Anisotropy of turbidity and elastic constants of liquid-crystalline polypeptide solutions

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The light scattering method was utilized to measure the anisotropy of turbidity and to determine elastic constants K_1, K_2 and K_3 in lyotropic solutions of poly(γ-benzyl-L-glutamate) (PBLG). Because of surface-induced orientation of the PBLG molecules, one of the turbidity components showed unexpectedly large values. The order of magnitude of the evaluated elastic constants was within the 10^{-7}–10^{-9} dyn range, and the characteristic anisotropy trend was $K_1 \geqslant K_3 \geqslant K_2$. The elastic constants correlated with molecular weight and concentration of the polymer, and were also affected by the solvent type. The dependence of the elastic constants was affected by the solvent. Correlation of K_1 and K_1/K_3 with molecular weight was in qualitative agreement with the polymer chain flexibility model.

INTRODUCTION

The elastic constants of liquid crystals are a bulk manifestation of the anisotropy of molecular symmetry and interactions. Knowledge of these continuum force constants is important from both fundamental and application viewpoints. In monomeric liquid-crystalline systems, the elastic constants have been relatively well studied, and, within the rigid-rod concept, have been shown to reflect directly the molecular geometries and interactions[1-7]. The existing nematic hard-rod theories suggest that the ratio K_1/K_3 should decrease with increasing molecular aspect ratio, L/D (L=length and D=diamater), of the rigid moiety. Experimentally, these predictions have been quantitatively verified in a number of monomeric nematogens[8]. Accordingly, elastic constant measurements in nematic homologues having various flexible alkyl segments have shown that the K_1/K_3 ratio usually increases with the length of the flexible segment[8,9].

Generally, theoretical predictions and experimental data of the elastic constants of nematic monomer systems are in qualitative agreement with each other. They indicate that both absolute and relative values of K_i are directly correlated with molecular asymmetry and interactions, and with the degree of orientational order.

In liquid-crystal polymers (LCPs), theoretical studies and experimental data of the elastic constants are scarce. Existing theoretical models based on a simple continuum elasticity concept[10,11] predict an increase of K_1 with molecular length due to the partial flexibility of the polymer chain. A more recent theory on the statistical description of the elastic constants in semi-rigid mesogenic polymers predicts a decrease of these moduli with chain flexibility and an increase with the degree of polymerization[12]. The same theory anticipates that the ratio of the elastic moduli should be independent of the molecular parameters.

Measurements of the elastic constants in LCPs with conventional methods, particularly with the Freedericks distortion technique, have been faced with experimental difficulties. This has been due mainly to the lack of strong surface anchoring, large-viscosity and thermal degradation of polymers. Among recent experimental investigations on LCPs, most studies have been carried out on lyotropic solutions of poly(γ-benzyl glutamate) (PBG) using both the field-induced distortion (FD)[13-21] and the quasi-elastic light scattering (QELS)[22,23] methods. The elastic constants of other LCP solutions[24,25], melts[26-28], as well as their mixtures with nematic monomer[29,30], have also been reported in the literature.

Existing elastic-constant data of PBG mesophase solutions are in disagreement with each other and are difficult to interpret. For example, studies on poly(γ-benzyl-L-glutamate) (PBLG) mesophase solutions in the molecular weight range of 70 000–300 000 with the QELS method[22] have shown that $K_1/K_3 \simeq 10^{-5}$, which is in discord with the result $K_1/K_3 \simeq 40$–1000 obtained by the FD technique on the same system[18,19]. On the other hand, application of QELS on a racemic poly(γ-benzyl-L-glutamate)/poly(γ-benzyl-D-glutamate) (PBLG/PBDG) solution[23] has reported that K_1 and K_3 are of the same order of magnitude. The most recent study with FD methods[21] showed that the type of solvent induces different chain flexibility, where $K_1 \simeq 10^{-6}$ dyn and a general trend $K_1 > K_3 \geqslant K_2$ has been observed.

In thermotropic LCP systems, there have been only a few attempts to study the elastic moduli. A recent application[28] of the FD method to the nematic melt of a polyester has shown that $K_1/K_3 \simeq 10$, and two other studies in mixtures of polyesters with low-molar-mass nematogens have indirectly demonstrated an increase of K_1[25] and K_3[26] with the degree of polymerization.

Regardless of the diversity of the mesogenic materials and the methods utilized, the elastic properties of the LCP systems are shown to be sensitive probes of the physico-chemical parameters and their quantitative knowledge should provide further insight into the polymer chain structure and the nature of the polymer–solvent interactions.

Following our current effort to introduce the present method as an experimental approach in characterization of liquid-crystalline materials, we report on the measurement of turbidities and elastic constants in PBLG mesophase solutions. This technique has been primarily developed to study the anisotropy of turbidity and to evaluate the elastic constants of monomeric nematogens[31]. Later, it has been extended to investigate the temperature dependence of these moduli in nematic homologues and mixtures[32,33], and recently its application to study the turbidities and elastic constants near the nematic–smectic A phase transition has also been demonstrated[34]. The results of current measurements with modified instrumentation[35] have shown the quantitative reliability of this technique, which has been its major drawback in the previous reports.

In this work, we studied the turbidities and elastic constants of oriented nematic phases of PBLG solutions in dioxane (DO) and dichloromethane (DCM) solvents. The elastic constants were evaluated from the experimental turbidity data in two geometries and the inspected turbidity in the third. The inspection method was similar to that utilized in thermotropic nematogens[34,35]. The results indicate that both the order of magnitude and trends of the elastic moduli depend on the molecular weight, concentration and nature of the solvent. The reported elastic data demonstrate their qualitative correlations with the PBLG molecular parameters and the chemical environment of the system. The results signify the occurrence of chain flexibility and polymer–solvent interactions, which are manifested by the order of magnitude and divergence of the elastic constants. Further quantitative correlation between the molecular properties and the elastic moduli requires more detailed and systematic investigations.

METHOD

It is well known that the turbidity of nematic liquid crystals is due to light scattering from long-wavelength orientational fluctuations of the nematic director. The first mathematical formulation of turbidity in terms of the scattering cross section σ has been derived by de Gennes[36]. Langevin and Bouchiat[31] made an exact computation of the scattering cross section for light scattering in an oriented nematic phase and showed that

measurement of the total absorption coefficients in selected geometries allows the determination of all three elastic constants. Accordingly, they calculated the total scattering cross section σ for the three following geometries:

$$1: k \parallel v_0 \qquad 2: k \perp v_0, i \perp v_0 \qquad 3: k \perp v_0, i \parallel v_0$$

where k is the wavevector of the incident beam, v_0 is the direction of the nematic director and i is the unit vector representing the polarization direction of the incident light beam. The expressions for σ (equation (6) of ref. 31) in these three geometries are:

1: $\qquad \sigma_1/\sigma_0 = [I_0(a_1) + I_0(a_2)]/4$ (1a)

2: $\qquad \sigma_2/\sigma_0 = I_1(a_2) + I_2(a_1) - I_2(a_2)$ (1b)

3: $\qquad \sigma_3/\sigma_0 = I_3(a_2) + I_4(a_1) - I_4(a_2) + I_5(a_1)$

$\qquad\qquad\qquad + I_6(a_2) - I_6(a_1)$ (1c)

where I_0 to I_6 are seven complex integrals (see appendix of ref. 31), which consists of the following reduced quantities:

$b = n_e/n_0$ (2a)

$a_\alpha = K_\alpha/K_3 \qquad (\alpha = 1, 2)$ (2b)

$\sigma_0 = k_\beta T \omega^2 \varepsilon_a^2 / 4\pi c^2 K_3 n_0^2$ (2c)

The values of σ_j/σ_0 were evaluated for different values of the parameters a_α and b by numerical analysis via a Gaussian quadrature integration procedure and a Romberg extrapolation. The results were stored in the computer as 2×2 matrices with a_1 rows and a_2 columns for each b value, where each matrix element consists of a pair of σ_1/σ_2 and σ_1/σ_3 ratios. A section of such a theoretical matrix for a wide range values of a_1 and a_2 is shown in *Table 1*. Overall, such a theoretical calculation suggests that, in spite of the diversity of the elastic constants, the turbidities of the nematic phase should always exhibit a $\sigma_3 > \sigma_2 > \sigma_1$ inequality trend.

Evaluation of the elastic constants requires exact experimental measurement and input of σ_j, n_0, n_e and T in the computer program. The experimental data are then processed and compared with those in the theoretical matrix elements. The computer search routine uses the necessary iterations to converge and find the best set of a_1, a_2 and σ_0 with a tolerance of less than 0.1%. From

Table 1 A portion of the theoretical a_1–a_2 matrix from equations (1); $b = n_e/n_0 = 1.448/1.444$

		0.001	0.01	0.1	1.0	10	100	1000
1000	$\sigma_1/\sigma_2 = 0.0570$		0.1030	0.1328	0.1188	0.0760	0.2135	0.0492
	$\sigma_1/\sigma_3 = 0.0553$		0.0974	0.1201	0.1059	0.0730	0.1786	0.0330
100	0.0570		0.1030	0.1325	0.1184	0.0774	0.1079	0.0702
	0.0554		0.0973	0.1197	0.1050	0.0726	0.0976	0.0652
10	0.0577		0.1042	0.1350	0.1266	0.1110	0.2074	0.1869
	0.0560		0.0982	0.1213	0.1107	0.0983	0.1260	0.1457
1.0	0.0625		0.1143	0.1585	0.1945	0.2874	0.4383	0.5088
	0.0604		0.1070	0.1403	0.1638	0.2404	0.3243	0.3547
0.1	0.0763		0.1420	0.2204	0.3248	0.4821	0.6003	0.6364
	0.0734		0.1318	0.1925	0.2691	0.3846	0.4621	0.4799
0.01	0.0821		0.1628	0.2383	0.3037	0.3548	0.3795	0.3859
	0.0796		0.1515	0.2129	0.2678	0.3143	0.3354	0.3397
0.001	0.0915		0.1237	0.1428	0.1437	0.1447	0.1463	0.1469
	0.0879		0.1180	0.1350	0.1371	0.1393	0.1439	0.1416

these extracted values and equations (2b) and (2c), evaluation of the corresponding K_1, K_2 and K_3 moduli is a straightforward procedure.

EXPERIMENTAL

The PBLG was purchased from Sigma with reported molecular weights of 70 000, 150 000, 240 000 and 296 000. The polymer samples were used without further purification. The solutions of PBLG in dioxane (DO) and dichloromethane (DCM) were prepared at mesophase concentrations in rectangular Helma optical cells with 0.1 and 0.2 cm inside thicknesses. The optical cells were sealed with Teflon caps and the solutions were allowed to mix completely at room temperature over a 2–4 week period. As the cholesteric mesophase of PBLG solutions is randomly oriented, the cells were placed between the gap poles of a 60 mHz Varian electromagnet with a field intensity of about 1.4 T. The magnetic field direction H served to create a uniaxial orientation and to define the direction of nematic direction v_0. The alignment of the samples was frequently examined under a polarizing microscope for textural orientation and homogeneity. The beam of a 7 mW laser was directed through a $\lambda/2$ polarization rotator into the sample located between the pole faces of the electromagnet, and a series of intercavity and exit mirrors served to direct the beam through the sample in the three required geometries. The mirrors were about 95% reflective and the direction of polarization of the incident beam was not affected by reflecting through them. The transmitted light was detected by a photodiode after passing through an adjustable calibrated diaphragm which defined the solid angle of detection Ω. The absorption coefficients σ_j in each geometry were measured

from the corresponding total light intensity I_j according to:

$$I_j = I_j^0 \exp(-l\sigma_j) \qquad (j=1,2,3) \qquad (3)$$

where I_j^0 is the corresponding intensity of an isotropic PBLG solution and l is the sample thickness. The apparatus and experimental details of these measurements have been mentioned elsewhere[31-33]. The elastic constants were evaluated with a computer fitting algorithm based on the theoretical model[31] and the calculation procedure reported elsewhere[33]. The required values of the refractive indices n_0 and n_e were extracted from the reported data[37] for the solutions with the same solvents and molecular weights used in this work. All experiments were carried out at the ambient temperature of 25°C. The uncertainties of the experimental values in the measured turbidities and estimated refractive indices are within 15%. Since the computer search routine provides the calculated elastic constants within 0.1% tolerance range, the overall uncertainties in the elastic moduli are only due to the limits of the experimental errors. In *Tables 2* and *3* we tabulate the experimental parameters, refractive indices and turbidities of the studied PBLG solutions in dioxane (DO) and dichloromethane (DCM), respectively. Each reported turbidity value is the average of three measurements at various sample locations. In order to reduce the viscosity and response time to the magnetic field, trifluoroacetic acid (TFA) was added to the PBLG/DO solutions in amounts of about 2–6%. The presence of TFA is known to reduce the association and increase the rate of solubilization of PBLG in DO, without any effect on the K_2 modulus of the solution[21,38]. Here, we found that the presence of TFA usually increases the overall turbidity of the solution without any noticeable effect on the elastic-constant values.

Table 2 Turbidities and refractive indices of PBLG/DO solutions at $C=18\%$ and $T=298$ K for samples A, B and C

			σ_j (cm^{-1})			
MW (10^{-3})	n_e/n_0	Sample	σ_1	σ_2	σ_3	$\langle\sigma_1\rangle$
70	1.448/1.444	A	1.52	0.56	0.69	0.15–0.21
		B	1.65	0.64	0.78	0.18–0.24
		B^a	5.50	1.25	1.45	0.35–0.45
150	1.447/1.443	A	0.95	0.86	0.95	0.24–0.32
		B	0.75	0.43	0.55	0.12–0.16
		C	0.95	0.69	0.88	0.19–0.25
		C^a	0.60	1.60	2.10	0.46–0.62
296	1.445/1.441	A	1.54	0.45	0.55	0.12–0.18
		B	2.47	0.72	0.98	0.20–0.26
		C	2.56	0.56	0.76	0.15–0.21

^{a} Sample with addition of 2–6% TFA

Table 3 Turbidities and refractive indices of PBLG/DCM solutions at $MW=240 000$ and $T=298$ K for samples A and B

			σ_j (cm^{-1})			
C (w/v%)	n_e/n_0	Sample	σ_1	σ_2	σ_3	$\langle\sigma_1\rangle$
18	1.448/1.443	A	0.50	0.18	0.20	0.050–0.064
		B	0.45	0.15	0.21	0.042–0.054
29.5	1.458/1.446	A	1.43	0.88	1.00	0.25–0.33
		A^a	1.75	1.30	1.50	0.36–0.48
37	1.480/1.450	A^a	13.1	7.8	9.2	2.2–2.8

^{a} Sample with addition of 2–6% TFA

RESULTS AND DISCUSSION

Anisotropy of turbidity

The lyotropic solutions of PBLG usually exhibit a cholesteric helix structure with low birefringence, large viscosity and large response time to the external fields. In these systems, the uniaxial orientation of the nematic polymer and the turbidity measurements are more difficult than in the nematic monomers. We found that the achievement of well oriented and defect-free nematic monodomains of PBLG solutions with a continuous and strong magnetic field requires at least 24 h. Even after such a long residence time, the achievement of an appropriate uniaxial nematic texture was not always ensured. The presence of local cholesteric helix as well as surface and bulk disclinations can create unwanted scattering centres, which often interfere with the light intensity measurements. These interfering effects are noticeable because the turbidity range of the PBLG solutions $(0.1-2.0 \, \text{cm}^{-1})$ is about one order of magnitude less than that in ordinary nematogens. Consequently, the measurements of the transmitted light intensities I_j in PBLG solutions are sensitive and require more experimental care. In a uniaxially oriented nematic phase, the measured scattering intensities as a function of the solid angle of detection usually exhibit a characteristic plateau value, which is used to calculate the corresponding σ_j values (see equation (3)). *Figure 1* shows the variation of the transmitted intensities of a typical well oriented nematic phase in a PBLG solution in three geometries as a function of half solid angle $\Omega/2$ of detection. The observed intensities in a well oriented sample converge to constant plateau values well within the limit of the aperture opening. The minimum aperture diameter was always kept larger than the angular divergence of the laser beam.

All measurements in this work as well as in another independent study[39] indicates that I_j in geometry 1 is always the lowest of the three intensities (see *Figure 1*). Although the absolute values of I_j depend on the sample thickness, solution concentration, polymer molecular weight and solvent type, their trends were similar in all
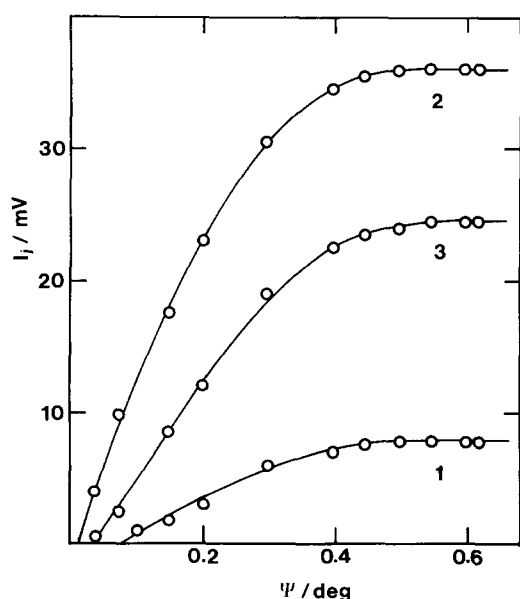

Figure 1 Variation of total light intensity I_j with the solid angle of detection ψ ($=\Omega/2$) in the three geometries

studied samples and showed a typical turbidity anisotropy trend of $\sigma_1 > \sigma_3 \geqslant \sigma_2$ type. This is in disagreement with both theoretical calculations (see *Table 1*) and experimental measurements[31-34], where the anisotropy of turbidity in nematics should obey the $\sigma_3 > \sigma_2 > \sigma_1$ inequality trend. In order to explain the origin of this discrepancy we refer to a recent study on the turbidity of 4-octyl-4-cyanobiphenyl $(8CB)$[34,35], where in the smectic A phase σ_1 is always larger than σ_2 and σ_3 values, and even in the nematic phase σ_1 has been found to increase significantly with surface effect (i.e. decrease of sample thickness). This effect is due to surface-enhanced smectic-like ordering near the surface boundary, which causes a significant decrease of light absorption or increase of turbidity in geometry 1. In fact, a current turbidity study on the cyanobiphenyl (nCB) series has shown that the nematic–surface interactions can dramatically increase the σ_1 values with samples as large as $1.0 \, \text{cm}$ thickness[40]. The significant contribution of surface effects to the σ_1 values of thermotropic systems and the possibility of smectic-like orientation of PBLG molecules near the surface boundary via strong end-chain effects[11] can explain the qualitative nature of the large σ_1 values in PBLG solutions.

Since the experimental values of σ_1 were not directly useful for the evaluation of the elastic constants, we utilized a simple inspection method to estimate the range of their values in the present system. The method is based on the approximation used in previous studies[34,35]. Considering that the ratios and the trends of turbidities in nematics (thermotropic and lyotropic) are the same, the appropriate range of σ_1 can be obtained for PBLG solutions. Namely, the σ_1/σ_2 and σ_2/σ_3 ratios in nematic homologues[32] and mixtures[33] have been found to fall within limits 0.28–0.36 and 0.72–0.92, respectively. From the experimental values of $\sigma_2/\sigma_3 = 0.70$–0.92 found in the PBLG solutions, it is conceivable that their σ_1/σ_2 ratios should also fall within the same range as that of the thermotropics. Also, inspection of the theoretical turbidity ratios from *Table 1* indicates that, in spite of large variations in the elastic moduli, the σ_1/σ_2 and σ_2/σ_3 ratios vary only within limits 0.049–0.636 and 0.67–0.99, respectively. In view of the compatibility between the experimental and theoretical data, we evaluated an expected range of σ_1 for all PBLG solutions on the basis of the limits $0.28 < \sigma_1/\sigma_2 < 0.36$ and the experimental values of σ_2. The results are tabulated in column 7 of *Tables 2* and *3*.

The evaluation of the elastic constants was then carried out by the computer search routine using the corresponding turbidities (columns 5, 6 and 7) and refractive indices (column 2) of *Tables 2* and *3*. As mentioned previously, the absolute values of turbidities were systematically increased by addition of TFA but did not have a noticeable effect on the order of magnitude of the elastic constants. Although, owing to the nature of the present inspection approach, we did not determine the exact values of the elastic moduli in PBLG solutions, the results are in qualitative agreement with the concept of polymer chain flexibility.

Elastic constants

Order of magnitude. The results of the calculations of the elastic moduli of the PBLG solutions from the turbidity data are tabulated in *Tables 4* and *5*. The evaluation of K_i was based on the computer search

Table 4 Elastic constants of BPLG/DO solutions, $C = 18\%$, $T = 298$ K

MW (10^{-3})	K_i (10^9 dyn)			
	K_1	K_2	K_3	K_1/K_3
70	6–18	0.2–2.0	0.6–2.2	$\langle 1.5 \rangle$
150	30–80	1.3–3.7	0.8–5.2	$\langle 30 \rangle$
296	140–210	3.0–4.5	1.0–2.3	$\langle 220 \rangle$

Table 5 Elastic constants of PBLD/DCM solutions, $MW = 240\,000$, $T = 298$ K

C (w/v%)	K_i (10^9 dyn)			
	K_1	K_2	K_3	K_1/K_3
18	90–130	0.9–1.3	100–160	$\langle 0.8 \rangle$
29.5	70–120	1.5–2.0	80–130	$\langle 0.9 \rangle$
37	60–120	1–10	80–140	$\langle 1.2 \rangle$

routine used in the previous studies[31–35,40]. *Table 4* provides the elastic data in PBLG/DO solutions as a function of polymer molecular weight, and *Table 5* shows the elastic moduli in PBLG/DCM solutions as a function of polymer concentration.

Since the σ_1 data are available at the upper and lower limits, the corresponding elastic constants cannot be reported as single values. In this respect, for each set of turbidity data we calculated the elastic constants as a function of σ_1. The upper and lower limits of these ranges were determined from the estimated $\langle \sigma_1 \rangle$ in *Tables 2* and *3*. In *Figure 2* we show calculated examples of K_i vs. σ_1 plots at three different molecular weights in PBLG/DO solutions. These data clearly demonstrate the non-linear behaviour of the elastic constants. Within the studied σ_1 range, K_1 ususually passes through a minimum, K_3 passes through a maximum and K_2 decreases almost linearly with turbidity. The elastic constants reported in *Tables 4 and 5* are the result of such a calculation at the upper and lower limits of σ_1. The order of magnitude of the elastic moduli reported here falls within the 10^{-9}–10^{-7} dyn range, where K_1 is the largest and the most variable, and K_2 is the smallest and the least variable of the three moduli. Depending on the solvent and the molecular weight and concentration of PBLG, K_1 and K_3 may be of the same order of magnitude (10^{-8}–10^{-7}) or can be different by as much as 100 times. The K_2 modulus, which is usually the smallest of the three constants, falls within the 10^{-9} dyn range.

Owing to the diversity of the PBLG solutions and the inconsistencies in the literature data of the elastic constants, any quantitative comparison of the data should be viewed with caution, particularly in view of the lack of information on the behaviour of the temperature dependence of K_i in these systems. This is not only lacking in this work, but has been basically neglected in the literature studies of PBLG solutions. It is well known that the elastic moduli of nematics decrease and converge with temperature below their nematic–isotropic (T_{NI}) transitions. This general behaviour has been supported by the relevant theories[1–7] and experiments for the monomeric nematogens (see for example refs. 8 and 9). In the literature of PBLG systems, only the temperature dependence of K_2 has been studied and reported to exhibit similar behaviour as those in monomeric nematogens[14]. In spite of the importance of the temperature behaviour of K_i for quantitative comparisons in various

solutions, at present we can only speculate that the lack of knowledge on differences in the T_{NI} of the investigated PBLG solutions could be the basic reason for the discrepancies of results in the literature. The quantitative verification of this important factor should await future systematic studies.
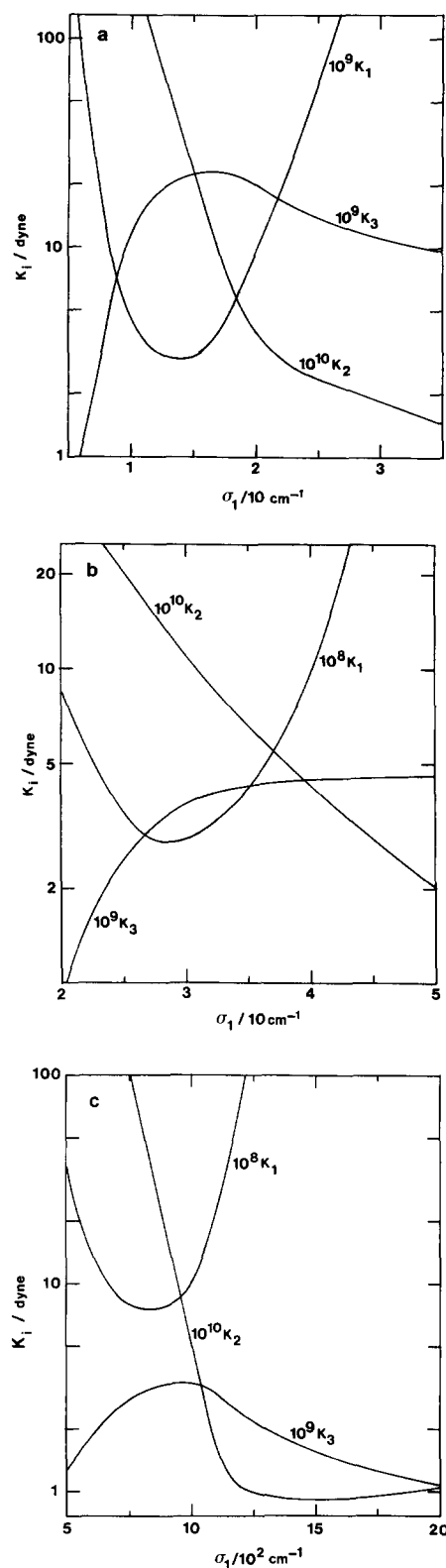

Figure 2 Calculated elastic moduli K_i as a function of σ_1 in the PBLG/DO solutions with molecular weight (a) 70×10^3, (b) 150×10^3, (c) 296×10^3. Other experimental data are from the related sample A in *Table 2*
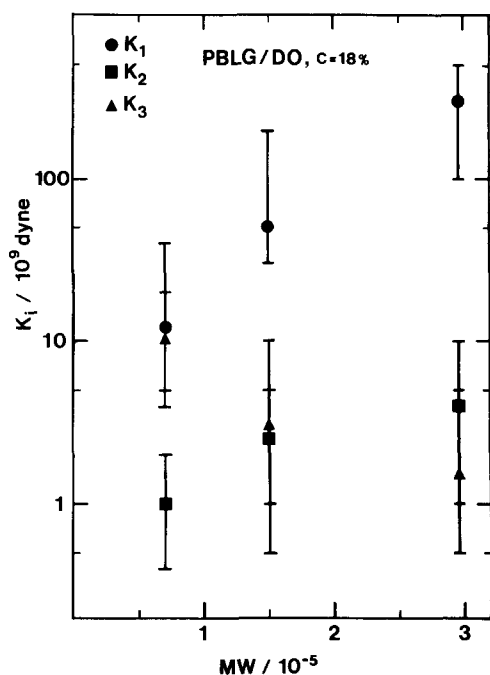
Figure 3 Molecular-weight dependence of the three elastic moduli in PBLG/DO solutions, $C = 18\%$, $T = 298$ K. The error bars represent the variation range of K_i based on the estimated limits of $\langle \sigma_1 \rangle$ (see *Table 2*). The points are the mean values of data from *Table 4*

Molecular-weight effect. The turbidities of PBLG/DO solutions do not exhibit a noticeable dependence on the molecular weight of the PBLG (see *Table 2*), but their elastic constants are significantly affected by the molecular weight of the polymer (see *Table 4*). This behaviour is better demonstrated in the semi-logarithmic plot of *Figure 3*, where the elastic constants of *Table 4* are plotted against the molecular weight of the PBLG. Note that the assigned data points in *Figure 3* represent the average mean of the moduli from all measurements and the error bars signify the K_i limits obtained from the corresponding $\langle \sigma_1 \rangle$ range. The results clearly show that, at the same concentration ($C = 18\%$), K_1 and K_2 increase whereas K_3 decreases with the molecular weight of the PBLG. Within the experimental limits, variations in the elastic constants are within one order of magnitude and their correlations with molecular weight can be linear. The opposing trends of K_1 and K_3 result in a significant increase of the K_1/K_3 ratio as the molecular weight increases. This ratio changes by 100 times within the molecular weight range 70 000–296 000.

The effect of molecular weight on the elastic moduli is also evident from the calculated data of *Figure 2*, where K_1 and K_3 curves exhibit a systematic separation from each other as the molecular weight increases. This qualitative comparison shows that, at lower molecular weight, the K_1 and K_3 curves can intercept with each other (*Figure 2a*) and approach the rigid-rod model, i.e. $K_1 \simeq K_3$. Whereas at larger molecular weights (*Figure 2c*) the K_1 is always larger than K_3.

The overall results of the elastic constants and their correspondence with the molecular weight in PBLG/DO solutions are in agreement with the theoretical model, which predicts that the splay modulus becomes forbidden when the molecular length and chain flexibility are increased[10,11]. Our results are also in qualitative agreement with recent studies using the field-induced distortion

methods[20,21]. These studies have reported a similar trend in the anisotropy of elastic moduli, but the reported molecular-weight dependence of K_1/K_3 is in disagreement with both the chain flexibility model and the present results. Although the sources of these experimental discrepancies are as yet difficult to explain, it is worth while pointing out that an increase of the polymer chain flexibility with molecular weight can be deduced from the variation of both K_1 and K_3 with the molecular weight, which is the consequence of presently lacking knowledge of more complex energetic and entropic contributions.

Concentration effect. In the PBLG/DCM solutions the turbidities exhibit a systematic increase with concentration of the PBLG (see *Table 3*), and from the corresponding elastic data (see *Table 5*) it is possible to deduce a qualitative correspondence with concentration. *Figure 4* shows a semi-logarithmic plot of the elastic moduli in PBLG/DCM solutions as a function of their concentrations at a molecular weight of 240 000. Within the experimental limits, the data indicate that K_1 and K_3 are of the same order of magnitude (about 10^{-7} dyn) and are almost unaffected, whereas K_2 exhibits a moderate increase with concentration. The trend of the concentration dependence of K_2 is in qualitative agreement with that in the PBLG/DO solutions reported previously[14]. Since the K_1 and K_3 data scatter (*Figure 4*) is within the experimental limits, their concentration dependence, if any, cannot be elaborated further at the present time.

The apparent concentration invariance of K_1 and K_3 moduli can also be explained according to the polymer–solvent interactions. That is, owing to a weak PBLG–DCM associations, the overall rigidity of the α-helix backbone structure of PBLG in the mesophase is less disturbed by the presence of DCM. The trend of the concentration behaviour of K_i in this solution also
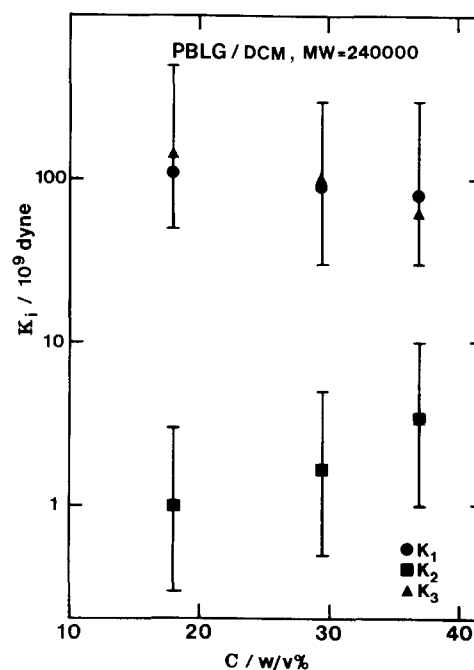

Figure 4 Concentration dependence of the three elastic moduli in PBLG/DCM solutions, $MW = 240 \times 10^3$, $T = 298$ K. The error bars represent the variation range of K_i based on the estimated limits of $\langle \sigma_1 \rangle$ (see *Table 3*). The points are the mean values of data from *Table 5*

indicates that the values of these moduli at higher concentrations may reach those in the thermotropic nematic rigid rods.

Solvent effect. Although the present data do not provide direct correspondence of the solvent effect with the elastic constants, it can be obtained indirectly from data of *Figures 3* and *4*. Namely, in the PBLG/DO solution (*Figure 3*), a linear interpolation of the elastic moduli to a molecular weight of 240 000 gives the estimated values of $K_1 \simeq 1 \times 10^{-7}$, $K_2 \simeq 3 \times 10^{-9}$ and $K_3 \simeq 2 \times 10^{-9}$ dyn. On the other hand, the average values of K_i in the PBLG/DCM solution at the same concentration and molecular weight (see *Table 5* and *Figure 4*) are $K_1 \simeq 1 \times 10^{-7}$, $K_2 \simeq 1 \times 10^{-9}$ and $K \simeq 1 \times 10^{-7}$ dyn. A comparison between the elastic data in the two solutions indicates that their K_1 and K_2 are effectively unchanged, whereas the K_3 in DCM is about 50 times larger than that in DO. Since such a large difference could not be due to either concentration or molecular weight, it should then be due to the nature of the solvent and the degree of polymer–solvent interaction. In this respect, we speculate that the stronger molecular associations of PBLG with DO can destabilize the rigidity of the α-helix structure of the polymer more than with DCM. The consequence of this effect in the PBLG/DO solution is the reduction of PBLG chain rigidity and the increase of its K_3 modulus. Furthermore, as the molecular weight of polymer and the K_1 modulus in both solutions are equivalent, the subsequent chain flexibility of PBLG should be dominated by solvent–polymer interactions, which is manifested by the K_3 increase in PBLG/DO solution.

The solvent effect may also be argued on the basis of induced aggregation of the polymer. In this respect, the aggregation of PBLG with DO would be more than DCM, where a larger variation of K_i with molecular weight is expected in solutions with DO. In fact, a recent study by the field-induced distortion method[21] has shown that the molecular-weight dependence of K_1 and K_1/K_3 is more significant with solvents that give smaller persistence lengths (larger polymer aggregations).

CONCLUSIONS

In the present work, we studied the anisotropy of turbidity in uniaxially oriented nematic solutions of PBLG, from which the ranges of the corresponding elastic constants were obtained. The reported elastic constants showed a pronounced anisotropy with K_1 as the largest and K_2 as the smallest of the three moduli. In the PBLG/DO system, the molecular-weight dependence of K_1/K_3 was in agreement with the theoretical prediction of polymer chain flexibility. We found a significant increase of K_1 and K_1/K_3 over a molecular-weight range of 70 000 to 296 000. Also the elastic moduli exhibited a pronounced solvent dependence, which, owing to the lack of theoretical and experimental knowledge, could not be fully explained. On the basis of the present results, the molecular weight, concentration and aggregation of the polymer as well as the nature of the solvent and the polymer–solvent interactions are found to influence both the absolute and relative values of the elastic constants. In one studied PBLG/DCM solution, the elastic moduli K_1 and K_3 did not show any significant dependence on the polymer concentration, but some increase in K_2

modulus was noticed. The knowledge of temperature-dependence of the elastic constants is an important consideration for meaningful comparison of data. This is yet lacking in the present work as well as in the literature and must be included in future studies to obtain a better understanding of the structure–property relations in PBLG solutions. Application of the present method to study the turbidities and elastic constants in other lyotropic and thermotropic polymer systems is the subject of our current research activities[40].

REFERENCES

1   Nehring, J. and Saupe, A. *J. Chem. Phys.* 1971, **54**, 337
2   Priest, R. *Mol. Cryst., Liq. Cryst.* 1972, **17**, 129; *Phys. Ref. (A)* 1973, **7**, 720
3   Straley, J. P. *Phys. Rev. (A)* 1973, **8**, 1181
4   Poniewierski, A. and Stecki, J. *Mol. Phys.* 1979, **38**, 1931; *Mol. Phys.* 1980, **41**, 145
5   Flapper, S., Vertogen, G. and Leenhouts, F. *J. Physique* 1981, **42**, 1647
6   Vertogen, G. *Phys. Lett. (A)* 1982, **89**, 448
7   Gelbart, W. and Ben-Shaul, A. *J. Chem. Phys.* 1982, **77**, 916
8   Leenhouts, F. Ph.D. Thesis, University of Goringen, WG, 1980
9   de Jeu, W. H. 'Physical Properties of Liquid Crystalline Materials', Gordon & Breach, New York, 1980, Ch. 6
10 de Gennes, P. G. *Mol. Cryst., Liq. Cryst. (Lett.)* 1977, **34**, 177
11 Meyer, R. B. 'Polymer Liquid Crystals' (Eds. A. Ciferri, W. R. Krigbaum and R. B. Meyer), Academic Press, New York, 1972, Ch. 6
12 Ten Bosch, A. and Sixou, P. *J. Chem. Phys.* 1987, **86**, 6556
13 Duke, R. W. and DuPré, D. B. *J. Chem. Phys.* 1974, **60**, 2759
14 DuPré, D. B. and Duke, R. W. *J. Chem. Phys.* 1975, **63**, 143
15 Patel, D. L. and DuPré, D. B. *Rheol. Acta* 1979, **18**, 662
16 Lonberg, F. and Meyer, R. B. *Phys. Rev. Lett.* 1985, **55**, 718
17 Hurd, A. J., Fraden, S. and Meyer, R. B. *J. Physique* 1985, **46**, 905
18 Fernandes, J. R. and DuPré, D. B. *Liq. Cryst. Ordered Fluids* 1984, **4**, 393
19 Fernandes, J. R. and DuPré, D. B. *Mol. Cryst., Liq. Cryst. (Lett.)* 1981, **72**, 67
20 DuPré, D. B. and Fernandes, J. R. *J. Appl. Polym. Sci., Appl. Polym. Symp.* 1985, **41**, 221
21 Parthasarathy, R., Houpt, D. J. and DuPré, D. B. *Liq. Cryst.* 1988, **3**, 1973
22 Duke, R. W. and DuPré, D. B. *Mol. Cryst., Liq. Cryst.* 1977, **43**, 33
23 Taratuta, V. G., Hurd, A. J. and Meyer, R. B. *Phys. Rev. Lett.* 1985, **55**, 246
24 Hurd, A. J., Fraden, S., Lonberg, F. and Meyer, R. B. *J. Physique* 1985, **46**, 905
25 Se, K., Suresh, A., Srubuvasari, M. and Berry, G. C. 'International Conference on Liquid Crystal Polymers', Bordeaux, 1987
26 Gilli, J. M., Sixou, P. and Blumstein, A. *J. Polym. Sci., Polym. Lett. Edn.* 1985, **23**, 379
27 Tsvetkov, V. N. 'International Conference on Liquid Crystal Polymers', Bordeaux, 1987
28 Zheng-Min, S. and Kleman, M. *Mol. Cryst., Liq. Cryst.* 1984, **111**, 321
29 Hopewood, A. I. and Coles, H. J. *Mol. Cryst., Liq. Cryst.* 1985, **130**, 281
30 Sefton, M. S., Bowdler, A. R. and Coles H. J. *Mol. Cryst., Liq. Cryst.* 1985, **129**, 1
31 Langevin, D. and Bouchiat, M. A. *J. Physique Coll.* 1975, **36**, C1-197

32 Hakemi, H., Jagodzinski, E. F. and DuPré, D. B. *J. Chem. Phys.* 1983, **78**, 1513

33 Hakemi, H., Jagodzinski, E. F. and DuPré, D. B. *Mol. Cryst., Liq. Cryst.* 1983, **91**, 129

34 Hakemi, H. *Mol. Cryst., Liq. Cryst.* 1987, **153**, 99

35 Hakemi, H. *Liq. Cryst.* 1989, **5**, 327

36 de Gennes, P. G. *C. R. Hebd. Seanc. Acad. Sci. Paris* 1968, **299**,

15; 'The Physics of Liquid Crystals', Clarendon Press, Oxford, 1974, p. 303

37 DuPré, D. B. and Lin, F. *Mol. Cryst., Liq. Cryst.* 1981, **75**, 217

38 Duke, R. W., DuPré, D. B. and Samulski, E. T. *Mol. Cryst., Liq. Cryst.* 1977, **40**, 247

39 Lin, F., personal communication

40 Hakemi, H., in preparation