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Three-Dimensional Order in Magnetically Oriented Poly(γ-benzyl L-glutamate) Films

Orientation of rodlike polymers using strong magnetic fields has been investigated for quite some time.[1-8] The diamagnetic anisotropy of such polymers is small, and as a consequence the magnetic orientational energy is not sufficient to orient individual molecules. However, if the molecules aggregate into an ordered array (e.g., virus particles[5,6] or fibrils[7,8]) or form an ordered fluid phase (liquid crystalline phase[1-3]), the diamagnetic anisotropy is enhanced considerably and highly oriented films can be easily obtained with magnetic fields of strength 0.2–2 T. Oriented DNA-containing bacteriophage was obtained by suspending a 2% solution of the virus over a 2-mm gap formed between horizontal glass rods: a magnetic field was used to enhance the uniaxial orientation induced mechanically by the glass rods during the slow evaporation of the solvent.[5,6] Experiments with oriented fibrin gels[7] obtained by polymerization in a magnetic field have shown that although the fibrin monomers (length 450 Å) are arranged in a crystalline lattice within a fiber (diameter ca. 1000 Å), the gel (network of fibers) as such is rotationally symmetrical about the molecular axis (direction of the magnetic field) with little long-range rotational order between the fibers. In the optical microscopy work reported on magnetically oriented collagen reconstituted from rat tail tendon,[8] no effort was made to determine the presence or absence of rotational symmetry around the orientation direction.

In one of the earliest works on magnetic orientation of polymers,[2] it was concluded that α-helical poly(γ-benzyl L-glutamate) (PBLG) films exhibit uniaxial orientation similar to mechanically oriented[9] polypeptide fibers. We now show that magnetically oriented PBLG has a symmetry higher than that of uniaxially oriented fibers. Unlike fibrin gels[7], the magnetically oriented PBLG film is not rotationally symmetric but possesses three-dimensional order extending over the entire film (0.5 cm × 1 cm and 0.1–0.5 mm thick) to a resolution of at least 2.6 Å.

Homogeneous solid films of high molecular weight PBLG (Sigma Chemical Co., stock no. P-5136, lot 074F5082, MW $\simeq$ 150 000–300 000) were prepared by slowly evaporating solutions of PBLG in CH_2Cl_2 over a period of ~24 h. Oriented films (thickness of 0.1–0.5 mm) were obtained when the solutions were evaporated in a 2-T magnetic field with the field direction parallel to the casting surface. A control film was made under similar conditions but in the absence of a magnetic field. A second control specimen was prepared by drawing a fiber from a concentrated solution of PBLG in CH_2Cl_2. X-ray diffraction (XRD) photographs were obtained at room temperature on a flat film by using a Unicam camera or a Supper precession camera with Ni-filtered Cu radiation (sample-to-film distance of 6.0 cm).

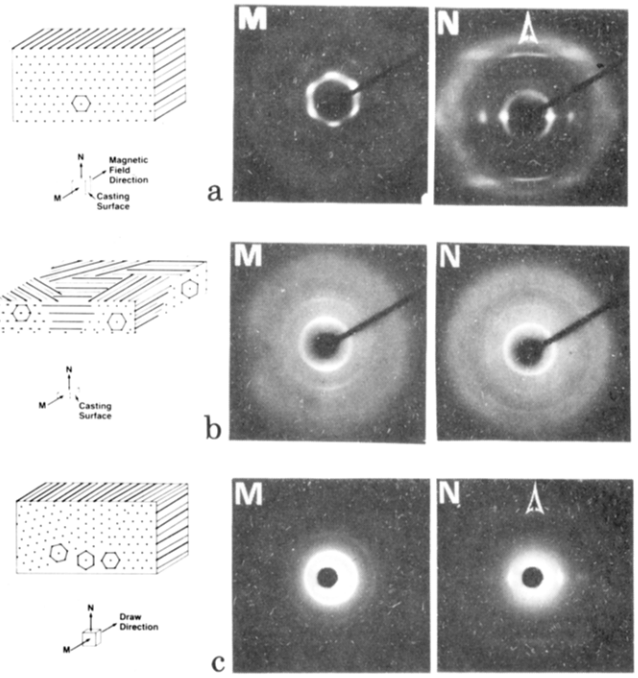

Figure 1. X-ray diffraction photographs of poly(γ-benzyl L-glutamate) (PBLG) samples. Such patterns can be indexed on a hexagonal lattice of side 14.8 Å. (a) Magnetically oriented film; (b) film prepared in the absence of a magnetic field but otherwise under conditions similar to those in (a); (c) fiber drawn from a concentrated PBLG solution. Left-hand side photographs, labeled M, were obtained with the film horizontal and with X-rays along the "machine" direction (respectively, direction of the field in (a), a direction parallel to the surface of the film in (b), and the direction of drawing in (c)). Right-hand side photographs, labeled N, were obtained with the film vertical and with X-rays normal to the surface of the film ((a) and (b)) or to the draw direction (c). The orientation of the sample with respect to the X-ray beam for the M and N photographs is illustrated next to each set of photographs. The direction of the magnetic field or drawining is also shown in these diagrams as well as in (a) and (c). The photographs of the magnetically oriented film obtained with X-rays perpendicular to the direction of the field and to the film normal are similar to the N photograph of (a). This similarity arises from the overlapping of the equatorial reflections.[10] (a) Shows three-dimensional order up to 2.6-Å resolution, (b) shows planar order with the crystallites of PBLG molecules randomly oriented in the plane of the film, and (c) shows uniaxial orientation with PBLG molecules oriented along the draw direction. These three states of order are schematically shown adjacent to each of the figures.

Figure 1a shows typical XRD photographs obtained with X-rays along the direction of the magnetic field (M direction) and along the normal to the casting surface (N direction).[14] For comparison, photographs from films made under identical conditions but with no magnetic field are shown in Figure 1b, and photographs of a fiber drawn from a concentrated solution are given in Figure 1c. In the absence of the field, there is no preferred orientation within the plane of the film (Figure 1b,N). While the N photograph of the magnetically oriented film (Figure 1a,N) shows a diffraction pattern similar to that of a uniaxially drawn fiber (Figure 1c,N), the M photograph (Figure 1a,M) shows a hexagonal array of reciprocal lattice points when one looks down the chain axis, i.e., the direction of the magnetic field. This hexagonal pattern persists up to a Bragg spacing of at least 2.6 Å, and the pattern from any region of the 0.5 cm × 1 cm magnetically oriented film appears in this same orientation. This indicates that the rotational disorder of the mosaic blocks common to cast films (Figure 1b,N) and uniaxially drawn fibers (Figure 1c,M) is absent and that in magnetically oriented PBLG films the crystalline domains or mosaic blocks show

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long-range register. Since these correlations exist over the entire sample, the magnetically oriented film can be regarded as a somewhat disordered macroscopic single crystal.

Although the magnetically oriented PBLG film possesses substantial three-dimensional order over the entire sample, the size of the mosaic blocks is small, being 220 Å perpendicular to the chain axis (from the width of the (110) reflection at 13 Å) and 110 Å along the chain axis (from the (0,0,43) reflection at 1.5 Å, indices based on the unit of Squire and Elliott;[10] *c*-chain axis). The corresponding values for the drawn fiber are 175 and 145 Å. The molecules within a mosaic block always possess three-dimensional order, whether or not there is a magnetic field. Therefore, we conclude that the mosaic blocks formed during the final stages of solvent evaporation from the magnetically oriented PBLG liquid crystal carry over into the solid film the long-range hexagonal order found in the precursor ordered fluid phase. In these polypeptide liquid crystals (10%–40% polymer), presumably the PBLG helices are molecularly dispersed with the helix axes approximately parallel to each other locally, even in the absence of a magnetic field. (The polymer solution in the bulk is cholesteric. The cholesteric pitch, as measured by the spacing of the retardation lines, is large and varies from 2 to 100 μm.[11] However, on a scale of few hundred angstroms, the local order in the PBLG liquid crystal is virtually nematic.[12]) This parallelism in solution defines a local nematic director which, due to the enhanced diamagnetic anisotropy of a domain of mutually oriented helices, aligns itself along the direction of the magnetic field. Thus, in a magnetic field, bulk cholesteric texture is destroyed (untwisted), and the whole solution shows nematic ordering. The resulting macroscopically oriented liquid crystal is still a fluid[3] in which the PBLG rods can exhibit facile self-diffusion parallel to the director (field). As the solvent is evaporated in the presence of the field, the nascent hexagonal packing present in the fluid liquid crystal (ref 13 and our unpublished results) improves. We speculate that above some limiting polymer concentration, crystalline aggregates (mosaic blocks) are formed. Within such a mosaic block there is extensive three-dimensional order. More importantly, because the mosaic blocks coalesce from the homogeneously oriented liquid crystal, there results substantial interblock alignment, giving rise to an apparent three-dimensional order over the entire sample.

The above argument differs from the mechanism proposed to explain the orientation of fibrin[7] and collagen[8] gels. In PBLG we have evidence[3] for the orientation of an ordered fluid (liquid crystal), with the nematic director parallel to the magnetic field, prior to the formation of mosaic blocks. In the case of fibrin and collagen, it was proposed[7,8] that aggregates are first formed; these aggregates, due to their enhanced diamagnetic anisotropy, independently align themselves with respect to the magnetic field (fibrin parallel to the field[7] and collagen perpendicular to the field[4,8]) during crystallization. It is likely that interactions between such aggregates are weak; hence, even magnetically oriented specimens have rotational disorder. Thus, in magnetically orientable materials, if the mosaic blocks independently align themselves in the field, then one obtains only a uniaxially oriented (rotationally symmetric) specimen; however, rotationally correlated mosaic blocks are formed from a magnetically oriented polypeptide liquid crystal to yeild a specimen which bears resemblance to a macroscopic single crystal.

We might speculate whether such single crystals can be obtained from other polymers and proteins. The existence of a liquid crystalline phase with sufficient positive diamagnetic anisotropy appears to be the primary requirement. Rod- or disklike synthetic macromolecules, virus particles, and proteins with high aspect ratios may be suitable candidates for producing "single crystals" using a magnetic field.

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(14) In these magnetically oriented films, the sides of the hexagonal crystal lattice are always parallel to the casting surface (mercury–polymer interface). This is probably due to the favorable interaction between the aromatic side chains and the surface of the mercury. In one experiment in which the film was cast with the polymer–air interface both at the top and at the bottom of the film, we found that the corners of the hexagonal lattice were on the air–polymer interface. The lateral spacing per PBLG molecule at the interface was 14.8 Å when the film was in contact with mercury and was 25.6 Å when the mercury–polymer contact was missing.

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