

Electric Birefringence of Poly(γ -benzyl-L-glutamate) in Ethylene Dichloride

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Robinson was the first to report that a poly(γ -benzyl-L-glutamate)(PBLG) solution in solvents such as chloroform, methylene chloride, dioxane, etc., undergoes a lyotropic phase change from isotropic to liquid-crystalline (cholesteric) phase with increasing concentration.^{1,2} Since then, the liquid-crystalline nature of concentrated solutions of PBLG has attracted great attention. The concentration region of the phase change was reported to be dependent on both temperature and molecular weight.² It has been found that PBLG molecules in liquid-crystalline solution orient in the direction of an external field when placed in a magnetic and/or electric field, as shown by NMR, X-ray, and IR dichroism.³⁻⁹ Electric birefringence measurements for the liquid-crystalline solution of PBLG were reported by Iizuka.⁶ On the other hand, electric birefringence studies of the dilute solution of PBLG have been reported by many authors.¹⁰⁻¹⁵ The electric birefringence measurement is thought to be very useful for examining the lyotropic phase change, since the electric birefringence will depend on the molecular association. In this work the electric birefringence measurements were carried out for a PBLG solution in ethylene dichloride (EDC) in a concentration range from 0 to 9 g/100 ml, in order to examine the lyotropic phase change.

The PBLG used was synthesized from the *N*-carboxyanhydride in dioxane, using triethylamine as an initiator. The molecular weight of the

polymer was 145000, as estimated from the measured intrinsic viscosity in dimethylformamide.¹⁶

Ethylene dichloride was washed with pure water after treating with a 50-% aqueous KOH solution, dried over CaCl₂, and then fractionally distilled.

The apparatus for birefringence measurements consisted of two nicol prisms, a $\lambda/4$ plate, a Kerr cell, a 4370-Å mercury-arc-lamp light source, a photomultiplier tube, and an amplifier. Chauvin's method was used to detect retardation δ . A glass cell for spectrophotometry (Takahashi Giken Glass Works Co., Ltd.) was used as the Kerr cell, with an optical-path length of 1 cm. The parallel-plate electrodes, 0.06 \times 9 \times 4.5 mm, made of stainless steel, were placed 6 mm apart in the cell. A voltage ranging from 0 to 2500 V was applied across the electrodes by means of a variable voltage supply. The temperature of solution was regulated at 22°C by circulating water around the cell.

The Kerr constants B were obtained from Kerr's equation by plotting values of δ vs. E^2

$$B = \delta / 2\pi l E^2$$

where the path length l is in centimeters and the applied field E is in statvolts/centimeter. The plots were linear up to the highest value of applied field, 5000 V/cm, indicating that no saturation occurs.

Figure 1 shows the specific Kerr constant B/c plotted vs. concentration. At low concentra-

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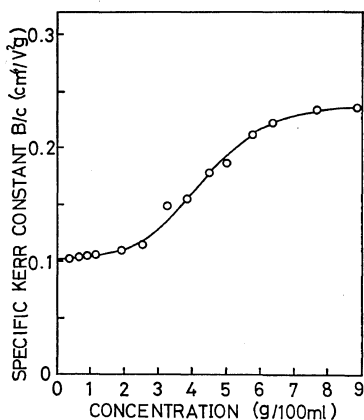


Figure 1. The specific Kerr constant B/c vs. concentration for poly(γ -benzyl-L-glutamate) in ethylene dichloride.

tions, the specific Kerr constant increases very gradually with increasing concentration. The intrinsic specific Kerr constant [B/c] extrapolated to zero concentration¹⁵ was $0.10 \text{ cm}^4/\text{V}^2\text{g}$. In the concentration range of 3–6 g/100 ml the specific Kerr constant shows a drastic increase with increasing concentration. At higher concentrations B/c was again found to increase gradually. Extrapolation of B/c to zero concentration from a higher-concentration region gives a much larger intrinsic specific Kerr constant of $0.20 \text{ cm}^4/\text{V}^2\text{g}$.

Measurements at much higher concentrations were impossible because of the intense light scattered from the solution. Observation through a polarizing microscope of solutions at concentrations above 9 g/100 ml shows that these solutions are in the liquid-crystalline phase. Therefore, the observed change in the specific Kerr constant is likely to be due to the lyotropic phase change.

Robinson, *et al.*,² reported the molecular weight dependence of the A point (the concentration above which the birefringent phase can exist) and the B point (the highest concentration at which the isotropic phase can exist). They also stated that A and B have much the same values for the solvents: dioxane, methylene

chloride, and probably chloroform, *m*-cresol, and dichloroacetic acid. A and B for the polymer used here are estimated to be 9–15 g/100 ml from Figures 2 and 3 in ref 2. This concentration region is much higher than the 3–6 g/100 ml region observed in the present work. This may suggest that the A and B points depend on solvent. Detailed investigations are still required to establish this point.

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