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MOLECULAR STRUCTURE

Solid "Liquid Crystal" Films of Poly- γ -benzyl-L-glutamate

WE present here evidence for a planar layered structure in solid films of poly- γ -benzyl-L-glutamate (PBG) made by casting from solution. The (idealized) structure is composed of successive layers of planes parallel to the film surface. The planes themselves consist of "domain" regions of parallel helical molecules. In a given domain the molecules in adjacent planes show a slight angle of twist relative to one another, characteristic of cholesteric liquid crystal structures. An interesting manifestation of this suggested structure is the unusually anisotropic swelling of these films. Films plasticized with a non-volatile solvent also maintain this layered cholesteric structure with a uniform separation of the PBG planes as shown by birefringence studies.

The structure of reasonably concentrated solutions of PBG has already been extensively characterized¹⁻⁵ and these solutions, which were in a fluid condition in contrast to our solid films, were shown to have a cholesteric liquid crystal structure. Close to the container surface, the molecular planes were parallel to the surface. Within the fluid, however, the molecular planes of the cybotactic regions were isotropically arranged.

The structure of the solid films (unplasticized and plasticized) which are discussed here was inferred from (a) swelling studies, (b) birefringence studies, and (c) X-ray observations⁶.

Films of PBG of high molecular weight (Pilot Chemicals; molecular weight, 10^5) 0.1 cm thick were prepared by slow evaporation of chloroform solutions. Solutions with initial concentrations of approximately 10 per cent PBG were contained in cylindrical polyethylene rings placed on a mercury surface. Homogeneous films plasticized with 'Aroclor' (chlorinated polyphenyls) were prepared by similar casting of predetermined ratios of 'Aroclor' and PBG dissolved in chloroform, then evaporating the chloroform.

The mechanical properties of these films are dependent on the concentration of plasticizer. The room temperature torsional modulus, G , measured after 10 sec, is shown in Table 1.

The PBG molecule has been shown to retain its α -helical conformation in the solid state⁷, and oriented plasticized films (20 per cent PBG) also exhibit the characteristic infrared dichroism associated with a helical molecular conformation.

When the completely dried films (100 per cent PBG) were introduced into benzene immediate anisotropic swelling of the films was observed. The film shape was retained

and dimensions of apparent equilibrium were attained within several minutes. There was a 400 per cent increase in the thickness of the film in a direction N normal to the surface of the film while the other dimensions (parallel to the film surface) increased about 20 per cent. The film remained in a solid condition and could be handled without change of shape.

Plasticized films also showed the same anisotropic swelling in benzene. The swelling was reversible, and the film approached its original dimensions as the solvent evaporated.

The structure of the swollen film was studied in further detail with a polarizing microscope. A thin section (2-3 μ) was cut perpendicular to the surface of a 100 per cent PBG film and swollen in benzene as described. Between crossed polars, the direction of viewing was in the plane of the original film. In the swollen condition, regularly spaced retardation lines were seen parallel to the surface of the film (and perpendicular to N). At maximum swelling the spacing S between retardation lines was about 2 μ .

In concentrated fluid solutions of PBG, the existence of retardation lines was regarded as very strong evidence for the liquid crystalline (cholesteric) structure²⁻⁵. Robinson also gave a relation between the spacing S and the concentration of PBG in solution². We find the relation to be approximately valid for our swollen (but solid) film.

It is possible that retardation lines on the 100 per cent PBG film (unswollen) cannot be resolved under a microscope because the value of S is smaller than the wavelength of visible light, and this may be why they were not observed by Elliott and Ambrose¹. The retardation lines can, however, be observed in films sufficiently plasticized with 'Aroclor', just as they can in films swollen in benzene.

The structure of solid films of PBG cast from chloroform solutions has also been examined by X-ray measurements in this laboratory. This structure was tentatively interpreted in terms of co-existing paracrystalline and mesomorphic regions with uniplanar orientation of the molecules in the plane of the film⁶. The new results reported here support this interpretation.

Films (100 per cent PBG) moderately crosslinked in the solid state by gamma irradiation also showed anisotropic swelling, which indicates the preservation of anisotropic order in the crosslinked solid. Perhaps the crosslinks form preferably in the parallel planes. The plasticized films can be readily handled in their original form but may also be crosslinked to lock in permanently the cholesteric structure.

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Denaturation Kinetics of Biopolymers by Differential Thermal Analysis

SEVERAL workers have described equations to calculate the activation energy of a reaction from the exothermic or endothermic peaks which occur during a differential thermal analysis (DTA) experiment¹⁻³. There is a second type of differential thermal analysis curve, one not

Table 1

Per cent PBG	$3G$ (dynes/cm ²)
100	5×10^9
80	2.3×10^9
50	1.2×10^9
30	2×10^8
20	3.5×10^7