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K. Czarniecka [a] & E. T. Samulski [a]
[a] Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, CT 06268, U.S.A.
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Polypeptide Liquid Crystals: A Deuterium NMR Study†‡

K. CZARNIECKA‡ and E. T. SAMULSKI

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, CT 06268 U.S.A.

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In polypeptide liquid crystals deuterium NMR spectra of labeled guest molecules and labeled Polybenzylglutamate exhibit a characteristic doubling (anisochronism) of the quadrupolar splittings of enantiotopic deuterons. The anisochronism is a reflection of local chirality. For achiral guests the chirality is acquired in collision complexes with the chiral polypeptide. The labeled polypeptide results suggest that the observed anisochronism is related to specific sidechain secondary structures. The observations are consistent with a model of solvent and/or temperature compensation in these lyotropic cholesteric phases wherein a polypeptide sidechain conformational transition is invoked.

INTRODUCTION

The *anomalous* compensation exhibited by the lyotropic liquid crystals formed from Poly-γ-benzyl-L-glutamate, abbreviated PBLG, in various solvents continues to provoke discussion. Robinson observed that the sign of the form optical rotation, an indicator of the sense or handedness of the cholesteric structure, depended on the solvent used to prepare the liquid crystal.[1] In the mixed solvent, 1,4-dioxane (D) plus methylene chloride (MC) 2:8 by volume, the pitch is infinite; a compensated (nematic) texture is present in PBLG liquid crystals. Subsequently, compensated liquid crystals have been reported for the mixed solvent D plus nitrobenzene (4:6 by volume)[2] and, moreover, a compensated phase occurs at specific temperatures for PBLG liquid crystals in a variety of solvents.[3] In all of these liquid crystals, the only chiral component is the polypeptide, and PBLG persists as a right-

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§ On leave from Department of Chemistry, Jagellonian University, Cracow, Poland.

handed α-helix in these liquid crystals. This is the anomaly: the cholesteric sense changes but the sense of the chiral component (PBLG) is unaltered. *Normal* compensated polypeptide liquid crystals can be prepared from a racemic mixture of the right- and left-handed helices, PBLG and PBDG, respectively.

The properties of polypeptide liquid crystals have been reviewed several times in current literature.[4] Herein we pursue a microscopic description of the phenomenon of *anomalous* compensation by expanding an earlier investigation[5] of polypeptide liquid crystals using deuterium nuclear magnetic resonance (DMR). We focus on the behaviour of the quadrupolar splittings of deuterium labeled PBLG in liquid crystals compensated via solvent mixture, temperature, and polypeptide chirality. Our findings suggest that *anomalous* compensation may be attributed to subtle changes in the average sidechain secondary structure on the periphery of the helix.

EXPERIMENTAL

Deuterium labeled polypeptide PBLG-d_7 was synthesized via the Leuchs anhydride of L-glutamic acid esterified with benzyl alcohol-d_7.[6] The PBLG-d_7 was used to prepare polypeptide liquid crystals (20% and 30% polypeptide by wt.) as reported earlier.[4] Some liquid crystals employed mixtures of PBLG-d_7 with PBLG (Sigma Chemicals, MW = 150,000) and PBDG (Miles-Yeda Ltd., MW = 98,000). The deuterium NMR spectra were recorded on a standard FT NMR (Bruker WH-90) operating at 13.8 MHz; moderate signal averaging was required. The temperature was controlled to ± 1 Kelvin. The samples were not spinning and care was taken to insure that equilibrium alignment was achieved in the spectrometer before recording the spectra.

RESULTS

We begin by contrasting the DMR spectra of "free" guest molecules dissolved in the PBLG-dichloromethane liquid crystals. Figure 1(a) and (b) shows the quadrupolar splittings of toluene-d_8 and benzyl alcohol-d_7, respectively. In the case of the toluene-d_8, the three observed splittings correspond to the para (1), methyl (2), and ortho-meta deuterons (3), respectively. On the other hand, the benzyl alcohol-d_7 exhibits four doublets; intensity and chemical shift measurements enable the following asignment: para (1), ortho-meta (2), and *two* doublets for the benzyl deuterons (A) and (B), respectively. An identical spectrum to Figure 1 (b) is observed for benzyl alcohol-d_7 in liquid crystals prepared from PBDG.

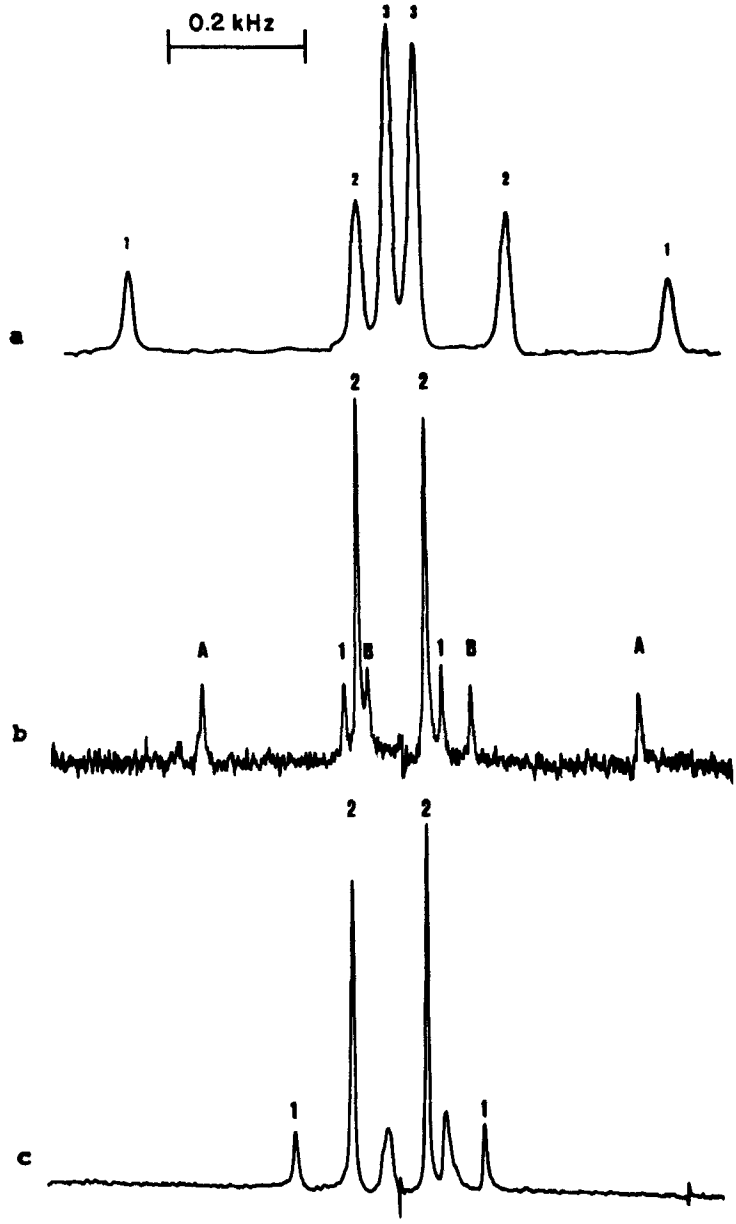

FIGURE 1 Quadrupolar splittings of labeled guest molecules (~5% wt.) solubilized in polypeptide liquid crystals (300 Kelvin); (a) toluene-d_8; PBLG-MC (20 wt % polymer); (b) benzyl alcohol-d_7; PBLG–MC (30 wt % polymer); (c) benzyl alcohol-d_7; racemic PBLG–PBDG–MC (30 wt % polymer). (See text for resonance assignments.)

The observed difference $\Delta\nu_A \neq \Delta\nu_B$ for the benzyl deuterons may be accounted for in the following manner. The "free" labeled guest molecules are partially oriented in the liquid crystal through non-specific repulsive interactions (anisotropic diffusion through the array of nearly parallel polypeptide helices) and specific attractive interactions between the guest and the chiral polypeptide molecules. These latter interactions in effect, confer chirality to the guest molecule. The homotopic deuterons in the CD_3 group of toluene are not differentiated in the chiral guest-PBLG collision complexes. However, the enantiotopic benzyl deuterons of the alcohol become diasteriotopic in such complexes leading to the observed anisochronism, $\Delta\nu_A \neq \Delta\nu_B$, of the benzyl deuterons.

In order to prove that the anisochronous benzyl deuterons are in fact caused by conferred chirality originating in specific chiral guest-PBLG interactions, we illustrate in Figure 1(c) the DMR spectrum of benzyl alcohol-d_7 dissolved in a nematic polypeptide liquid crystal consisting of a racemic mixture of helices with opposite chiralities, PBLG and PBDG. The para (1) and ortho-meta (2) doublets are indicated; the slightly broadened doublet that remains corresponds to the apparent isochronous benzyl deuterons. Rapid chemical exchange of the guest between complexes exhibiting opposite chirality (guest-PBLG and guest-PBDG) averages the conferred chirality to zero and $\Delta\nu_A = \Delta\nu_B$. We now try to exploit the behavior of enantiotopic deuterons in the PBLG sidechain to determine whether or not conformational changes are relevant to *anomalous* compensation in polypeptide liquid crystals.

As reported previously, PBLG-d_7 prepared from the amino acid esterified with benzyl alcohol-d_7 exhibits quadrupolar splittings in the liquid crystalline phase.[5] Figure 2(a) schematically illustrates the primary structure of PBLG-d_7. In the NMR spectrometer the solvated helices are aligned parallel to the magnetic field ($\Delta\chi > 0$) and consequently the rotational isomerism within the pendant sidechains only partially averages the quadrupolar interactions. As this "bound" species is considerably more constrained than the "free" guest molecules discussed initially, the resulting quadrupolar splittings of the labeled sidechain (Figure 2(b)) are correspondingly larger than those presented in Figure 1. In this PBLG-d_7-MC liquid crystal, the benzyl deuterons are anisochronous, and $\Delta\nu_A \neq \Delta\nu_B$.

The observed anisochronism within the CD_2 group is *not* a consequence of supramolecular chirality, i.e., chiral constraints imposed on the sidechain in the cholesteric texture caused by intermacromolecular packing. The cholesteric structure, macroscopically absent in the presence of the magnetic field, spontaneously reappears on removal of the field. This undoubtedly reflects an incipient local cholesteric packing of the neighbouring helices. In the compensated nematic texture of the racemic liquid crystal (PBLG-d_7

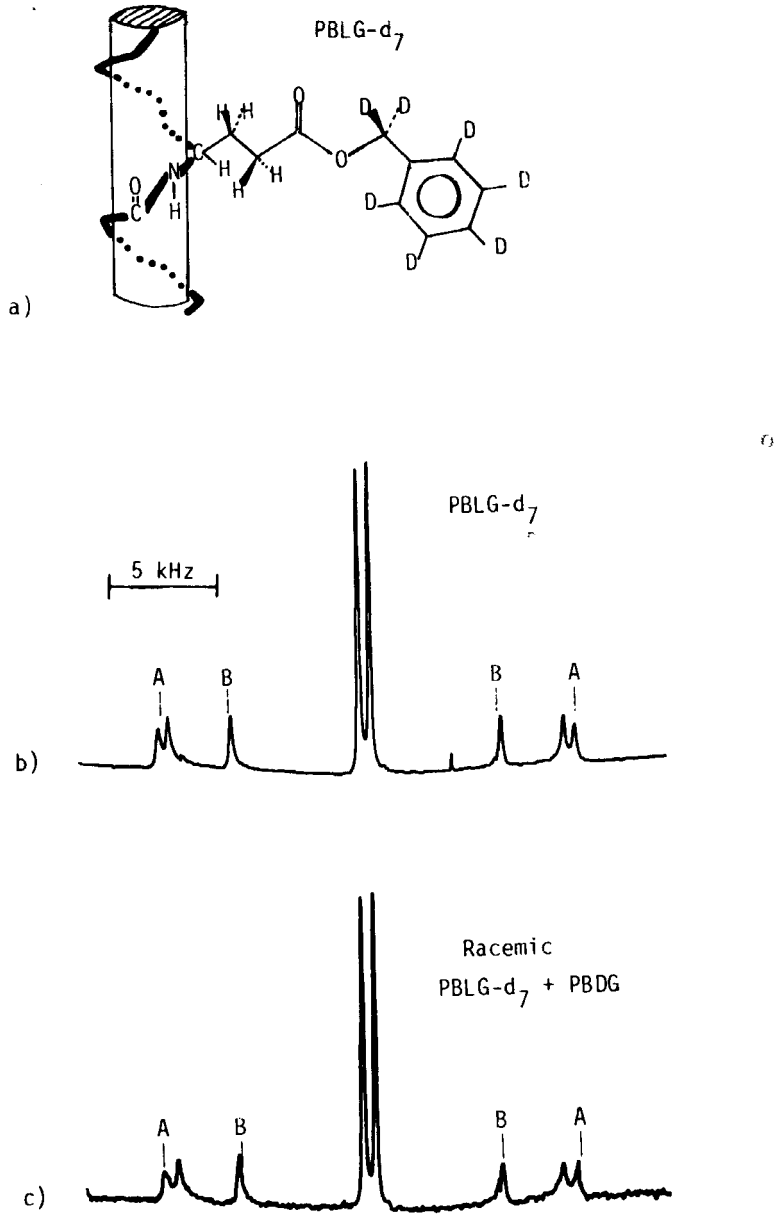

FIGURE 2 (a) Primary structure of PBLG-d_7; Quadrupole splittings of labeled PBLG-d_7 in the liquid crystal phase (300 Kelvin): (b) PBLG-d_7–MC (30 wt % polymer); (c) racemic PBLG-d_7 + PBLG–MC (15 + 15 wt % polymer). The letters A and B denote the benzyl CD_2 resonances.

+ PBDG-MC), the local packing of the helices and concommitant constraints on the sidechain are presumably different. In this compensated phase, however, anisochronism similar to that reported for the pure L-isomer is found (Figure 2(c)). We therefore conclude that the observation $\Delta\nu_A \neq \Delta\nu_B$ is indicative of specific intramacromolecular effects related to the chirality of the average sidechain secondary structure. In the remainder of this paper we focus on the changes in $\Delta\nu_A$ and $\Delta\nu_B$ with temperature and solvent composition of polypeptide liquid crystals prepared with PBLG-d_7.

Figure 3 shows the temperature dependence of $\Delta\nu_A$ and $\Delta\nu_B$ for the two liquid crystals described in Figure 2. Both liquid crystals exhibit a coincidence ($\Delta\nu_A = \Delta\nu_B$) of the CD_2 doublets at the same temperature, 261 K. In the case of the PBLG-d_7 liquid crystal, the coincidence temperature is identical to that at which the liquid crystal is *anomalously* compensated (in the absence of the field). There is, of course, no corresponding textural transition in the racemic liquid crystal. Thus, the observation that $\Delta\nu_A = \Delta\nu_B$ in both liquid crystals at the same temperature (independent of the equilibrium texture) reinforces our contention that the coincidence of the CD_2 doublets is of intrapolypeptide origin.

The coincidence of the two CD_2 doublets is also readily observed in PBLG-d_7 liquid crystals prepared with mixed solvents. Table I shows the coincidence temperature and the magnitude of the quadrupolar splitting, $\Delta\nu_A = \Delta\nu_B$ in mixtures of D:MC. The quadrupolar splittings are larger in the more concentrated liquid crystals (the orientational order improves with increasing polypeptide concentration). The change in coincidence temperature with polymer concentration is not very strong (see 8:2 MC:D samples, Table I).

At a fixed temperature, the difference between $\Delta\nu_A$ and $\Delta\nu_B$ closely parallels the behavior of the cholesteric pitch in the mixed solvent liquid crystals. In Figure 4 the cholesteric pitch and the inverse of the difference in the quadrupolar splittings $(\Delta\nu_A - \Delta\nu_B)^{-1}$ are shown as a function of solvent composition; the coincidence composition coincides with the *anomalous* pitch compensation (2:8 D:MC; $T = 293$ K).

DISCUSSION

In the late 1960's Sackmann *et al.*[7] used NMR to demonstrate that optically active guest molecules sense the chirality of the liquid crystal solvent even when no macroscopic chirality is present (e.g. nematic solvents were fabricated by using compensated mixtures of cholesterol derivatives). Here we have demonstrated that for the case of enantiotopic deutrons on an achiral guest molecule, interactions of the guest with the chiral component of the

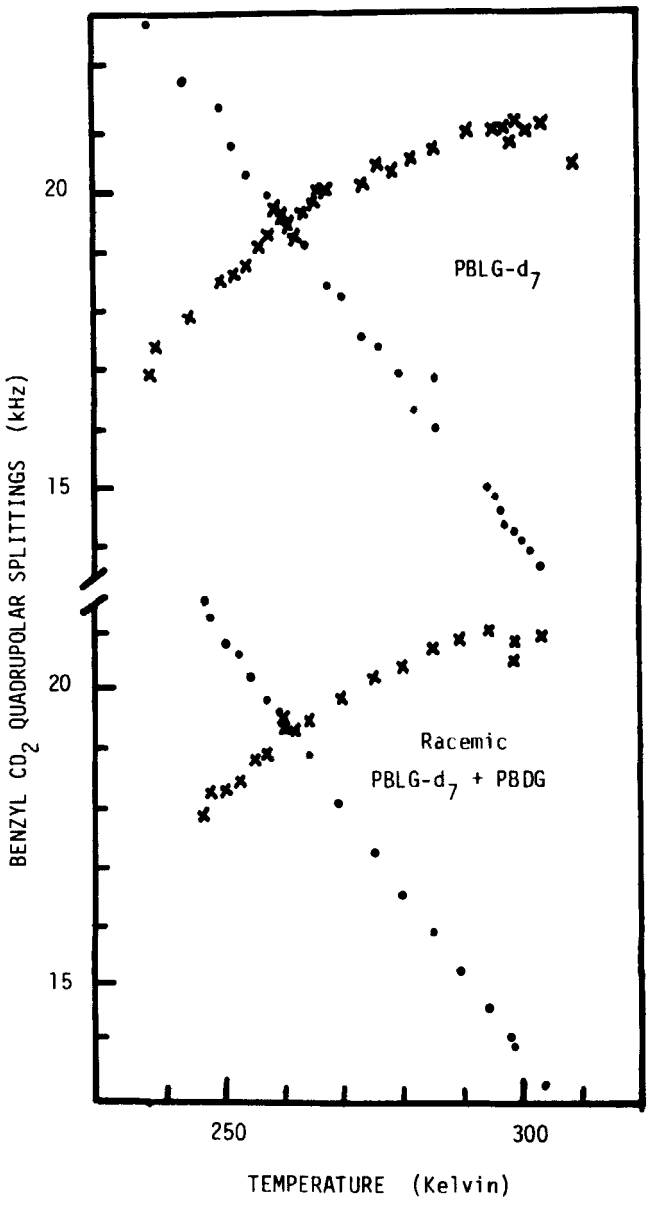

FIGURE 3 Temperature variation of the benzyl CD_2 quadrupolar splittings $\Delta\nu_A$ and $\Delta\nu_B$ indicated by the crosses and dots, respectively, in PBLG-d_7 and racemic (PBLG-d_7 + PBDG) liquid crystals. The coincidence temperature ($\Delta\nu_A = \Delta\nu_B$) is 261 Kelvin.

TABLE I

Coincidence Temperature in Polypeptide Liquid Crystals.

Polypeptide	Polymer wt. %	Solvent[a]	Coincidence temperature	$\Delta\nu_A = \Delta\nu_B$ (kHz)
PBLG-d_7	30	MC	261.5	19.5
PBLG-d_7 + PBDG	15 + 15	MC	261.0	19.3
PBLG-d_7	30	MC:D = 8:2	292.5	17.4
PBLG-d_7	20	MC:D = 9:1	276.5	17.9
PBLG-d_7	20	MC:D = 8:2	295.0	17.0
PBLG-d_7	20	MC:D = 7:3	296.0	16.6
PBLG-d_7	20	MC:D = 6:4	299.0	16.4

[a] MC = methylene chloride; D = 1,4-dioxane.

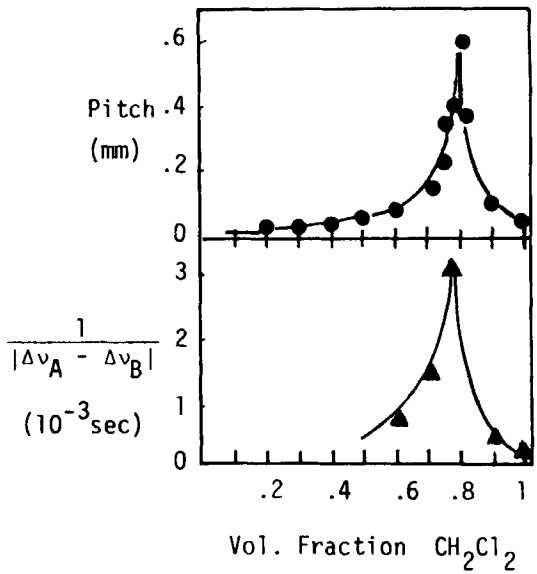

FIGURE 4 Cholesteric pitch (Ref. 8) and benzyl deuteron differences $(\Delta\nu_A - \Delta\nu_B)^{-1}$ versus solvent composition for mixed solvent (MC + D) PBLG liquid crystals.

polypeptide liquid crystal (the α-helix) confers chirality to the guest transforming the enantiotopic deuterons to diasteriotopic deuterons. This demonstration provides a starting point for an explanation of the appearance of two doublets for the benzyl deuterons in the DMR spectra of PBLG-d_7 liquid crystals. In the case of PBLG-d_7 the labeled probe is not a free guest molecule but the covalently attached polypeptide sidechain. The chirality sensed by the sidechain CD_2 group is not conferred via intermolecular associations as in the case of the guest-host interactions, but rather results from an average

over many possible sidechain conformations. This average yields for the CD_2 group a local environment with a net chirality. Most importantly, the sense of this averaged local sidechain chirality (right- or left-handed) appears to be dependent on the temperature and solvent composition on the polypeptide liquid crystal. While this local chirality of the sidechain secondary structure appears to determine the handedness of the macroscopic texture (right- or left-handed cholesteric liquid crystals), changes in the macroscopic texture (untwisting the cholesteric structure with a magnetic field or compensating the cholesteric structure by using racemic mixtures of polypeptides) does not perturb the local sidechain chirality.

All of the observations reported here lead to the following mechanism of

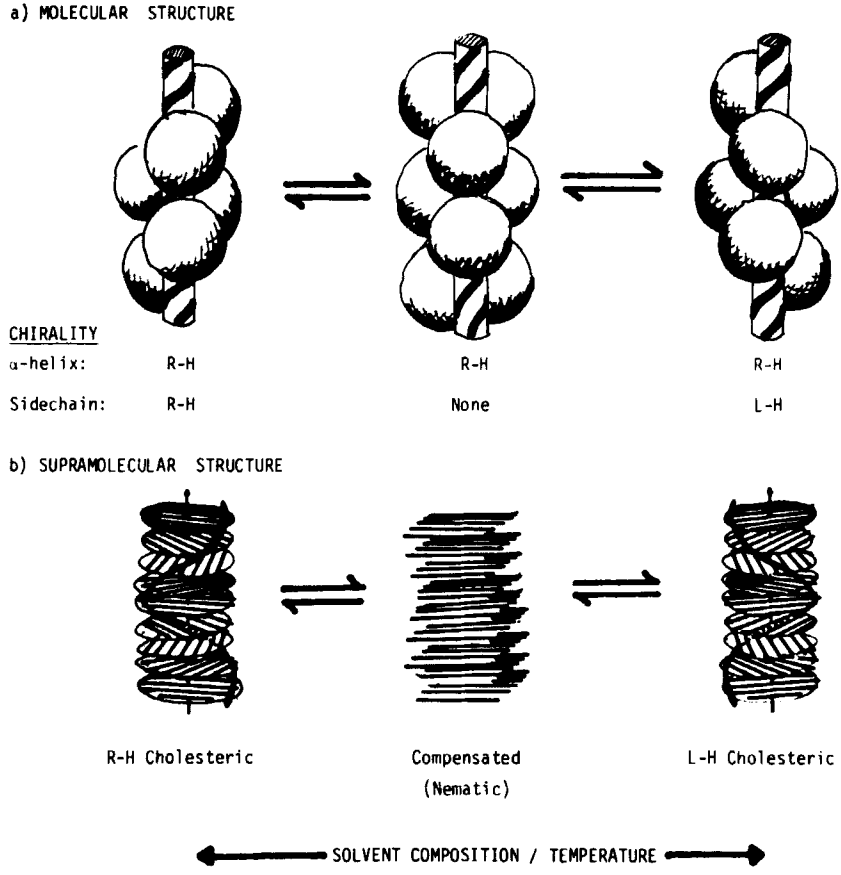

FIGURE 5 Schematic transformation in PBLG sidechain secondary structure corresponding to a change in apparent chirality for the polypeptide (a) and consequent reversal of cholesteric pitch sense (b); R-H and L-H denote right- and left-handed senses, respectively.

the *anomalous* compensation induced in the cholesteric polypeptide liquid crystals by mixtures of achiral solvents and/or temperature (Figure 5). The sense of the chirality of the average sidechain secondary structure on the exterior of the α-helical core of PBLG dictates the sense of the cholesteric structure in polypeptide liquid crystals. The sidechain secondary structure is delicate and is a complex function of solvation, intrasidechain dihedral angle constraints, and thermal energy. Changes in solvation and/or temperature can shift the average chirality of the sidechain secondary structure from right- to left-handed thereby changing the *apparent* chirality of the polypeptide. This change in *apparent* chirality causes the transition from a right- to a left-handed cholesteric texture although the core of the PBLG retains the low energy right-handed α-helical conformation.

This mechanism is not at variance with an earlier model of *anomalous* compensation involving the dielectric properties of the polypeptide and the solvent medium. While the polypeptide polarizability would be a function of sidechain secondary structure,[8] at the present time there is no straightforward quantitative accounting for the variation of the coalescence temperature with solvent composition (Table I). The proposed mechanism of *anomalous* compensation is also consistent with a recent theory of the cholesteric texture which focuses on the dipolar interactions among rod-like particles that possess a helicoidal array of permanent transverse dipoles;[9] the proposed change in sidechain secondary structure would alter the sense of the transverse dipolar array and thereby produce a transition form right- to left-handed cholesteric twist via a compensated texture. Lastly, this mechanism is consistent with a crude steric model for the origin of the handedness of the cholesteric sense; the screw-sense of the van der Waals surface of the polypeptide (the sidechain secondary structure) was invoked earlier by one of the authors as the source of cholesteric sense.[10]

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