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# Correlation of Pitch with Concentration and Molecular Weight in Poly($\gamma$-benzyl glutamate) Lyophases

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ABSTRACT: The variation of helical pitch in multicomponent mixtures consisting of a solvent and one or more different molecular weight polymeric species can be described by an equation in which the pitch is a quadratic function of the number densities of polymeric chiral solutes and achiral solvent, each of which has characteristic molecular twisting powers. The equation is shown to apply to literature data on the pitch of poly($\gamma$-benzyl glutamate) (PBLG) in *m*-cresol, 1,2,3-trichloropropane, and dioxane and to a large body of new data presented herein on PBLG in chloroform, by using samples of known polydispersity with molecular weights varying from 85 000 to 660 000.

## Introduction

The synthetic polypeptide PBLG adopts an $\alpha$-helical conformation in a wide variety of organic solvents and behaves like a typical rigid-rod type structure.[1,2] Above a certain critical concentration, the PBLG rods form a cholesteric liquid-crystalline phase.[3,4] The structure of the liquid crystal is strongly influenced by solvent; in dioxane[5] and chloroform[5] a right-handed cholesteric structure forms as the critical concentration is reached, whereas in 1,2-dichloroethane and dichloromethane[5,6] a left-handed structure is obtained. Indeed in solvent mixtures, the system can be compensated[5]—that is, the cholesteric structure changes to an untwisted nematic structure. It is further typical to see the pitch of the helix change thermally, frequently undergoing inversion at some characteristic "nematic" compensation temperature.

PBLG is a model system for a wide variety of chiral (and achiral) polymers that form lyotropic liquid-crystalline phases, and a large number of investigations have been conducted in an attempt to understand and correlate the effects of concentration, temperature, molecular weight, and solvent on the phase diagram and chirality of the medium.[5-9] In particular, the helical pitch of solutions of PBLG is known to depend on these variables, but the precise nature of the relationships has been difficult to define.

It is the purpose of this work to examine both literature data on PBLG solutions and a large body of new data presented herein on PBLG in chloroform solution to develop correlations that will allow the prediction of pitch in multicomponent mixtures of PBLG in a given solvent system.

## Theory

It occurred to us that the perturbations introduced into a solvent medium by chiral rods could be treated by an approach previously used by Bak and Labes[10,11] to predict pitch–concentration relationships in multicomponent thermotropic liquid–crystal mixtures consisting of cholesteric and nematic species. Although solvents such as chloroform are clearly not nematic liquid crystals, when they are participants in a liquid-crystal lyophase, they behave as though they were "virtual" nematic molecules: that is, their orientation and director field distribution are made chiral by the presence of the chiral rod.

When chiral rods are introduced into an achiral liquid, the induced distortions in that nematic (or, in the case treated here, "virtual nematic") liquid were calculated by de Gennes[12] for the case of low concentrations. The new director $n(r)$ is

$$n = n_0 + \delta n \qquad (1)$$

The local rotation at a distance $r$ from the chiral solute is described by the vector $\mathbf{w}$, defined as

$$\delta n = \mathbf{w} \times n_0 \qquad (2)$$

This perturbation gives rise to the twist of the nematic director having the form

$$\mathbf{w} = -\beta \nabla (1/r) \qquad (3)$$

The $\beta$ parameter has the dimensions of a surface (square centimeters) and is the interaction parameter—"molecular twisting power". Bak and Labes[11] generalized this treatment and extended eq 3 to the general case.

The expressions derived by Bak and Labes for multicomponent cholesteric–nematic mixtures can therefore be applied to the case in question in the following manner. For a mixture of cholesteric rods (A) in a solvent (B), the pitch is a quadratic function of the number densities of the components as shown in

$$\frac{1}{2p} = \frac{1}{n_A + n_B}\{\beta_A n_A^2 + 2\beta_{AB} n_A n_B + \beta_B n_B^2\} \qquad (4)$$

where $n_A$ ($n_B$) is the number of A (B) molecules per cubic centimeter in the mixture. This equation is, most likely, valid only for polymeric rods in the fully semiflexible limit, i.e., where the contour lengths greatly exceed the deflection lengths.[13]

The helical pitch of a multicomponent mixture can be generalized into

$$\frac{1}{2p} = \frac{1}{\sum_i n_i}\{\sum_i \beta_i n_i^2 + 2\sum_{i<j} \beta_{ij} n_i n_j\} \qquad (5)$$

where $n_i$ ($i$ = 1,2,3) is the partial number density of the component molecules in the mixture.

To analyze data on a two-component system, a convenient form of the above generalized equation is

$$\frac{1}{2pMm_A} = (N\beta_A - 2N\beta_{AB})m_A + 2N\beta_{AB} \qquad (6)$$

where

$m_A = \dfrac{n_A}{n_A + n_B} =$ mole fraction of the cholesteric component A

$M = \left[\left(\dfrac{M_A}{d_A} - \dfrac{M_B}{d_B}\right)m_A + \dfrac{M_B}{d_B}\right]^{-1} =$ molar density of the mixture

$M_A$ ($M_B$) = molecular weight of A (B) component

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$d_A$ ($d_B$) = density (g/cm$^3$) of pure A (B) component

$N$ = Avogadro's number

The equation can be rewritten as

$$\frac{M_A + (M_B - M_A)w_A}{2pdw_A} = \left\{N\beta_A\frac{M_B}{M_A} - 2N\beta_{AB}\right\}w_A + 2N\beta_{AB} \qquad (7)$$

where $w_A$ = weight fraction of the cholesteric PBLG component A and $d = d_B/[1 + (d_B/d_A - 1)w_A)$ = density (g/cm$^3$) of the mixture. The density of PBLG is taken as 1.271 g/cm$^3$ independent of its molecular weight.

For a binary mixture of PBLG (component A) in solvents such as chloroform (component B), since $M_A \gg M_B$, eq 7 can be simplified into

$$\frac{M_A(1 - w_A)}{2pdw_A} = \left\{N\beta_A\frac{M_B}{M_A} - 2N\beta_{AB}\right\}w_A + 2N\beta_{AB} \qquad (8)$$

It is also possible to analyze data on multicomponent mixtures consisting of several different molecular weight samples of polymer in a given (virtual nematic) solvent. In this work, data were obtained on ternary systems consisting of two different samples of PBLG of differing molecular weights in chloroform. We treat the mixtures in a manner identical with the Bak and Labes treatment[11] of thermotropic data on two cholesteric (A and B) components and one nematic (C) component (in this case, the "virtual" nematic solvent chloroform). Equation 5 becomes ($\beta_C = 0$)

$$\frac{1}{2pd} = N\left\{\frac{\beta_A}{M_A}\alpha(1 - w_C) + \frac{\beta_B}{M_B}(1 - \alpha)(1 - w_C)\right\} + NM'\left\{\frac{\delta\beta_{AB}}{M_AM_B}\alpha(1 - \alpha)(1 - w_C)^2 + \frac{\delta\beta_{AC}}{M_AM_C}\alpha w_C(1 - w_C) + \frac{\delta\beta_{BC}}{M_BM_C}(1 - \alpha)w_C(1 - w_C)\right\} \qquad (9)$$

where

$\alpha$ = weight fraction of A component in the mixture of A and B only

$w_C$ = weight fraction of C component in the total mixture of A, B, and C compounds

$$2\beta_{AB} = \beta_A + \beta_B + \delta\beta_{AB}$$

$$2\beta_{AC} = \beta_A + \delta\beta_{AC}, \text{ etc.}$$

$$M'^{-1} = \frac{\alpha(1 - w_C)}{M_A} + \frac{(1 - \alpha)(1 - w_C)}{M_B} + \frac{w_C}{M_C}$$

The definition of $M'^{-1}$ was incorrect in the Bak and Labes paper.[11] $M_B$ should be the denominator of the second term, *not* $M_A$. For the PBLG system, $M_AM_B \gg M_AM_C$ or $M_BM_C$. Consequently the equation can be simplified into a more convenient form for data analysis:

$$\frac{1}{2pd(1 - w_C)} = N\left\{\left(\frac{2\beta_{AC}}{M_A} - \frac{2\beta_{BC}}{M_B}\right)\alpha + \frac{2\beta_{BC}}{M_B}\right\} \qquad (10)$$

Further, when $w_C$ is constant, eq 10 can be reduced to the form

$$1/p = k\alpha + k'$$

A plot of the left-hand side of eq 10 vs $\alpha$ for a known $w_C$ value should give linear behavior over the entire composition range. By extrapolation of the straight line in these plots to $\alpha$ = 0 and 1, molecular twisting powers can be obtained.

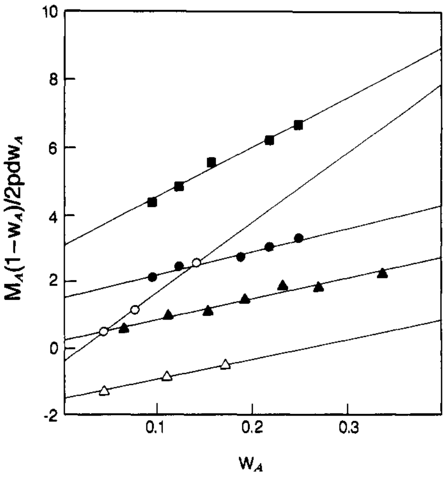

**Figure 1.** Test of the validity of eq 8 applied to literature data on PBLG in dioxane (● MW = 3.1 × 10$^5$, 25 °C; ■ MW = 5.5 × 10$^5$, 25 °C), *m*-cresol (▲ MW = 2.46 × 10$^5$, 35 °C), and 1,2,3-trichloropropane (○ MW = 2.46 × 10$^5$, 40 °C; △ MW = 1.84 × 10$^5$, 95 °C); $x$ axis, dimensionless; $y$ axis in units of 10$^8$ cm$^2$.

## Analysis of Literature Data

Equation 8 can be applied to the analysis of data on PBLG in the following solvent systems: dioxane, *m*-cresol, and 1,2,3-trichloropropane. Dupre and Duke[7] treated their data on the change of pitch with concentration by plotting log pitch vs log concentration for two different molecular weight samples of PBLG and find $p \approx C^{-1.8}$. Although Toriumi et al.[9] do not specifically plot their data on *m*-cresol or 1,2,3-trichloropropane as a function of concentration, it is possible to extract sufficient data from their plot of the temperature dependence of helical twisting power at various concentrations to assess the applicability of eq 8. Robinson[1] finds that pitch is proportional to $C^{-2}$ in *m*-cresol and dioxane. The data of all of these authors can be successfully treated by the approach represented by eq 8. A test of the validity of eq 8 for these data is shown in Figure 1. Good fits to a linear function are obtained over the entire range of concentrations examined.

## Experimental Procedures: PBLG in Chloroform

PBLG used in these studies was supplied by Sigma Chemical Co. with molecular weights from 85 000 to 345 000. Additional samples were provided by Dr. C. Matheson (Du Pont), molecular weight 435 000, and by Prof. T. Asaka (University of Kyoto), molecular weight 660 000. The values of the polydispersity ($M_w/M_n$) of the samples were estimated by gel permeation chromatography, and all samples were of low polydispersity (1.15–1.22).

PBLG (10–30 mg) was placed in an 0.6-mm-thick rectangular glass capillary (purchased from Vitro Dynamics, NJ), typically 6 mm wide and 2.5 in. long and sealed at one end. The appropriate amount of chloroform was added with a syringe, and the sample was sealed with a microtorch. Samples were incubated for at least 1 week to ensure complete homogeneity, the very high molecular weight samples requiring longer times for the textures to develop and remain stable. Optical observations were made between crossed polars on a Nikon microscope fitted with a video camera to allow images to be recorded on videotape. Samples were annealed for several days in an electromagnet for alignment and critical magnetic field studies.

## Analysis of Data

**PBLG in Chloroform.** In this section, we shall analyze the general behavior of pitch with concentration, tem-

**Table I**
**Phase Transition Behavior of PBLG in $CHCl_3$[a] Giving the Phase Sequences as One Proceeds from Low to High Temperature**

| MW | concn (w/v), % 30 | 35 | 40 | 45 | 50 |
|---|---|---|---|---|---|
| 85 000 | $N \rightarrow C_L$ | | $N \rightarrow C_L$ | | $C_R \rightarrow N \rightarrow C_L$ |
| 110 000 | $C_R \rightarrow N \rightarrow C_L$ | | $C_R \rightarrow N \rightarrow C_L$ | | $C_R \rightarrow N \rightarrow C_L$ |
| 210 000 | | $C_R \rightarrow N \rightarrow C_L$ | $C_R \rightarrow N \rightarrow C_L$ | $C_R \rightarrow N \rightarrow C_L$ | |
| 345 000 | | $C_R \rightarrow N \rightarrow C_L$ | $C_R \rightarrow N$ | $C_R \rightarrow N$ | |
| 435 000 | N | $C_R \rightarrow N$ | | | |
| 660 000 | N[b] | $C_R \rightarrow N$[c] | | | |

[a] The symbols N, $C_R$, and $C_L$ represent nematic, right-handed cholesteric, and left-handed cholesteric, respectively. [b] Concentration = 31%. [c] Concentration = 37%.

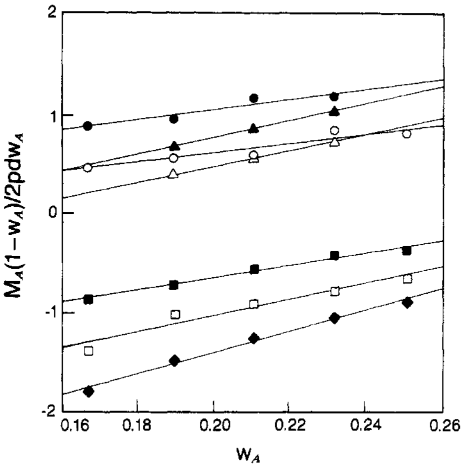

Figure 2. Test of the validity of eq 8 applied to PBLG (MW = 2.1 × $10^5$) in chloroform at 10, 20, 25, 30, 60, 70, and 80 °C reading from top to bottom; $x$ axis, dimensionless; $y$ axis in units of $10^8$ cm$^2$.

perature, and molecular weight of PBLG. PBLG solutions typically show an increase in pitch with temperature to an infinite pitch (nematic phase) at some characteristic temperature, which we shall call $T_N$ (where N = nematic). Above this temperature pitch decreases in value with temperature. $T_N$ depends on solvent, as does the sign of the helix; in this discussion, we restrict ourselves to chloroform. In chloroform, there is a helical sense inversion at $T_N$, with the low-temperature phase having a right-handed helicoidal sense, and the high-temperature phase forming a left-handed helix. The phase-transition behavior of various PBLG samples is described in Table I. Note that when concentration and molecular weight are low, the right-handed cholesteric phase is not seen at all, whereas at high concentration and molecular weight, the left-handed cholesteric phase is not observed.

Typical data on pitch, $T_N$, the critical magnetic field $H_c$ for helix unwinding, the elastic constant $k_{22}$ determined from the critical magnetic field value,[7] and the coefficient of the temperature dependence of pitch are listed in Table II.

A typical plot of data showing the pitch–concentration relationship as described in eq 8 is shown in Figure 2. As can be seen, the fit to a linear function is very good and allows a correlation of data at any concentration and temperature. Similar plots are obtained for PBLG of different molecular weights.

**Ternary Mixtures.** Data were accumulated for solutions of PBLG of two *different* molecular weights in chloroform. In the first series of experiments, bimodal mixtures consisting of a total of either 45 or 51% of two different samples of PBLG in chloroform were prepared. Table III summarizes the properties of these solutions. If one attempts to mix PBLG of very disparate molecular weights, one would expect to obtain biphasic samples.

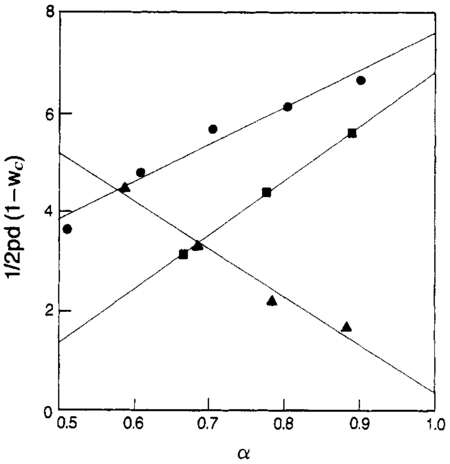

Figure 3. Test of the validity of eq 10 applied to ternary mixtures at room temperature in which the weight fraction of chloroform is constant: ● MW = 2.1 × $10^5$, major PBLG component, MW = 8.5 × $10^4$, minor PBLG component; ▲ MW = 8.5 × $10^4$, major; MW = 2.1 × $10^5$, minor; ■ MW = 2.1 × $10^5$, major; MW = 1.1 × $10^5$, minor; $x$ axis, dimensionless; $y$ axis in units of $10^2$ cm$^2$/g.

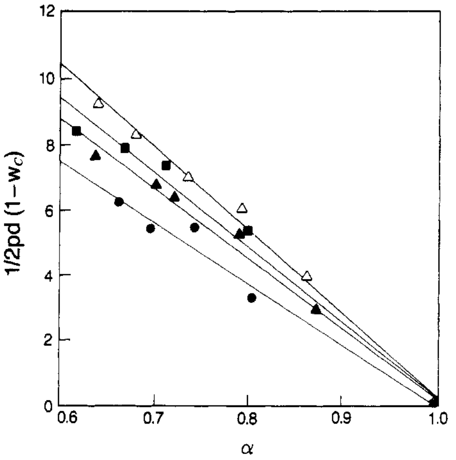

Figure 4. Test of the validity of eq 10 applied to ternary mixtures at room temperature, in which one component of PBLG (MW = 3.45 × $10^5$) is major and another component of PBLG (● MW = 8.5 × $10^4$, ▲ MW = 1.1 × $10^5$, ■ MW = 2.1 × $10^5$, △ MW = 6.6 × $10^5$) is minor; $x$ axis, dimensionless; $y$ axis in units of $10^2$ cm$^2$/g.

Provided the molecular weights are not too different, bimodal monophasic samples can be prepared. In this work, bimodal mixtures with molecular weight ratios of 1.9–2.5 were studied. These data were analyzed in accord with eq 10, and good linear plots were obtained, indicating the validity of the treatment. A typical data set is shown in Figure 3.

In a second series of experiments, small (varying) amounts of PBLG (component B) of different molecular weights were added to a solution of a large amount of cholesteric PBLG (component A) in chloroform (component C). Again good linear plots were obtained in accord

Table II
Summary of the Properties of Solutions of PBLG in Chloroform at 25 °C

| MW × $10^3$ | concn, g | pitch, $\mu$m | $-dp^{-1}/dT$, $mm^{-1}$ °$C^{-1}$ | $T_N$, °C | $H_c$, kG | $10^7k_{22}$, dyn |
|---|---|---|---|---|---|---|
| 85 | 30 | ∞ | 0.73 | 6.0[a] | | |
| 85 | 40 | ∞ | 1.04 | 17.9[a] | | |
| 85 | 50 | 56 ± 2 | 1.36 | 34.2 | 9.8 | 8.3 |
| 110 | 30 | ∞ | 0.78 | 23.8 | | |
| 110 | 40 | ∞ | 1.13 | 27.7 | | |
| 110 | 50 | 44 ± 2 | 1.45 | 37.5 | 10.1 | 5.4 |
| 210 | 35 | 54 ± 1 | 1.06 | 38.6 | 10.1 | 8.2 |
| 210 | 40 | 44 ± 1 | 1.22 | 43.9 | 10.0 | 5.3 |
| 210 | 45 | 28 ± 1 | 1.32 | 48.9 | 14.0 | 4.2 |
| 345 | 35 | 63 ± 3 | 0.10 | 62.0 | 12.3 | 16.5 |
| 345 | 40 | 22 ± 1 | 2.69 | 33.5[a] | ≈25 | ≈8.3 |
| 345 | 45 | 26 ± 1 | 2.00 | 34.5[a] | $22 < H_c < 25$ | $9 < k_{22} < 12$ |
| 435 | 35 | 42 ± 2 | 1.80 | 34.0[a] | 12.2 | 7.2 |
| 660 | 37 | 32 ± 2 | 1.82 | 33.8[a] | $21 < H_c < 25$ | $12 < k_{22} < 18$ |

[a] $T_N$ is obtained by extrapolation.

Table III
Properties of Ternary Mixtures of PBLG (A and B) and Chloroform (C) at 25 °C

| PBLG A, % | PBLG B (MW 210 × $10^3$), % | pitch, $\mu$m | $-dp^{-1}/dT$, $mm^{-1}$ °$C^{-1}$ | $T_N$, °C | $H_c$, kG | $10^7k_{22}$, dyn |
|---|---|---|---|---|---|---|
| MW 85 × $10^3$ | | | | | | |
| 5 | 46 | 23 ± 1 | 0.93 | 60.5 | 17.8 | 4.6 |
| 10 | 41 | 25 ± 1 | 0.99 | 58.5 | 17.8 | 5.4 |
| 15 | 36 | 27 ± 1 | 0.96 | 56.5 | 17.7 | 6.3 |
| 20 | 31 | 32 ± 1 | 0.98 | 51.7 | 12.2 | 4.2 |
| 25 | 26 | 42 ± 2 | 0.90 | 48.3 | 12.0 | 7.0 |
| 30 | 21 | 34 ± 1 | 0.89 | 52.5 | 12.2 | 4.7 |
| 35 | 16 | 46 ± 2 | 0.88 | 46.9 | 11.5 | 7.7 |
| 40 | 11 | 68 ± 5 | 0.82 | 41.4 | 10.8 | 14.8 |
| 45 | 6 | 88 ± 4 | 0.83 | 38.1 | 10.6 | 23.9 |
| MW 110 × $10^3$ | | | | | | |
| 5 | 40 | 30 ± 1 | 0.75 | 55.0 | 12.0 | 3.6 |
| 10 | 35 | 38 ± 1 | 0.64 | 51.3 | 12.3 | 6.0 |
| 15 | 30 | 53 ± 2 | 0.61 | 46.0 | 12.0 | 11.0 |
| 20 | 25 | 46 ± 2 | 0.70 | 46.5 | 11.8 | 8.1 |
| 25 | 20 | 62 ± 2 | 0.87 | 38.2 | 12.0 | 15.2 |
| 30 | 15 | ∞ | 1.20 | 38.7[a] | | |
| 35 | 10 | ∞ | 1.41 | 37.7[a] | | |
| 40 | 5 | ∞ | 1.28 | 34.5[a] | | |

[a] $T_N$ is obtained by extrapolation.

with eq 10, as is shown in Figure 4.

From both of these experiments, values of $\beta_A$, $\beta_B$, and the two-component interaction parameters ($\beta_{AB}$, $\beta_{AC}$, $\beta_{BC}$) could be obtained. In the next section we shall examine the meaning of these $\beta$ parameters.

## Molecular Twisting Powers

From the analyses of data on binary and ternary solutions of PBLG in chloroform as well as from the literature data on binary solutions of PBLG in other solvents, one obtains a series of molecular twisting powers. These values show wide variation with the nature of the solvent, but some systematic dependence on molecular weight. Previous attempts to calculate the pitch in cholesteric solutions have in the main focused on chiral dispersion forces.[14-18] A theory based on the virial expansion of the free energy by Straley[19] has been recently expanded by Odijk,[13] and the predicted concentration dependence fits quite closely to the experimental data of Dupre and Duke.[7]

The molecular twisting powers obtained in this work are useful parameters in calculating the pitch of a given mixture in a given solvent provided the empirical parameters have been determined for a small data set. First, we examine the solute parameter $\beta_A$. Table IV lists this parameter as a function of temperature, molecular weight, and solvent. $\beta_A$ shows random fluctuations of ≈20% with

Table IV
$10^{11}N\beta_A$ ($cm^2$) of PBLG in Chloroform

| | $10^3$MW | | |
|---|---|---|---|
| T, °C | 85 | 110 | 210 |
| 0 | | 2.17 | |
| 10 | | 2.21 | 9.30 |
| 20 | | 1.77 | 13.60 |
| 25 | | 2.04 | 7.97 |
| 30 | | | 12.60 |
| 40 | 1.86 | | |
| 50 | 1.63 | | |
| 60 | 1.17 | | 7.88 |
| 70 | 1.30 | | 10.10 |
| 80 | 0.99 | | 13.20 |

Table V
$10^7N\beta_{AC}$ ($cm^2$) of PBLG in Chloroform

| | $10^3$MW | | |
|---|---|---|---|
| T, °C | 85 | 110 | 210 |
| 0 | | −0.48 | |
| 10 | | −1.08 | 0.05 |
| 20 | | | |
| 25 | | | −1.80 |
| 30 | | | −5.90 |
| 40 | −4.80 | | |
| 50 | −5.08 | −5.14 | |
| 60 | −5.20 | | −9.60 |
| 70 | | | −13.60 |
| 80 | −6.11 | | −18.10 |

**Table VI**
**Molar Twisting Powers Determined from Ternary Mixtures of Two Different Molecular Weight Samples of PBLG in Chloroform at 25 °C**

| $10^3$MW | $10^7N\beta_{AC}$, cm$^2$ | $10^8N\beta_{BC}$, cm$^2$ |
|---|---|---|
| 85 | 1.31 | 0.83 |
| 110 | | 1.01 |
| 210 | 3.87 | 2.20 |
| 345 | 5.76 | 3.45 |
| 435 | 7.96 | 5.22 |
| 660 | | 7.85 |

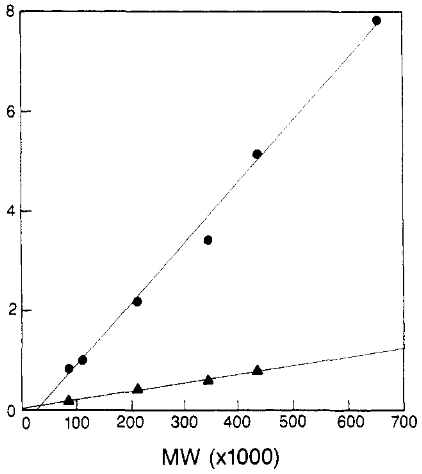

**Figure 5.** Relationships between the solute–solvent molar twisting powers and the molecular weight of the solute PBLG in ternary mixtures: ● $N\beta_{BC}$, ▲ $N\beta_{AC}$. $N\beta_{AC}$ and $N\beta_{BC}$ are in units of $10^8$ cm$^2$; A is the major cholesteric component, and B is the minor cholesteric component.

temperature and variations depending on the nature of the solvent. However, the average value of $\beta_A$ in chloroform solution shows a linear correlation with molecular weight.

The solute–solvent interaction parameters $\beta_{AC}$ or $\beta_{BC}$ can be obtained from data sets for both binary and ternary mixtures. These values are given in Tables V and VI as functions of molecular weight and temperature. These parameters also show a linear correlation with molecular weight of PBLG as is shown in Figure 5. In addition, $\beta_{AC}$ is linear in temperature, provided one is not close to the phase-transition temperatures, as is shown in Figure 6.

Finally, Table VII lists typical values of the parameter $\beta$ for solute ($\beta_A$) and solute–solvent ($\beta_{AC}$) in various solvents. There is a strong variation that does not correlate to any solvent property such as dielectric constant, polarity, etc. The solute–solute interaction parameters ($\beta_{AB}$) can also be calculated and are of similar magnitude to those relating to a single solute ($\beta_A$). Solute–solvent interaction parameters ($\beta_{AC}$ or $\beta_{BC}$) are similar in magnitude to each other but quite different in magnitude from those relating to solutes alone.

## Conclusions

The pitch–concentration relationship for multicomponent polymeric cholesteric lyotropic liquid crystals formulated in this work has been shown to be in accord with a wide variety of experimental data on PBLG in several solvents, as well as for PBLG mixtures in chloroform. Molecular twisting powers are obtained that correlate with the molecular weight of PBLG. If one is not close to the phase transition, the solute–solvent interaction parameters show a linear correlation with both molecular weight and temperature. This analytical approach will therefore allow prediction of chirality of polymeric lyotropic solutions once one has available from a small data set the appropriate values of $\beta$.

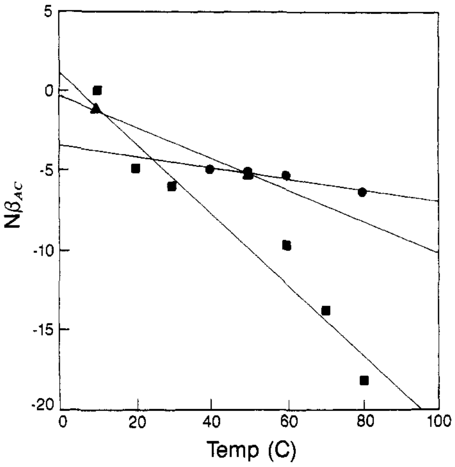

**Figure 6.** Relationship between solute–solvent molar twisting powers and temperature in PBLG–chloroform binary mixtures: $N\beta_{AC}$ in units of $10^7$ cm$^2$; ● MW = $8.5 \times 10^4$; ▲ MW = $1.1 \times 10^5$; ■ MW = $2.1 \times 10^5$.

**Table VII**
**Summary of Twisting Powers of PBLG in Different Solvents**

| $10^3$MW | solvent | temp, °C | $10^{12}N\beta_A$, cm$^2$ | $10^7N\beta_{AC}$, cm$^2$ | ref |
|---|---|---|---|---|---|
| 85 | chloroform | 25 | 0.14 | −4.10 | *a* |
| 110 | chloroform | 25 | 0.20 | −2.78 | *a* |
| 210 | chloroform | 25 | 1.07 | −4.20 | *a* |
| 310 | dioxane | 25 | 4.97 | 0.75 | 5 |
| 550 | dioxane | 25 | 18.30 | 0.80 | 5 |
| 246 | *m*-cresol | 25 | 3.21 | −4.00 | 9 |
| 246 | *m*-cresol | 35 | 2.60 | −4.80 | 9 |
| 246 | *m*-cresol | 45 | 2.20 | −6.40 | 9 |
| 184 | TCP[b] | 95 | 1.16 | −13.40 | 9 |
| 246 | TCP[b] | 40 | 6.13 | −22.20 | 9 |

[a] Data presented in this work. [b] TCP = 1,2,3-trichloropropane.

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**Registry No.** PBLG, 25014-27-1; PBLG (SRU), 25038-53-3.

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