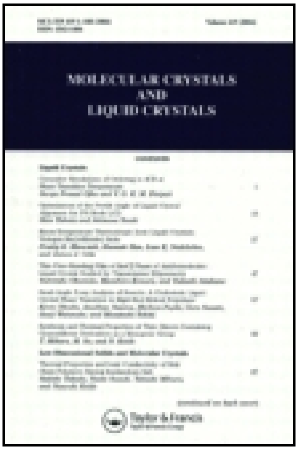

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E. T. Samulski [a] & A. V. Tobolsky [b]
[a] Department of Chemistry, Princeton University
[b] Textile Research Institute, Princeton, New Jersey

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The Liquid Crystal Phase of Poly-γ-benzyl-L-glutamate in Solution and in the Solid State

E. T. SAMULSKI and A. V. TOBOLSKY

Department of Chemistry,
Princeton University
and
Textile Research Institute,
Princeton, New Jersey

Abstract—Concentrated solutions and solid films of Poly-γ-benzyl-L-glutamate have been examined using proton magnetic resonance, X-ray diffraction and optical microscopy. The unusual findings can be correlated with the cholesteric-like liquid crystal phase known to exist in concentrated solutions of this polypeptide.

Introduction

Poly-γ-benzyl-L-glutamate (PBLG) assumes an α-helical molecular conformation in a number of solvents. In sufficiently concentrated solutions the rigid, rodlike molecules form ordered domains or cybotactic clusters. Robinson and coworkers have extensively characterized the structure of this ordered phase and have found it to be similar in many respects to the liquid crystal phase formed by derivatives of cholesterol.[1–5] The structure in the liquid crystal phase of PBLG may be described in the following manner. In any given volume element or domain, the helical axes of the molecules are essentially parallel. In such a domain it is possible to visualize a set of equi-spaced parallel planes in which the helical axes lie. The optically active molecular conformation causes molecules in a given plane to have a slight twist relative to those in adjacent planes about an axis of torsion perpendicular to the set of planes. The incorporation of successive layers of appropriately oriented molecules results in a helicoidal supramolecular structure. The texture axis (axis of torsion) adopts all orientations throughout the macroscopic fluid and the change in orientation of this axis from one region to another occurs in a continuous fashion. The observed high optical rotatory power and microscopically visible periodicities (retardation lines) are consistent with this helicoidal structure.

We wish to report on unusual manifestations of the liquid crystalline structure in concentrated PBLG solutions and in solid films, plasticized and unplasticized, using proton magnetic resonance, X-ray diffraction and optical microscopy.

1. PMR Spectra in Fluid PBLG Solutions

The formation of an ordered phase in solutions of rodlike molecules has been discussed theoretically and investigated experimentally. Flory,[6] using a statistical mechanical treatment of the lattice model for polymer solutions, has shown that the volume fraction of rod-like molecules at which the formation of an ordered phase occurs is a function of the axial ratio of the molecules. Robinson has studied the phase transitions in PBLG solutions as a function of axial ratio (molecular weight) in several helicogenic solvents by observing the formation of the spontaneously birefrigent liquid crystal phase with a polarizing microscope. We have observed that the phase changes in PBLG solutions are reflected in the p.m.r. spectra of the solvent. Table 1 summarizes our findings and gives a comparison with the optical observations for a sample of the same axial ratio.

The p.m.r. spectrum of dichloromethane consists of a single sharp absorption in ordinary isotropic solvents. In the PBLG–CH_2Cl_2 solutions, the normally observed singlet broadens and changes to a doublet as the concentration of PBLG is raised. Above a limiting concentration (12% for this molecular weight PBLG), the liquid crystal phase exists throughout the entire sample and can be oriented by the spectrometer magnetic field. The rotational motion of the CH_2Cl_2 molecules is restricted in this

TABLE 1 Solution of PBLG in Dichloromethane‡

% PBLG (vol.)	0–8%	8–12%	12%
Optical Measurements[3]	isotropic solution	two phases	liquid crystalline
nmr absorption signal of CH_2Cl_2§	singlet	broadening	doublet

‡ PBLG mol. wt. 275,000 Pilot Chemical Company.
§ sample tube stationary in spectrometer.

oriented liquid crystal matrix hence the direct dipolar interactions within the CH_2Cl_2 molecules are no longer averaged to zero. The appearance of the doublet in the liquid crystal phase of PBLG is a result of intramolecular direct dipole–dipole coupling between the CH_2Cl_2 protons. A recent review of this phenomenon using thermotropic liquid crystals as solvents in n.m.r. is contained in reference 7.

When the liquid crystalline fluid is initially placed in the spectrometer, the texture axis has many different orientations throughout the macroscopic sample. Hence, the domains of parallel PBLG molecules are randomly oriented. Consequently, the shape of the initial p.m.r. absorption line is similar to that observed in powdered crystalline hydrates in which the distribution of orientations of the rotationally restricted pair of protons is random.[8] The initial spectrum changes to a discrete doublet after the sample has been in the magnetic field form some time. This suggests a reorientation of the domains by the magnetic field. The resulting structure is nematic with the optic axis parallel to the magnetic field. Similar behavior was observed with the nematic liquid crystal phase of PBLG, e.g. an equi-molar mixture of the *D* and *L* isomers of polybenzyl glutamate;[2] PBLG–CH_2Cl_2: dioxane solutions 4 : 1 (vol.)[4]. The time dependent spectra of both solvents in the latter solution is shown in Fig 1.

During the course of this work two independent reports of this phenomenon in PBLG solutions appeared each with their respective observations interpreted in terms of an oriented nematic structure.[9,10] Although it has been reported that it is possible to

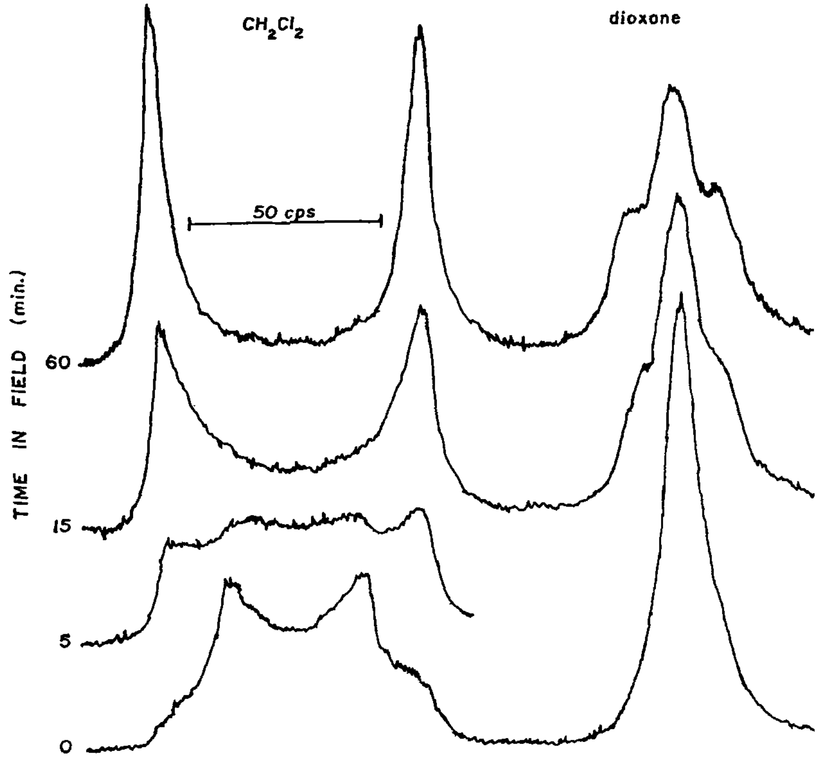


Figure 1. P.m.r. spectra of liquid crystal phase of PBLG–CH_2Cl_2: dioxane (4 : 1) solution, 12% PBLG (vol.). Temperature 40 °C; recorded with VARIAN A 60 A Spectrometer.

preserve the cholesteric structure and orient the axis of torsion in some systems,[11] X-ray diffraction and physical properties of PBLG films cast in a magnetic field indicate that the structure in the oriented liquid crystal phase is nematic.[12]

Due to the high viscosity of these PBLG solutions, the slow reorientation times of the nematic axis enables one to observe the characteristic $(3\cos^2\theta - 1)$ dependence of the dipolar interactions by turning the sample to different values of θ, the angle between the nematic axis and the spectrometer magnetic field. The separation of the doublet at the equilibrium orientation ($\theta = 0°$) is twice that observed when the nematic axis (direction of helical molecular axes) is perpendicular to the magnetic field ($\theta = 90°$). The maximum separation ($\theta = 0°$) can be increased by raising the concentration of PBLG in solution.[9]

2. PMR Spectra in Solid PBLG Films

Solid films of PBLG 1 mm thick were prepared by controlled evaporation of chloroform solutions (5–10% PBLG) contained in a cylindrical polyethylene ring placed on a mercury surface. Rectangular sections of the solid film were dried *in vacuo* at room temperature then exposed to the vapor of dichloromethane. The p.m.r. spectra of the swollen sections of film were recorded with the section of film at a known orientation in the spectrometer. Cross-linking films prior to swelling by gamma irradiation does not effect the p.m.r. spectra and allows the more highly swollen films to be readily handled without loss of shape. An example of the type of spectra obtained is shown in Fig. 2. In the diagram of Figure 2, N is normal to the film plane (casting surface) and the

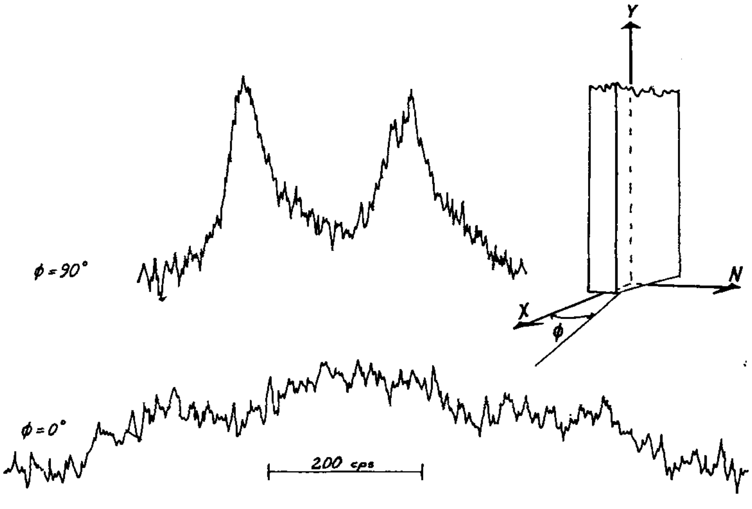


Figure 2. P.m.r. spectra of CH_2Cl_2 in swollen PBLG film, 60% PBLG (wt.). Temperature 40°C; average of 25 sweeps of VARIAN A 60 A using VARIAN C 1024 time averaging computer.

X and Y axes are in the plane of the film. The spectra were recorded with the Y axis coincident with the spectrometer sample tube axis and Φ is the angle which the X axis makes with the magnetic field. Analogous to the observations in the fluid phase, the maximum separation of the doublet is dependent on the concentration of PBLG in the swollen film.

Workers in these laboratories previously reported that X-ray diffraction patterns of PBLG films cast from solution indicated that the molecules had a uniplanar orientation in the plane of the film.[13] Assuming that the structure as indicated by these X-ray studies is not significantly altered by swelling, the p.m.r. spectra of the swollen films are consistent with this structure and the results of Section I. The spectra shown in Figure 2 support the view that the optic axis of domains of parallel PBLG molecules is perpendicular to N and the direction of the optic axis is random in the plane of the film (X, Y plane).

3. X-ray Study of Plasticized PBLG Films

The high degree of molecular order present in the fluid liquid crystal phase gives clearly observable X-ray diffraction patterns. A study of the fluid phase of PBLG in dioxane showed a diffuse reflection in the small angle region with the sharpness increasing and the spacing decreasing as the concentration of PBLG was raised.[3] The data was interpreted using the helicoidal structure assuming that the packing of the rod-like molecules is locally hexagonal. The small angle diffuse reflection was interpreted as the first reflection, d_{100}, of a two dimensional hexagonal lattice. In an attempt to extend these results to higher PBLG concentrations, we examined the d_{100} spacing as a function of PBLG concentration in solid plasticized films.

Plasticized films were prepared by casting predetermined ratios of PBLG and an inert, non-volatile component, chlorinated polyphenyls (Aroclor 1232 Monsanto Company), from a chloroform solution. In Fig. 3 the d_{100} spacing as a function of PBLG concentration in the solid plasticized films is shown with the data

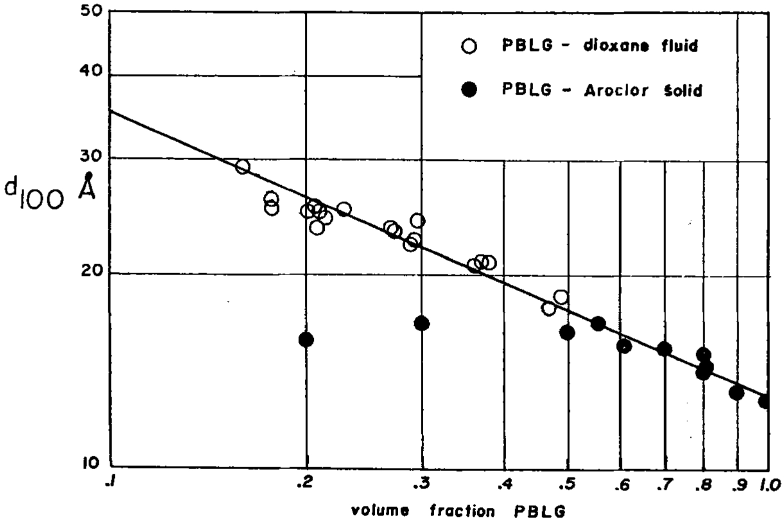


Figure 3. d_{100} spacing vs. PBLG concentration. ○ solution data of Robinson *et al.* *Discuss. Faraday Soc.* **25**, 29 (1958).
● d_{100} spacing in solid plasticized PBLG-Aroclor films taken from flat film photographs. Sample to film distance 6 cm; Cukα radiation; 0.5 mm collimator.

of Robinson *et al.* reported for PBLG in the fluid phase.[3] The d_{100} spacing increases continuously from 12.6 A in 100% PBLG to 17 A in 50% PBLG. At concentrations below 50% PBLG the d_{100} spacing is the same as that found in the film with 50% PBLG. This behavior is interpreted as a separation into two phases at 50 PBLG (Aroclor is not a solvent forPBLG). The initial continuous change of d_{100} is considered as evidence for the presence of a single, homogeneous phase rather than two phases (crystallites or liquid crystals and pools of plasticizer).

4. Optical Characteristics of PBLG Films

In concentrated PBLG solutions the appearance of regularly spaced retardation lines has been interpreted to be a manifestation of the presence of the helicoidal supramolecular structure.[1-5] In

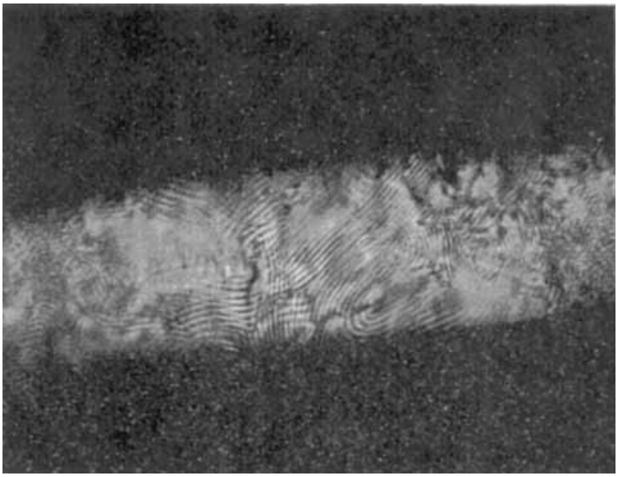
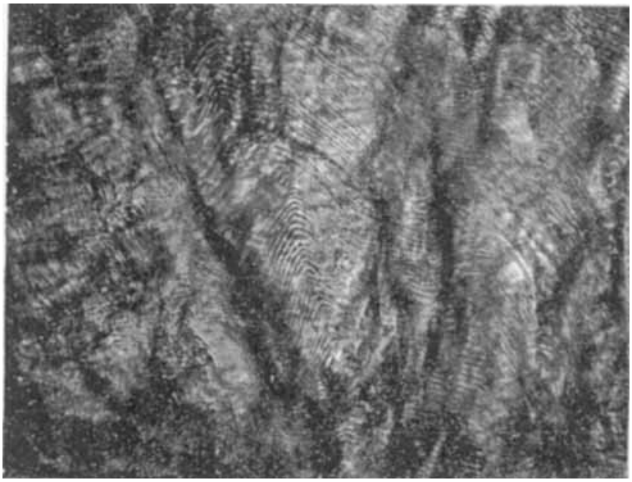


Figure 4. A. Retardation lines with spacing $S = 50$ microns observed in capillary containing 10% PBLG (vol.) in dioxane.



B. Twenty micron thick section of solid PBLG: 3,3′dimethylbiphenyl 7 : 3, $S = 2$ microns. In both photographs the microscope was used with crossed polars to improve contrast.

the fluid liquid crystal phase the continuous angular displacement of the molecules as one travels along the axis of torsion gives rise to a periodic variation in the refractive index appearing as alternating bright and dark equispaced lines. The spacing between these retardation lines is concentration dependent. In concentrated PBLG solutions, spacings as large as 100 microns were observed decreasing in size as the PBLG concentration was raised until they were too small to be observed with an optical microscope.[1-5] Figure 4(a) shows a typical photograph of the retardation lines in the fluid liquid crystal phase. The formation of the helicoidal structure is sensitive to the particular solvent being used hence solutions may require several days for the retardation lines to appear. Consideration of the molecular structure of the solvents which promoted the formation of the helicoidal structure prompted us to select the non-voltaile liquid, 3,3′-dimethylbiphenyl, as a plasticizer for the solid PBLG films. After standing several days, a chloroform solution of PBLG (15% vol.) and plasticizer (PBLG: plasticizer in ratio of 7 : 3), showed the miscroscopically visable retardation lines. The spacing between retardation lines decreased as the chloroform slowly evaporated over a two week period. The remaining solid plasticized PBLG film (70% PBLG) retained the helicoidal structure. Figure 4(b) shows a photograph of a thin section of this film. The retardation lines with spacing of about 2 microns extended throughout the entire solid.

Conclusions

The p.m.r. spectra and X-ray studies in the fluid state show no discontinuity on passing to the solid state suggesting that the local structure in each state must be quite similar. The presence of the retardation lines in the plasticized PBLG film indicates that it is possible for the helicoidal structure to exist in the solid state. These results along with Robinson's earlier observation,[4] slowly evaporated solutions of PBLG yield films reflecting iridescent colors as found in cholesteric liquid crystals, support the existence of a helicoidal structure in the solid state of PBLG derived from that found in the liquid crystal phase.

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