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Sin-Doo Lee; R. B. Meyer[a]
[a] The Martin Fisher School of Physics, Brandeis University, Waltham, Massachusetts, U.S.A.

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PRELIMINARY COMMUNICATION

The growth of highly ordered textures in planar poly(γ-benzyl glutamate) liquid crystals

by SIN-DOO LEE†
Bellcore, 331 Newman Springs Road, Red Bank, New Jersey 07701, U.S.A.
and R. B. MEYER
The Martin Fisher School of Physics, Brandeis University, Waltham, Massachusetts 02254, U.S.A.

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We have observed the growth of highly ordered textures in homogeneously aligned poly(γ-benzyl-glutamate) (PBG) liquid crystals as the polymer concentration increases. The textures are similar to the hexagonal columnar textures exhibited by recent studies on highly concentrated solutions of helical biological polymers. In a geometry of homeotropic alignment, no evidence of such texture growth was seen, which is probably due to strong binding interactions between PBG polymers and the substrates.

Concentrated solutions of long, rigid or semi-rigid polymers may exhibit a series of liquid-crystalline phases between a conventional liquid and a crystalline solid. Study of these phases provides us with fundamental knowledge about novel structural phase transitions and relevant intermolecular interactions in condensed matter systems. It has recently been reported that concentrated aqueous solutions of helical biopolymers such as DNA form multiple liquid-crystalline phases [1-3] with variation in the polymer concentration, temperature, and method of sample preparation. Of particular interest is the existence of a columnar longitudinal order and a hexagonal lateral order in highly concentrated DNA solutions, confirmed by freeze-fracture structures and X-ray diffraction [3].

We report in this communication the preliminary observation of the growth of highly ordered textures in a homogeneously aligned polymer liquid crystal, formed from a solution of poly(γ-benzyl-glutamate) (PBG) in mixed organic solvents, as the PBG concentration increases by slowly evaporating the solvents. PBG is one of the most extensively studied class of synthetic polypeptides due to its ready availability and good solubility properties [4-7]. The nematic solution was prepared by dissolving freeze-dried PBG with 50-50 weight ratio of PBLG ($8{\cdot}5 \times 10^4$) and PBDG ($15{\cdot}0 \times 10^4$), purchased from Sigma Co., in a solvent mixture composed of 18 per cent dioxane and 82 per cent dichloromethane to suppress the cholesteric helicity. The initial volume fraction of PBG nematic solution was approximately 0·29 determined by taking the specific volume of PBG as 0·791 ml/g [8] and the density of the mixed

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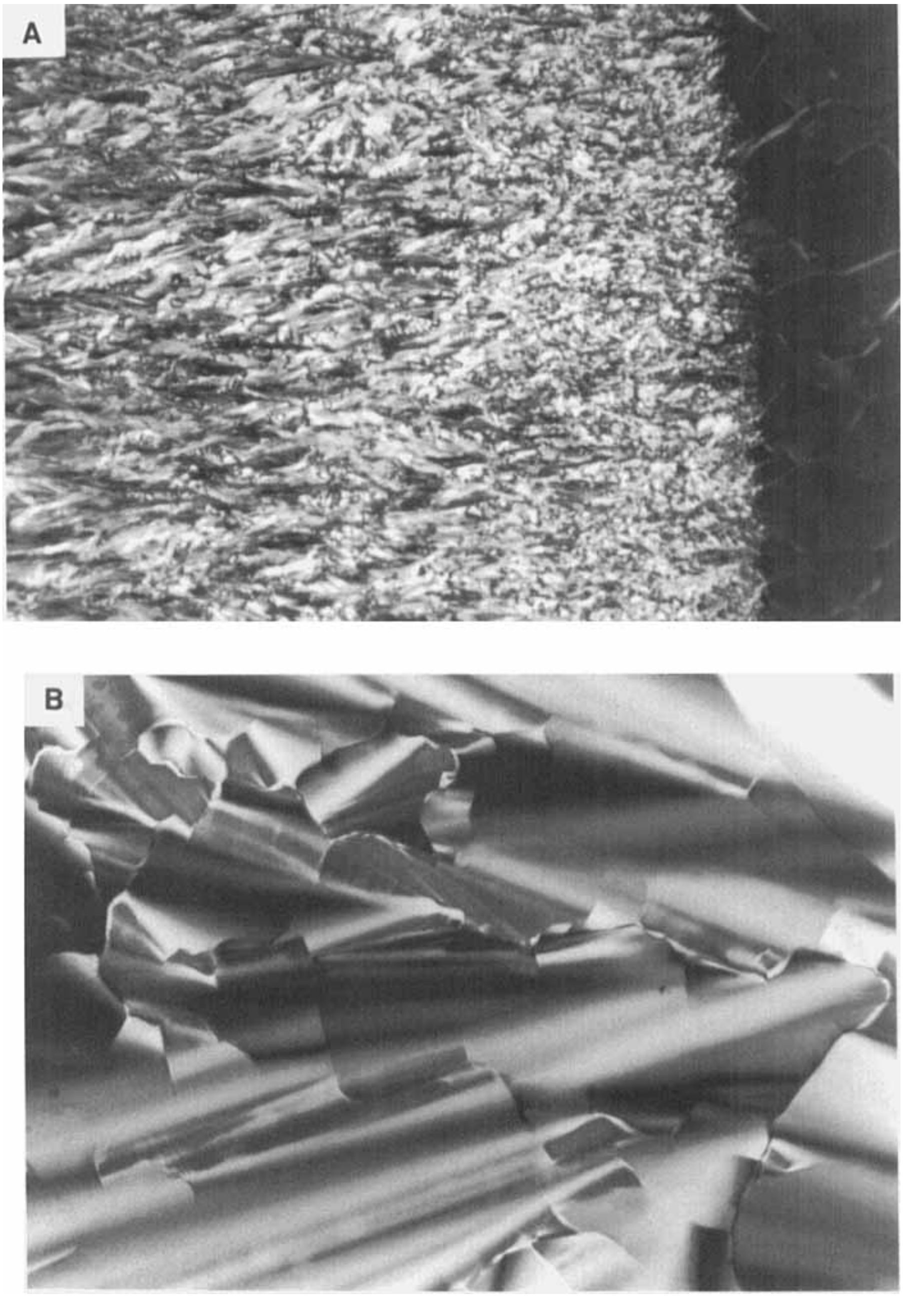
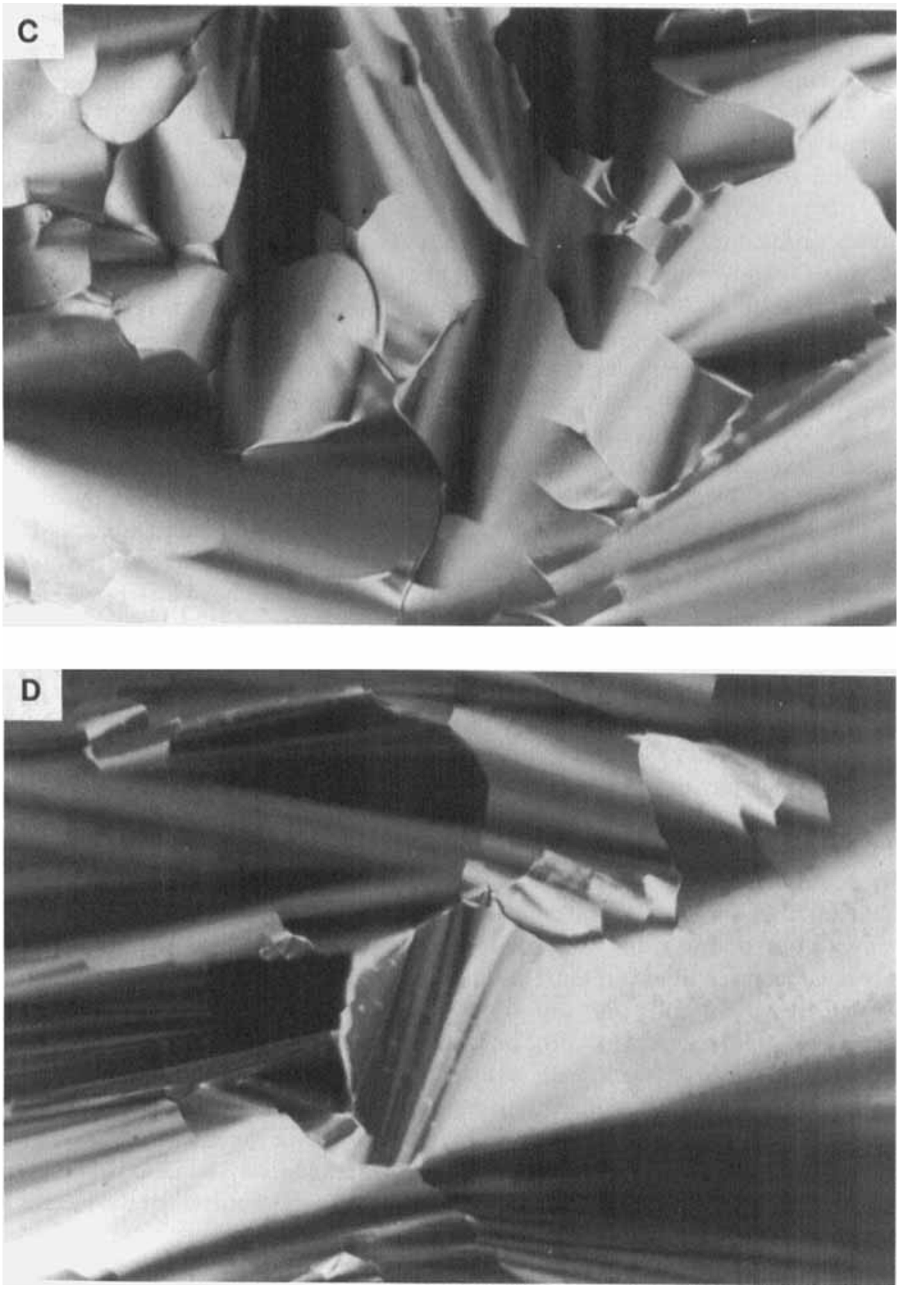
† Work done while at Brandeis University.



Photographs, taken between crossed polarizers, of the growth of highly ordered textures of PBG. (A) The ordered textures grew in a homogeneously aligned region but not in a region of homeotropic alignment (dark area) as the concentration was progressively increased by slow evaporation of the solvents (×40). (B) (×100), (C) (×100), (D) (×200); the structures formed a homogeneous phase. Most of the domains articulate around disclination lines.



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solvent at 1·28 g/ml. We first produced well-oriented PBG nematic samples, typically 50 μm thick, with planar as well as homeotropic alignments on the treated substrates. The solvents were then slowly evaporated from the nematic sample, assembled in an aluminium press with four screws, by transport between a teflon spacer and the substrate surface at room temperature. For long molecules, the nematic director tends to lie parallel to a substrate because condensation of many chain ends at the surface costs a great deal of entropy. For PBG, however, the previous experiments suggest that all of the standard procedures for producing planar alignment, that proved successful in low-molecular weight liquid crystals, have yielded only the homeotropic alignment [9, 10]. The detailed procedure for the planar alignment of PBG has been described elsewhere [11].

Several PBG samples composed of different molecular weights (6·6, 8·5, and $16{\cdot}5 \times 10^4$) of PBLG which we investigated produced the same results for the growth of highly ordered textures at high concentrations. A typical example of the growth of the textures is shown in the figure (A)–(D), photographs taken between crossed polarizers. For this sample ($8{\cdot}5 \times 10^4$ of PBLG) the volume fraction for the formation of the ordered phase was approximately 0·36, estimated from the solvent loss for 4 weeks. At the early stage, a number of microdomains began to appear in a homogeneously aligned region as the concentration was progressively increased by slow evaporation of the solvents. On the other hand, a homeotropic region exhibited only multiply connected domains due to the variation in the helical pitch as a function of concentration, and no further growth was observed. The fully developed, highly ordered textures resemble those of the hexagonal columnar phase observed in aqueous DNA solutions at high concentrations [3]. The birefringence became stronger as the ordered textures gradually grew. Note that the observed fan textures have a stepped appearance. Although more definite structural data such as diffraction patterns are needed, based on the microscopic observations, we speculate that the highly ordered textures grown in our PBG samples manifest the characteristics of the hexagonal columnar phase. Since the columnar phase has long-range ordering of the molecules in the three dimensions, the layers will not be easily curved or bent. Thus, in the fan domains of this phase, the conic sections become angled, and exhibit stepping patterns across the backs and along the edges of the fans, as shown in figure (B).

In helical PBLG solutions, previous studies [2] showed that the hexagonal patterns, dissimilar to those grown in our planar samples, sometimes nucleate in a homeotropic region near the interface with the isotropic phase. The results were in contrast to our studies where no such texture growth was realized in a homeotropic area of the racemic PBG samples. This is probably due to strong binding interactions between PBG chain ends and our substrates, which results in good homeotropic alignment. Also, in racemic PBG the benzene rings at the end of the side chains prefer to form a cooperative stack with a face-to-face arrangement between D and L molecules [12]. It might be noted that the degree of the cholesteric helicity and the strength of the surface anchorage play a significant role in the growth process of the structural order, particularly the columnar-like order. More systematic studies, however, would be required to establish the detailed growth mechanism for the hexagonal columnar-like textures in PBG liquid crystals.

Recent experimental works on PBLG solid films indicated that a three dimensional order can be induced by either slowly casting films from solutions in various solvents [13] or orienting solutions by the application of a strong magnetic field during the slow evaporation of the solvents [14]. The magnetically oriented PBLG films were found to possess the long-range hexagonal order revealed by the precursor ordered fluid phase [13]. In addition, during the solvent evaporation, the nascent hexagonal packing of PBLG present in the fluid phase was substantially improved in the presence of the magnetic field [4, 14]. In some of our PBG sample cells dissembled, we checked that the PBG samples, showing the highly ordered textures, were still in the liquid-crystalline state. In the light of the above arguments, the treated substrates, which produced well-oriented homogeneous alignment, probably facilitate and enhance the formation of highly ordered, hexagonal columnar-like textures of PBG as in the case of the applied magnetic field.

In conclusion, we observed the growth of highly ordered, columnar-like textures in well-oriented planar PBG liquid crystals at high concentrations. It might be interesting to study the effect of chain flexibility, in terms of the variation in temperature or molecular weight, on the growth of novel structural orders in polymer liquid crystals since the high degree of the flexibility may destroy the layered order, i.e. the smectic-like or the columnar-like order even at high concentrations.

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