

Light-Scattering Study of a Polymer Nematic Liquid Crystal

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We study the relaxation of thermally excited orientation fluctuations in a polymer nematic liquid crystal using photon correlation spectroscopy. The material studied is poly- γ -benzyl-glutamate at a concentration just above the isotropic-to-nematic transition point. The relaxation rates of elastic deformation modes exhibit large anisotropies. Quantitative measurements of ratios of Frank elastic constants and Leslie viscosities are described.

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Polymer liquid crystals composed of long rigid and semirigid molecules have already proven to be of considerable interest. They exhibit much more highly anisotropic properties than are found in the familiar low-molecular-weight liquid crystals. The high anisotropy is responsible for a number of newly observed macroscopic structural phenomena in these materials.¹⁻³ Theoretically, there have been simple discussions of the elastic and viscous properties of nematic liquid crystals composed of long semirigid chains,⁴ and more detailed models of the elastic^{5,6} and viscous⁷ properties of nematics composed of rigid rods, based on the Onsager theory.⁸ These theories predict large anisotropies, which have not until now been measured directly.

A traditional way of measuring elastic constants in a nematic liquid crystal has been a Fréedericksz transition.⁹ In long-chain nematics, however, the anisotropy of elasticity and viscosity produces unusual static and dynamic response to applied electric and magnetic fields. In fact, there may be no direct way of measuring the splay elastic constant with a Fréedericksz transition in these materials.¹⁰ Another well-established experimental method used to study the elastic and viscous properties in liquid crystals is quasielastic Rayleigh light scattering. This Letter presents quasielastic light-scattering measurements which we believe to be the first systematic experimental study of Frank elastic constants and anisotropic viscosities in a polymer nematic liquid crystal composed of long rigid or semirigid molecules.

It has been theoretically predicted¹¹ and experimentally confirmed¹² that long-wavelength fluctuations of the nematic director \mathbf{n} give rise to two overdamped, low-frequency, periodic distortion modes, associated with splay-bend and twist-bend elastic distortions of the nematic liquid crystal. In the limiting case of small optical-frequency dielectric anisotropy $\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$ (and therefore small optical birefringence $\Delta n = n_e - n_o$) of the uniaxial nematic, the differential light-scattering cross section per unit scattering volume per unit solid angle due to these two modes is given, in the

absence of external fields, by the relationship¹³

$$\sigma = \Delta\epsilon^2 (\pi\lambda^{-2})^2 \sum_{\alpha=1,2} k_B T G_{\alpha} / (K_3 q_{\parallel}^2 + K_{\alpha} q_{\perp}^2). \quad (1)$$

Here λ is a wavelength of light, $k_B T$ is the Boltzmann constant times temperature, and q_{\parallel} and q_{\perp} are components of the scattering wave vector \mathbf{q} parallel and perpendicular to the director. K_1 , K_2 , and K_3 are, respectively, splay, twist, and bend Frank elastic constants, and G_{α} is a geometrical factor involving incoming and outgoing polarizations of the light beams. The relaxation time of the fluctuations associated with the two elastic deformation modes described above is given by

$$\tau_{\alpha}(\mathbf{q}) = \eta_{\alpha}(\mathbf{q}) / (K_3 q_{\parallel}^2 + K_{\alpha} q_{\perp}^2), \quad \alpha = 1, 2, \quad (2)$$

where $\eta_{\alpha}(\mathbf{q})$ is a wave-vector-dependent effective viscosity, given by a combination of the five anisotropic Leslie viscosities, α_i .¹⁴

The problem with low-molecular-weight nematics is that the optical birefringence is large, on the order of 0.1. This condition produces strong multiple scattering and requires precise measurements of the ordinary and extraordinary indices of refraction of the scattering medium to identify the scattering geometry uniquely.¹² In our samples, on the other hand, because of the low birefringence of about 0.001, multiple-scattering effects are negligible, yet the intensity of the scattered light is strong enough to allow the use of an argon laser in this experiment, as seen from the power requirements below. Furthermore, the scattering medium can be treated as optically isotropic for the propagation of light. Corrections to the scattering wave vector due to finite optical birefringence remain less than 2% for total scattering angles of greater than 2°.

The particular liquid crystalline preparation studied is a racemic mixture of poly- γ -benzyl-glutamate (PBG, from Sigma Chemical Co.) in a mixture of methylene chloride and dioxane as solvents (to suppress any residual cholesteric torsion¹⁵), at a concentration just above a two-phase region, about 13% by volume. For the degree of polymerization of 700 for

this material the molecular length-to-diameter ratio is equal to 70. The sample is a 40- μm -thick nematic single crystal in a planar cell with parallel boundary conditions. To achieve a parallel alignment of PBG at sample surfaces the glass substrates were coated with a layer of obliquely evaporated silicon monoxide. A thin film of plasma-polymerized ethylene gas was then deposited on top of the silicon monoxide layer. The sample was aligned in a magnetic field immediately upon filling with liquid crystal. The procedure is described in detail elsewhere.¹⁶

The light source used is the 5145- \AA line of an argon laser at a power of about 100 mW. No evidence of sample heating was present during the experiment. The signal is detected with a photomultiplier; the photoelectron pulses are standardized and sent to a digital correlator which computes the temporal autocorrelation function of the intensity fluctuations of the scattered light in real time. We consider two basic geometries:

(1) The director is normal to the scattering plane with the cell normal bisecting the angle defined by the incident and scattered wave vectors, with \mathbf{q} lying in the plane of the sample. Incident polarization is parallel to the director and scattered polarization is normal to it in the scattering plane. In this situation we observe a superposition of splay and twist elastic distortion modes with the amplitudes proportional respectively to $\cos^2(\theta/2)/(K_1q^2)$ and $\sin^2(\theta/2)/(K_2q^2)$, where θ is the total scattering angle. The splay signal dominates at small scattering angles and for $2.5^\circ < \theta < 12^\circ$ the spectra were fitted to a single exponential. At $\theta > 25^\circ$ the superposition of splay and twist signals gives rise to

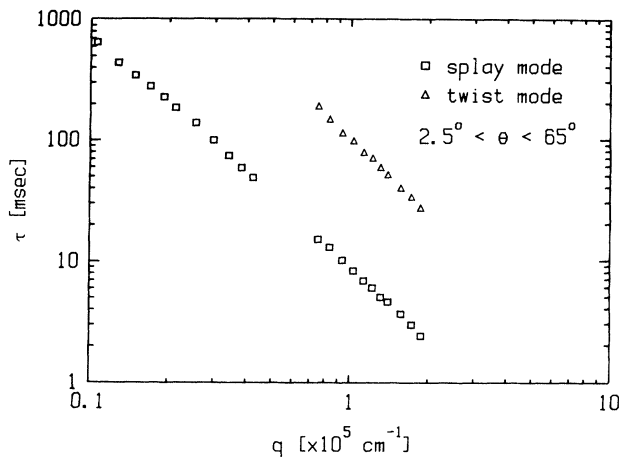


FIG. 1. Double logarithmic plot of the scattering-wave-vector dependence of relaxation times of splay and twist elastic deformation modes in configuration (1). Both modes display diffusive ($1/q^2$) behavior. For a given q there is a clear separation in relaxation times, the splay mode being an order of magnitude faster than the twist.

a homodyne correlation function consisting of a linear combination of three exponentials. A nonlinear least-squares fitting procedure was used to determine the relaxation times and the relative amplitudes of the two signals, which is relatively easy since the relaxation times are well separated. The \mathbf{q} dependence of the relaxation times for splay and twist modes is given in Fig. 1. The agreement between small and large scattering-angle results is good. With the angular factors taken into account K_1/K_2 was measured from the relative amplitudes consistently over the entire range of scattering angles.

(2) The sample then, for each θ , is rotated 90° around the axis normal to the plane of the cell such that \mathbf{n} is now in the scattering plane with $\mathbf{q} \parallel \mathbf{n}$. This is a pure bend mode with its amplitude proportional to $\cos^2(\theta/2)/(K_3q^2)$. Figure 2 shows the angular dependence of the relaxation time for the bend mode, obtained with a single-exponential fit to experimental data. For $\theta > 65^\circ$ the bend relaxation time becomes prohibitively small for photon-correlation spectroscopy, whereas the splay and the twist modes remain a few orders of magnitude slower, because of a large anisotropy of their respective viscosities as will be discussed below.

Note that in both configurations depolarized light scattering was used and background light was negligible. All spectra were fitted by homodyne correlation functions in the range of scattering angles studied and no evidence of heterodyne scattering was seen. In addition, a signal due to a concentration-fluctuation mode was observed independently in polarized scattering and with different geometrical conditions. Since the relaxation time constant associated with the concentration fluctuations was found to be very different

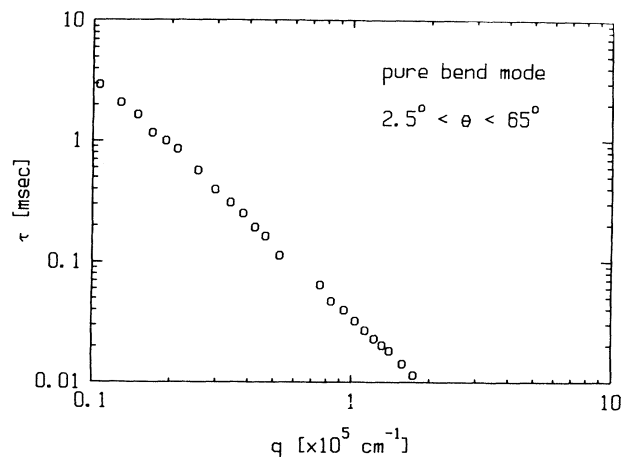


FIG. 2. Double logarithmic plot of the scattering-wave-vector dependence of relaxation time of bend elastic deformation mode in configuration (2). Diffusive ($1/q^2$) behavior is well established.

from both splay-twist and bend modes (it was faster than splay and slower than bend), one can conclude that the two elastic distortion modes described above are correctly identified.

We observe that in going from configuration (1) to configuration (2) none of the geometrical factors is changed. The focusing of the laser beam, the length of the scattering column subtended by the detector pinhole, the angles of incidence and refraction of the incoming and outgoing light beams, and their respective polarizations stay constant. While the correct analysis of absolute photometric intensities is difficult because of the variations in the factors described above with the beam orientation, the relative intensity of these two signals is well defined. Given that the intensity of the incident laser beam remains the same, the ratio of the total amplitudes of the spectra in configurations (1) and (2) is given by the relationship

$$\frac{a_1 + a_2}{a_3} = \frac{K_3}{K_2} \tan^2 \frac{\theta}{2} + \frac{K_3}{K_1}, \quad (3)$$

where a_1 , a_2 , a_3 are the amplitudes of splay, twist, and bend signals, respectively. A functional dependence of the relationship (3) is illustrated in Fig. 3. At small scattering angles the first term in Eq. (3) is suppressed by the angular factor and K_3/K_1 is measured directly. At larger θ the twist mode begins mixing in and the curvature in Eq. (3), as shown in Fig. 3, determines K_3/K_2 . In addition K_1/K_2 is determined from the spectra in configuration (1). All three measurements are in good agreement with each other.

Our main results are summarized in Table I. Note that the measured K_1 and K_3 are nearly equal to one another, and that K_1 and K_2 differ by a factor of 11.4.

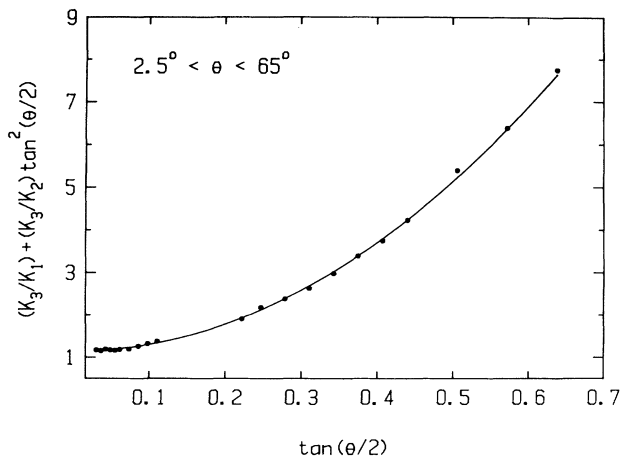


FIG. 3. Ratio of total scattering amplitudes of the elastic deformation modes in configurations (1) and (2). A solid line results from a fit by the theoretical relationship [Eq. (3)].

Existing calculations, based on a hard-rod model, while qualitatively in agreement with the present experiment, predict somewhat different ratios of elastic constants^{5,6}: $K_1/K_2=3$ and $5 \leq K_3/K_1 \leq 10$. An argument that offers a possible explanation for this discrepancy has been proposed in Ref. 4: Splay distortion at constant density lowers the entropy of the system and thus increases the free energy, which effectively increases the spaly elastic constant. Also, for molecules that are somewhat flexible, rather than rigid, K_3 should be reduced from the hard-rod limit. To test this idea, more data will be needed.

The viscosity associated with splay is $\eta_{\text{splay}} = \gamma_1 - \alpha_3^2/\eta_b$ and that for twist is $\eta_{\text{twist}} = \gamma_1$.¹⁴ We find that these are equal to each other within the accuracy of the fit. The splay distortion involves director rotations coupled to sliding of the molecules parallel to one another, the two processes facilitating each other. In the infinite-chain limit the viscosity for rotation of the director, γ_1 , becomes infinitely large compared to the viscosity for sliding of the molecules along one another, since director rotations become strongly coupled to macroscopic shear flow. In that limit η_{splay} is precisely equal to γ_1 . The measured equality of η_{splay} and η_{twist} indicates that at the length-to-diameter ratio of 70 PBG already approaches a behavior characteristic of the infinite chain limit.

Also in this limit, the bend mode has a characteristic viscosity of η_b , the Miesowicz viscosity of sliding of the chains parallel to one another.⁴ It is possible, therefore, to compare γ_1 and η_b directly. In a real system, composed of long but finite particles, the ratio of γ_1 to η_b is large but not infinite; for this sample, it is equal to 220, not in disagreement with the existing

TABLE I. Measured ratios of elastic constants and viscosities in PBG from light-scattering data.

$\frac{K_1}{K_2}$	11.4 ± 0.3
$\frac{K_3}{K_1}$	1.17 ± 0.03
$\frac{K_3}{K_2}$	13.0 ± 0.4
$\frac{\gamma_1}{\eta_b}$	220 ± 12
$\frac{\gamma_1}{\eta_{\text{splay}}}$	1 ± 0.02
$\frac{\alpha_3^2/\eta_c}{\gamma_1}$	1
$\frac{\alpha_3^2/\eta_b}{\gamma_1}$	≤ 0.02

TABLE II. Estimated values for elastic constants (in 10^{-7} dynes) and viscosities (in poises) in PBG obtained using the light-scattering results and the measurements of critical magnetic field in the bend Fréedericksz transition.

K_1	4.1 ± 0.2
K_2	0.36 ± 0.02
K_3	4.7 ± 0.3
γ_1	34.7 ± 2.1
η_b	0.16 ± 0.01
η_c	35.0 ± 2.1
$ \alpha_3 $	0.14 ± 0.01
$ \alpha_2 $	34.8 ± 2.1

theories for anisotropic viscosities.⁷

On the basis of these results one can speculate that α_2 and η_c are both large, on the order of γ_1 , while α_3 and η_b are small and of the same order of magnitude. Thus, our experiments indicate that the anisotropic viscosities can be classified into two distinct groups, with their magnitudes being very similar within each. In our sample the “small” viscosities are roughly comparable to those in low-molecular-weight nematics, while the “large” ones are larger by a factor of several hundred. This observation supports the theoretical prediction of Ref. 4 for limiting viscous properties of long-molecular-chain nematic liquid crystals.

To obtain the absolute values one needs an independent measurement of one of the material parameters, such as K_3 with a Fréedericksz transition. The critical field for the bend distortion mode was measured to be 6.5 kG in the same sample as in the present experiment.¹⁷ This result, in combination with a published value for a diamagnetic anisotropy of PBG,¹⁸ leads to a direct determination of the three K_i 's as well as of γ_1 and η_b ; the bounds for another three viscosities can be calculated from the ratios in Table I. These results are given in Table II. Other light-scattering measurements are being performed to determine η_a and α_1 , the remaining independent viscosities. In addition, the Fréedericksz transition measurements were used to obtain K_3/K_1 . Preliminary results indicate a reasonably good agreement with the light-scattering experiment.

A study of the molecular-length and concentration dependence of the material parameters in a polymer nematic liquid crystals remains to be done. Such a study will provide a better understanding of the funda-

mental viscous and elastic properties of these systems and help improve existing theoretical models.

To conclude, we obtained ratios of Frank elastic constants and certain anisotropic viscosities in a polymer nematic liquid crystal (PBG). The viscosities approach the behavior predicted for a system composed of infinitely long molecular chains, and the elastic constants are compatible with models for rigid or semirigid molecules.

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