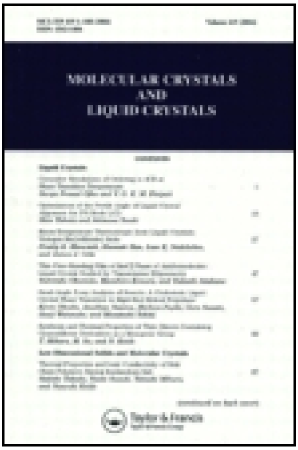

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On the Anisotropy of Turbidity and Elastic Constants of a Monomer and a Polymer Liquid Crystal

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ON THE ANISOTROPY OF TURBIDITY AND ELASTIC CONSTANTS OF A MONOMER AND A POLYMER LIQUID CRYSTAL

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ABSTRACT: The light scattering method was used to study the anisotropy of turbidity (σj) and elastic constants (Ki) of 8CB and PBLG nematics. σj and Ki are influenced by surface effects, the cybotactic structure and the magnetic field. The relative order of magnitude of Ki in the 8CB monomer was in support of the hard-rod model ($K1 < K3$), but in PBLG was in accord with partially flexible model ($K1 > K3$).

INTRODUCTION

The anisotropy of molecular interactions in liquid crystals is responsible for a number of interesting macroscopic phenomena including the viscoelastic properties. Knowledge of the elastic constants of mesophases for understanding structure-property relations is important from both fundamental and applied points of view. According to the hard-rod model, the well established moduli of "splay" K1, "twist" K2, and "bend" K3 in low molecular weight nematic compounds, are expected to be of the same order of magnitude, obeying the inequality: $K3 > K1 > K2$. This has been verified in nematogens by various experimental methods. In spite of experimental progress in the study of the elastic constants of the monomeric systems, their measurement in polymer liquid crystals with the Freedericksz transition (1-4) and light scattering (5,6) methods is the subject of current interest. The inconclusive results of these studies are in qualitative agreement with both the hard-rod model (7) (ref. 3,6), where $K1/K3 < 1$, and the forbidden splay concept of partially flexible polymers (8,9) (ref. 1, 5), where $K1/K3 > 1$. In this work, we utilized the previously developed anisotropy of turbidity method (10,11), to study two liquid crystal systems. In the first, we used the well characterized nematic monomer; 4-octyl-4'cyanobiphenyl (8CB). We studied the effect of the sample thickness and cybotactic nematic structure on the turbidity σ_j and the elastic constant Ki values of 8CB. In the second part we carried out primary measurements of σ_j and Ki of lyotropic liquid crystal polymer solution of poly(γ- benzyl -l-glutamate) (PBLG) solutions. Due to uncertainty of the turbidity data in one of the geometries, we estimated the range of the elastic constants by an approximation method. Detailed analysis of these studies are in progress.

EXPERIMENTAL

The compound 8CB was obtained from BDH Chemicals Ltd. with a stated purity of 99.9% and was used as such. The transition temperatures; T(NI)=314.5 and T(AN)=307.0°K, were determined by hot-stage microscopy. The samples were studied in optical precision cells with inside thickness ' of l = 0.02, 0.04, 0.1 and 0.2 cm. The PBLG samples were purchased from Sigma with molecular weights of 70,000 - 296,000. Solutions of PBLG in dioxane and dichloromethane were prepared at concentrations above the B point in rectangular optical cells with l=0.1 and 0.2 cm thicknesses. The 8CB and PBLG sample cells were placed in a temperature control unit, which was designed to fit between the poles of a 14 kG electromagnet. The magnetic field was used to induce uniaxial orientation in the nematic phase. σ_j values were determined by accurate masurements of total scattering cross sections of the oriented nematic medium in three selected geometries. Ordinary and extraordinary refractive indices, n_o and n_e, were extracted from the literature data for 8CB (12) and PBLG (13), with appropriate corrections for transition temperature differences. temperature was controlled to an accuracy of ±0.05 K. The experimental details and procedure for evaluation of the elastic constants have been mentioned elsewhere (10,11). The computer search routine was improved to calculate Ki values, as different as five order of magnitude. The overall estimated errors on measured turbidities is within 5% and on calculated elastic constants is within 20%.

RESULTS AND DISCUSSION

THERMOTROPIC 8CB MONOMER:

Figure 1 presents the temperature dependence of the three absorption coefficients σ_j in the nematic phase of 8CB at l=0.2-0.02 cm. In this mesophase, the nonlinear behavior and relative order of magnitude: $\sigma 1 < \sigma 2 < \sigma 3$ (see Fig. 1a), are in accord with our previous measurements in nematics systems (10). The nematic-surface interactions become more significant as the sample thickness decreases (see

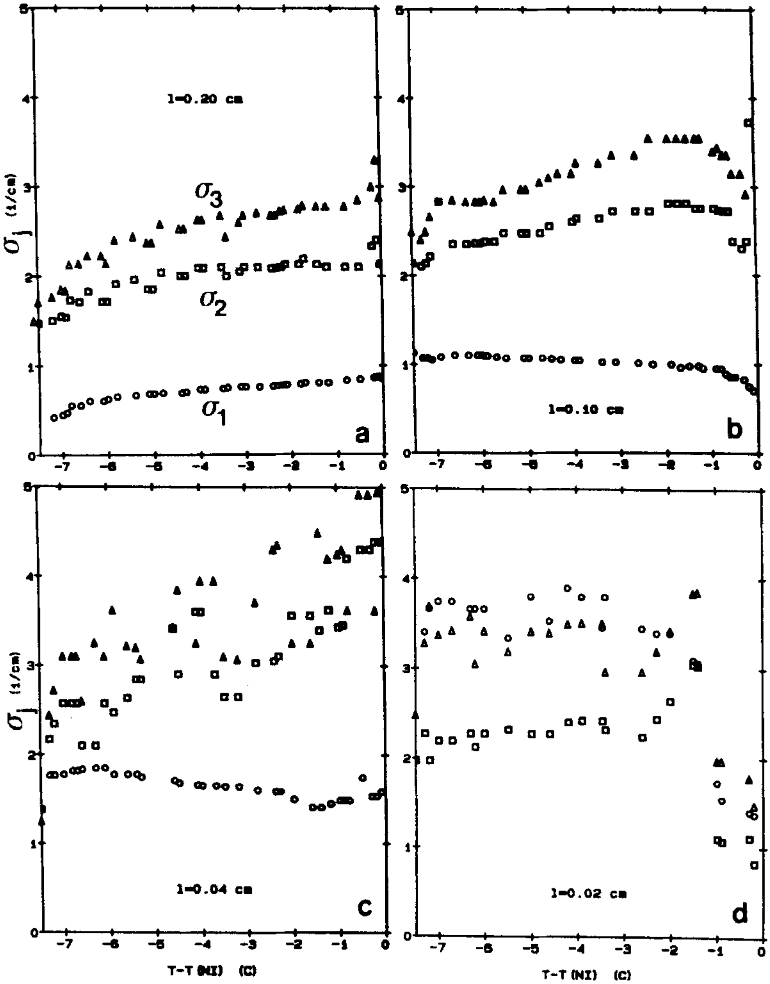

FIGURE 1. Turbidities of 8CB as a function of temperature and sample thickness.

Figures 1a-d). This surface effect is so significant in geometry 1 that, at l=0.02 cm, $\sigma 1$ becomes comparable with $\sigma 2$ and $\sigma 3$ (Figure 1d). In geometry 1, the direction of nematic director is always perpendicular to the glass surfaces. The inverse relation between $\sigma 1$ and the sample thickness can be directly attributed to the growth of the "cybotactic" nematic or the smectic-like structure (14). The enhancement of $\sigma 1$ over $\sigma 2$ and $\sigma 3$ is a result of both geometrical and surface effects. In determining the elastic constants, we found that surface effects of this type always give divergent values of K1. Examples of these calculations are given in Table I, where the experimental values of σj were used without correction (T=314 K, n_o=1.528, n_e=1.632).

TABLE I. Effect of thickness on Oj and Ki values of 8CB.

thickness	σj (1/cm)			Ki (10^7 dyne)		
l (cm)	$\sigma 1$	$\sigma 2$	$\sigma 3$	K1	K2	K3
0.20	0.81	2.35	2.86	12.3	4.6	13.2
0.10	0.83	2.30	3.15	18.8	4.3	10.5
0.04	1.40	3.70	4.40	273	1.2	7.9
0.02	1.54	3.05	3.85	855	1.6	5.8

The comparison of data indicate that, by decreasing sample thickness, K1 is increased but K2 and K3 are decreased. At $l<0.1$ cm, K1/K3 becomes much larger than unity, in contrast to the theoretical and the experimental results for rigid-rod nematics (12,15). For elimination of surface contributions to Ki values, we used a first-order approximation approach, assuming that the $\sigma 1/\sigma 2$ and $\sigma 1/\sigma 3$ ratios are independent of the sample thickness. Accordingly, all $\sigma 1$ data were corrected with respect to the standard l=0.2

cm sample. The results are presented in Figure 2, where temperature dependence of K2 and K3 are calculated for the corresponding sample thicknesses. Considering the correction procedure and the range of the experimental errors of the present study, the Ki values at different thicknesses are in good agreement with each other.

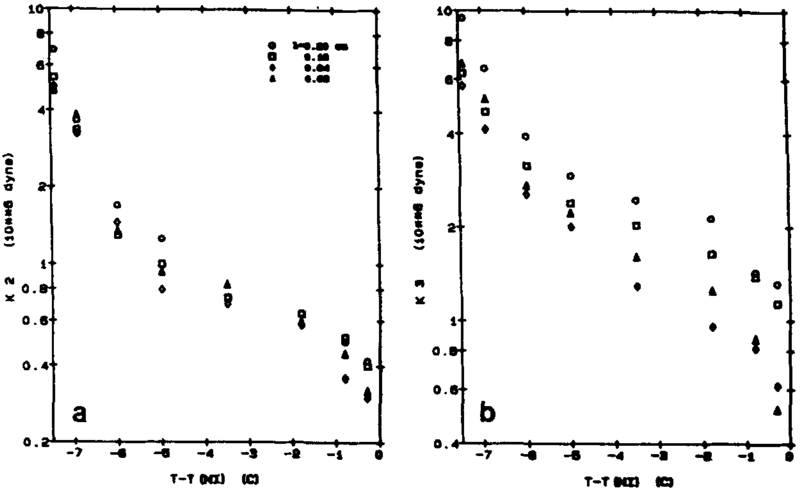

FIGURE 2. K2 and K3 values of 8CB vs sample thickness.

The well known K2 and K3 divergence near the AN transition and the second-order nature of this phase transition will be reported elsewhere (16). The Ki values reported here and in previous studies (11) are systematically larger than those found with the Freedericksz distortion method (12,15). This difference is mainly due to the dampening of the orientational fluctuations by the strong magnetic field used in the turbidity experiments. The field effect can result in smaller σ_j values, which in turn gives larger Ki than actual values. The effect of σ_j variations on the elastic constants of 8CB are presented by examples tabulated in Table II. Here, we assumed that $\sigma 1/\sigma 2$ and $\sigma 1/\sigma 3$ ratios are constant, independent of $\sigma 1$ changes. The results of Table II clearly indicate the inverse correlations between σj and Ki values.

TABLE II. Dampening effect of orientational fluctuations on σj and Ki of 8CB (T=314.0°K, l=0.2 cm).

σj (1/cm)			Ki (10^7 dyne)		
$\sigma 1$	$\sigma 2$	$\sigma 3$	K1	K2	K3
4.05	11.75	14.30	2.4	0.9	2.6
1.62	4.70	5.72	6.1	2.3	6.6
0.81	2.35	2.86	12.3	4.6	13.2 (exp)

From the study of the anisotropy of turbidity and elastic constants of 8CB we conclude that, both nematic-surface interactions and magnetic field can affect the anisotropy of turbidity and the elastic constant values of 8CB. But these parameters do not contribute to the qualitative behavior of temperature dependence of elastic constants and the growth of the cybotactic structure in the nematic phase. Improvements in the turbidity technique require direct empirical studies of the effects of magnetic field and laser beam intensities on σj and Ki values, which is the subject of our current investigations.

LYOTROPIC PBLG SOLUTIONS:

Due to large molecular weights and high viscosities of the mesophase PBLG solutions, their turbidity and refractive index anisotropies are much lower than those of thermotropic monomers, which results in diverse values of the principle elastic moduli. Assuming that relatively large $\sigma 1$

values of PBLG arise from the surface phenomena, the calculation of the elastic constants can be carried out by an approximation procedure similar to that used in 8CB system. Consequently, we calculated continuous functions of $\sigma1$ dependence of K1, K2 and K3 .

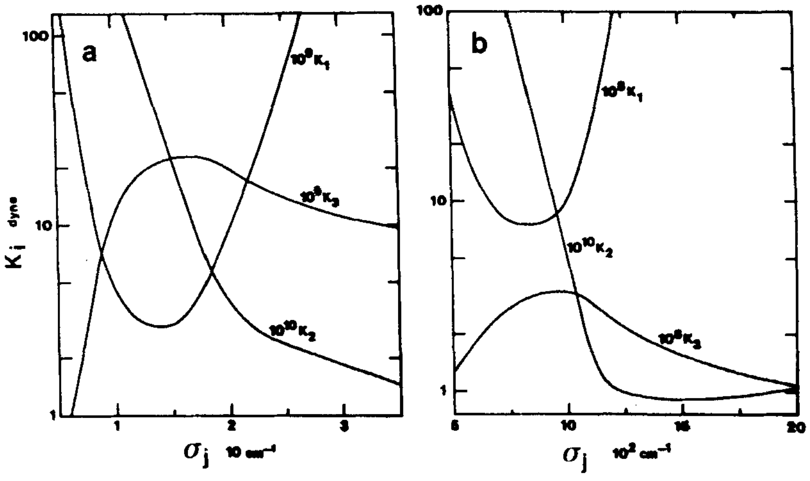

FIGURE 3. Variations of Ki with $\sigma1$ in PBLG/dioxane solutions. a) MW70000, $\sigma2/\sigma3=0.65/0.75$, $n_e/n_o=1.448/1.444$, b) MW296000, $\sigma2/\sigma3=0.50/0.55$, $n_e/n_o=1.444/1.441$.

The acceptable $\sigma1$ range was from the estimated $\sigma1/\sigma2=0.28-0.64$ ratio, extracted from a thermotropic nematic mixture (11b), where $\sigma2$ and $\sigma3$ are the measured values. Figure 3 shows the results of these calculation for two PBLG/dioxane solutions at 18.2%(w/w) concentration, l=0.2 cm thickness and T=298°K temperature. The results indicate that all K1 and K3 curves exhibit a minima and a maxima within a narrow $\sigma1$ range, which can be identified by the corresponding K1 (min) and K3(max), respectively. We didn't observe any extrema for K2 moduli in these calculations. The order of magnitude of Ki values were best estimated from the corresponding average $\sigma 1$ value (i.e., $\sigma 1/\sigma 2=0.46$), as well as at the extrema of the curves. The initial results tabulated

TABLE III. Estimated elastic moduli in PBLG solutions.

(w/w%) C	solvent	(1000) MW	Ki (10^9 dyne) K1	K2	K3	K1(min)	K3(max)
18.2	dioxane	70	40	0.2	15	30	23
18.2	dioxane	296	600	0.1	19	75	34
18.0	CH2Cl2	240	900	12	6	500	20
29.5	CH2Cl2	240	1500	0.1	15	450	9

in Table III indicate that, irrespective of the concentration, solvent and molecular weight, the K1 value is the largest of Ki, obeying the inequality: K1 > K3 > K2, where $1 < K1/K3 < 25$. This supports the the concept of forbidden splay modulus due to partial flexibility of the polymer chain (8,9). Although one can refer to other correlations, arising from the concentration, solvent and the molecular weight effects on Ki, futher discussions of the present data will require experimenal refinements of the turbidity method, which is in progress.

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