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The cholesteric liquid crystals formed by poly(γ-benzyl L-glutamate) (PBLG) in various solvents exhibit a cholesteric sense inversion when the temperature or the solvent composition is changed. The sense inversion in 1,2,3-trichloropropane and in *m*-cresol occurs from right- to left-handed *via* an untwisted nematic state with increasing temperature. The helical twisting power (reciprocal of the cholesteric half-pitch) in mixtures of these two solvents shows a quadratic dependence on the solvent composition, accompanied by a two-fold sense inversion (right → left → right) at low temperatures. The measurements of the twisting power are also reported for PBLG in a series of alkylchlorides in order to establish the role of solvent. In solvents with low dielectric constants PBLG forms the right-handed cholesteric structure while it changes to the left-handed one when the dielectric constant is increased beyond a critical value of *ca*. 9. The increase in temperature enhances the left-handed twisting power in all solvents studied here regardless of the cholesteric sense at room temperature. These observations clearly separate the effects of solvent and temperature on the cholesteric structure and are discussed in comparison with theories.

INTRODUCTION

A synthetic polypeptide, poly(γ-benzyl L-glutamate) (PBLG), in certain organic solvents adopts an α-helical conformation stabilized by a network

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of intramolecular hydrogen bonds and behaves as a typical rod-like molecule. When the concentration of PBLG in such a solution is increased beyond a critical value (*A* point) the solution begins to form small portions of an anisotropic liquid crystalline phase, and at a higher concentration (*B* point) the entire solution changes to the liquid crystalline phase. Robinson *et al.*[1,2] have found that PBLG liquid crystals exhibit a high form optical rotation and a striation pattern characteristic of cholesteric liquid crystals. In the liquid crystalline phase the long molecular axes of PBLG helices are arranged essentially parallel within a microscopic molecular layer, but the molecules lying in each layer have successive slight angular displacements along the torsion axis with respect to the molecules in the adjacent layers.

Although the critical concentrations, the *A* and *B* points, are rather insensitive to solvent, the structure of liquid crystal is strongly influenced by solvent. For instance, PBLG forms a right-handed cholesteric structure in 1,4-dioxane and chloroform, while it forms a left-handed structure in 1,2-dichloroethane and dichloromethane.[1,2] In an appropriate mixture of dioxane and dichloromethane, the right- and left-handed twists compensate, and the cholesteric structure changes to an untwisted nematic structure. Solvent-induced compensation has also been observed in mixed solvent systems such as dioxane—nitrobenzene,[3] dioxane—dichloroethane[4] and dichloroethane—*m*-cresol.[4] Samulski and Samulski[5] have developed a theory of the solvent-induced compensation in polypeptide liquid crystals based on the calculation of the van der Waals interactions between two chiral rods embedded in a dielectric medium. This theory shows that the cholesteric sense changes when the dielectric constant of the medium is increased by altering the solvent composition, and the calculation is in good agreement with experimental observations in the dioxane—dichloromethane mixed solvent. One may therefore anticipate that the cholesteric sense in a given solvent is determined by the magnitude of dielectric constant if there are no specific interactions between polymer and solvent.

Another important observation is a compensation induced by a change in temperature. In previous papers[4,6] we have reported that the PBLG—*m*-cresol liquid crystal shows this kind of compensation and the cholesteric sense reverses from right to left with increasing temperature. This finding was discussed in terms of the polymer—solvent interaction since *m*-cresol is a solvent which forms hydrogen bonds with the side-chain carbonyl groups of PBLG. However, our subsequent investigations reveal that the sense inversion also occurs in 1,2,3-trichloropropane (TCP) which does not have any particular functional groups. Similar findings have been reported for poly(γ-alkyl L-glutamate)s in chloroform[7] and for PBLG in tetrachloroethane.[8] These newly found inversions prompted us to study the effects of temperature and solvent on the cholesteric structure more extensively to establish an experimental basis for further detailed understanding of the mechanism of these so-called anomalous inversions.

In this paper, we first describe how the sense inversion occurs in TCP based on the optical rotatory dispersion (ORD), circular dichroism (CD) and microscopic measurements. The dependences of the cholesteric structure on the PBLG concentration in TCP and on the solvent composition in TCP—*m*-cresol mixed solvent are also described. In the latter section we focus on the temperature and solvent effects in a series of alkylchlorides which are chosen to avoid the specific polymer—solvent interactions such as the hydrogen-bond formation. The results are compared with microscopic theories for lyotropic liquid crystals.

EXPERIMENTAL

The two PBLG samples used in this study were synthesized by the *N*-carboxyanhydride method from γ-benzyl L-glutamate using triethylamine as the initiator. The average molecular weights of the samples were estimated from viscosity measurements to be $M_w = 18.4 \times 10^4$ and $M_w = 24.6 \times 10^4$; the latter sample was used in most experiments. All solvents were purified before use by simple distillation or vacuum distillation over proper desiccants. A weighed amount of PBLG was completely dissolved in solvent, and then the solution was sealed in a cell and matured at room temperature to allow the formation of the liquid crystalline structure. The concentration C, expressed in volume % of PBLG in solution, was calculated by assuming the specific volume of PBLG to be 0.787 ml/g.

The cholesteric half-pitch was determined by measuring the spacing between microscopically visible striation lines. The measurements were carried out at 5°C intervals in a glass cell of 2 mm thickness by using a polarizing microscope with a thermostated oven. In order to obtain the equilibrium pitch, the solution was kept at each temperature for more than 10 h. The ORD and CD spectra were measured using a Shimazu QV-50 spectrometer with ORD attachments and a JASCO J-20 recording spectropolarimeter, respectively. Water-jacketed quartz cells manufactured by JASCO, with pathlengths of 0.2 mm for ORD and 0.1 mm for CD, were used. These cells were cleaned with a concentrated solution of chromic acid, then rinsed with distilled water and acetone. The temperature of the sample was controlled by circulating water and monitored by a copper—constantan thermocouple. In order to eliminate the effect of birefringence upon the optical rotation, ORD measurements were repeated for different values of the angle between the vertical position of the sample cell and the plane of polarization of the incident beam. For this purpose the cell was mounted on a holder and both the polarizer and the analyzer were designed to be rotated in a plane perpendicular to the incident beam.

RESULTS AND DISCUSSION

A. Temperature and Concentration Dependences of the Helical Twisting Power in TCP

The cholesteric liquid crystalline structure can be described by the handedness and the strength of the twist. For cholesteric phases of PBLG, the latter quantity can be measured directly from the spacing S between striation lines, which is equal to half the cholesteric pitch. Figure 1 shows the temperature dependence of S for PBLG liquid crystals in TCP (C = 15.0 vol %). Initially S increases with temperature to an infinite value at T_c = 53°C, and then begins to decrease with further increase in temperature. The liquid crystalline solution at temperatures around T_c shows no regular striations but a random thread-like pattern corresponding to the nematic phase. The observed S values for the two PBLG samples

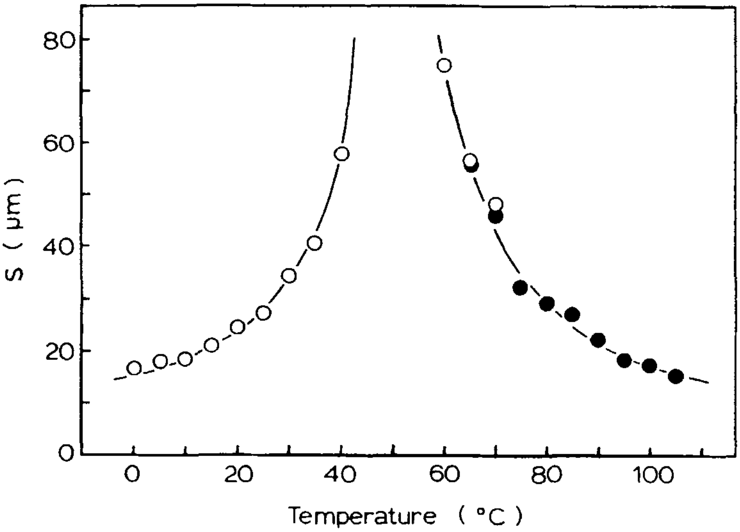


FIGURE 1 Plot of the cholesteric half-pitch S vs temperature for PBLG liquid crystals in TCP (C = 15.0 vol%). Open and closed circles represent data points for the PBLG samples with M_w = 24.6 × 10^4 and M_w = 18.4 × 10^4, respectively.

with molecular weights of 18.4×10^4 and 24.6×10^4 can be fitted to one experimental curve (see also Figure 4), so there appears to be no significant effect of molecular weight on the cholesteric pitch. This may be due to the rather small difference in molecular weight between two samples.

A divergence of S at a specific temperature has already been observed for PBLG in *m*-cresol, where the cholesteric sense inverts at T_c.[6] In order to prove the sense inversion in TCP, we measured the ORD spectra. According to the theory of de Vries,[9] the wavelength dispersion of optical rotatory power Θ is approximately given as follows:

$$\Theta = 45(\Delta n)^2 P \lambda^{-2} \text{ (degree } \mu\text{m}^{-1}\text{)} \tag{1}$$

where $P = 2S$ is the cholesteric pitch, λ is the wavelength of incident light and Δn is the birefringence of the molecular layer. Figure 2 shows the plots of Θ *vs* λ^{-2} in TCP. A positive optical rotation at 20°C, which varies in proportion to λ^{-2}, indicates the presence of a right-handed cholesteric structure. The sign inversion to negative at 100°C corresponds to an in-

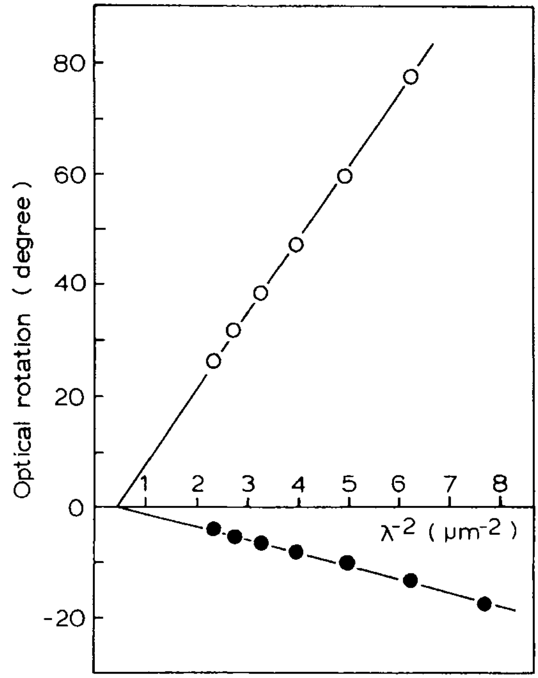


FIGURE 2 de Vries plot of the optical rotatory power of the PBLG liquid crystal in TCP at (○) 20°C and (●) 100°C. The molecular weight of the PBLG sample is $M_w = 24.6 \times 10^4$ and the concentration is $C = 15.0$ vol%.

version of the cholesteric sense from right to left. The magnitude of Θ at 100°C is much lower than that at 20°C, although S in Figure 1 has almost the same value at these temperatures. This may be associated with the reduction of orientational order due to larger thermal fluctuations at the higher temperature.

The sense inversion was also exhibited for the same solution by the CD measurements. Figure 3 shows the ultraviolet CD spectra of the cholesteric phase in TCP at 20°C and 82°C. The shape and the peak wavelengths (254, 259 and 265 mμ) of these CD spectra are identical to those of an absorption spectrum for the terminal phenyl groups in the side chain of PBLG. Such an intense circular dichroism does not appear until the solution forms the cholesteric phase; therefore, it can be attributed to a helical organization of the chromophors in the cholesteric structure. Saeva[10] has termed this "liquid crystal induced circular dichroism (LCICD)", and has suggested that the cholesteric sense can be determined by the sign of LCICD. Since the PBLG—dioxane liquid crystal displays a positive LCICD spectrum,[11] we conclude that the cholesteric phase in TCP at 20°C has the same sense as in dioxane, *i.e.*, right-handed. When the temperature is increased to 82°C, the positive LCICD band changes its sign to negative while maintaining the same shape. This negative sign, which is the same as that in EDC at room

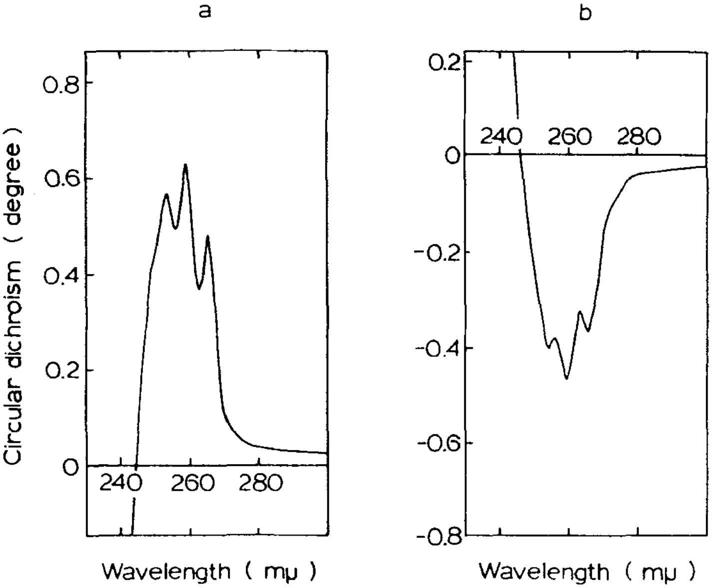


FIGURE 3 LCICD spectra of the side-chain phenyl groups of PBLG in the liquid crystalline solution in TCP at (a) 20°C and (b) 82°C.

temperature,[12] indicates a left-handed cholesteric structure. The sense inversion from right- to left-handed determined from LCICD is consistent with the conclusion of ORD studies.

The results of pitch measurements in TCP are summarized in Figure 4, where the reciprocal of S is plotted against temperature T. The S^{-1} value has been used as a measure of the helical twisting power since it is proportional to the twist angle between neighboring molecules. The sign of S^{-1} reflects the cholesteric sense; a positive sign is identified with the right-handed twist. The right-handed twist first decreases linearly with tem-

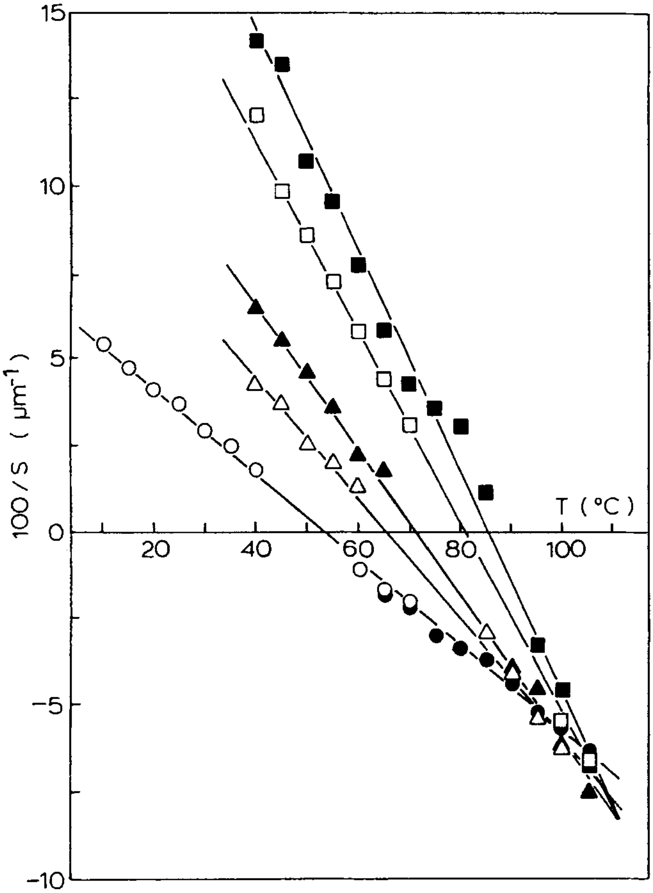


FIGURE 4 Temperature dependence of the helical twisting power of PBLG—TCP liquid crystals of various concentrations; (○)(●) 15.0%, (△) 17.5%, (▲) 20.0%, (□) 22.5%, and (■) 25.0%. Closed circles are data points for the PBLG sample with M_w = 18.4 × 10^4, and others are for the sample with M_w = 24.6 × 10^4.

perature toward zero at T_c, and then changes to the left-handed twist. In other words, an increase in temperature results in a continuous increase in the left-handed twisting power. The observed relationship between S^{-1} and T can be represented by,[6,7]

$$S^{-1} = A(T - T_c) \tag{2}$$

where A is a temperature coefficient of the twisting power.

The S^{-1} value is essentially an increasing function of concentration at low temperatures; however, this relationship varies with temperature. In particular, in a narrow range of temperature below 100°C, the magnitude of the left-handed twisting power decreases as the PBLG concentration is increased. This behavior occurs as a consequence of a shift of T_c to higher temperatures with increasing in concentration. Robinson[2] has already noted that the change in S^{-1} is porportional to C^2 in dioxane and in

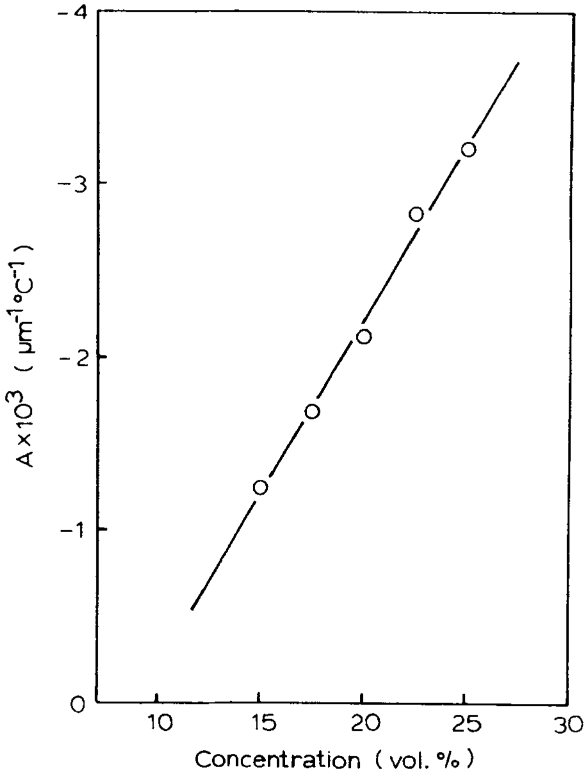


FIGURE 5 Plot of the temperature coefficient of the helical twisting power *vs* the PBLG concentration for the PBLG—TCP liquid crystal.

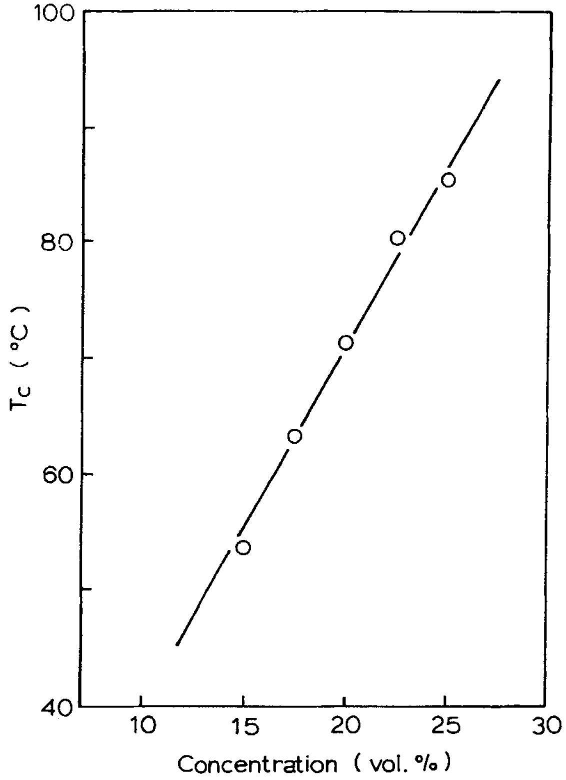
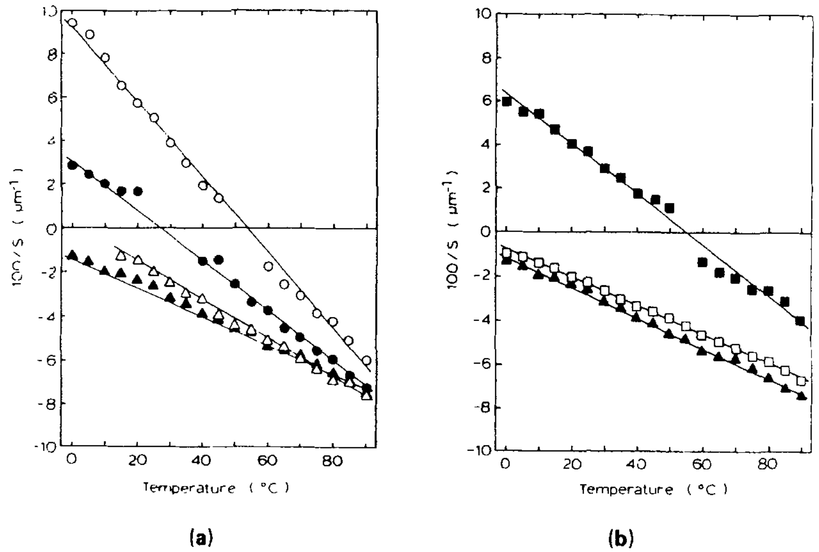


FIGURE 6 Plot of the compensation temperature T_c *vs* the PBLG concentration for the PBLG—TCP liquid crystal.

m-cresol, but his observation should be regarded as valid at a particular temperature. The relationship between the twisting power and concentration, valid for any temperature, can be developed in terms of *A*, which corresponds to S^{-1} at a given value of the temperature difference $T - T_c$. The plot of *A* *vs* *C* in Figure 5 demonstrates that *A* increases linearly with concentration. The compensation temperature T_c is also an increasing function of concentration as seen in Figure 6. These results agree with earlier observations in *m*-cresol.[13]

B. Helical Twisting Power in TCP—*m*-Cresol Mixed Solvents

Figure 7 shows the temperature dependence of S^{-1} in TCP—*m*-cresol mixed solvents. In *m*-cresol, S^{-1} changes linearly with temperature from positive to negative, passing through zero at T_c = 53°C. When 20 mol %



(a)

(b)

FIGURE 7 Temperature dependence of the helical twisting power of PBLG liquid crystals in TCP—*m*-cresol mixed solvents (M_w = 24.6 × 10^4 and C = 15.0 vol%). The contents of TCP in solvent mixtures (mol%) are: (a) (○) 0, (●) 20, (△) 40, and (▲) 60; (b) (▲) 60, (□) 80, and (■) 100.

of *m*-cresol is substituted by TCP, the right-handed twisting power and the magnitude of its temperature coefficient are markedly decreased, and T_c shifts to 27°C. A further increase in the TCP content is accompanied by further decreases in the right-handed twisting power and the T_c value. In a mixture of 40% TCP and 60% *m*-cresol, T_c falls below room temperature; hence the liquid crystal retains the left-handed structure over the entire range of temperature. The formation of the left-handed structure in this solvent was confirmed by a negative ORD spectrum at 25°C. The S^{-1} *vs* T curve is shifted to lower values of the ordinate as the TCP content is increased to 60% (Figure 7a). But a further increase in the TCP content causes an upward shift (Figure 7b). This observation indicates a quadratic dependence of the twisting power on the solvent composition, accompanied by a twofold sense inversion.

Figure 8 illustrates how the twisting power changes with the solvent composition. At low temperatures, a right → left → right sense inversion can be induced by increasing the TCP content. The twofold inversion disappears above 60°C since the cholesteric structure becomes left-handed in both TCP and *m*-cresol; however, the quadratic variation of the twisting

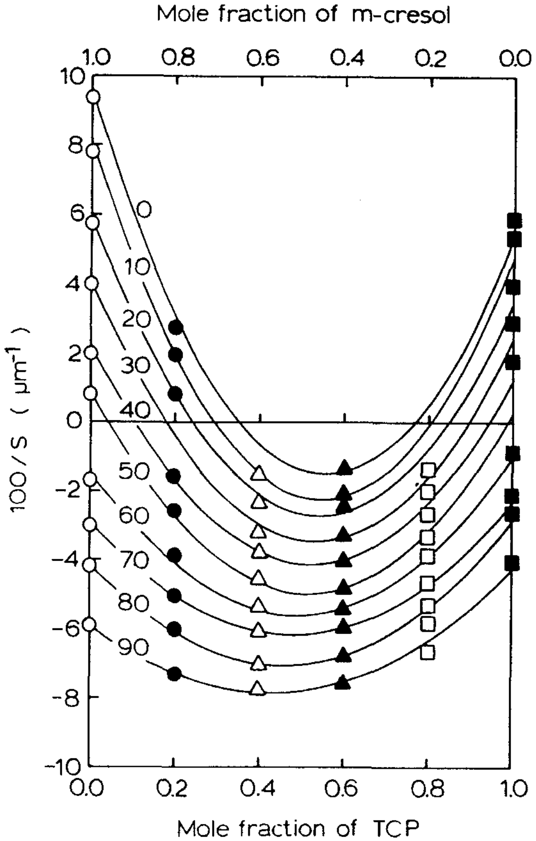


FIGURE 8 Dependence of the helical twisting power on the solvent composition in TCP—*m*-cresol mixtures. Numerals indicate the temperatures in °C.

power still remains. The following equation has been proposed to describe the dependence of the twisting power on the solvent composition in dichloroethane—*m*-cresol mixture;[4]

$$S^{-1} = S_{11}^{-1}x^2 + 2S_{12}^{-1}x(1 - x) + S_{22}^{-1}(1 - x)^2 \qquad (3)$$

where S_{11}^{-1} and S_{22}^{-1} represent the intrinsic twisting powers in the two separate solvents, S_{12}^{-1} represents the induced twisting power and x is the mole fraction of solvent 1 in the solvent mixture. The least-square fits of Eq. 3 shown by solid lines in Figure 8 reproduce the experiment satisfactorily. The values of S_{ij}^{-1} used for fitting are summarized in Table I, together with the critical mole fraction x^* of solvent 1 for compensation. According to

TABLE I

Temperature dependence of the helical twisting power S_{ij}^{-1} and the critical mole fraction of solvent 1 for compensation x^*.

solvent 1	solvent 2	Temp.	S_{11}^{-1}	S_{22}^{-1}	S_{12}^{-1}	x^*	
		°C	$\mu m^{-1} \times 10^2$				
TCP	*m*-cresol	0	5.4	9.5	−10.3	0.35	0.77
		10	4.8	8.0	−10.8	0.29	0.80
		20	3.4	5.9	−10.0	0.24	0.85
		30	2.4	4.1	−10.1	0.17	0.89
		40	1.2	2.2	− 9.9	0.10	0.94
		50	0.2	0.8	−10.4	0.04	0.99
		60	−1.0	−1.4	− 9.9		
		70	−2.3	−2.9	− 9.6		
		80	−2.8	−4.1	−10.5		
		90	−4.2	−5.9	−10.5		

Eq. 3, the twofold sense inversion can be expected under the following conditions: (i) $S_{11}^{-1}S_{22}^{-1} > 0$, (ii) $S_{11}^{-1}S_{12}^{-1} < 0$ or $S_{22}^{-1}S_{12}^{-1} < 0$, and (iii) $(S_{12}^{-1})^2 > S_{11}^{-1}S_{22}^{-1}$. In other words, the twofold inversion occurs only when the induced twisting power has a sufficiently large magnitude and a sign opposite to those of the intrinsic twisting powers in pure solvents. These conditions are indeed achieved in the TCP—*m*-cresol system in the temperature range below 60°C, where x^* can be given as;

$$x^* = \frac{S_{22}^{-1} - S_{12}^{-1} \pm [(S_{12}^{-1})^2 - S_{11}^{-1}S_{22}^{-1}]^{1/2}}{S_{11}^{-1} - 2S_{12}^{-1} + S_{22}^{-1}} \tag{4}$$

Above 60°C, all S_{ij}^{-1} values possess negative values, hence condition (ii) vanishes and the twofold inversion disappears.

The twofold inversion was first reported by Stegemeyer and Finkelmann[14] in binary mixtures of thermotropic cholesteric materials. The induced twisting power in such systems was considered to result from the dipole-quadrupole interactions between optically active species 1 and 2. However, there exists only one chiral constituent in our system, *i.e.*, PBLG, and it retains the right-handed α-helical conformation in both TCP and *m*-cresol. So far no satisfactory theory has been developed to explain the origin of this anomalous twofold inversion.

C. Solvent Effect on the Twisting Power

The aforementioned studies show that the thermally induced sense inversion is not a peculiar behavior of the cholesteric phase of PBLG in *m*-cresol, but it also occurs in TCP. This finding implies that the short range polymer—solvent interaction such as the hydrogen-bond formation is not the predominant reason for the thermally induced inversion and, that the inversion can occur in various solvents if T_c appears in a proper range of temperature. Thus, we are faced with the problem of explaining the solvent effect: how does T_c or the twisting power at a given temperature depend on the nature of solvent?

In this section we examine the temperature dependence of the twisting power in various solvents at a fixed PBLG concentration to answer this question. Figure 9 illustrates the results in five different alkylchlorides. In dichloroethane PBLG forms the left-handed cholesteric structure in the temperature range below the boiling point of the solvent.[4] The cholesteric sense in dichloromethane was also shown to be left-handed by the negative LCICD spectrum for the side-chain phenyl groups. Unfortunately, the

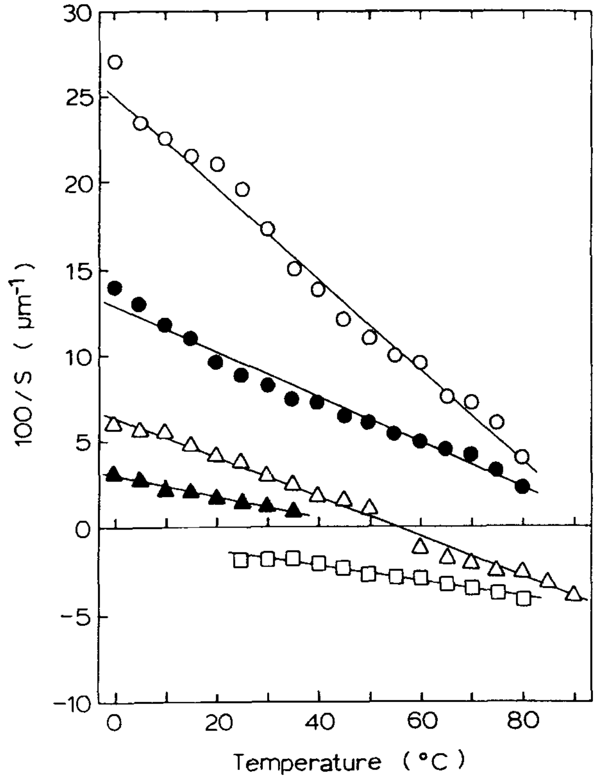


FIGURE 9 Temperature dependence of the helical twisting power of PBLG liquid crystals (M_w = 24.6 × 10^4 and C = 15.0 vol%) in various alkylchloride solvents: (○) pentachloroethane, (●) 1,1,1,2-tetrachloroethane, (△) TCP, (▲) chloroform, and (□) 1,2-dichloroethane.

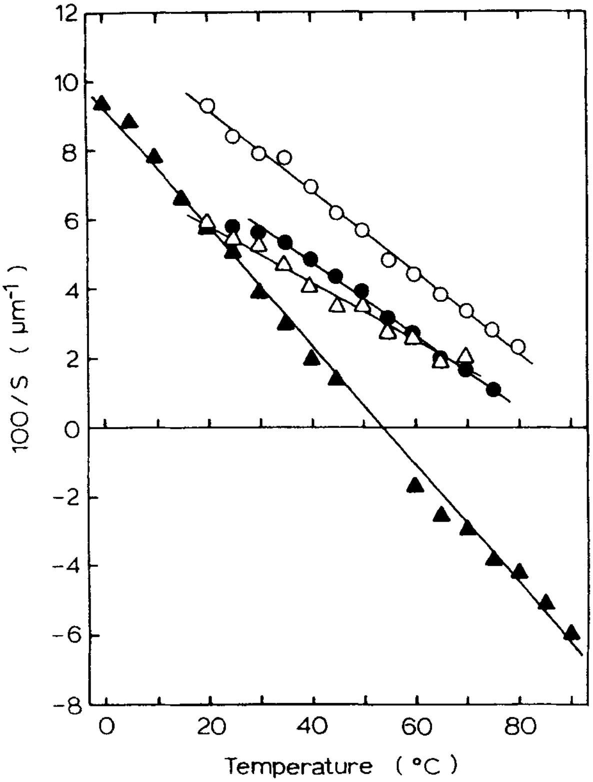


FIGURE 10 Temperature dependence of the helical twisting power in (○) tetrahydrofuran, (●) *N*,*N*-dimethylformamide, (△) 1,4-dioxane, and (▲) *m*-cresol.

cholesteric pitch in this solvent was too large to allow an accurate determination of its dependence on temperature. A rough estimate at 25°C gives an S^{-1} value of -0.01 μm^{-1}. On the other hand, the sign of the phenyl group LCICD was positive in chloroform, confirming the right-handed cholesteric sense.[1,2] The structure is also right-handed in pentachloroethane and 1,1,1,2-tetrachloroethane, and the S^{-1} values are much larger than in chloroform. Extrapolation of the S^{-1} *vs* T curves gives the compensation temperatures in the range 90 ~ 100°C, so that left-handed structures are expected at temperatures higher than our range of measurements. In fact, a sense inversion was recently reported in 1,1,2,2-tetrachloroethane around 83°C by Hashimoto *et al.*[8] TCP, as described above, is also a solvent which supports the thermally induced sense inversion. In spite of the apparent dependence of the cholesteric sense on solvent, plots of S^{-1} *vs* T in all these systems give straight lines with the negative slope.

Figure 10 summarizes the results of pitch measurements in four solvents which have chemically different structures from those studied in Figure 9. The cholesteric structure of PBLG is right-handed in tetrahydrofuran, *N,N*-dimethylformamide and dioxane. Values for *m*-cresol from Figure 7a are included in Figure 10 for comparison. The temperature coefficient of S^{-1} is again found to be negative in these solvents.

Samulski and Samulski[5] have derived the following equation for the twisting angle between two chiral rods $\phi = \pi d/S$ (d is the distance between rods) embedded in solvent with the dielectric constant ε_m:

$$\phi = \frac{1}{2}\tan^{-1}\{\varepsilon_m(J_{11} - J_{22})/C\} \tag{5}$$

Here C is an adjustable constant and J_{ij} are parameters proportional to $(\varepsilon_i - \varepsilon_m)(\varepsilon_j - \varepsilon_m)$ where ε_i and ε_j are the principal dielectric constants normal to the rod major axis. If the ε_m value is changed passing through a critical value $\varepsilon_m^* = (\varepsilon_1\varepsilon_2)^{1/2}$, the cholesteric twist will change its sign. Although the Samulski and Samulski theory was originally developed for the sense inversion in mixed solvents, it is also applicable to an analysis of the variation of the twisting power in various solvents. We should, however, note that such an application must be restricted to certain classes of solvents since the theory does not include the short range polymer—solvent interactions. In fact, the twofold sense inversion observed in a mixed solvent including *m*-cresol was not anticipated by their theory. We believe the best comparison of experiment with their theory to be achieved for a series of non-interactive, chemically similar solvents which covers a wide range of the dielectric constant. The result of such a comparison is shown in Figure 11 where the S^{-1} value at 25°C is plotted against ε_m. We find in alkylchlorides (shown by closed circles) that the positive S^{-1} value gradually decreases to zero with increasing ε_m and becomes negative in dichloromethane and dichloroethane. The experimental value for chloroform shows a displacement from the general trend, nevertheless, it still exhibits a positive sign. The sense inversion from right to left is in the correct direction of the Samulski and Samulski prediction. Furthermore the ε_m^* value of *ca.* 9 estimated from Figure 11 has a comparable magnitude to that found in the dioxane—dichloromethane mixed solvent ($\varepsilon_m^* = 7.9$). These agreements strongly suggest that the dielectric property of solvent plays an important role in determining the helical twisting power in this particular series of solvents. Anomalous S^{-1} values, for example in *m*-cresol, should be attributed again to the short range interactions of solvent with the PBLG sidechains.

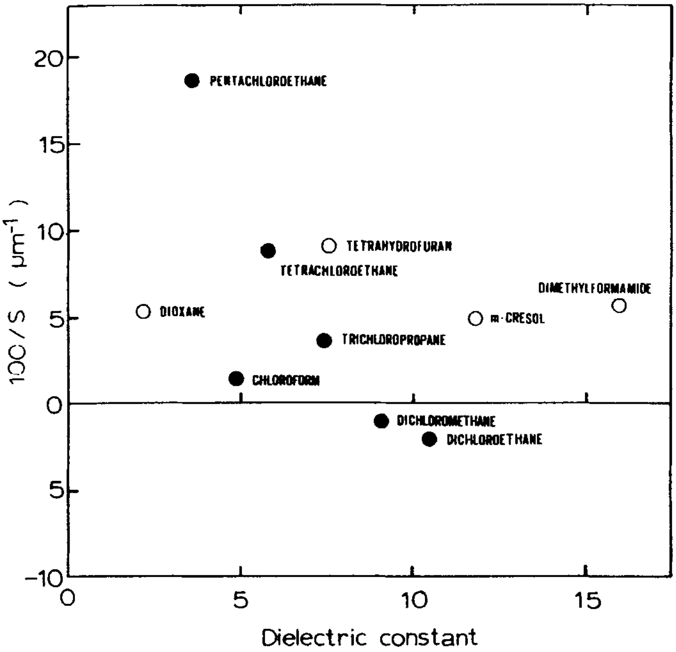


FIGURE 11 Plot of the helical twisting power *vs* the dielectric constant of solvent at 25°C.

CONCLUDING REMARKS

The cholesteric structure of lyotropic PBLG liquid crystals has been investigated in various solvents. We have described some new findings which can be summarized as follows: (i) The cholesteric liquid crystal in TCP exhibits a thermally induced inversion of its cholesteric sense. The observed dependence of the twisting power on temperature can be represented by $S^{-1} = A(T - T_c)$, where both A and T_c increase linearly with concentration; (ii) The twisting power in TCP—*m*-cresol mixed solvents depends quadratically on the solvent composition and shows a twofold inversion of sign at low temperature; (iii) In a series of alkylchlorides, the twisting power changes monotonically from positive to negative when the dielectric constant of solvent is increased; and (iv) In all solvents studied here, S^{-1} *vs* T plots give straight lines with negative slopes.

The combined influence of temperature and solvent on the cholesteric structure has obstructed a total understanding of the mechanism of twist in lyotropic polypeptide liquid crystals. We believe that this difficulty is now overcome to a certain extent by observations (i), (iii) and (iv). The cholesteric sense and pitch in alkylchlorides at room temperature are essentially dictated by the dielectric constant of solvent in accordance with the theory,[5] and the increase in temperature causes a linear increase in the left-handed twisting power. This effect of temperature is independent of the solvent effect, *i.e.*, the cholesteric sense at room temperature, therefore, can be discussed separately. One possible explanation for the thermal behavior, especially the linear dependence of the twisting power on temperature, is given from the phenomenological theory of Keating.[15] If it is assumed that the PBLG molecule undergoes a hindered rotation in a plane normal to the axis of cholesteric torsion, Eq. 2 can be derived from the Keating equation simply by adding a temperature-independent term AT_c which represents the inherent twist.[6] Recently, Kimura *et al.*[16] have developed a molecular theory of the cholesteric ordering in polypeptide solutions, including both the hard-rod repulsive and angle-dependent attractive interactions. The latter contribution is represented by the Maier-Saupe potential[17] and the Goossens term[18] which is responsible for generating the cholesteric twist. This theory predicts that a thermally induced sense inversion can occur and that the twisting power is inversely proportional to temperature. The theoretical dependence is contrary to our observations; however, they point out that in a temperature range of $|T\text{-}T_c| \ll T_c$ their equation can be rewritten in the form of Eq. 2.

The twofold sense inversion observed in TCP—*m*-cresol mixed solvents can not be explained by the Samulski and Samulski theory,[5] which successfully explains the behavior in alkylchlorides. Within the limit of their model (long-range van der Waals attractions), it may be possible to expand the theory to the above situation by introducing a change in the local dielectric property of PBLG (especially the reorientation of the side-chain permanent dipole moment)[19] and/or a deviation of the dielectric constant from an ideal additive law.

The theory of Kimura *et al.*[16] can also be expanded to the binary solvent systems as the Goossens theory[18] was expanded by Finkelmann and Stegemeyer[20] and Hanson *et al.*[21] Because of the nature of Kimura's potential, this expansion would result in an expression of the twisting power similar to Eq. 3, but which also includes the contributions from hard-core repulsions. The magnitude of latter contributions has been estimated to be proportional to the side chain length. Hence, for a system in which the shape anisotropy of PBLG is insensitive to the solvent composition one may expect Eq. 3 to be still applicable. In fact, the good agreement of Eq. 3 with experiment in TCP—*m*-cresol seems to indicate such a situation. However, we are not going to conclude from this agreement that the attractive interaction dominates the energy between PBLG helices. The above discussion implicitly assumes that a three-component system (chiral PBLG plus two achiral solvents 1 and 2) can be reduced to a two-component system which consists of PBLG 1 ideally solvated by solvent 1 and PBLG 2 solvated by solvent 2. This simplification ignores the interactions between multiple centers possessing different properties, which should be important for molecules with lengths much longer than the lateral distance to the neighbors. The theories featuring both attractive and repulsive interactions have recently shown their usefulness in variety fields of liquid crystal physics;[22] nevertheless, we claim that the application to PBLG liquid crystals in binary solvent mixtures should be done very carefully. We would suggest that they are to be tested at first by rather simple observations (i) and (iii) concerning the temperature, concentration and solvent effects.

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