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Electrically Oriented X-ray Diffraction Patterns of Liquid Crystalline Solutions of Poly-γ-Benzyl-L-Glutamate

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Electrically Oriented X-ray Diffraction Patterns of Liquid Crystalline Solutions of Poly-γ-Benzyl-L-Glutamate

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Abstract—Oriented X-ray diffraction patterns of liquid crystalline solutions of Poly-γ-benzyl-L-glutamate formed with *m*-cresol and *p*-dioxane were produced by applying constant electric fields. The patterns confirm electrically induced molecular orientation and are essentially identical to shear oriented solution patterns. The patterns indicate that the polypeptide maintains its α-helical conformation while oriented under an electric field.

1. Introduction

In a recent article, Toth and Tobolsky(1) indicated that concentrated solutions of Poly-γ-benzyl-L-glutamate (PBLG) oriented under the influence of an electric field. It was suggested that the electric field induced a phase transformation from a cholesteric mesophase to either an aligned smectic phase or an aligned nematic phase. Their conclusions were based upon optical transmission and optical birefringence observations. However, interpretation of optical transmission data with regard to molecular orientation becomes more difficult in light of work by Gregson *et al.*(2) which indicates that PBLG aggregates in solution. As a result, the solution may consist of liquid crystalline aggregates under the influence of an electric field as opposed to a uniform phase. This may complicate transmission data with optical diffraction effects.

Parry and Elliott(3) have produced oriented X-ray diffraction patterns using shear forces to induce orientation. These patterns strongly suggest that PBLG exists as an α-helix in concentrated *m*-cresol solutions.

As a logical extension of that work, preliminary study in this laboratory has been directed toward obtaining oriented diffraction patterns of concentrated PBLG solutions produced by a constant electric field. Such an experiment has two objectives. First, the patterns would verify molecular orientation induced by constant electric fields. Second, the patterns would detect any major conformational changes between shear oriented molecules and electrically oriented molecules.

2. Experimental

For this study, PBLG was obtained from New England Nuclear Co., Pilot Chemicals Division (lot #G-152). The polypeptide had a molecular weight of 310,000.

The solutions were contained between two thin glass disks, 1 in. in diameter and 0.076 mm thick. The disks were separated by a 1.6 mm thick teflon spacer. The assembly was placed inside a cylindrical teflon tube and pressure sealed with threaded teflon rings which were inserted on either side of the glass windows. Electric fields were applied via two parallel platinum wires suspended in the solution at a 1 cm separation. The X-ray beam passed through the solution along the teflon tube axis so that it was perpendicular to the glass disks and the electric field.

All diffraction photographs were taken with a Picker X-ray unit using a 0.5 mm pinhole collimated beam. Cu Kα radiation was obtained using a Ni filter. A flat plate camera was used at a sample to film distance of 10 cm.

3. Results and Discussion

Figure 1(a) is a control X-ray photograph of *m*-cresol at room temperature under a potential difference of 300 V applied over 1 cm. Three diffuse halos at 38.5A, 11.2A, and 4.9A were recorded (measurements were made at the center of the halos' widths except for the 38.5A halo in which the outer edge was measured).

Figure 1(b) is an X-ray photograph of a concentrated solution of *m*-cresol and PBLG (0.240 g PBLG/g of solution). No electric field was applied. Two changes were observed. First, diffuse scattering

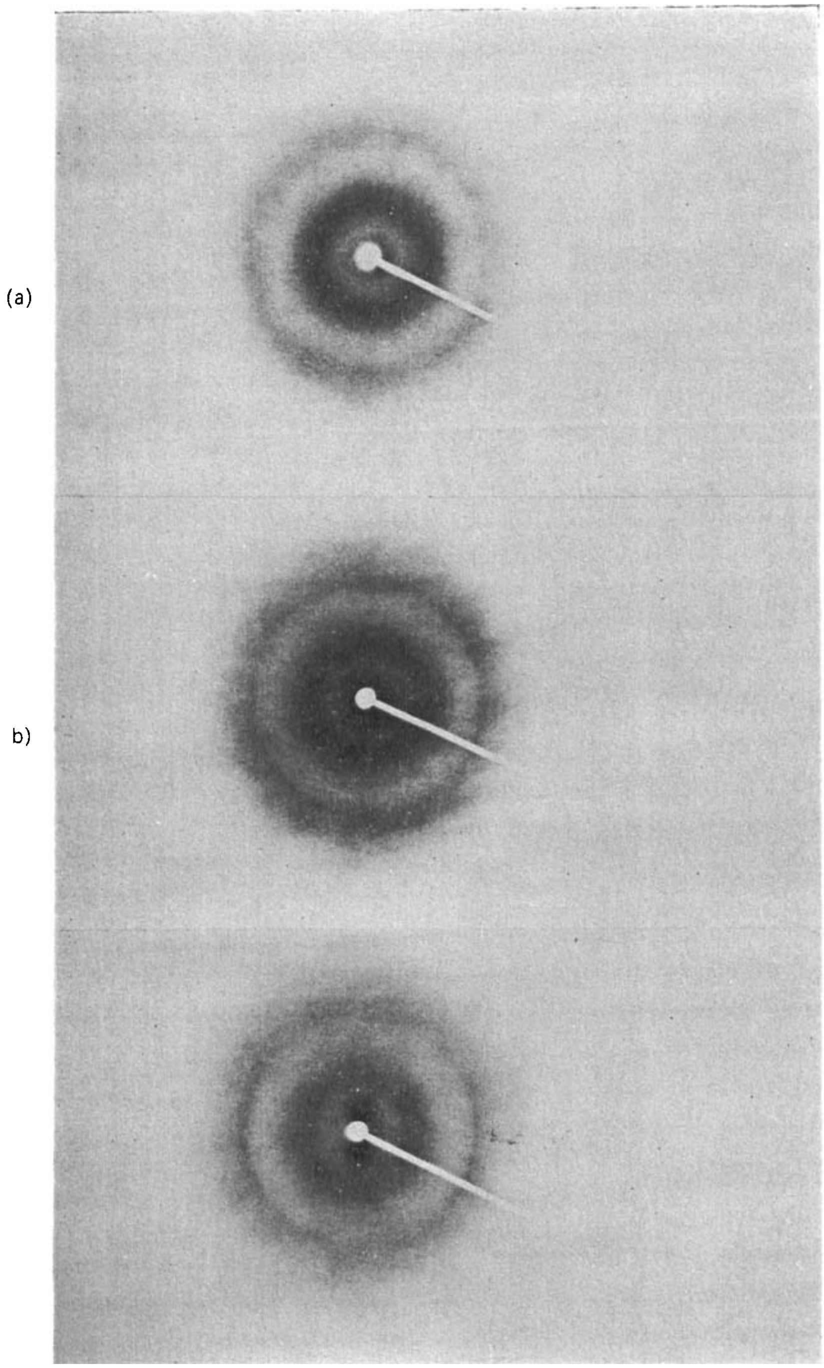

Figure 1. (a) *m*-cresol under 300 V over 1 cm. (b) PBLG + *m*-cresol under no electric field. (c) PBLG + *m*-cresol under 300 V over 1 cm.

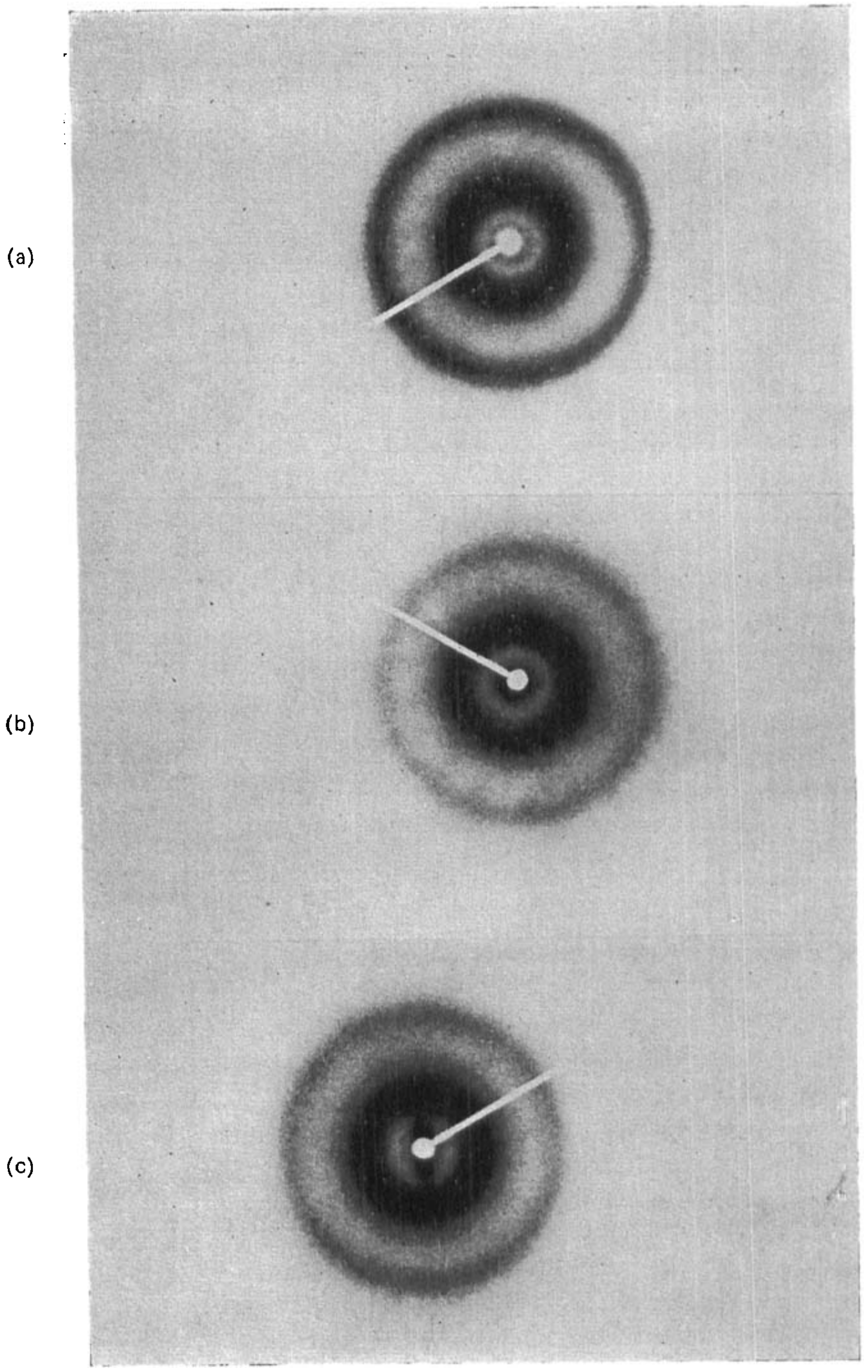

Figure 2. (a) p-dioxane under 500 V over 1 cm. (b) PBLG + p-dioxane under no electric field. (c) PBLG + p-dioxane under 3000 V over 1 cm. Reduced $\frac{1}{2}$ times.

about the origin has increased. The outer edge of this halo now corresponds to a Bragg spacing of 22.1A. Second, the outer solvent halo has sharply terminated on the inside edge at 5.24A.

Figure 1(c) is an X-ray photograph of the same solution under a potential difference of 300 V over 1 cm. Orientation is indicated by an equatorial streak terminating at 20.8A and the meridional arc at 5.24A. Assuming that PBLG has maintained its α-helical conformation, the meridional arc indicates that the molecular axis is parallel to the electric field.

Initial studies have also been performed with solutions of PBLG and *p*-dioxane. Figure 2(a) is a control X-ray photograph of *p*-dioxane under a potential difference of 500 V over 1 cm. Again three halos appear at 38.5A, 17.5A, and 4.46A (measurements were made, as before, at the center of the halos' widths except for the 38.5A halo in which the outer edge was measured). The 17.5A halo has some structure (possibly a series of rings).

Figure 2(b) is an X-ray photograph of the concentrated solution of PBLG with *p*-dioxane (0.297 g of PBLG/g of solution). No electric field was applied. Diffuse scattering has increased at the origin. The outer edge of this halo now corresponds to a Bragg spacing of 24.1A.

Figure 2(c) is an X-ray photograph of the same solution under a potential difference of 3000 V over 1 cm. The only observable change is the presence of an equatorial streak terminating at 22.1A.

Further work has indicated that orientation initiates at a concentration of 10% by weight in both solvents. The patterns undergo little change until the concentration exceeds 30% by weight. At this point, the equatorial streak begins to separate into a streak plus a discrete spot.

Orientation initiates in 29% by weight solutions with *m*-cresol between 100 and 125 V over 1 cm. For 20% by weight solutions with *p*-dioxane orientation initiates between 2000 V and 3000 V over 1 cm. Additional changes in the patterns have not been produced by applying higher electric fields.

4. Conclusion

The results show that molecular orientation is induced by constant electric fields in concentrated solutions of PBLG formed with *p*-

dioxane or *m*-cresol. The X-ray patterns for *m*-cresol solutions do not differ appreciably from those produced by Parry and Elliott.(3) These patterns have already been interpreted as showing an α-helical conformation.(3,4)

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