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Poly(γ-benzyl-L-glutamate) Liquid Crystals in Benzene

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Contrary to reports that the synthetic polypeptide, poly(γ-benzyl-L-glutamate), adopts a smectic molecular organization in benzene solution we find this lyotropic system to be a cholesteric liquid crystal. Direct optical and optical rotatory dispersion measurements are reported that support this conclusion. The influence of a magnetic field and small amounts of halogenated organic acids on the cholesteric structure was also examined.

Concentrated solutions of the synthetic polypeptide poly (γ-benzyl-L-glutamate) (PBLG) from lyotropic liquid crystals in a number of solvents. Benzene is unusual.

Doty *et al.*[1] noted the extremely high viscosity of PBLG in benzene and dioxane. The extraordinarily high viscosity built in solutions of the polymer in these solvents is suggestive of the formation of large molecular aggregates present even in dilute solution. Powers and Peticolas[2,3] studied the viscosity and electric field induced birefringence (Kerr effect) of PBLG in mixed solvents, including benzene and dioxane, over a range of concentrations. Their results are indicative of a lateral, antiparallel aggregation of the polymer α-helices in these solvents of low dielectric constant which does not occur in solvents of higher polarity. The magnitude of the effect in benzene is most pronounced and the authors concluded that PBLG/benzene solutions are probably smectic liquid crystals.

Tobolsky *et al.*[4] observed a distinctly different morphology of PBLG films cast from benzene solution than found in those formed from polar solvents such as chloroform and methylene chloride. The films cast from benzene exhibited a much greater permeability to liquid benzene than films prepared from CH_2Cl_2. The 550 fold difference in the diffusion constant of the penetrant could not be explained on the basis of differences in film density or solubility coefficient. The authors thus accounted for the enhanced transport of the solvent in terms of a locked-in smectic organization of the polymer in the film as proposed by Powers and Peticolas[2,3] for the liquid crystal.

In this article, we report the results of our observations in polarized light on concentrated PBLG solutions in benzene. We find the texture visible in the polarization microscope to be that of a *cholesteric* liquid crystal. Furthermore the optical rotatory dispersion of the solutions is consistent with a helicoidal (twisted nematic) superstructure of the macromolecules in this solvent. The cholesteric to nematic phase transition was also followed as a function of magnetic field strength and values of the twist elastic constant, K_{22}, determined. The presence of small amounts of third component, halogenated organic acids was found to dramatically alter the viscoelastic properties of the liquid crystal, as noted in other mixed solvent systems with this polymer.[5] The effect of the polar acid moeity on the cholesteric pitch is however remarkably different in PBLG/benzene liquid crystals than previously found in similar PBLG/dioxane solutions.

EXPERIMENTAL

PBLG and the enantiomer poly(γ-benzyl-D-glutamate) both of molecular weight 150,000 were obtained from Sigma Chemical Company and used without further purification. The solvent benzene was of spectral grade and was purified by shaking with concentrated sulfuric acid and distillation from metallic sodium. Dichloroacetic acid was vacuum distilled but trifluoroacetic acid was used as purchased.

Optical rotatory powers as a function of wavelength were determined in 1 mm pathlength quartz spectrophotometric cells with a Perkin Elmer Model 241 MC polarimeter using a tungsten lamp source. Optical rotations are reported in terms of $[\alpha]_\lambda$, the specific rotation at wavelength λ.

Liquid crystal solutions of PBLG were prepared in standard 2 mm pathlength spectrophotometric cells. Solubility problems with the polymer in pure benzene were overcome by heating the preparation to 40°C in a thermostat for several weeks. In mixed solvents with a small acid component, solutions were completely formed in a few days at room temperature.

The pitch of the cholesteric preparations was determined from an average of the separation between striations observed in a Nikon polarization microscope equipped with a micrometer eyepiece. Samples were subjected to the field of a 4 inch variable electromagnet and pitch measurements taken as a function of field strength in programmed steps. Field intensities were determined using a rotating coil fluxmeter.

RESULTS AND DISCUSSION

Cholesteric pitch

Figure 1 is a photomicrograph of a 21.7% wt/v solution of PBLG of molecular weight 150,000 in benzene. Birefringence regions with swirl-like, fingerprint patterns characteristic of cholesteric liquid crystals are clearly evident throughout the preparation. The observed periodicity between the approximately equidistant striations is equal to one half the pitch, p, of the twisted molecular organization. The pitch was found to increase in a regular manner with increasing temperature (Figure 2) in contrast to the usual behavior of thermotropic cholesterics which have a negative temperature coefficient,[6] i.e. $dp/dT < 0$. The anomalous temperature dependence is the same however as reported in PBLG liquid crystals in other solvents such as chloroform and dioxane.[5,7] PBLG solutions do not exhibit iridescent coloration when viewed in reflected white light as the pitch is well beyond the wavelength of light.

Optical rotatory dispersion

PBLG/benzene solutions also display high optical rotatory powers that increase markedly upon the formation of the liquid crystal. We have investigated the optical rotatory dispersion (ORD) of dilute solutions of PBLG and

FIGURE 1 Photomicrograph of PBLG/benzene liquid crystal (21.7% wt/v of polymer) in the polarization microscope showing cholesteric texture. The distance between the equispaced retardation lines is one-half the pitch of the cholesteric structure.

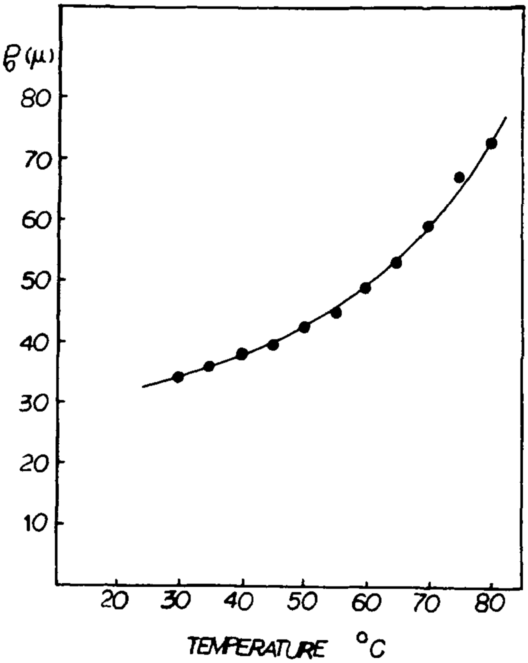

FIGURE 2 Temperature dependence of the pitch for PBLG/benzene liquid crystal (21.7 % wt/v).

the enantiomer poly(γ-benzyl-D-glutamate) (PBDG) in benzene and concentrated solutions of PBLG in benzene held just below the critical volume fraction for the appearance of cholesteric spherulites. In this latter concentration regime, which is just below the "A" point discussed extensively by Robinson,[8-10] the solution is uniformly birefringent and strongly optically active. To our knowledge, this pretransition region of the liquid crystal has not been previously examined. It is a curious region in that a small change (½–1 %) in polymer concentration will cause the solution to turn completely isotropic (dilution of polymer) or will precipitate the formation of cholesteric spherulites (concentration of polymer to the "A" point).

Figure 3 shows the ORD curves from 300 to 600 nm of ~5 % wt/v PBLG and PBDG solutions in benzene. The dispersion curve of PBLG is similar to that obtained by Yamaoka[11] for a lower molecular weight sample of this isomer in chlorobenzene, with a crossover point at 355 nm. The behavior of the D-isomer is essentially the mirror image of that of PBLG, as expected. ORD curves were fitted to a two term Drude equation of the form:[11]

$$[R']_\lambda = \frac{3}{n_\lambda^2 + 2}\cdot\frac{MRW}{100}\cdot[\alpha]_\lambda = \frac{A_0\lambda_0^2}{\lambda^2 - \lambda_0^2} + \frac{A_1\lambda_1^2}{\lambda^2 - \lambda_1^2}, \tag{1}$$

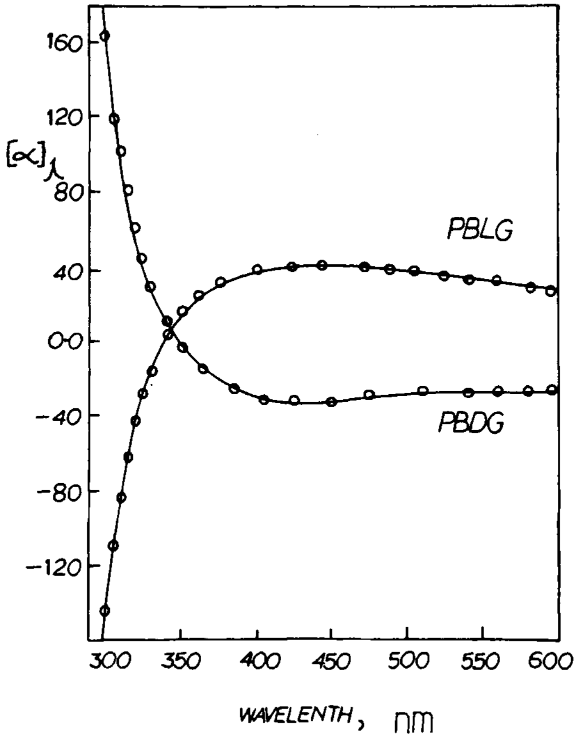

FIGURE 3 Optical rotatory dispersion curves for dilute solutions in benzene of PBLG (4.95 %) and PBDG (5.18 %) at 22°C.

where $[R']_\lambda$ is the reduced mean residue rotation at wavelength λ, MRW is the mean residue weight (219) of the polypeptide, and n_λ is the refractive index of the solvent. The critical wavelengths λ_0 and λ_1 were taken to be 193 and 226 nm, respectively.[11] For PBLG, the Drude parameters were $A_0 = +2660$ and $A_1 = -1590$; for PBDG, $A_0 = -2430$ and $A_1 = +1490$.

Upon concentration of the polymer to the pretransition region, the optical rotatory power increases approximately one thousand fold. Figure 4 is a plot of the specific rotation versus wavelength for PBLG in this region (16.2 % wt/v at 22°C). The high form optical rotation observed has its origin in the twisted superstructure of the cholesteric phase. Rotations are all positive as reported for PBLG in dioxane by Robinson.[9] We infer therefore that the sense of the cholesteric twist is the same in the two solvents. Optical rotations of the complete liquid crystal phase itself were too large to measure at this sample thickness.

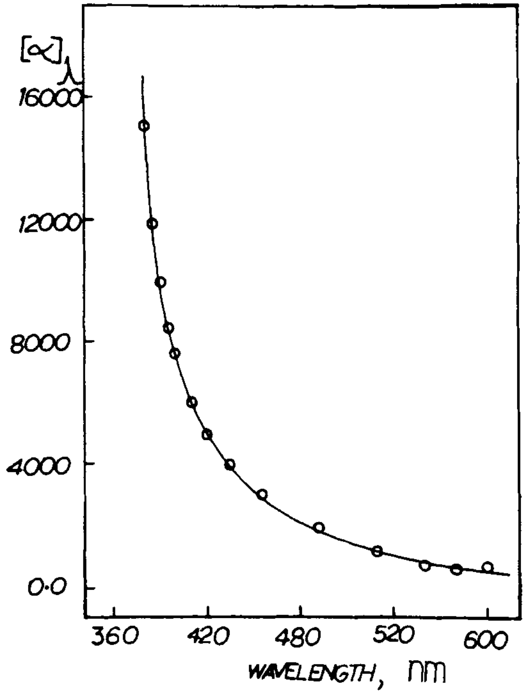

FIGURE 4 Plain positive ORD curve for PBLG/benzene solution in the pretransition region (16.2% wt/v) before the appearance of cholesteric spherulites.

Effect of halogenated organic acids

Solution properties of polypeptides are quite sensitive to even trace amounts of halogenated organic acids. In mixed solvent systems containing a helicogenic solvent and a denaturant such as dichloroacetic acid (DCA) or trifluoroacetic acid (TFA), PBLG and similar polypeptides undergo an intramolecular phase transition from the α-helical conformation to a flexible random coil. This occurs at about 10–30% acid by volume with TFA but a higher concentration of ~75% of the weaker acid DCA is required. More subtle alterations of the polypeptide helix in a pretransition region have been reported.[12–14] At even lower concentrations the effect of the acid is still noteable, particularly in the modification of the solution viscosity. The acid apparently acts to break up loosely formed polymer aggregates and solutions adopt the viscoelastic behavior more characteristic of a dispersion of discrete polymer molecules. The interaction of TFA with PBLG helices has also been examined in the liquid crystal. Reorientation rates of the polymer in a magnetic field were found to be remarkably sensitive to the presence of the

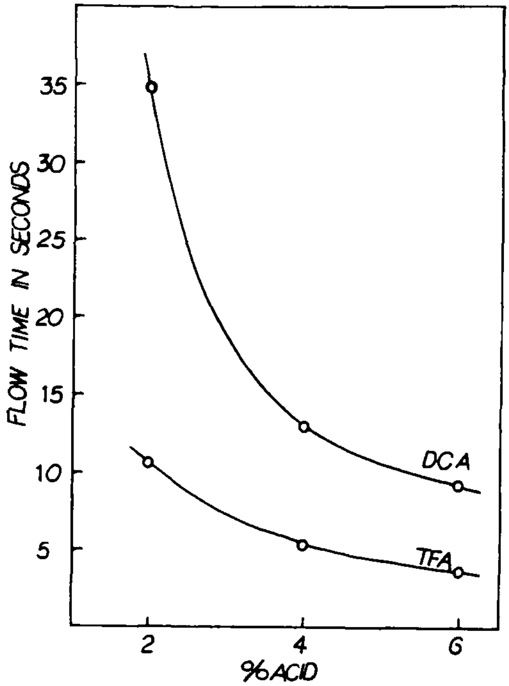

FIGURE 5 Bulk flow time of PBLG/benzene liquid crystals with added DCA or TFA. Ordinate is the time in seconds for a one centimeter travel of the edge of the meniscus of the liquid crystal after inversion in a 2 mm path length spectrophotometric cell. The abscissa is the volume percent of acid in the binary solvent.

acid.[15] The abrupt decrease in the rotational viscosity coefficient found is most likely due to the breakdown of polypeptide aggregates as in dilute, isotropic solution. In the liquid crystal, aggregation of PBLG could result in an intermittant and tenuous three dimensional network impeding flow. The destruction of the network by the acid therefore is accompanied by increased fluidity. It is remarkable however that only a trace amount of the acid is required. Figure 5 demonstrates the effect of a few percent of TFA and DCA on the bulk viscosity of PBLG/benzene liquid crystals. At a given concentration, TFA is seen to be more effective in viscosity reduction than the weaker acid DCA.

The pitch of the cholesteric structure of PBLG/benzene liquid crystals was also found to be sensitive to small quantities of DCA or TFA as a second solvent component. The pitch was found to increase with increasing acid, added in such a manner to keep the volume fraction of polymer the same (Figure 6). The stronger acid (TFA) results in a greater alteration of the helical twist of the medium being about 1.5 times as effective as DCA. The influence

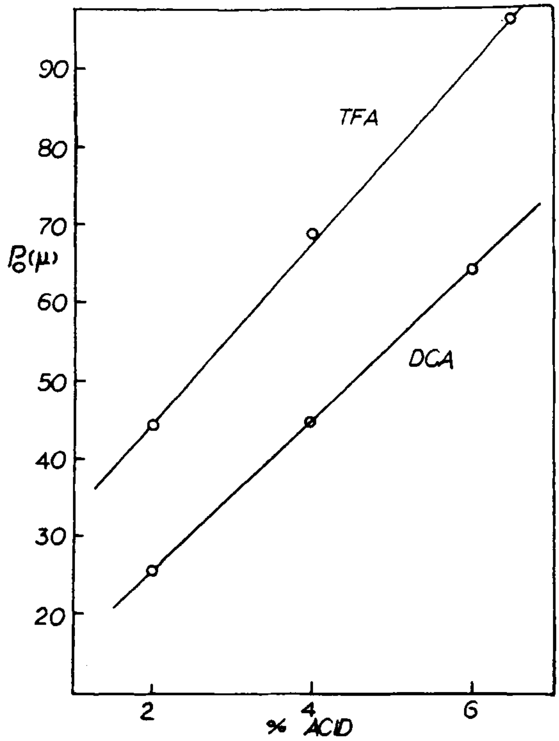

FIGURE 6 The dependence of the zero field pitch, p_0, on acid concentration. PBLG/benzene liquid crystals (23% wt/v).

of TFA on the cholesteric structure of polypeptide liquid crystals has been previously discussed[5] but the effect seen here with benzene as the major solvent is quite different from that observed in the case of the similar solvent dioxane. In PBLG/dioxane liquid crystals, small quantities of TFA result in a pitch *decrease*. The PBLG/dioxane system thus far is unique, being the only polypeptide liquid crystal exhibiting a pitch decrease with increasing polarity of the solvent medium. The difference in action of halogenated acids in these two systems is most likely a result of different specific polymer-solvent and solvent-solvent interactions.

Samulski and Samulski[16] have developed a theory of the origin of the cholesteric twist based upon van der Waals-Lifschitz forces between large rod shaped chiral molecules. The role of the solvent is articulated *via* its dielectric permittivity. Theory predicts an increase in pitch with increasing dielectric constant of the medium, as would occur in binary solvents when a polar solvent is substituted for a nonpolar component. An increase in pitch with added TFA or DCA is the observation here with PBLG/benzene liquid crystals but is not the case with dioxane as the major solvent. The physical properties of benzene and dioxane are similar (dielectric constants at 25°C of 2.274 and 2.209, respectively) so we must look for additional factor to understand the variance. Although the theoretical model contains easily visualized parameters such as the chirality and polarizability of the macromolecule and the dielectric constant of the intervening solvent, the effect of specific polymer-solvent, solvent-solvent interactions is not directly obvious. It is known that small amounts of TFA protonate the N-terminal amide group of PBLG and associate with the polymer by H-bonding to the carboxyl groups of the side chain ester.[17] The result is a reduction in the overall dipole moment of the helical macromolecule and a modification of the polarizability of local segments that figure into calculations with the model. Such modifications of the polymer would occur by acid attack in both benzene and dioxane solvents. In the case of dioxane however there is a competitive pathway that can draw a portion of the acid away from the polymer chain. A strong acid such as TFA or DCA reacts with dioxane to form a solvated proton and the acid anion. The ions of the titrant acid are thus present mostly as ion pairs involving the molecules of the more ubiquitous solvent.[18] Hydrocarbon solvents such as benzene do not form such ion pairs. The magnitude of the proposed shift in acid association from polymer to solvent apparently is sufficient to reverse the sense of the cumulative twist in the two otherwise similar liquid crystals.

Cholesteric-nematic transition induced by a magnetic field

Application of a magnetic field causes the regions of well formed striations observed under the polarization microscope to turn and order such that the striations run parallel to the field direction. This rotation is accompanied by a dilation of the pitch which increases with increasing field strength. At a high enough applied field the striations disappear and the solution takes on the appearance of an aligned nematic phase. Meyer[19] and deGennes[20] have considered such a field distortion of the cholesteric structure and find that the transition to complete nematic order occurs at a critical field strength given by:

$$H_c = \frac{\pi^2}{2}\left(\frac{K_{22}}{\Delta\chi_m}\right)^{1/2} \cdot \frac{1}{p_0}, \tag{2}$$

where p_0 is the zero field pitch; $\Delta\chi_m$, the diamagnetic anisotropy of the liquid crystal; and K_{22}, the twist elastic constant. A functional form for the dependence of the cholesteric pitch, p, on magnetic field was also derived:[19,20]

$$\frac{p}{p_0} = \left(\frac{2}{\pi}\right)^2 K(k)E(k) \tag{3}$$

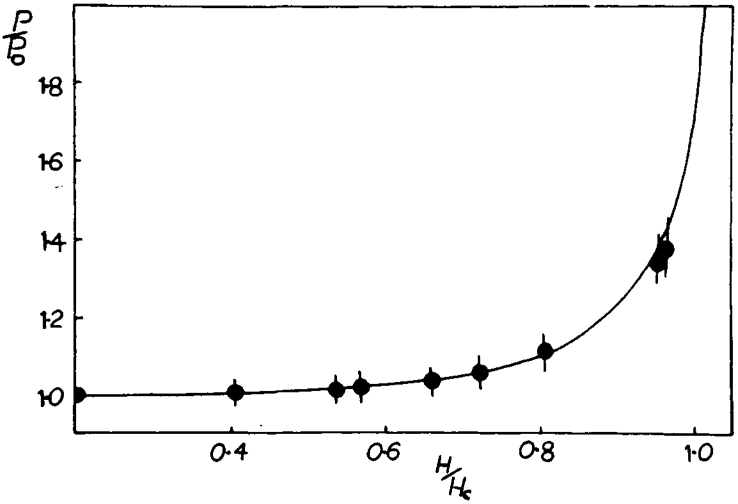

FIGURE 7 Dependence of the pitch, p, on magnetic field strength, H, for PBLG/benzene liquid crystal (23 % wt/v) with 4 % added TFA. Reduced plot where p_0 is the pitch in the absence of the field and H_C is the critical field. The solid curve is after the theory of Meyer[19] and deGennes.[20]

where $K(k)$ and $E(k)$ are elliptical integrals of the first and second kind, respectively, and k is defined through the relation, $H/H_c = k/E(k)$ and varies between 0 and 1. As the field increases the pitch is predicted to increase slowly at first and then diverge logarithmically as the critical field is approached. The theory has been verified for thermotropic liquid crystals[6] and for lyotropic liquid crystals of this polymer in a number of different solvents.[5,7,15,21,22] Figure 7 is a plot of the field dependence of the observed pitch for a PBLG/benzene liquid crystal with 4 % TFA. The solid curve is that of theory Eq. (3) and is seen to conform quite well to the data of this system. Similar behavior has been observed for solutions of the polymer in benzene with 6 % TFA and 4 % and 6 % DCA added. Table 1 is a list of the measured parameters of these transitions. The zero field pitch, p_0, of the polymer in the single solvent benzene liquid crystal with 4% TFA. The solid curve is that of theory [Eq. (3)] field, H_c, is beyond the range of our magnet. Experimental values of $\Delta\chi_m$ and its dependence on acid concentration are not available for this solvent system. $\Delta\chi_m$ has been shown to be acid dependent in PBLG/dioxane liquid crystals where the side chain organization of the polypeptide is considerably modified.[5,15] The extent of the interplay of the acid component with the peptide and the solvent is not easily calculable. We would predict however that in the solvent benzene, which avoids acid association, the effect on a per molecule basis of TFA or DCA on $\Delta\chi_m$ would be greater than in dioxane which draws a portion of the acid away from the polymer.

TABLE I

Parameters of the Magnetic Field Induced Cholesteric-Nematic Transition in PBLG/Benzene Liquid Crystals. Solutions are 23 % wt/v of Polymer of Molecular Weight 150,000 with the Indicated Additions of DCA or TFA.

% Acid	$P_0(\mu)$	$H_c(kG)$	$K_{22}/\Delta\chi_m$ (emu · cgs)
2% DCA	25.5	—	—
4% DCA	44.8	10.8	96.3
6% DCA	59.1	6.10	53.5
2% TFA	44.4	—	—
4% TFA	69.2	6.20	75.8
6% TFA	96.6	3.20	39.3

CONCLUSION

The optical, ORD, and magnetic field transitions described above definitely support the categorization of PBLG/benzene liquid crystals to the cholesteric texture in contrast to previous suppositions that this unusual solvent yields the smectic organization.

We have considered the possibility that these concentrated PBLG/benzene solutions are twisted smectics exhibiting therefore properties characteristic of both smectic (large viscosity) and cholesteric (high form optical rotatory power) liquid crystals. We find it unlikely that these long (~15Å × 1000Å), partially flexible helices would order in the regular two-dimensional register of smectic planes. The temperature dependence of the pitch noted in Figure 2 also speaks against this alternative model. In the thermotropic chiral smectics studied to date, the optical rotation[23] and pitch[24] are insensitive to temperature as would be expected if the cumulative twist were controlled by the interaction between smectic layers rather than by individual molecules as in cholesteric phases. The strong temperature dependence of the pitch suggests that these layers do not exist in PBLG/benzene liquid crystals.

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