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Chain flexibility and elastic constants of solutions of a polymer liquid crystal

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Measurements of the splay, twist, and bend elastic contants have been made on a series of lyotropic liquid crystals of poly-γ-benzyl-L-glutamate formed in concentrated solutions of non-aggregating solvents. The solvent dependence of the persistence length of the macromolecule was also examined. The influence of solvent on the elastic properties of the liquid crystal is distinguished from that of polymer conformation. With such separation of variables, the results are broadly in accord with predictions of flexible rod models. The variation of the elastic constants with molecular weight, however, depends upon solvent.

1. Introduction

Recent developments [1, 2] in models describing the elastic response of polymer liquid crystals have emphasized the flexible nature of the macromolecule and have led to predictions that are at variance with those obtained from hard-rod formulations [3–5]. Tests of both types of modelling have generally been inadequate due to the paucity of experimental data in the literature. Such data as is available has been gleaned from studies of systems [1] in which there is much ambiguity regarding macromolecular conformation as well as the nature and extent of polymer aggregation. The validity of these models in predicting trends in elastic response with such microscopic molecular properties as molecular weight will remain in question until reliable experiments isolate conformational variables and the state of aggregation of polymers in solution. We describe in this paper the molecular weight and solvent dependence of the elastic constants of a polymer liquid crystal in which the responding unit can be identified with confidence. Measurements of the splay (K_1), twist (K_2) and bend (K_3) elastic constants of lyotropic solutions of the polypeptide, poly-γ-benzyl-L-glutamate (PBLG), were made using field-induced distortions of the liquid crystal director. Polymers in the molecular weight range between 85 000 and 345 000 were examined in a number of nonaggregating solvents. Included for comparison purposes are similar measurements on liquid crystals of the polymer maintained in an aggregating solvent. This solvent choice also allows the exploration of the effects of interchain polymer segment interactions on elastic response.

The extent of conformational flexibility of the polypeptide was determined by measurements of the persistence length in all of the solvents of this study. Our data indicate that treatment of the macromolecule as a flexible rod results in closer agreement with theory of liquid crystal elasticity. The nature of the variation of the elastic constants with molecular weight depends on solvent, however. The molecular weight dependence of the elastic constants is thus oversimplified in both hard- and flexible-rod models.

2. Experimental section

(*a*) *Viscosity measurements*

The solvents chosen for this study were pyridine, nitrobenzene, *m*-cresol, cyclohexanone, dioxane, and a mixture of dioxane and 6 per cent trifluoroacetic acid (TFA). Four-bulb Cannon–Ubbelohde shear dilution viscometers were used to make viscosity measurements of solutions of this polymer as a function of concentration and shear rate. Times were measured with a stop-watch accurate to 0·01 s. The accuracy of our measurements was verified with known solvent viscosities. Each run was repeated to ensure the reproducibility of the data obtained. Shear rate dependence in the viscosity, when observed, was corrected by extrapolation to zero shear rate as suggested by Schurz and Immergut [6]. Intrinsic viscosities were obtained by extrapolation of this data to zero concentration using the Martin equation [7]:

$$\log \frac{\eta_{\mathrm{sp}}}{c} = \log[\eta] + kc. \tag{1}$$

The use of the Huggins equation [8]:

$$\frac{\eta_{\mathrm{sp}}}{c} = [\eta] + k[\eta]^2 c \tag{2}$$

provided concordant results in a few cases. Concentrations of the solutions were less than, or equal to, 1 percent w/v. Persistence lengths were obtained from logarithmic plots of intrinsic viscosity versus molecular weight (85 000–345 000) using the hydrodynamic theory of wormlike chains as developed by Yamakawa and Fujii [9] with numerical corrections as reported by Conio *et al.* [10]. Data for PBLG in five of the six solvents studied could be fitted well to these theoretical equations. However, data for the polymer in dioxane would not fit the model. This is not surprising as this solvent promotes considerable aggregation [11] among the polypeptide macromolecules and the hydrodynamic unit must differ considerably from a single, semiflexible cylinder.

(*b*) *Measurement of* $K_2/\Delta\chi$

Concentrated solutions of PBLG form spontaneously twisted (cholesteric) liquid crystals in all of the solvents of this study. All of the liquid crystalline samples discussed here were prepared with polymer concentrations just above the B-point where a uniform anisotropic phase is first observed upon increasing solute volume fraction from dilute solution [12]. The twist elastic constants, K_2, may be measured by monitoring the dilation of the pitch of the cholesteric structure through the field-induced cholesteric to nematic transition. The pitch, which may be observed and measured optically through diffraction rings or in the polarization microscope, diverges to infinity at the transition point which occurs at a critical electric or magnetic field strength. For the magnetic case [13, 14],

$$K_2/\Delta\chi = 4P_0^2 H_c^2/\pi^4, \tag{3}$$

$K_2/\Delta\chi$ thus may be determined from the critical field strength, H_c, and a measure of the zero-field, equilibrium pitch, P_0. $\Delta\chi$ is the diamagnetic susceptibility anisotropy of the liquid crystal, which must be separately determined for absolute values of K_2 to be obtained. Error in the values of $K_2/\Delta\chi$ so obtained are estimated to be ~ 15 per cent for this liquid crystal.

(c) Measurement of $K_1/\Delta\chi$ and $K_3/\Delta\chi$

Measurements of the splay and bend elastic constants may be made from the detection of the onset of the respective field-induced distortions (Frederik's transitions) of the liquid crystal director in a sample confined to a planar geometry of thickness d. The liquid crystal was held between two glass slides that were cleaned in a manner reported earlier [15] in order to obtain a homeotropically aligned sample. A suitable mylar spacer was used to define the thickness and the whole assembly was sealed with an epoxy adhesive to prevent solvent loss by evaporation. Sample orientation was achieved in about 8–12 hours. We could not observe the Frederik's transition in liquid crystals containing pyridine and the dioxane-TFA mixture; in the former, the solvent rapidly attacked the adhesive, while the acid in the latter solvent mixture caused the orientation to be rather unstable. The unavailability of appropriate molecular weights from time to time in the course of our study made it impossible in some cases to measure all of the three elastic constants on samples of the same molecular weight. However, approximately the same range of molecular weights (100 000 to 250 000) of PBLG has been used for each of the solvents in this study.

For the magnetic case, the splay and bend distortions occur at:

$$H_{c,i}^2 = \frac{\pi^2}{d^2}\cdot\frac{K_i}{\Delta\chi} \tag{4}$$

where $H_{c,i}$ is the threshold field for the splay ($i = 1$), or bend ($i = 3$) distortion. In our homeotropic samples, the magnetic field was placed at right angles to the unperturbed macroscopic liquid crystal director. As the field strength was slowly raised, the subsequent distortion was monitored by changes in the birefringence of the sample. These changes, though quite small, may be measured by an optical arrangement as shown in figure 1 [16]. A lower power ($\sim$ 7 mW) He–Ne laser is directed perpendicular to the surfaces of the glass plates holding the liquid crystal. The polarization of the laser beam is adjusted to be 45° to the magnetic field axis with a Glan–Thompson crystal polarizer. The polarization incident to the liquid crystal sample is subsequently modulated using a photoelastic device (PEM) consisting of a glass plate that is stressed by a piezoelectric transducer operating at a frequency, ω, of 50 kHz. This generates a time dependent retardation, $\Delta n_{\mathrm{PEM}} = A \sin \omega t$, where A is a maximum amplitude. Light received by an analyser whose axis is crossed ($-45°$) with the original polarization state thus oscillates in intensity. In the absence of the liquid crystal, the output of the detector will oscillate at even multiples of 50 kHz according to [16]

$$I = (1/4)(1 - J_0(A) + 2J_2(A)\cos 2\omega t + 2J_4(A)\cos 4\omega t + \ldots), \tag{5}$$

where the J_i are Bessel's functions of the first kind of order i. With a birefringent sample in the optical train, the detector also senses a frequency component at 50 kHz whose intensity is in proportion to the sine of the birefringence, Δn, [16] as

$$I = (1/4)(1 - J_0(A)\cos\Delta n + 2J_1(A)\sin\omega t \sin\Delta n \\ - 2J_2(A)\cos 2\omega t \cos\Delta n + \ldots). \tag{6}$$

The 100 kHz component now contains the cosine of Δn. The 50 kHz component may be captured by lock-in amplification. A typical field-induced distortion is imposed incrementally over about 15 hours to assure equilibration. To correct for long term drifts in the laser output and system optics, the laser beam is sampled before it reaches

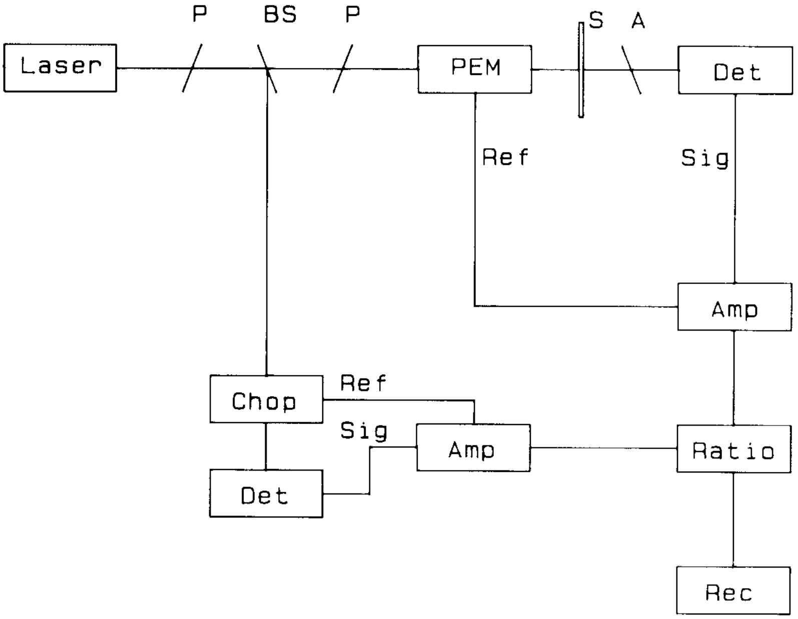

Figure 1. Schematic diagram of the apparatus used to measure birefringence. P: polarizers (0°); BS: beamsplitter; PEM: a photoelastic device that modulates the polarization state of the laser beam at a frequency of 50 kHz (0°); S: sample (0°); A: analyser (−45°). The azimuthal angles of the components are given in parentheses. The undisturbed liquid crystal director is parallel to the laser beam and the field is perpendicular to both.

the PEM and is chopped and ratioed with the modulated beam. The output signal of the ratio meter is used to drive the Y-axis of an XY recorder, the X-axis being proportional to the applied magnetic field strength as measured with a calibrated Hall-effect probe and gaussmeter.

Problems associated with Frederick's distortion measurements on PBLG liquid crystals have been discussed previously [15]. In the homeotropic sample geometry utilized in this work, the threshold field is indistinct and yields only an upper limit to the value of K_3. K_1 values are obtained by a curve fitting procedure [16] to the shape of the recorder traces beyond the threshold field. The curve fitting algorithm required the diamagnetic anisotropy of the polymer as an input and the reported value, 8×10^{-9}, [17] was used with the assumption that it was independent of solvent and molecular weight. Resolution of the value of K_1 is also limited due to the thin samples necessary to guarantee stable homeotropic alignment. We estimate that the splay and bend elastic constants (divided by the constant magnetic susceptibility anisotropy) are in error by ~ 20 per cent.

3. Results and discussion

(*a*) *Persistence lengths*

Persistence lengths of polymers in solution may be determined by a variety of physical methods including light scattering, dielectric constant and translation diffusion measurements, flow birefringence and viscometry [18]. Values obtained from these studies for a given polymer are not often in good agreement even in the same solvent [11, 19]. The discrepancies are most likely due to the different and invariably

Table 1. Persistence lengths of poly-γ-benzyl-L-glutamate polymers in dilute solution with physical constants of solvents.

Solvent	Persistence length, q (± 100 Å)	Solubility parameter, δ of solvent [21]	Dielectric constant of solvent at 25°C
Pyridine	1500	10·6	12·4
Nitrobenzene	1200	10·3†	34·8
m-Cresol	900	11·1	11·8
Cyclohexanone	700	9·55	18·3
Dioxane + 6 per cent TFA	1100	10·0‡	3.3

†We have taken an average of the value we obtained from equation (7) (10·6) and that given by Hildebrand and Scott (10·0) in [21].

‡The δ for this solvent mixture has been approximated by the δ of pure dioxane, alone.

inadequate models employed for the geometric shape and dynamics of the macromolecule. The simplifying assumption of rigid rod behavior of elongated macromolecules is apparently inadequate even at low molecular weights [19]. We have, for this study, relied on a single viscometric method of obtaining persistence lengths based on the wormlike chain model of polymer dynamics [9, 20]. We have also restricted our study to solvents that are known to prevent substantial aggregation of the polymer. (Persistence lengths were not measured for this polymer in the solvent dioxane.) We thus have some assurance that these reasonably stiff polymer chains are acting as independent hydrodynamic units and conform well to the assumptions of theory.

The Yamakawa–Fujii development [9] requires an estimate of the diameter of the wormlike cylinder in solution, which we have taken to be 18 Å for PBLG in all of the solvents except *m*-cresol where a fit of the data to the equations of theory was obtained with a diameter of 15 Å. (X-ray measurements place the diameter of α-helical PBLG between 15–25 Å [11].) Values of the persistence length, q, so obtained are listed in table 1. The persistence length of PBLG is found to be distinctly lower in *m*-cresol ($q = 900$ Å) and cyclohexanone ($q = 700$ Å) than in the other solvents where q is greater than 1000 Å. This is likely a solubilization effect as 'good' solvents tend to stretch out the polymer. For example, pyridine dissolves PBLG very readily and supports a persistence length of 1500 Å; in the range of solvents of this study, cyclohexanone (with $q = 700$ Å) is relatively poor.

The solvation ability of a given solvent may be quantified by resort to the Hildebrand solubility parameter, δ, defined through [21]

$$\delta = (\Delta H_{\mathrm{vap}}/v)^{1/2}, \qquad (7)$$

where ΔH_{vap} is the molar enthalpy of vaporization and v is the molar volume. When the solubility parameter of the solvent and solute are equal, a solution of the two will be regular in a thermodynamic sense [21, 22]. For our purposes, we note that a smaller enthalpy of mixing between polymer and solvent, as would occur when their δ values are similar, results in a more negative free energy of mixing and hence greater solubilization of the polymer. (This is strictly correct only in non-polar solutions, but we use the concept anyway as the solubility parameter does seem to correlate well with a solvent's ability to dissolve PBLG [23]). The values of the Hildebrand solubility parameter for the solvents of this study are also listed in table 1.

Based upon the assumption that the intrinsic viscosity of a polymer solution is maximal when the δ of the solute matches that of the solvent (i.e., when the solution is athermal) [24], we estimate that δ of PBLG is around 10.6. The intrinsic viscosities of only the four single-component, non-aggregating solvents were taken into account and the maximum is found to be better defined at the lower molecular weights. The assumptions underlying this approach are open to question in the case of PBLG, but the only alternative method of obtaining the δ of the polymer involves a calculation of the cohesive energy by summing the contributions of the chemical moieties [22]. Given the uncertainties in these values, an empirical approach to this quantity seems preferable.

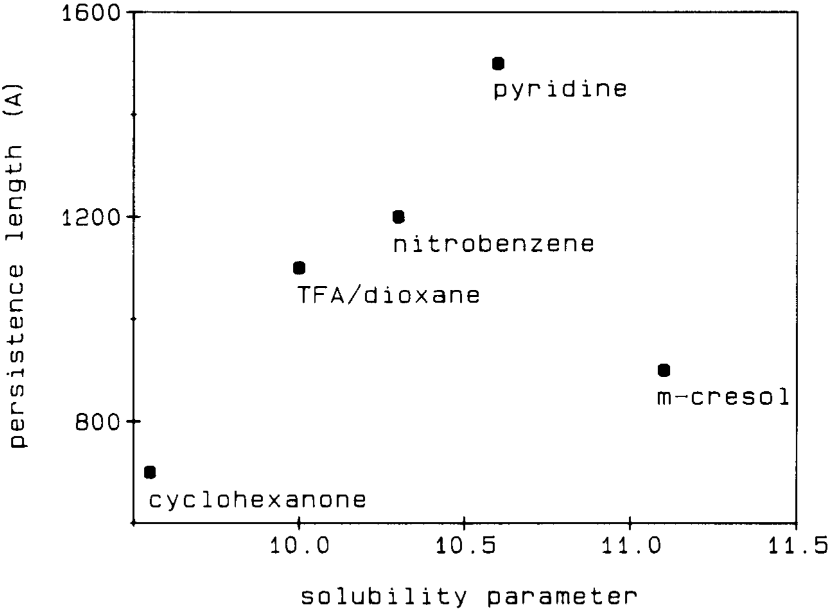

Figure 2. Correlation of the measured persistence length of PBLG with the Hildebrand solubility parameter, δ, of the solvents of this study. The estimated δ of PBLG is 10·6.

A plot of persistence length versus the solubility parameter of the solvent in figure 2 shows the effect of greater extension of the macromolecular worm-like cylinder with solvents of progressively greater effectiveness. The point for *m*-cresol could not be expected to follow the trend as its direct hydrogen bonding is not accounted for in this measure of solubility.

(*b*) *Twist elastic constant, K_2*

The molecular weight dependence of $K_2/\Delta\chi$ is tabulated in table 2 and shown graphically in figure 3 for the solvents indicated. A pronounced solvent effect is seen in the molecular weight dependence of this ratio. Assuming insignificant changes in the diamagnetic susceptibility, the twist modulus is found to be relatively low in value and independent of molecular weight in some solvents, and higher and considerably more molecular weight dependent in others. We find a rough correlation with molecular weight dependence and the degree of association of polymer chains. This is most distinctly shown in the comparative data in dioxane and dioxane with 6 per cent TFA. TFA is known to dramatically reduce macromolecular association and increase the rate of solubilization of this polymer in dioxane [25]. The trend is exemplified in figure 4, where the intrinsic viscosity of dilute solutions of the polymer at a constant

Table 2. Solvent and molecular weight dependence of elastic constants of PBLG liquid crystals ($K_i/\Delta\chi$ in dynes).

	MW					
	85 000	110 000	150 000	190 000	210 000	260 000
Dioxane						
ϕ	0·165		0·157		0·143	0·16
$K_1/\Delta\chi$	500		1250			1250
$K_2/\Delta\chi$		7·7	9·5		45	40
$K_3/\Delta\chi$	9		5·8			10
K_1/K_3	56		216			125
Cyclohexanone						
ϕ	0·34			0·26		0·18
$K_1/\Delta\chi$	2500			1250		750
$K_2/\Delta\chi$		4·6	4·7		4·8	10·5
$K_3/\Delta\chi$	19			12·5		12·5
K_1/K_3	132			100		60
m-Cresol						
ϕ		0·277		0·25		0·23
$K_1/\Delta\chi$		1250		1000		625
$K_2/\Delta\chi$		13·8	22		32·6	38·3
$K_3/\Delta\chi$		9·4		9·6		19
K_1/K_3		130		104		33
Nitrobenzene						
ϕ	0·25	0·215				0·17
$K_1/\Delta\chi$	750	500				1000
$K_2/\Delta\chi$			18·1		47·6	44·2
$K_3/\Delta\chi$	8·0	10·5				15
K_1/K_3	94	48				66
6 per cent TFA + dioxane						
ϕ		0·291	0·290		0·247	0·219
$K_2/\Delta\chi$		15·6	14·4		17·8	21·8
Pyridine						
ϕ		0·312			0·206	0·184
$K_2/\Delta\chi$		11·3			35·8	39·4

ϕ = volume fraction of polymer at the solution B-point.

molecular weight (150 000) is taken as a measure of the degree of association in the solvents of this study. The rate of change of the twist modulus with molecular weight roughly correlates with polymer association as measured by the intrinsic viscosity of the solution.

We have also attempted a kind of corresponding states analysis by comparing solvent effects under the same condition of inter- and intra-molecular order of the polymer solute. As noted above, all liquid crystal solutions of this study were prepared with polymer concentrations just above the solution B-point. The liquid crystal order parameter is thus approximately the same for all samples of this study. The degree of intrachain flexibility among samples may also be matched if we choose data at a molecular weight where all polymer chains have a common contour length at or below the lowest persistence length (as measured in dilute solution). This occurs at a common molecular weight of 150 000 except for the cyclohexanone sample, which shows little variation anyway in $K_2/\Delta\chi$. At this molecular weight we may assume that all polymer solute molecules are rigid rods of the same length and focus on solvent

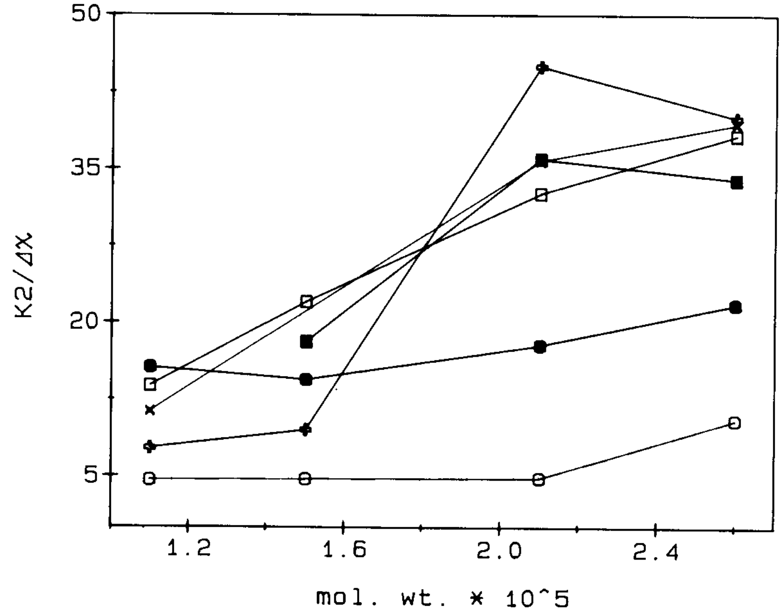

Figure 3. Molecular weight dependence of the twist modulus (divided by the diamagnetic susceptibility anisotropy, $\Delta\chi$) for TFA/dioxane (open circles); cyclohexanone (filled circles); dioxane (open crosses); nitrobenzene (filled squares); pyridine (X); *m*-cresol (open squares).

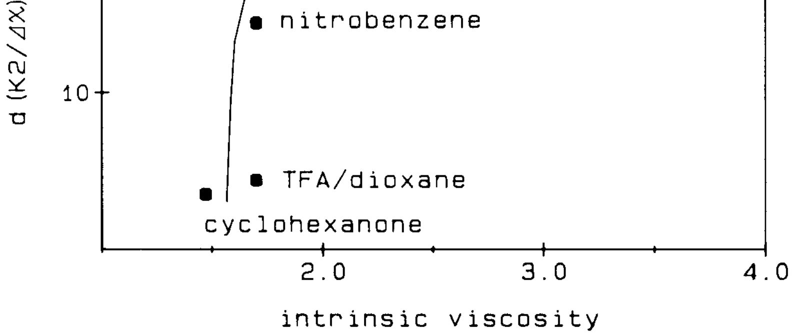

Figure 4. Rate of change of $K_2/\Delta\chi$ with respect to molecular weight as a function of the intrinsic viscosity of dilute solutions of the polymer in the solvents indicated. Intrinsic viscosity at a constant molecular weight (MW = 150000) is taken as a measure of the degree of association of polymer chains. The curve drawn is a visual guide.

Table 3. Corresponding state values of $K_2/\Delta\chi$ (dynes) in various solvents polymer MW = 150 000; rigid rod length ~1000 Å.

Solvent	$K_2/\Delta\chi$
Cyclohexanone	4·7
Dioxane	9·5
Dioxane/6 per cent TFA	14·4
Pyridine	20†
Nitrobenzene	18·1
m-Cresol	22·0

†Interpolated.

effects alone. Adopting this standard state for the PBLG α-helix, $K_2/\Delta\chi$ values are significantly solvent dependent as seen in table 3.

One contribution to this isolated solvent dependence of K_2 could arise from modification of the side-chain conformation of the macromolecule. As the side chains become more extended perpendicular to the main chain axis, they are more likely to interfere with one another in twist distortions of the liquid crystal director. X-ray data [26] on liquid crystals of this polypeptide indicate that the helices lie in hexagonal close packing with an interhelical distance of only ~22 Å. (Molecular models show that fully extended side chains would, in fact, overlap at this separation.) Entanglement of extended side-chains would require a higher degree of cooperative motion as polymer chains adapt to a twist deformation in the liquid crystal and K_2 should thus rise due to this effect. The twist modulus is seen to be larger in the aromatic solvents that would draw out the benzyl moiety. To quantify this observation, we plot the corresponding state $K_2/\Delta\chi$ ratio versus the solubility parameter for the respective solvents in figure 5.

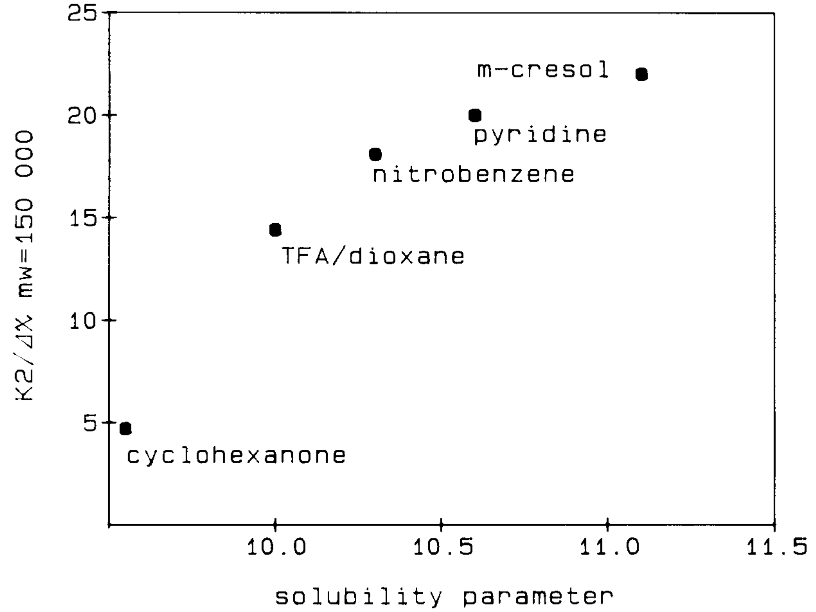

Figure 5. Values of the twist modulus at the corresponding state molecular weight (MW = 150 000) versus solubility parameter of solvent.

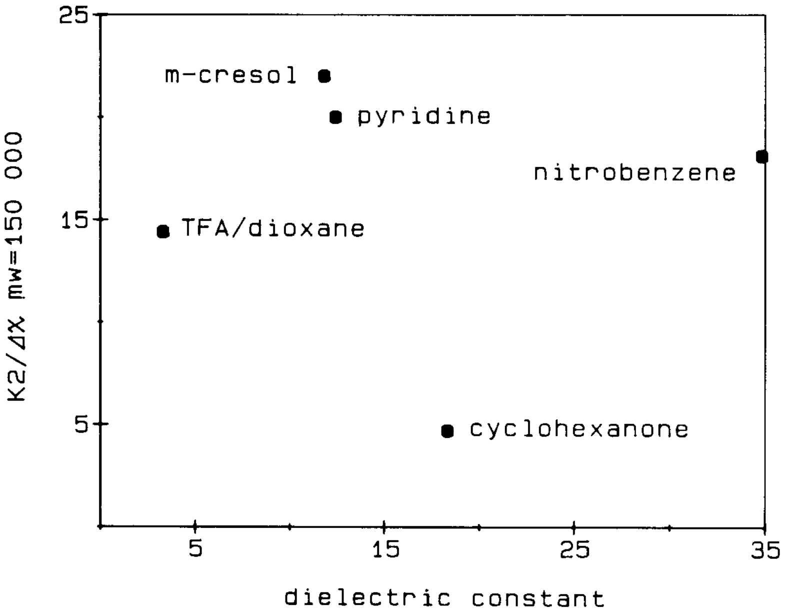

Figure 6. Values of the twist modulus at the corresponding state molecular weight (MW = 150 000) versus dielectric constant of solvent.

The solubility enhancement of the polymer (along with the presumed extension of its side-chains) correlates well with an increase in the twist modulus. The figure also shows that the value of K_2 approaches a limit at large δ which is consistent with the finite extensibility of the side chains. The behaviour of *m*-cresol is also found to be in line with the trend of the other solvents. The specific hydrogen bonding capability of *m*-cresol in this case would stabilize the extension of the side chains and contribute to greater solubility of the polymer. We have also examined the variation of $K_2/\Delta\chi$ with the dielectric constant of the solvent as another physical parameter that might correlate with the extension of the polar side chains. The plot shown in figure 6 is not so regular and we can draw few conclusions, except that the behaviour of cyclohexanone is unusual in this case.

(*c*) *Splay and bend elastic constants, K_1 and K_3*

Values of $K_1/\Delta\chi$ and $K_3/\Delta\chi$ obtained from the Frederick's transition procedure are listed in the compendium of table 2 and plotted versus polymer molecular weight in figures 7 and 8. As much as a hundredfold variation in the elastic response is seen to occur with changes in the solvent and molecular weight parameters at this liquid crystal. This wide variation in the splay and bend distortions is similar to that found previously for the twist mode in PBLG liquid crystals [15] and is notably greater than variations of the moduli found for small molecule liquid crystals [27]. The order of magnitude differences among the elastic constants also is significantly different from that found with small molecules, with $K_1 > K_3 \geqslant K_2$.

Values of K_1 ten times larger than K_2 and K_3 have been found in measurements of the three elastic constants of a thermotropic, polyester liquid crystal [28]. In table 4 we compare our measurements of the elastic constants with those reported for the thermotropic polyester, a small molecule nematic (MBBA), and the predictions

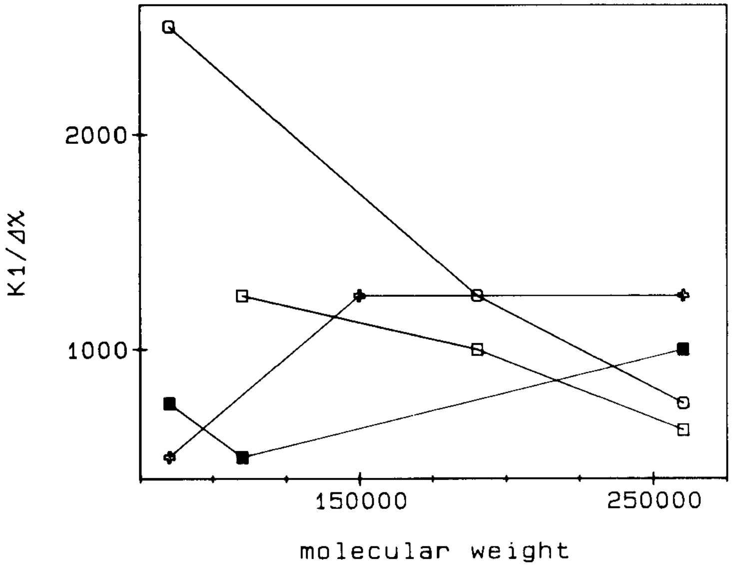

Figure 7. Molecular weight dependence of the splay modulus in the solvents indicated (symbols used are defined in the caption to figure 3).

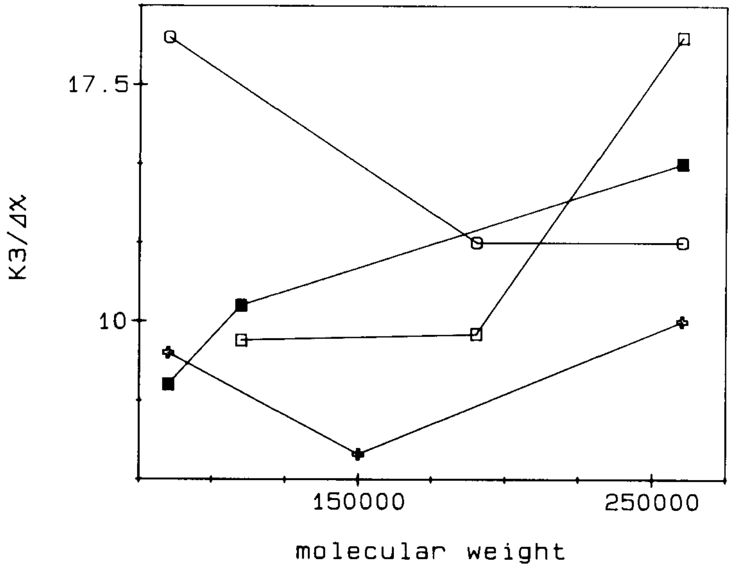

Figure 8. Molecular weight dependence of the bend modulus in the solvents indicated (symbols used are defined in the caption to figure 3).

of hard-rod [29] and flexible-rod [29] models. Values selected for PBLG liquid crystals correspond to the lowest molecular weight of our study. The range of values for the K_i in this column thus reflects the solvent dependence. The twist elastic constant is the smallest for thermotropic as well as lyotropic liquid crystals, irrespective of the axial ratio of the constitutent molecules. The splay elastic constant tends to be the largest in polymeric liquid crystals except in the case of tobacco mosaic virus (TMV) solutions where the bend elastic constant is by far the largest [30].

Table 4. A comparison of the elastic constants of small molecular nematic, lyotropic and thermotropic polymer liquid crystals with theoretical calculations (K_i in dynes)

Elastic constants	PBLG MW = 75 000 or 85 000 (lowest available MW)	Thermotropic polyester oligomer [28]	MBBA [27]	Flexible-rod (Meyer) (MW ~70 000) [29]	Hard-rod (Straley) (MW ~130 000) [29]	Hard-rod (Priest) (MW ~130 000) [29]
K_1	$4 \times 10^{-6} - 2 \times 10^{-5}$	3×10^{-6}	6×10^{-7}	$15{\cdot}5 \times 10^{-7}$	$4{\cdot}2 \times 10^{-7}$	$2{\cdot}8 \times 10^{-7}$
K_2	$4 \times 10^{-8} - 1{\cdot}2 \times 10^{-7}$	2×10^{-7}	4×10^{-7}	–	$1{\cdot}4 \times 10^{-7}$	9×10^{-8}
K_3	$7 \times 10^{-8} - 1{\cdot}4 \times 10^{-7}$	3×10^{-7}	$7{\cdot}5 \times 10^{-7}$	$6{\cdot}88 \times 10^{-7}$	$2{\cdot}60 \times 10^{-7}$	$6{\cdot}7 \times 10^{-7}$

In small molecule thermotropic liquid crystals, the splay and bend elastic constants are similar.

It is evident that K_1 is much higher in PBLG liquid crystals than in the thermotropic systems considered; its magnitude also significantly exceeds theoretical predictions although the flexible-rod model provides a better match with experimental data than the hard-rod models, probably due to the inclusion of entropic contributions. K_2 is similar in the three systems and is quite close to Straley's result for hard-rod systems. However, K_3 is smaller in PBLG than in the thermotropic systems and is also less than theoretical predictions. That the hard-rod model overestimates the bend elastic constant is not very surprising, but the discrepancy between experiment and flexible-rod models is intriguing.

We speculate that the force necessary to induce the bend distortion in an assembly of macromolecules interacting through their sidechains is less than that required in the absence of such interaction. If the polymer sidechains are fully extended in certain solvents, the distortion of the backbone of one macromolecule may cooperatively induce the distortion of its neighbors since the (interdigitated) sidechains would maintain their energetically favorable orientations with respect to one another. The operation of such an effect may serve to explain the reduction in the bend elastic constant. In this context, it is interesting that table 2 reveals an inverse relation between K_3 (interpolated at a molecular weight of 150 000) and the solubility parameter in cyclohexanone, nitrobenzene, and *m*-cresol. Considering that polymer sidechains are probably more extended in solvents of higher δ, this relation may reflect the operation of a sidechain mediated cooperative interaction between polymer molecules.

The similarity in the bend constants of the two thermotropic liquid crystals (whose axial ratios are quite different) in table 4 may corroborate the notion that the bend elastic constant is not solely determined by the rigidity of individual molecules. However, we emphasize that no discussion of the solvent dependence of elastic properties of lyotropic liquid crystals can be definitive if only the polymer molecules are taken into account. Thus, it is quite possible that variation of the bend elastic constant with solvent is due to solvent-solute interactions that are still not perfectly understood.

Figures 7 and 8 do not display the molecular weight dependence expected in current theories of polymer liquid crystal behaviour. A pronounced increase in the splay modulus is predicted in hard and extended rod theories, with $K_1 \sim L^4$ in the Onsager approach [3] and $K_1/K_3 \sim L^2$ or $\sim L$ in continuum developments [1]. No such dependence is found in our data over the molecular weight range studied. In fact, depending on solvent, both K_1 and K_3 may increase or decrease with polymer length. This lack of correspondence with theory has a probable cause in the flexibility of the macromolecule and the solvent interaction of its sidechains in the molecular weight range of this study. At a molecular weight of 100 000 most of the polymer chains are near or above the measured persistence lengths (table 1). Polymer chains with $L > q$ may more easily adapt to the voids and compressions created in the splay and bend distortions, thus lowering the expectation on the trend of the values of these moduli with molecular weight. In this context, it is seen that PBLG liquid crystals in solvents with the lowest persistence length values show the greatest decrease in the splay modulus (and K_1/K_3 ratio) with molecular weight.

4. Conclusion

In conclusion, the twist elastic constant and its molecular weight dependence in the liquid crystalline solutions of this study are clearly correlated with the solubility of the polypeptide in the different solvents. There is extensive scatter in plots of splay and bend elastic constants as a function of molecular weight; furthermore, general trends in the data do not agree with theoretical predictions of a logarithmic scaling of the elastic constants with contour length, independent of solvent. The scatter may be due to statistical fluctuation in sparse data or to inherent uncertainties in the measurement of the Frederiks distortion in weakly anisotropic media. The discord with theoretical predictions, however, is also apparent in the work of Meyer and co-workers, who used a light scattering approach [1, 29]. It is likely that the molecular weight dependence of K_1 and K_3 in different solvents is influenced by the flexibility of the polymer and solvent interaction of its sidechains. The latter aspect has received little attention in the theoretical models proposed to date.

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