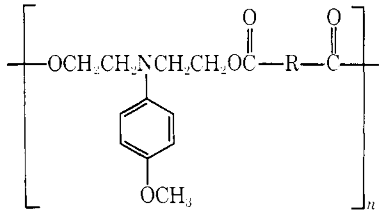
TABLE I

PROPERTIES OF DONOR POLYMER I, ACCEPTOR POLYMER II, AND A 50:50 MIXTURE

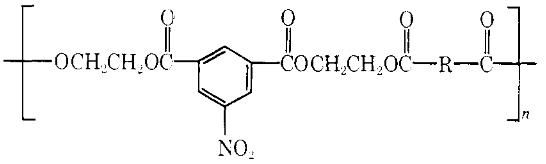
Property[a]	I	50:50 mixture[b]	II
Color	Colorless	Yellow-orange[f]	Colorless
Reduced viscosity[c]	0.80	0.60	0.40
Lowest energy absorption maximum,[d] mμ	298	398[e,f]	330
Glass transition temp (T_g), °C	50–60	60–70	70–80
Tensile modulus, psi	335,000	360,000	260,000

[a] Films prepared by solution casting from chloroform. [b] This mixture was prepared from 10% solutions (by weight) of I and II. [c] Determined in chloroform at 25° at 0.2 g/100 ml. [d] Determined on a Cary 14 spectrophotometer in chloroform. [e] Determined by scanning a mixture of solutions of I and II in a 2-cm cell against individual 1-cm cells containing I and II. [f] The possibility that the color was caused by the presence of unreacted monomers was ruled out since the individual polymers were refluxed for 3 days with methanol prior to spectroscopic study. This treatment would remove *p*-anisyliminodiethanol and the bishydroxyethyl ester of 5-nitroisophthalic acid since they are soluble, at room temperature, to the extent of 50 and 10 g in 100 ml of methanol. Based on the probable molecular weight distribution for condensation polymers obtained in high yield and molecular weight, no extraordinary amounts of low molecular weight oligomers should be present to interfere with the color measurements.

A typical donor polymer–acceptor polymer composition was prepared either by solution casting or melt mixing poly(*p*-anisyliminodiethanol bisphenol A carbonate) (I) and poly(bis(2-hydroxyethyl)-5-nitroisophthalate bisphenol A carbonate) (II). The 50:50 mixture (by weight) which gives clear, uniform and flexible films, possesses a bright yellow-orange color. Some of the mechanical and physical properties of this blend are given in Table I. This composition is an example of a polymeric donor–polymeric acceptor charge-transfer complex possessing usable mechanical properties, and as such, is the first representative of this class of materials.



I



II

R = bis(4,4′-oxyphenyl)-2, 2-propane

We prepared condensation polymers as donors since suitable choice of the functional groups therein should impart toughness. Previous work mainly utilized poly(vinyl aromatics). Polycarbonate I, containing the free tertiary amine group, was prepared in >95% yield by a low-temperature solution polycondensation between bisphenol A dichloroformate and *p*-anisyliminodiethanol. The latter compound was synthesized from *p*-anisidine and ethylene oxide. Since polyesters of isophthalic acid are known to be tough materials, we prepared a poly(mononitroisophthalate) for evaluation as one type of acceptor species. Reaction of 5-nitroisophthalic acid with ethylene oxide gives the requisite bis(hydroxyethyl ester) monomer.[6] This compound was polymerized with bisphenol A dichloroformate in the presence of pyridine to give the poly(ester carbonate) (II) in over 90% yield.

Other aspects of the synthesis and properties of this and other novel donor polymer–acceptor polymer charge-transfer systems will be reported in subsequent publications.

(6) Suitable elemental analyses were obtained by Galbraith Laboratories, Knoxville, Tenn.

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Some Unusual Properties of Poly(γ-benzyl L-glutamate) Films Cast in Strong Magnetic Fields

Poly(γ-benzyl L-glutamate) (PBLG) is known to have an α-helical molecular conformation in solution and in the solid state.[1,2] We present evidence for unusual supramolecular structures in cast films of PBLG, emphasizing the effect of magnetic fields. The nature of the cast films composed of these rodlike molecules is discussed in terms of (a) X-ray observations, (b) swelling characteristics of the films and (c) nmr of solvent molecules in the swollen film. The X-ray observations are correlated with the earlier work of Robinson, *et al.*, on the fluid liquid crystal phase of PBLG.[3] We observed the ability of concentrated solutions of this polypeptide to act as a liquid crystal solvent for nuclear magnetic resonance experiments as recently reported by other workers.[4,5]

Films of high molecular weight PBLG (Pilot Chemicals, lot G-98, mol wt, 275,000) 1 mm thick were prepared by slow evaporation of chloroform solutions.

(1) J. T. Yang and P. Doty, *J. Amer. Chem. Soc.*, **79**, 761 (1957).

(2) M. F. Perutz, *Nature*, **167**, 1053 (1951).

(3) C. Robinson, J. C. Ward, and R. B. Beevers, *Discussions Faraday Soc.*, **25**, 29 (1958).

(4) S. Sobajima, *J. Phys. Soc. Jap.*, **23**, 1070 (1967).

(5) M. Panar and W. D. Phillips, *J. Amer. Chem. Soc.*, **90**, 3880 (1968).

Solutions of initial concentrations of 5–10% PBLG (all concentrations given in volume per cent) were contained in cylindrical polyethylene rings placed on a mercury surface. Plasticized films were prepared by similar casting of predetermined ratios of PBLG and an inert nonvolatile component, Aroclor (Monsanto Co. Aroclor 1232), dissolved in chloroform, then evaporating the chloroform. Unusually oriented films were prepared by performing the casting in a 10-kG magnetic field. Nmr spectra were recorded with a Varian A60A at 40°.

X-Ray Studies. It was previously reported that films of PBLG cast from solutions in the absence of magnetic fields gave X-ray diffraction patterns which indicated that the molecules had a uniplanar orientation in the plane of the film.[6]

Casting films in a strong magnetic field can change the molecular orientation in the film. During the casting procedure, the concentration of PBLG continuously increases. At approximately 12% PBLG the solution changes to a liquid crystal phase which has been extensively characterized.[7] In this phase the cybotactic regions of high molecular order accentuate the magnetic anisotropy of the component molecules. Consequently a magnetic field produces a marked orientation of these ordered domains. This orientation is retained in the film when the remaining solvent is removed in the presence of the magnetic field. The orientation of the molecules is in the direction of the magnetic field H. The direction normal to the film surface is N; axes in the plane of the film are X and Y.

Fiberlike X-ray diffraction patterns obtained from 100% PBLG films cast in a magnetic field are similar to those reported for mechanically oriented films of PBLG.[8] When the magnetic field is parallel to N, the molecules tend to line up normal to the surface of the film. When the magnetic field is in the plane of the film, *e.g.*, parallel to the X axis, the molecules line up parallel to the X axis. The resulting X-ray diagrams along the three coordinate axes are the same for both cases provided the reference axis is the molecular axis. Figure 1 shows the X-ray results.

When casting with the magnetic field parallel to N, there is competition between the uniplanar orientation (Figure 1a and b) and the orientation imposed by the magnetic field. Figure 1f indicates regions of high orientation where the molecular axis is tilted approximately 30° out of the film plane.

The 1.5-Å meridional reflection characteristic of the α-helix is observed on both sides of the equator when the fiber axis (magnetic field direction, H) is perpendicular to the cylindrical camera axis and also to the incident beam.

X-Ray investigation of Aroclor plasticized films indicated that the lateral spacing between molecules changed with the concentration of PBLG in a manner similar to that found for the fluid liquid crystal phase in dioxane.[3] The d_{100} spacing increases continuously from 12.6 Å in 100% PBLG to 17 Å in 50% PBLG.

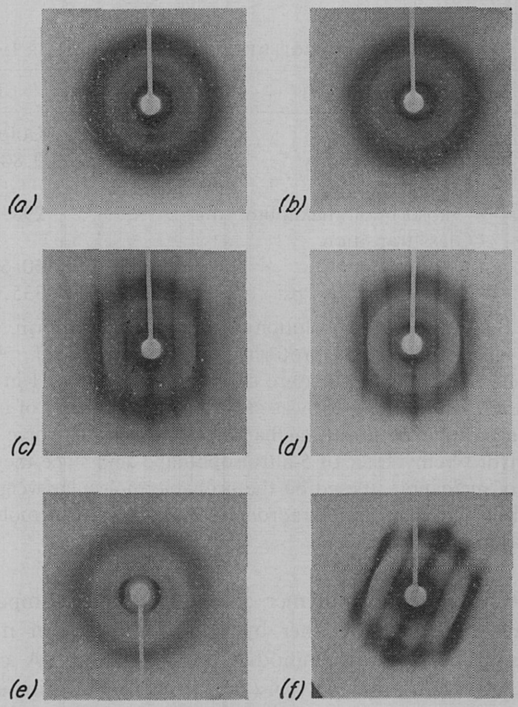

Figure 1. Flat film X-ray photographs, sample to film distance 6 cm, Cu Kα radiation, 0.5 mm collimator. No magnetic field present during casting: (a) X-ray beam in the X–Y plane with N direction vertical in the photograph; (b) X-ray beam parallel to N. Magnetic field in the plane of the film parallel to the X axis during casting: (c) X-ray beam parallel to Y axis with N vertical in the photograph; (d) X-ray beam parallel to N with the Y direction vertical in the photograph. Magnetic field parallel to N during casting; X-ray beam is in the X–Y plane and the N direction vertical in both e and f.

Casting plasticized films in a magnetic field allowed observation of equatorial reflections from films containing less than 20% PBLG. At concentrations of PBLG below 50% the d_{100} spacing was the same as that found in the 50% film. We interpreted this behavior to be a separation into two phases which occurs below 50% PBLG concentration. The initial continuous variation of d_{100} with concentration of PBLG varying from 100 to 50% is interpreted as evidence for a single, homogeneous phase rather than two phases (crystallites or liquid crystals plus pools of plasticizer).

Swelling. An interesting manifestation of the structure in the solid state of PBLG is the observed anisotropic swelling of the cast films. When the completely dried films are placed in a liquid such as benzene, the initial dimensions of the film immediately begin to change and approach apparent steady state values in about 1 hr.

The changes in dimensions are reported as the fractional per cent increase in a given dimension, *i.e.*, $(l_e - l_0)100/l_0$ where l_e is the apparent equilibrium dimension and l_0 is the initial dimension. The l_e's were recorded 48 hr after the films were introduced into the liquid. Table I summarizes the data obtained from films cast under different conditions. The swelling is reversible; the films approach the original dimensions on removing the solvent.

With a knowledge of the initial structure present in

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[6] A. J. McKinnon and A. V. Tobolsky, *J. Phys. Chem.*, **70**, 1453 (1966).

[7] C. Robinson, *Mol. Cryst.* **1**, 467 (1966), and references cited therein.

[8] C. H. Bamford, A. Elliot, and W. E. Hanby, "Synthetic Polypeptides," Academic Press, New York, N. Y., 1951.

TABLE I
PER CENT FRACTIONAL INCREASE ON SWELLING[a]

Film	*N*	*X*	*Y*
A. No field	640	10	20
B. H∥N	5	300	350
C. H∥X	366	11	132

[a] Films contained ~90% benzene by weight.

the dry films obtained from X-rays, the data in Table I suggest that the swelling of the films results primarily from an increase in the lateral spacing between the molecules and translations in the direction parallel to the molecular axis are highly restricted.

Nmr Observations. The unusual structure of PBLG films is also reflected in the proton magnetic spectra of solvent molecules swollen into the films. We have observed the nmr spectra of dichloromethane in the presence of PBLG over the entire concentration range of PBLG. These observations enabled us to follow the phase transitions which occur in PBLG solutions.[7]

In dilute molecular solutions (PBLG less than 8% concentration) the nmr spectra of dichloromethane consists of the normally observed singlet which is characteristic of pure CH_2Cl_2. On increasing the concentration of PBLG (in the range between 8 and 12%) the signal broadens as the liquid crystal phase begins to form. When the concentration of PBLG is sufficiently high (higher than 12%) such that the liquid crystal phase exists throughout the entire sample, the phase is oriented by the magnetic field. The spectra of dichloromethane then changes to a doublet indicative of intramolecular direct dipole–dipole coupling. This observation suggests that the dichloromethane is partially ordered by the anisotropic liquid crystal matrix. The splitting of the signal followed the angular dependence characteristic of dipolar interactions. An independent study of the same effect reported an increase in the separation of the doublet as the PBLG concentration was further increased.[4]

PBLG films cast in the absence of a magnetic field were exposed to dichloromethane vapor and examined with the *X* (or *Y*) axis coincident with the spectrometer sample tube axis. The orientation dependent splitting of the dichloromethane signal is shown in Figure 2. Cross-linking films by γ irradiation did not affect the nmr spectra and allowed the more highly swollen films to be readily handled without loss of shape.

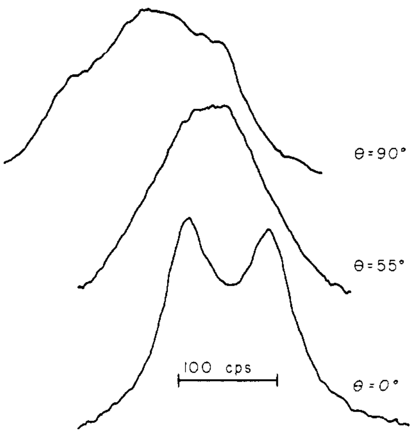

Figure 2. Nmr spectra of dichloromethane (30% by weight) swollen into a cross-linked film of PBLG cast in the absence of a magnetic field. θ is the angle between *N* and the spectrometer magnetic field direction. Examination of films swollen with chloroform suggest that the shift of the center of the doublet with angle can be attributed to the magnetic susceptibility of the swollen film.

The spectra shown in Figure 2 support the structure suggested by X-ray observations.[6] These spectra are consistent with a structure having the optical axis of domains of parallel polymer molecules perpendicular to *N* but randomly oriented in the plane of the cast film (*X*, *Y* plane). Analogous to observations reported for the fluid phase, the maximum separation of the doublet was dependent on the concentration of PBLG in the swollen film.

The nmr results show no discontinuity in the spectra of CH_2Cl_2–PBLG mixtures when these mixtures are in a demonstrably fluid liquid crystal phase or when these mixtures are solid swollen films, indicating that the local structures in each case must be quite similar.

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