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Frank Elastic Constants and Leslie-Ericksen Viscosity Coefficients of Nematic Solutions of a Rodlike Polymer

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FRANK ELASTIC CONSTANTS AND LESLIE-ERICKSEN VISCOSITY COEFFICIENTS OF NEMATIC SOLUTIONS OF A RODLIKE POLYMER

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Abstract The formation of a monodomain nematic liquid crystal with a solution of the rodlike poly[1,4-phenylene-2,6-benzobisthiazole] will be described, along with the results of elastic and quasi-elastic light scattering on the oriented solution. The latter are analyzed to give the ratios K_S/K_T = 15.8 and K_B/K_T = 7.3 for the Frank elastic constants and η_S/η_T = 0.86 and η_B/η_T = 0.14 for the Leslie-Ericksen viscosities. These are compared with theoretical models and with results observed for the shear stress and the flow birefringence in steady flow.

1. INTRODUCTION

A monodomain liquid crystal has been prepared with a solution of poly(1,4-phenylene-2,6-benzobisthiazole), PBT, in methane sulfonic acid, MSA. (0.0406 weight fraction polymer with molecular weight $M_W = 3.4 \times 10^4$ or average length L_W = 155nm). As shown elsewhere, PBT is rodlike and optically anisotropic [1]. Elastic and quasi-elastic light scattering measurements have been used to study the Frank elastic constants K_S, K_T and K_B and the viscosity coefficients η_S, η_T and η_B, where the subscripts S, T and B designate splay, twist and bend distortions of the director field, respectively.

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2. MONODOMAIN FORMATION

The monodomain was prepared by slow extrusion of the nematic solution into tubing with a rectangular cross section (0.04 cm x 1 cm) at a flow rate sufficient to cause appreciable molecular orientation in the stretching flow of the advancing front. On cessation of flow the sample exhibited a mottled texture, was highly turbid, and developed striations perpendicular to the flow direction through which no light was transmitted under crossed polars for any orientation of sample and polarizer. Otherwise, the sample transmission between crossed or parallel polars was about equal. On aging, the sample developed what will be referred to as a smooth texture, with the formation of disclinations loops near either bounding plane of the cell. The smooth texture was markedly birefringent and dichroic, with a preferred direction along the original flow direction, and scattered light weakly (low turbidity). With additional aging (10-20 days) most of the disclinations loops contracted and disappeared. The back fluoresence emission was determined using incident light with a wavelength that is strongly absorbed, so that fluoresence was observed only from the solution within about 1 μm from the surface. This fluoresence was strongly anisotropic, indicating orientation of the rodlike chains in the original flow direction. Moreover, this orientation at the surface was present immediately after the cell was filled, and remained on heating the sample above its clearing temperature, where order was lost in the bulk. We postulate that the oriented chains presented to the surface by the advancing front as the cell was filled with solution are strongly adsorbed in the oriented state, and remain in that state indefinitely. The monodomain alignment is then driven by these oriented adsorbed chains.

The motiled appearance observed immediately on cessation of flow is attributed to flow instabilities, perhaps involving tumbling of the director orientation in the flow plane along the flow direction, see below. Thus, the nonbirefringent striations may represent regions of nearly homeotropic orientation formed where the tumbling has oriented the molecular axis perpendicular to the flow direction, see below. Additional details of the monodomain formation will be discussed elsewhere [2].

3. ELASTIC AND QUASI-ELASTIC LIGHT SCATTERING

The light scattering apparatus used incorporates a

Krypton-ion laser (647 nm wavelength), and a computer-based data acquistion system and autocorrelator; details may be found elsewhere [1, 2]. Following convention [3–5], the scattering plane (containing the incident and scattered rays) *is taken as a plane of reference, and use is* made of an orthonormal coordinate system spanned by the basis vectors $\mathbf{e}_0$, $\mathbf{e}_1$, $\mathbf{e}_2$; defined as $\mathbf{e}_0 = \mathbf{n}$, $\mathbf{e}_1 = \mathbf{e}_2 \times \mathbf{n}$ and $\mathbf{e}_2 = (\mathbf{n} \times \mathbf{q})/|(\mathbf{n} \times \mathbf{q})|$. Here $\mathbf{n}$ is a unit vector in the direction of the director field and $\mathbf{q}$ is the scattering vector:

$$\mathbf{q} = \mathbf{k}_I - \mathbf{k}_S \tag{1a}$$

$$q^2 = (k_I - k_S)^2 + 4k_I k_S \sin^2(\theta/2) \tag{1b}$$

where $\mathbf{k}_I$ and $\mathbf{k}_S$ are the wave vectors of the incident and scattered beams, respectively, and θ is the scattering angle. Thus, $k_I = 2\pi n_I/\lambda$ and $k_S = 2\pi n_S/\lambda$, where λ is the wavelength of the incident light in vacuum and n_I and n_S are the refractive indices for propagation of the incident and scattered beams, respectively. Then, with unit vectors i and f along the polarization direction of the incident and scattered rays, respectively, the Rayleigh ratio may be expressed as [3–5]

$$R_{f,i,n}(q_\perp, q_\parallel) = K \sum_{\mu=1,2} \Gamma_\mu \tag{2a}$$

$$\Gamma_\mu = F_\mu(f,i,n)/\hat{K}_\mu(q_\perp, q_\parallel) \tag{2b}$$

where K is proportional to the square of the dielectric anisotropy, F_μ depends only on the geometrical arrangement of the scattering experiment and $\hat{K}_\mu$ depends on the three Frank elastic constants:

$$\hat{K}_\mu(q_\perp, q_\parallel) = K_\mu q_\perp^2 + K_3 q_\parallel^2 \tag{3}$$

Here, $q_\parallel = \mathbf{q} \cdot \mathbf{n}$ and $q_\perp^2 = q^2 - q_\parallel^2$, and subscripts 1, 2 and 3 designate splay, twist and bend, respectively. The arrangement used here is confined to the use of horizontal and vertical orientations of the polarization of the scattered and incident rays, respectively, using n perpendicular or parallel to the scattering plane, such that

$$\frac{R_{H,V,\perp}(q_\perp, 0)}{R_{H,V,\parallel}(0, q_\parallel)} = \frac{K_B}{K_S} + \frac{K_B}{K_T} \tan^2(\theta/2) \tag{4}$$

As pointed out by Taratula *et al* [6] the use of Eqn. (4)

provides complete data on the ratios of the Frank elastic constants. The data obtained here are fitted by Eqn. (4), with the results given in Table 1. Consistent results obtained with other geometries will be discussed elsewhere [2].

The photon count correlation function may be expressed as [3-6]

$$g^{(2)}_{f,i,n}(\tau;q_\perp,q_\parallel) = \tag{5}$$

$$1 + f\left\{\frac{\sum_{\mu=1,2}\Gamma_\mu \exp[-\tau/\tau_\mu(q_\perp,q_\parallel)]}{\sum_{\mu=1,2}\Gamma_\mu}\right\}^2$$

where f, equal to $g^{(2)}_{f,i,n}(0;q_\perp,q_\parallel) - 1$, is an optical coherence factor, and

$$\tau_\mu(q_\perp,q_\parallel) = \hat{\eta}_\mu(q_\perp,q_\parallel)/\hat{K}_\mu(q_\perp,q_\parallel) \tag{6a}$$

$$\hat{\eta}_1(q_\perp,q_\parallel) = \eta_B + m_1(q_\perp/q_\parallel)(\eta_S - \eta_B) \tag{6b}$$

$$\hat{\eta}_2(q_\perp,q_\parallel) = \eta_B + m_2(q_\perp/q_\parallel)(\eta_T - \eta_B) \tag{6c}$$

Here m_1 and m_2 depend on $q_\perp/q_\parallel$ and the Leslie-Ericksen viscosity coefficients [2,5], with limiting values for small $q_\perp$ and small $q_\parallel$ that give $\hat{\eta}_1(0,q_\parallel) = \hat{\eta}_2(0,q_\parallel) = \eta_B$, $\hat{\eta}_1(q_\perp,0) = \eta_S$ and $\hat{\eta}_2(q_\perp,0) = \eta_T$. The data on $g^{(2)}$ were analyzed to give the first cumulant:

$$k = -\frac{1}{2}\lim_{\tau=0}\frac{\partial \ln[g^{(2)}(\tau) - 1]}{\partial\tau} \tag{7}$$

with results shown in Fig. 1 for three geometries. As shown in Fig. 1, k is proportional to q^2. Data obtained with additional geometries discussed elsewhere [2] gave consistent results. Two of the geometries correspond to the arrangement described above, with $k = K_T q^2/\eta_T$ over the angular range studied for perpendicular orientation of n and $k = K_B q^2/\eta_B$ for horizontal polarization of n. With the third geometry, horizontal orientation is used for both incident and scattered rays, with parallel orientation of n such that in general, $k = \hat{K}_1(q_\perp,q_\parallel)/\hat{\eta}_1(q_\perp,q_\parallel)$. However, over the angular range studied, $m_1 \approx 1$ and this result simplifies [2] to $k = K_S q^2/\eta_S$. The results calculated from Fig. 1 are given in Table 1.

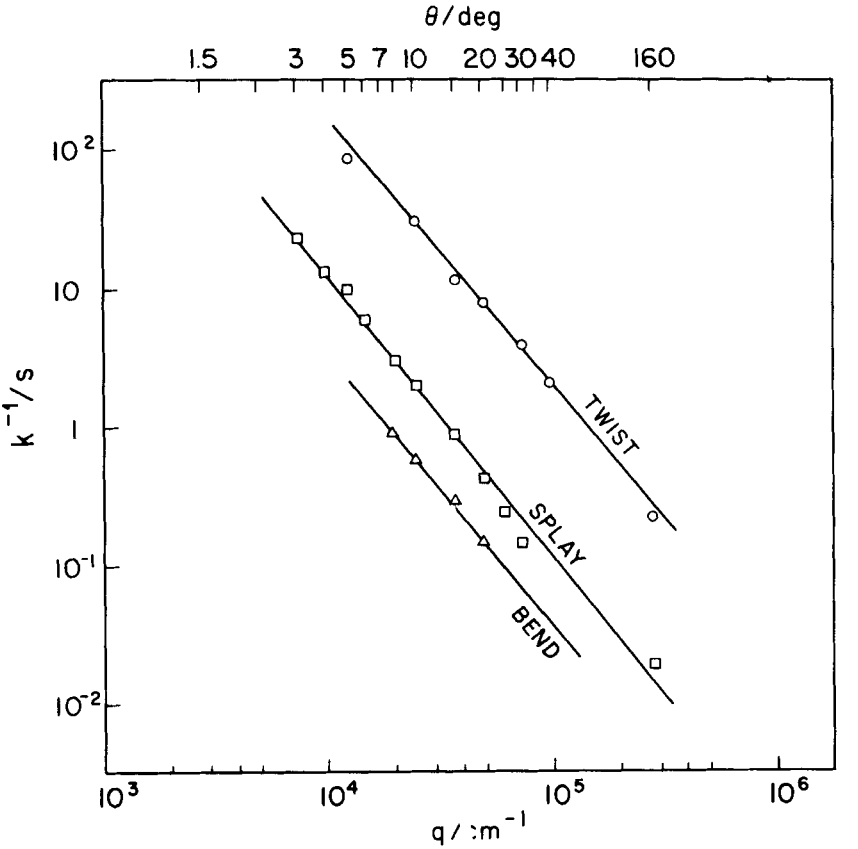

Fig. 1 The inverse k^{-1} of the first cumulant versus q^2 for three geometries: $g^{(2)}_{H,V,\perp}(\tau;q_\perp,0)$, O; $g^{(2)}_{H,V,\parallel}(\tau;0,q_\parallel)$, Δ; and $g^{(2)}_{H,H,\parallel}(\tau;q_\perp,q_\parallel)$, □. The identification of k/q^2 with splay, bend or twist distortion of the director field is indicated on the figure.

3. DISCUSSION

As shown in Table 1, for the nematic solution studied, $K_S > K_B > K_T$ and $\eta_T > \eta_S >> \eta_B$. As will be discussed elsewhere [2], based on the magnitude of the absolute scattering, we estimate that $K_T \approx 2.4$ pN, which is of the order frequently observed with small molecule liquid crystals [3,4]. According to a theoretical treatment [7] the Frank elastic constants for a nematic fluid comprising volume fraction ϕ of impenetrable rods of length L and diameter D takes the form

$$K_i = \frac{(\phi/\phi_C)^2 kT}{D} k_i(S) \qquad (8)$$

where the threshold volume fraction ϕ_C for formation of the ordered phase is nearly proportional to D/L, S is the order parameter for the director field, and i = 1,2,3 for splay, twist and bend, respectively. With this model, $K_S/K_T = 3$ and $K_B/K_T \approx 18.7$, in contrast with the results found here.

The enhanced value of K_S observed here is consistent with a model whereby the local change $\delta\rho$ in the number density ρ of chains induced by splay results in the inclusion of a term $(E_{OSM}/2)\ \langle\delta\rho/\rho\rangle^2$ to the elastic free energy density, leading to a term proportional to $(\text{div } n)^2$ that dominates K_S [8]. Here, E_{OSM} is an osmotic modulus, reflecting the change in the free energy accompanying the concentration of chain ends in a splay distortion. Work is in progress to determine the Frank elastic constants as a function of c and M for nematic solutions of PBT.

Statistical mechanical treatments have been given for the viscosity coefficients α_i(i = 1-6) that appear in the constitutive equation of Leslie and Ericksen [9]. The parameters η_S, η_T and η_B may be expressed using four of the α_i(i = 2-5). With one of the statistical treatments of these [10], both η_S and η_B are zero, which is not in accord with our results. With another treatment [11].

$$\eta_S/\eta_T = 1 - 35/(80S^2 + 108S - 21) \qquad (9)$$

$$\eta_B/\eta_T = 1 + \frac{35(4S - 1)^2}{3(40S^4 - 76S^3 - 96S^2 + 20S + 7)} \qquad (10)$$

$$\alpha_1/\eta_T = -(5S - 2)(4S - 1)/9 \qquad (11)$$

where S is the order parameter of the director field and α_1 is a Leslie-Ericksen viscosity coefficient that does not occur

in representations of η_S, η_B or η_T in terms of the α_i. With Eqn. (9), η_S/η_T increases from 0.34 to 0.79 as S increases from 0.5 to 1.0. Over this same range η_B/η_T decreases from 0.17 to 0, and α_1/η_T decreases from - 0.06 to - 1. There is no value of $S < 1$ for which Eqn. (9) gives the η_S/η_T observed here. With use of Eqn. (10), the observed η_B/η_T corresponds to $S = 0.62$, for which Eqn. (9) gives $\eta_S/\eta_T = 0.54$, in comparison with the observed value of 0.86, and Eqn. (11) gives $\alpha_1/\eta_T = -0.06$.

According to the Leslie-Ericksen constitutive equation [9], in the absence of boundary effects (see below) shear flow is expected to be stable with a steady state shear viscosity that may be expressed in the form

$$\frac{\eta_0}{\eta_T} = Z\left[\frac{\eta_S}{\eta_B} - 1\right]^{-1} + \frac{1}{2}(Z - 1)\left\{1 + \frac{(\alpha_1/\eta_T)(1 + Z)}{4Z^2}\right\} \tag{12a}$$

if $Z > 1$, where

$$Z = [r + (r^2 - 4)^{1/2}]/2 \tag{12b}$$

$$r = 2\left[\frac{\eta_S}{\eta_T} - 2\,\frac{\eta_S}{\eta_T}\cdot\frac{\eta_B}{\eta_T} + \frac{\eta_B}{\eta_T}\right]\left[\frac{\eta_S}{\eta_T} - \frac{\eta_B}{\eta_T}\right]^{-1} \tag{12c}$$

and α_1 is one of the Leslie-Ericksen viscosity coefficients. Shear flow is predicted to be unstable of $Z < 1$, see below. In the stable flow, the director is in the flow plane, tilted at the alignment angle $\theta_0 = (1/2)\arccos(Z^{-1})$. With Eqns. (9) and (10), $Z < 1$ for all S, so that shear flow is predicted to be unstable. With the values given in Table 1, $Z > 1$, so that stable shear flow is predicted, with $\theta_0 = 22$ deg., and $\eta_0/\eta_T = 0.46 + 0.06(\alpha_1/\eta_T)$.

Typically, with nematic solutions of PBT in steady flow between parallel plates or in a cone and plate, the ratio M/Ω of the torque M to the angular velocity Ω is found [12] to decrease continuously with increasing Ω before reaching a plateau of constant M/Ω for a range of Ω, and then decreasing with further increase in Ω. With the sample used here, M/Ω was found to be constant at low Ω, decreasing at larger Ω [13]; the lowest Ω used corresponded to a shear rate of $10^{-3}s^{-1}$. If the steady flow with M/Ω independent of Ω is taken to be proportional to η_0, then $\eta_0 = 200$ Pa·s for the temperature used here (20°C). By comparison, with the

data in Table 1, $\eta_T K_T^{-1} = 191$ Pa·s pN^{-1}, or $\eta_0/\eta_T = 0.44$, making use of the estimate for K_T given above. With this value, $\alpha_1/\eta_T < 0$, in accord with Eqn. (1), but the uncertainty in the estimate of α_1/η_T is large owing to the small prefactor (0.06).

Since the separation between the surface in the parallel plate or the cone and plate rheometers is not large (ca 1mm), it is possible that the substantial orientational correlation lengths characterizing the nematic solutions of PBT can affect the relation between M and Ω. Thus, defining η_δ as $\sigma h/V$, where σ is the shear stress, V is the relative velocity and h the separation of the confining surfaces, it can be expected that a static, oriented boundary layer near either surface will give $\eta_\delta \neq \eta_0$, and in general, $\eta_\delta > \eta_0$ similar to behavior often observed with PBT at low Ω [12]. A treatment for such an effect based on the Leslie-Ericksen constitutive equation gives the general result [14]

$$\eta_\delta = \eta_0 \{1 - E^{-1/2} H_\delta(\theta_2, \theta_1, \theta_0)\}^{-1} \qquad (13)$$

where H is a function of the alignment angle θ_0 and the orientation angles θ_1 and θ_2 (in the shear plane) between the flow direction and the direction of $\mathbf{n}$ for the adsorbed layers at the two surfaces, and E_i is the Ericksen number ($i = 1,2,3$)

$$E_i = Vh\,\eta_i/K_i \qquad (14)$$

for shearing deformation between surfaces separated by distance h and moving at relative velocity V. For cone and plate geometry, $E_i \square (2\pi R)^2 \Theta\Omega\eta_i/K_i$, where R is the radius, Θ is the angle between the cone and plate, and Ω is the angular velocity [14]. For the apparatus used in reference (13), $E_i \approx 1500\eta_i/K_i$, and in the experiments used to determine the steady state viscosity, $\Omega > 3\times10^{-6}$ rad/s. Thus, with the values of η_i/K_i entered in Table 1, $E_i > 10^5$. Consequently, the oriented boundary layer is expected to be small for the Ω used, such that $\eta_\delta \approx \eta_0$, (By contrast, since the K_i are comparable for small molecule and polymer liquid crystals, η_i/K_i is much smaller for the small molecule case, so that E_i is typically smaller for small molecules).

In the steady flow observed in the Ω-range with M/Ω nearly independent of Ω, the flow birefringence was found to be lower than expected, and to fluctuate with time at a fixed place, with the birefringence dropping nearly to zero, then increasing to a large value quasiperiodically [13]. This behavior suggests that the director tumbles in flow, an

effect consistent with the appearance of nonbirefringent striations described in section 2. Such tumbling is predicted [15] for shear flows with $Z < 1$, but are not expected if $Z > 1$ and $E_i >> 1$. The tumbling could result if some or all of the η_i depend on the deformation rate, so that the effective value of Z could be less than unity at the flow conditions, giving unstable flow. In that case, the observed constant M/Ω could not be taken as η_0 for use with Eqn. (12), and the estimate for α_1/η_T given above would not be meaningful. In fact, if still lower Ω is required to reach the slow flow of the Leslie-Ericksen constitutive equation, then E_i may be reduced to such a low value that Eqn. (13) becomes meaningful, with $\eta_\delta > \eta_0$, and at the increase of M/Ω with decreasing Ω would be viewed as the result ot two separate effects: 1) a boundary layer reflecting the orientation of adsorbed layers, such that η_δ calculated from M/Ω is much larger than η_0 at small Ω, and 2) dependence of the η_i on deformation rate, causing M/Ω to increase with decreasing Ω, and resulting in unstable shear flow. We are unaware of theoretical predictions on the effects of deformation rate on the Leslie-Ericksen viscosity coefficients.

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TABLE 1 Frank Elastic Constants and Leslie-Ericksen Viscosities for a Nematic Solution of PBT[a]

K_S/K_T	15.8	η_S/η_T	0.86
K_B/K_T	7.3	η_B/η_T	0.14
$\eta_S K_T^{-1}$/Pa·s·pN^{-1}	165	$\eta_S K_S^{-1}$/Pa·s·pN^{-1}	10
$\eta_T K_T^{-1}$/Pa·s·pN^{-1}	191	$\eta_T K_T^{-1}$/Pa·s·pN^{-1}	191
$\eta_B K_T^{-1}$/Pa·a·pN^{-1}	27	$\eta_B K_B^{-1}$/Pa·s·pN^{-1}	3.7

a) K_T is estimated to be 2.4 pN for this material [2]. Weight fraction of polymer equals 0.0406 in methane sulfonic acid.

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