relative intensities and orientations can be used to deduce relative molecular dispositions within the aligned monodomains. How this can be done in practice is illustrated in the following two publications.

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Figure Legends

Fig. 1 Intensity distribution in reciprocal space (cross section) for parallel extended periodic chains.

Fig. 2 Effect of small random displacements from ideal lattice sites on intensity distribution shown in Fig. 1.

Fig. 3 Intensity distribution for smectic-A ordering of a semiflexible LCP.

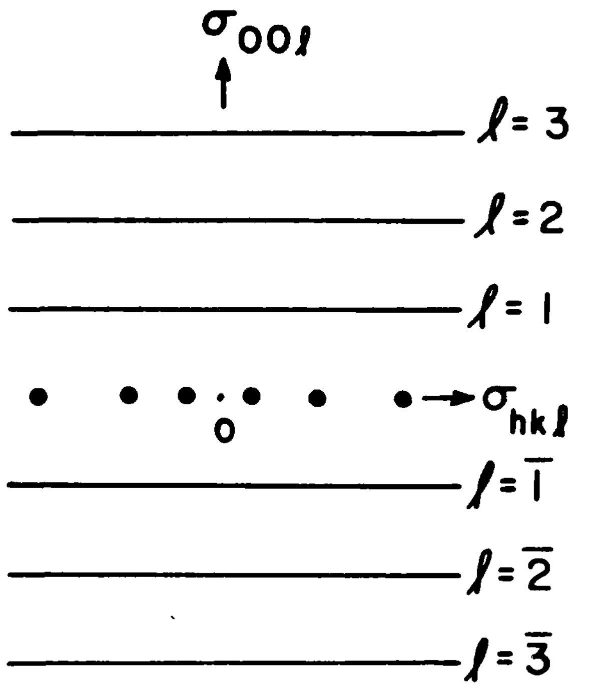
$\sigma_{00\ell}$
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Fig. 1

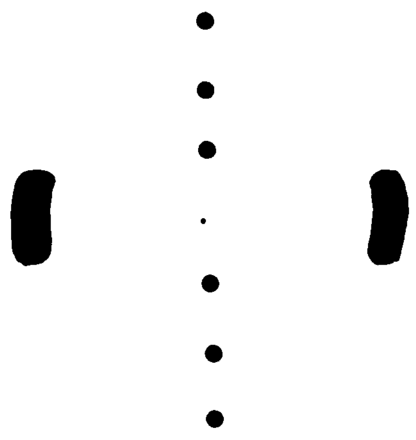

Fig. 3

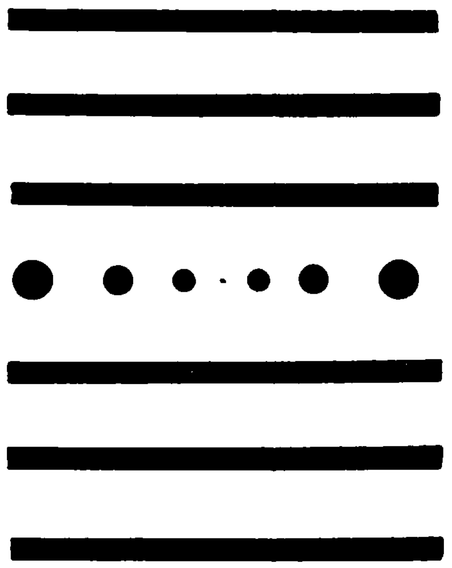

Fig. 2

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