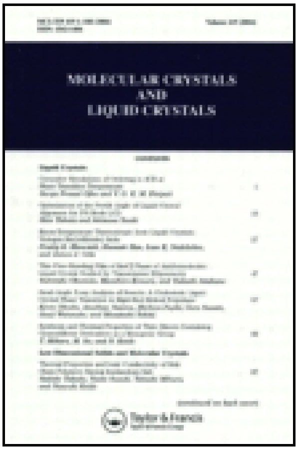

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Control of the Pitch of Synthetic Polypeptide Lyotropic Phases Utilizing a Chiral Solvent†

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The addition of the chiral solvent, phenethyl alcohol to the cholesteric lyotropic phases of the synthetic polypeptides poly-(γ-benzyl-L-glutamate) or poly-(γ-benzyl-D-glutamate) (PBLG and PBDG) causes a strong perturbation of the pitch. Both polymers are in the α-helical conformation and, in both cases, *l*-alcohol increases and *d*-alcohol decreases the pitch relative to the racemic alcohol.

INTRODUCTION

The synthetic polypeptide, poly-γ-benzyl-L-glutamate (PBLG) and its enantiomer poly-γ-benzyl-D-glutamate (PBDG), in appropriate organic solvents adopt an α-helical conformation stabilized by a network of intramolecular hydrogen bonds and behave as typical rod-like structures. Robinson *et. al.*[1–4] pioneered the detailed optical investigations of PBLG solutions and found that the liquid crystals exhibit high degrees of optical rotation and form striation textures characteristic of cholesterics.

Although the critical concentrations for liquid crystal phase formation are relatively insensitive to solvent, the actual structure of the liquid crystal is strongly influenced by the nature of the solvent. For instance, PBLG retains its right-handed chirality in 1,4-dioxan, while it changes to left-handed in 1,2-dichloroethane and dichloro-

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methane.[2,3] Compensated nematic structures occur at critical solvent ratios, for example 4:1 dichloromethane: dioxan (by vol.).[3] Molecular chirality has long been known to be a requisite for cholesteric structure. A nematic liquid crystal can be transformed into a cholesteric by adding an optically active solute and conversely a racemic mixture of PBLG and its mirror image PBDG can adopt a nematic texture *via* compensation. These properties have been reviewed recently by Samulski and DuPre.[5]

The purpose of this work was to establish whether pitch can also be controlled in polymer solutions by using a chiral solvent which would interact with the chiral or achiral rods. It is known that in thermotropic systems small optically active molecules can induce a chiral interaction among achiral molecules and several generalized theories have been developed for these interactions predictive of the pitch of the medium.[6] The pitch of PBLG cholesterics is, however, thus far, considered an ". . .ill-defined function of the temperature, the polymer concentration, the rod aspect ratio and the solvent quality."[5] In this work the chirality of the solvent medium itself is shown to be an extremely important additional factor that can profoundly alter the chirality of the phase.

EXPERIMENTAL

The synthetic polypeptides were obtained from Sigma Chemical Co. The molecular weights, based on viscosity determinations of PBLG and PBDG were given by the manufacturer as 210,000 (PBLG, lot #23F-5023) and 150,000 (PBDG, lot #70F-5011). In all cases the polymers were used without further purification. Optically active (+ and −) α-phenethyl alcohol were obtained from Chemical Dynamics Corp., N. J., and their optical rotation verified. Dibromomethane was obtained from Aldrich Chemical Co. (Gold Label grade). 10-30 mg of PBLG or PBDG were placed in 0.6 mm rectangular glass capillaries from Vitro Dynamics, Inc., N. J., the appropriate amount of solvent/solvents added, and the sample sealed with a torch. Samples were incubated for at least one week to assure complete homogeneity of the solutions. Optical observations were made between crossed polars on a Nikon microscope. Samples were annealed in an electromagnet for several days for alignment and critical magnetic field studies.

RESULTS AND DISCUSSION

Table I lists values for the pitch measured optically from the so-called "finger-print pattern" of cholesterics. When the helix axis of a cholesteric lies parallel to the glass walls of a capillary, the appearance between crossed polars is that of a series of parallel lines.[7] As the director, or rod axis, passes through every 180° of rotation, these positions of extinction produce the line pattern and hence one simply

TABLE I

Pitch and Critical Magnetic Field of a 20% (W/V) Solution of PBLG (M.W. 210,000) in Phenethyl Alcohol and Dibromomethane at 25°

Volume Ratio Alcohol/CH_2Br_2	Pitch P μm	H_c kG	Elastic Constant k_{22} dyne × 10^7
l-alcohol			
3:7	150.0	3.4	7.3
4:6	90.0	5.0	5.6
5:5	37.6	8.6	2.9
5:5	37.8	8.5	2.8
2:1	18.5	14.6	2.0
2:1	20.2	14.5	2.3
3:1	14.0	17.2	1.6
3:1	14.6	16.0	1.5
4:1	11.6	21.0	1.6
4:1	12.7	20.8	1.9
dl-alcohol			
3:7	140.0	3.8	8.0
4:6	55.0	6.1	3.1
5:5	36.0	8.8	2.7
5:5	33.8	9.2	2.6
2:1	14.1	17.0	1.6
2:1	17.4	14.8	1.8
3:1	12.4	20.6	1.8
3:1	12.8	20.0	1.8
4:1	8.7	23.0	1.1
4:1	10.0	21.4	1.2
d-alcohol			
3:7	90.0	4.6	4.8
4:6	45.0	6.8	2.6
5:5	30.4	9.4	2.2
5:5	28.9	9.9	2.2
2:1	12.2	20.7	1.8
2:1	14.2	15.2	1.3
3:1	10.6	21.2	1.4
3:1	11.7	20.9	1.6
4:1	6.3	>23.9	>0.62
4:1	7.3	23.5	0.81

measures the distance between two such lines to obtain a value for half of the pitch of the helix.

Also listed in Table I are experimental measurements of the critical magnetic field H_c required to deform, or untwist the cholesteric of pitch P into a nematic[8,9] which allows a calculation of the elastic constant k_{22} from the equation:

$$H_c = \left(\frac{\pi^2}{2}\right)\left(\frac{k_{22}}{\chi_a}\right)^{1/2}\left(\frac{1}{P}\right)$$

χ_a, the anisotropy of the magnetic susceptibility, is assumed to be invariant and have a value = 6.7×10^{-9} emu cm^{-3}.[10] The elastic constant k_{22} is known to be solvent dependent. For example, it has a value of 5.4×10^{-7} in dichloromethane, 6.2×10^{-8} in dioxan, and 2.1×10^{-7} in chloroform.[10] The values in Table I therefore seem quite reasonable for a mixture of dibromomethane and phenethyl alcohol.

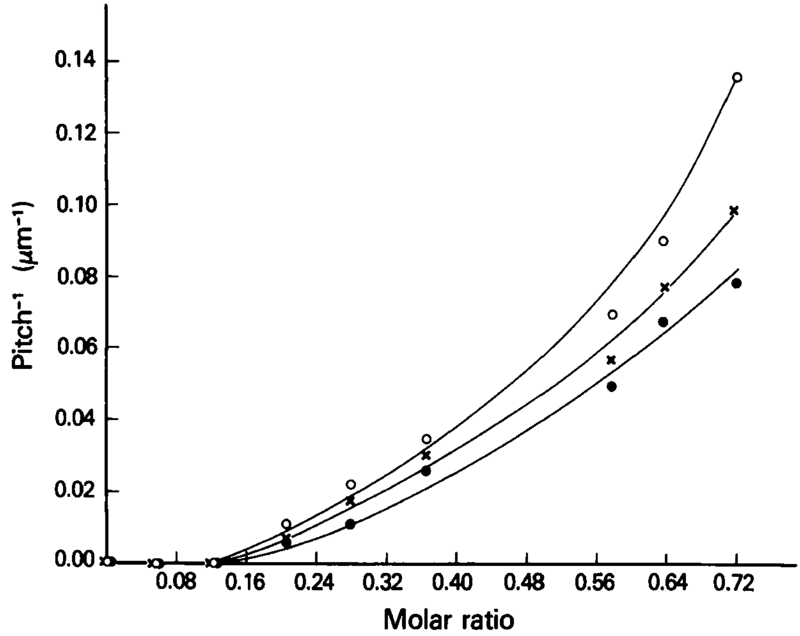

FIGURE 1 Inverse pitch of PBLG solution (20% W/V, M.W. 210,000) *vs.* mole ratio of phenethyl alcohol/phenethyl alcohol + dibromomethane at 25°. ●, *l*-alcohol; X, *dl*-alcohol; ○, *d*-alcohol.

TABLE II

Pitch of 30% PBDG (M.W. 150,000) Solution in Phenethyl Alcohol-Dibromomethane Mixtures at 25°

Volume Ratio Between Alcohol/CH_2Br_2	Pitch, μm *l*-PhOH/CH_2Br_2	*dl*-PhOH/CH_2Br_2	*d*-PhOH/CH_2Br_2
1:1	10.4 ± 0.2	9.6 ± 0.2	8.8 ± 0.3
2:1	5.0 ± 0.3	4.5 ± 0.1	4.1 ± 0.1
3:1	3.7 ± 0.1	3.2 ± 0.1	2.9 ± 0.1

P^{-1} is plotted in Fig. 1 as a function of the mole ratio of phenethyl alcohol to total moles of solvent. As phenethyl alcohol is added, the system remains nematic up to ~ 0.12 mole ratio. *l*-alcohol increases and *d*-alcohol decreases the pitch up to a mole ratio of 0.70. Beyond this concentration the system is biphasic. P^{-1} is ~ proportional to mole ratio except at very high and very low concentrations of alcohol.

Some measurements were performed in pure phenethyl alcohol with a somewhat higher concentration of PBLG—25 % (wt/vol) of M.W. 210,000. The pitches of *l*, *dl*, anf *d* alcohol solutions were 9.8 ± 0.6, 8.8 ± 0.6, and 8.1 ± 0.7, respectively.

Table II gives a few measurements on PBDG solutions, and again *l*-alcohol increases and *d*-alcohol decreases the pitch. Since it is known that both PBDG and PBLG are in the α-helix conformation, the interaction of phenethyl alcohol appears to be primarily a delocalized interaction with the entire polymer rod.

It is clear from this work that a chiral solvent environment can cause a profound change in the arrangement of chiral polymer rods in solution. The effect seems to involve an interaction between the long polymer rods and the solvent molecules which are relatively very small and no adequate model exists to explain how size distribution of chiral objects affects the long range distortion. Further work on this topic is in progress.

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