Rheological, Rheo-Optical and Light Scattering Studies on Nematic Solutions of Poly(1,4-Phenylene-2,6-Benzobisthiazole)

Rheological and rheo-optical properties of mesogenic solutions of rodlike polymers are discussed. Some of the salient features of the observed behavior with isotropic solutions described, including a single-integral constitutive equation that is found to be useful, and a review of certain aspects of theoretical treatments of the viscosity of nematic fluids. The light scattering experiments are discussed, including studies on a monodomain formed with a PBT solution. Aspects of the rheological behavior of nematic solutions of PBT are considered, first for recently small strain and then for deformation with large strain rates.
INTRODUCTION

Rheological and rheo-optical properties of mesogenic solutions of rodlike polymers are discussed in the following. In the remainder of this section, some of the salient features of the observed behavior with isotropic solutions will be described, including a single-integral constitutive equation that is found to be useful, and a review of certain aspects of theoretical treatments of the viscosity of nematic fluids. The light scattering experiments are discussed in the next section, including studies on a monodomain formed with a PBT solution. In the final two sections, aspects of the rheological behavior of nematic solutions of PBT are considered, first for recently small strain and then for deformation with large strain rates.
Isotropic Solutions

Important rheological properties of isotropic solutions of the rodlike polymers poly(1,4-phenylene-2,6-benzobisthiazole), PBT, and poly(1,4-phenylene terephthalamide), PPTA, can be represented by a single-integral constitutive equation of the BONZ type [1-5]. With this relation, the components \( \sigma_{\alpha\beta}(t) \) of the stress tensor are given by

\[
\sigma_{\alpha\beta}(t) = -\int_0^\infty ds \frac{\partial G_0(s)}{\partial s} Q_{\alpha\beta}(t, t-s). \tag{1}
\]

Here \( G_0(t) \) is the shear relaxation modulus determined in a linear viscoelastic response [6] and \( Q_{\alpha\beta} \) depends only on the strain-history. Expressions of \( Q_{\alpha\beta} \) for shear deformation and uniaxial elongation are available [5]. For recently small deformations, \( Q_{\alpha\beta} \) reduces to \( Q^0_{\alpha\beta} \) of linear viscoelasticity. For example, for a shear deformation, \( Q^0_{12}(t_1, t_2) = \gamma(t_1, t_2) = \gamma(t_1) - \gamma(t_2) \), where \( \gamma(t) \) is the shear strain at time \( t \) [6]. With this deformation, nonlinear effects can be represented by [2,4,6,7]

\[
Q_{12}(t_1, t_2) = \gamma(t_1, t_2) T_3[\gamma(t_1, t_2)]. \tag{2}
\]

The nonlinear strain-measure is approximately given by [2,7]

\[
T_3(\gamma) \approx \exp\left(-m(\gamma - \gamma')/\gamma^*\right) \tag{3}
\]

where \( m \) is zero for \( |\gamma| < \gamma' \) and unity otherwise. Application of these relations to give the dependence on shear rate \( \kappa \) of the steady-state viscosity \( \eta_k \), the recoverable compliance \( R_k \) obtained after steady flow, and the first-normal stress function \( N_x(1) \) are discussed elsewhere [2,7]. (Here \( R_k = \gamma_R/\eta_k \gamma_k \), with \( \gamma_R \) the recoverable strain, and \( N_x(1) = \nu^{(1)}/2(\kappa\eta_k) \) with \( \nu^{(1)} \) the first-normal stress difference). In particular, with \( G_0(t) \) in the form

\[
G_0(t) = \eta_k \tau_i^{-1} \exp(-t/\tau_i) \tag{4}
\]

these relations may be integrated to give \( \eta_k \), \( R_k \) and \( N_x(1) \) in the forms [7]

\[
\eta_k = \Sigma \eta_j[1 - q(\beta\gamma^{*1}\kappa/\tau_i)] \tag{5}
\]

\[
\eta_0 R_k = \Sigma \eta_j[1 - q(\beta\gamma^{*1}\kappa/\tau_i) \exp(-\eta_0 R_k/\tau_i)] \tag{6}
\]

\[
\eta_k^2 N_x(1) = \Sigma \eta_j[1 - p(\beta\gamma^{*1}\kappa/\tau_i)] \tag{7}
\]

The functions \( q, p \) and \( \beta \) are determined elsewhere [2]; \( \beta \approx 1 \) is a weak function of \( \gamma'\gamma^* \). Study of the linear viscoelastic behavior can give the \( \eta_k \), \( \tau_i \) parameters [6]. The flow birefringence \( \Delta n(13) \) in the [1-3] flow plane (i.e., shear gradient in direction-2 with flow in direction-1) has been represented in terms of the preceding by use of the stress-optic law [1]:

\[
M_x = \Delta n(13)/(\kappa \eta_k) = 2C'N_x(1) \tag{8}
\]

with \( C' \) a constant equal to the limiting value of \( M_x/2R_k \) for small \( \kappa \).

The same constitutive equation may be used to determine the stress relaxation function \( \eta_x(\tau) \) and the flow birefringence relaxation \( \hat{M}_x(\tau) \), each determined following cessation of steady flow at shear rate \( \kappa \) (\( \eta_x(\tau) = \sigma(\tau)/\kappa \) and \( \hat{M}_x(\tau) = \Delta n(13)(\tau)/(\kappa \eta_k)^2 \) where \( \sigma(\tau) \) and \( \Delta n(13)(\tau) \) are, respectively, the stress and birefringence at time \( \tau \) after cessation of flow). Thus,

\[
\hat{\eta}_x(\tau) = \Sigma \eta_j[1 - q(\beta\gamma^{*1}\kappa/\tau_i) \exp(-\tau/\tau_i)] \tag{9}
\]

and

\[
\hat{M}_x(\tau) = 2C'N_x(1)(\tau), \quad \text{with}
\]

\[
\eta_k^2 N_x(1)(\tau) = \Sigma \eta_j[1 - p(\beta\gamma^{*1}\kappa/\tau_i)] \exp(-\tau/\tau_i). \tag{10}
\]

A theoretical estimate [8] of \( \eta_0 \) for isotropic solutions of rodlike chains given by the relation
$$\eta_0 = (1 - B c \text{cL.} / a M_1)^{-2}$$  \hspace{1cm} (11a)$$

$$\eta_{\text{ISO}} = KN^2 M[\eta]_0 [c \text{cL.} / M_1]^{-3}$$  \hspace{1cm} (11b)$$

provides a satisfactory representation of experimental data [1,2]. Here, $M_1$, $[\eta]$ and 1.c are the molecular weight, intrinsic viscosity and length, respectively, of the chain, $M_1 = M / 1$, $c$ is the concentration (wt/vol), $\eta_0$ is the solvent viscosity, $a$ is the value of $c \text{cL.} / M_1$ for onset of the nematic state, $B$ is a constant near unity, and $K$ is a constant (ca. $1.5 \times 10^{-4}$ in cgs units) [2].

In many cases, the parameter

$$\tau_c = \eta_0 R_0 = \lim_{\xi \to 0} \eta_0 R_0$$  \hspace{1cm} (12)$$
is useful in reducing data over a range of temperature or concentration [1,2,7]. Typical data on $\eta_0 / \eta_0$, $R_0 / R_0$ and $M_1 / M_0$ versus $\tau$, for an isotropic solution of PBT [2] are shown in Figs. 1 and 2. The representation of the experimental curves by Eqs. (5-8) is satisfactory, provided the experimental $G_0(t)$ is used. The latter decays more slowly than a theoretical estimate according to Doi and Edwards [5]. Typical data on $\eta_0(t) / \eta_0$ and $\eta_0(t) / \eta_0$ versus $t / \beta_0$ for isotropic solutions of PBT [2] are shown in Fig. 3. Here, $\beta_0$ is an empirical parameter, about equal to $\eta_0 R_0$. 

Figure 2. The steady-state flow birefringence versus the reduced shear rate $\eta_0 R_0$ for an isotropic solution of PBT (0.0255 weight fraction) at several temperatures. The curve is calculated with Eq. (7) and (8) using experimentally determined values of $\tau_1$ and $\eta_1$ (from reference 2).
for recently small deformations with \( n \) fixed by an external field (e.g., a magnetic field) with, respectively, \( \eta \) parallel to the velocity gradient, \( n \) parallel to the flow direction, and \( n \) perpendicular to both the flow and the velocity gradient (i.e., the Miesowicz viscosities) [10]. According to the Leslie-Ericksen constitutive equation [9], these viscosities are given by

\[
\eta_a = -\frac{1}{2} a_2 + a_4 + a_5 - \frac{1}{2} \eta_c + \frac{1}{2} (a_5 - a_2) \tag{13}
\]

\[
\eta_b = -\frac{1}{2} a_3 + a_4 + a_6 - \frac{1}{2} \eta_a + \frac{1}{2} a_3 + a_2 \tag{14}
\]

\[
\eta_c = a_4 / 2 \tag{15}
\]

Here, use is made of Parodi's relation: \( a_6 = a_2 + a_3 + a_5 \) [11]. The \( a_i \) coefficients also appear in the viscosity parameters occurring in the analysis of light scattering data discussed below. For example, a viscosity \( \eta_T \) associated with twist of the director field (without deformation of the sample) is given by [12-14]

\[
\eta_T = \eta_3 - a_2 \tag{16}
\]

Frequently, \( -a_2 > |a_3| \) [13], in which case \( \eta_T \) is close to the quantity

\[
\eta_{ab} = \eta_a - \eta_b = - (a_2 + a_3) \tag{17}
\]

Additional viscosities \( \eta_B \) and \( \eta_s \) associated, respectively, with bend and splay of the director field are given by [12-14]

\[
\eta_B = \eta_T - \frac{(\eta_T + \eta_{ab})^2}{4 \eta_a} \tag{18}
\]

\[
\eta_s = \eta_T - \frac{(\eta_T - \eta_{ab})^2}{4 \eta_b} \tag{19}
\]

If \( \eta_T \approx \eta_{ab} \), then \( \eta_s \approx \eta_T \) and \( \eta_B < \eta_T \), as has been observed for low molecular weight nematic fluids [12].

**Nematic Solutions**

With nematic solutions of rodlike polymers, it can be anticipated that much of the preceding will not be valid owing to the long orientational coherence lengths of the nematic state. For example, since an isotropic fluid has no inherently preferred direction, the properties described by Eq. (1) do not depend on the flow direction. By contrast, under certain circumstances the rheological properties of a nematic fluid may depend markedly on the orientation of the director \( n \); for the solutions of interest here, this may be assumed to be coincidental with the orientation of the rodlike chains. According to the Leslie-Ericksen constitutive equation [9], the viscometric properties of such a fluid may be represented in terms of six viscosity coefficients \( a_i \) (i = 1-6). A well-known example of this behavior is demonstrated by the viscosities \( \eta_a, \eta_b, \) and \( \eta_s \) calculated as \( a_{12}/\pi \).

**Figure 3.** The reduced flow birefringence relaxation function \( M_a(t)/M_a \) (open circles) and stress relaxation function \( \dot{\gamma}_a(t)/\gamma_a \) (filled circles) for an isotropic solution of PBT (0.0294 weight fraction) for several shear rates. With \( \beta_a = \tau_a R_a \) (From reference 7).
If there are no constraints to maintain a preferred orientation of \( n \), then the steady-state shear viscosity \( \eta_0 \) for recently small deformation is given by [9]

\[
\eta_0 = \eta_b + \frac{1}{2} (\eta_{ab} - \eta_1) \left\{ 1 + \frac{\alpha_1 (\eta_{ab} + \eta_1)}{4 \eta_{ab}} \right\}.
\] (20)

In this flow, the director orients at an angle \( \theta_0 \) to the flow direction (in the shear plane), with

\[
2\theta_0 = \arccos (\eta_1 / \eta_{ab}).
\] (21)

Stable shearing flow requires \( \eta_1 < \eta_{ab} \); if \( \eta_{ab} \approx \eta_1 \), then \( \eta_0 \approx \eta_b \). Finally, in elongational flow (with no constraints on the director), the elongational viscosity \( \eta_0 \) is given by [15]

\[
\eta_0 = 3 \eta_b + (\eta_{ab} - \eta_1) + \eta_d
\] (22)

where \( 2 \eta_d = \alpha_3 - \alpha_2 + 2 \alpha_1 \). If \( \eta_d \) and \( \eta_{ab} - \eta_1 \) are much less than \( 3 \eta_b \), then \( \eta_0 \approx 3 \eta_b \).

With many nematic fluids, it is possible to create a preferred direction in a sample confined between two surfaces by adsorption on the surfaces in a preferred direction [13]. The long orientational coherence of the nematic then provides the globally preferred direction. In this situation, if one plate is moved parallel to the other with velocity \( V \), the deformation is expected to result in orientation at the angle \( \theta_0 \) at distances far from the surface, but near the surfaces the orientation remains that of the adsorbed layer [9,16]. Currie and coworkers [16] have used the Leslie-Ericksen constitutive equation to compute the viscosity as a function of \( \kappa = V / h \) for a number of geometries in terms of the Ericksen number \( E_3 \) defined as

\[
E_3 = a(V/\kappa)^2 / K_4
\] (23)

where \( a \) and \( \kappa \) are the shear stress and shear rate, respectively, at a position with deformation at velocity \( V \), and \( K_4 \) is the bend free energy coefficient. For simple shear flow, \( V / \kappa \) is equal to the separation \( h \) of the two parallel surfaces. With this treatment, the boundary layer with thickness \( \delta \) and the orientation of the adsorbed layer decreases with increasing \( \kappa = V / h \), and the apparent viscosity \( \eta_\delta = \sigma h / V \) is given by [16]

\[
\eta_\delta = \eta_0 \left[ 1 + \frac{1}{2} \left( \frac{\partial}{\partial \delta \phi} \right)^2 \right]^{-1/2}
\] (24)

where \( \eta_0 \) is given by Eq. (20), with \( \theta_1 \) and \( \theta_2 \) the orientation angles (in the plane of shear) between the flow direction and the direction of \( \eta \) for the adsorbed layers at the two surfaces, and \( \partial_\delta \phi \) depends on the viscosity coefficients \( \alpha_i \). Questions of flow stability have been explored within the frame of this model [9,16]. With Eq. (24), \( \eta_\delta \) decreases toward \( \eta_0 \) with decreasing \( \kappa \), until the boundary layer is negligibly thin. For small \( \kappa \), \( \eta_\delta \) increases toward a limiting value specified by \( \theta_1 \) and \( \theta_2 \) and the viscosity coefficients.

Theoretical treatments for nematic fluids comprising long rodlike macromolecules have given estimates for the viscosity coefficients \( \alpha_i \) in terms of the order parameter \( S \) characterizing the nematic fluid [15,17,18]. \( S \) is expected to increase with increasing \( \kappa \). Values of \( \alpha_i / \eta_0 \) for two such treatments [17-18] are given in Table 1. (For these treatments \( \alpha_6 = \alpha_5 + \alpha_2 + \alpha_3 \) so that only five of the six coefficients are independent.) The principal difference between the two

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Reference 18</th>
<th>Reference 17(b)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( a_1/\kappa )</td>
<td>(-S^2 )</td>
<td>(-S^2 )</td>
</tr>
<tr>
<td>( a_2/\kappa )</td>
<td>(-S(1+2S)/(2+S) )</td>
<td>(-S(2)(r -1) + 2(1+2S)/(3(r -1) + 2+S) = -S(4S -1)/(5S - 2) )</td>
</tr>
<tr>
<td>( a_3/\kappa )</td>
<td>(-S(1+S)/(2+S) )</td>
<td>(-S(2)(r -1) + 2(1-S)/(3(r -1) + 2+S) = -S(1+S)/(5S - 2) )</td>
</tr>
<tr>
<td>( a_4/\kappa )</td>
<td>( (1/3) )</td>
<td>( (7.5S -2S^2)/35 -(-1+S)(1/2)S/(7+4S) )</td>
</tr>
<tr>
<td>( a_5/\kappa )</td>
<td>( S )</td>
<td>( S(5+2S)/7 -S[S(1+S)/(2+S)] = S(3-4S) )</td>
</tr>
<tr>
<td>( a_6/\kappa )</td>
<td>( 0 )</td>
<td>(-2S(1+S)/(7-S[S(1+S)/(2+S)] )</td>
</tr>
<tr>
<td>( a_7 )</td>
<td>( 1/(1+S) )</td>
<td>( r(S)(1+S)/(3+S) = r(1+S)/(3+S) )</td>
</tr>
<tr>
<td>( a_8 )</td>
<td>( 1 -1/(1+S) )</td>
<td>( 1/(1+S) )</td>
</tr>
</tbody>
</table>
treatments is in the estimate for \( \alpha_3 \), which is different in sign for the two treatments. This difference is critical as it affects the sign of \( \eta_{ab} - \eta_1 \), which must be positive for stable flow. Thus, for the treatment in reference 18, \( \eta_1 < \eta_{ab} \) and shear flow is predicted to be stable, with

\[
\eta_0 = \frac{\eta_b (1 + 2S)(2 + 3S)}{2(1 + S)} \quad (25)
\]

\[
\eta_b = \frac{\eta_0}{(1 + S)^{4/(1 + S/2)}} \quad (26)
\]

where \( \eta_0^{SO} \) is given by Eq. (11b). For the treatment in reference 15, \( \eta_1 > \eta_{ab} \), and shear flow is predicted to be unstable. For the latter treatment,

\[
\eta_b = \eta_0 \frac{2(1 - S)^4}{2l} \left[ (4S + 7) + 35(5S - 2) \right]^{-1} \quad (27)
\]

which is larger than \( \eta_b \) given by Eq. (26) for the same \( S \). According to Eqs. (25-26), \( \eta_0 \) is expected to decrease as \( c_l/M_1 \), exceeds \( \alpha \), through both of the factors \( (1-S)^4 \) and \( (1-B)^2 \):

\[
\left( \frac{\eta_0}{\eta_0^{max}} \right) = \left( c_l / M_1 a \right)^3 (1-S)^4 (1-B)^2 f(S) \quad (28)
\]

where \( f(S) \approx 10/(1 + 2S) \) and \( (\eta_0)^{max} \) is the value of \( \eta_0 \) given by Eq. (11a) with \( c_l / M_1 a = 1 \). Behavior similar to this has been reported [3], provided viscometric data are interpreted in a particular way (see below).

a) \( k = k_0 (1 - S)^2 \); \( \eta_0^{SO} \) given by Eq. (11b) and \( k' = 10 \) in reference 17 or 6 in reference 18 (The factor \( k' \) was omitted in reference 24). Since \( \alpha_2 + \alpha_3 = \alpha_6 - \alpha_5 \), only five of the \( \alpha_i \) are independent.

b) Based on asymptotic behavior for \( \alpha_i \), given in reference 17 and approximate relations for \( \lambda \) and \( r \) [24].

c) \( \lambda = \eta_{ab}/\eta_1 \), see Eqs (16) and (17).

CHAPTER 7

LIGHT SCATTERING STUDIES OF LIQUID CRYSTALLINE PBT SOLUTIONS

Solutions of PBT (or PPTA) of a suitable concentration undergo a phase transformation from an isotropic to a nematic solution with decreasing temperature, passing through a biphasic region for a narrow temperature range [1-3]. Data on the Rayleigh ratios \( R_{IV}(\theta) \) and \( R_{IVV}(\theta) \) determined through such a transformation are shown in Fig. 4 for scattering with \( \theta = 20^\circ \). Here the symbols \( IV \) and \( VV \) denote the horizontally and vertically polarized components of the scattering with vertically polarized light, respectively. Details of this experiment will be published elsewhere [20]. A solution of PBT \( (M_w = 3.4 \times 10^4) \) in methanol-sulfuric acid (weight fraction \( w \) of the polymer equal to 0.041) was placed between parallel glass plates. The assembly was sealed to prevent contamination by atmospheric moisture. As shown in Fig. 4, both \( R_{IV}(20) \) and \( R_{IVV}(20) \) increase with decreasing \( T \) as the sample is cooled \( (dT/dt \approx -0.003K/s) \), with the ratio \( R_{IV}(20) / R_{IVV}(20) \) increasing from about 0.02 at 110°C to 0.9 for \( T<70^\circ C \).

Immediately after being cooled to 25°C, the sample exhibited a mottled texture with transmission, \( T \), and \( T_1 \) between either crossed or parallel polarizers, respectively, being low (<4%). Upon annealing at 25°C, both \( R_{IVV}(20) \) and \( R_{IV}(20) \) decreased, with the ratio \( R_{IV}(20) / R_{IVV}(20) \) remaining nearly unchanged. The scattered intensity decreased exponentially on annealing, with a time constant of about 100 hrs. After annealing, the sample exhibited a smooth texture when viewed between parallel or crossed polarizers, with the exception of a few large, looped disclinations, see Fig. 5. When viewed between crossed polarizers, the sample exhibited a blotchy pattern of extinction that varied as the sample was rotated between the crossed polarizers; in some areas extinction never obtained. This appearance is attributed to smooth variations of the director orientation throughout the fluid; the rodlike chains tend to be parallel, with a preferred orientation, but that orientation varies smoothly throughout the sample. Adsorption of the polymer on the glass surfaces could serve to stabilize such a texture.
Figure 4. The Rayleigh scattering ratio (20 deg scattering angle) determined as a function of temperature for a nematic solution of PHT (0.041 weight fraction). The thermal history is indicated by the arrowheads; the temperature was changed continuously over the range 20 to 110 to 20°C over 16 hr. The symbols H_v and V_v designate, respectively, the horizontally and vertically polarized components of the scattering with vertically polarized incident light.

Figure 5. Photomicrograph of a nematic solution viewed between crossed polars. Except for a few disclinations, the texture is smooth, but not uniformly oriented. The disclinations are found only near the bounding surfaces, e.g., the disclinations near the upper surface are in sharp focus and those at the opposite surface appear diffuse. The larger grid has a 220 µm spacing.

As shown in Fig. 4, both R_VV(20) and R_HV(20) passed through a maximum with increasing temperatures when the annealed specimen was reheated (dT/dq ≈ 0.003K/s), with the maximum scattering occurring near the temperature (92°C) for the onset of a biphasic state visible by polarized microscopy. As the temperature exceeded 60°C, the smooth texture was replaced by an increasingly complex texture and increased scattering.

Photon correlation data were obtained for the sample with smooth texture with both the VV and HV scattering, giving G(VV)(τ) and G(HV)(τ) intensity correlation functions, respectively. In both cases the correlation function, decayed over a wide range of time, e.g., with the representation
\[ \frac{G^{(2)}(\tau)}{G^{(2)}(\infty)} = 1 - f(\Lambda) \sum r_i \exp(-\gamma_i \tau) \]  

(29)

the distribution of the coherence times \( \gamma_i \) spanned from 0.1 to 10^3 ms. (Here, \( f(\Lambda) \) is an instrumental coherence factor equal to \( [G^{(2)}(0) - G^{(2)}(\infty)]/G^{(2)}(\infty) \), and \( \sum r_i = 1 \).

A monodomain sample better suited for light scattering studies was prepared by slow extrusion of the sample into a rectangular channel (cell dimensions: 0.03 cm thick, 1 cm wide and 1.5 cm along the flow direction). It was reasoned that this procedure would cause a preferential orientation (along the flow direction) of the polymer adsorbed on the glass surfaces, resulting in a globally preferred orientation throughout the solution at equilibrium. Shortly after cessation of flow, the sample exhibited strong birefringence, with a preferred orientation in the flow direction, and scattered light very strongly. In addition, the sample exhibited several nonbirefringent narrow bands precisely perpendicular to the flow direction. As the sample aged, these bands were converted to large loop disclinations going completely around the sample in a plane normal to the former flow direction. These features may be related to flow instabilities related to complete rotation of the director in the shear plane, so that the orientation is nearly homeotropic in the center of the narrow, nonbirefringent bands (see below). Several hours subsequent to cessation of flow, the fluid developed strong birefringence, which extinguished between crossed polars for cell orientation with the cell axis (the flow direction during the extrusion) parallel to the axis of either the polarizer or the analyzer. At this stage, a dense field of disclinations obtained near either surface, but the interior was free of such defects. After several days, almost all of the disclinations disappeared, leaving a few loop disclinations at the surfaces, with a sharpened extinction between crossed polars, see Fig. 6. The solution was also dichroic, with preferred directions parallel and perpendicular to the cell axis (maximum extinction for light polarized along the cell axis). For wavelengths near the absorption maximum (440 nm) the extraordinary ray is completely extinguished, and the sample performed as a polarizer. Viewed in natural light, the solution appeared transparent (yellow in color), being nearly featureless.

Figure 6. Photomicrograph of an oriented nematic solution of PBT obtained between cross polars. The sample orientation of the nematic being parallel to the polarizer. The loop disclination shown in the micrograph gradually shrank, and disappeared after several weeks. The larger grid has an 80 \( \mu \)m spacing.

For a liquid crystal monodomain, the Rayleigh ratio depends on the orientation of the director relative to the plane containing the incident and scattered rays, the polarization of these, and the scattering angle \( \theta \). Thus, the Rayleigh ratio may be expressed in the form \( 12-14 \).

\[ R_\Lambda, p, n(q_1, q_2) \propto (n_e - n_0)^2 \sum_{\alpha = 1, 2} \Gamma_\alpha \]  

(30a)

\[ \Gamma_\alpha = F_\alpha (P, \Lambda, n)/\tilde{K}_\alpha (q_1, q_2) \]  

(30b)

where \( P, \Lambda \) and \( n \) designate the unit vectors defining the orientation of the polarizer, analyzer and director, respectively, with respect to the scattering plane containing the incident ray,
the scattered ray and the scattering vector $q$. In Eq. (30), $F_0(P', \Lambda, n)$ depends only on the geometrical arrangement used in the scattering experiment, and $\hat{K}_a$ depends on the Frank free energy coefficients $K_1 = K_s$, $K_2 = K_T$ and $K_3 = K_B$ for splay, twist and bend deformations of the director field, respectively, through the expression

$$\hat{K}_a(q_\perp, q_\parallel) = K_a q_\perp^2 + K_3 q_\parallel^2$$  \hspace{1cm} (31)

$$q_\perp = (q \cdot n)$$  \hspace{1cm} (32)

$$q_\parallel = (q^2 - q_1^2)^{1/2}.$$  \hspace{1cm} (33)

For example, for the horizontal component of the scattering obtained with vertically polarized incident light,

$$\frac{R_{HV, \perp}(q_\perp, 0)}{R_{HV, \parallel}(0, q_1)} = \frac{K_B}{K_s} + \frac{K_B}{K_T} \tan^2 \theta / 2$$  \hspace{1cm} (34)

where the subscripts $\perp$ and $\parallel$ designate the director orientation perpendicular and parallel to the scattering plane, respectively. In another arrangement with the vertical component of the scattering obtained with horizontally polarized incident light,

$$R_{VH, \parallel}(q_\perp, 0) \propto \frac{(n_c - n_0)^2}{K_T} \left( 1 + \frac{K_T}{K_s} \cot^2 \frac{\theta}{2} \right)$$  \hspace{1cm} (35)

Data, obtained according to these two cases for the PBT solution studied, are shown in Fig. 7.

The dynamic scattering depends on the elastic constants along with the viscosities for twist, bend and splay:

$$G^{(2)}_{\Lambda, P, n}(q_\perp, q_\parallel; \tau) = G^{(2)}_{\Lambda, P, n}(q_\perp, q_\parallel; 0)$$

$$+ \left| \sum_{\alpha = 1, 2} \Gamma_{\alpha} \exp[ -\tau/\tau_{\alpha}(q_\perp, q_\parallel)] \right|^2$$  \hspace{1cm} (36a)
where

\[ \tau_a(q_L, q_T) = \hat{\eta}_a(q_L, q_T)/K_a(q_L, q_T) \]  \hspace{1cm} (36b)

and \( \Gamma_a \) is given by Eq. (30b). The function \( \hat{\eta}_a(q_L, q_T) \) is complex, but simplifies for special values of \( q_L \) and \( q_T \):

\[ \hat{\eta}_1(0, q_T) = \hat{\eta}_2(0, q_T) = \eta_B \]  \hspace{1cm} (37)
\[ \hat{\eta}_1(q_L, 0) = \eta_s \]  \hspace{1cm} (38)
\[ \hat{\eta}_2(q_L, 0) = \eta_I \]  \hspace{1cm} (39)

Experimental arrangements were used to permit evaluation of \( \tau_1 \) and \( \tau_2 \) with either \( q_L \) and \( q_T \) equal to zero, with the results shown in Fig. 8 [20].

Values of the Frank free energy constants and the viscosities determined for \( \eta_I \), etc. are given in Table 2, along with similar data reported [21] for nematic solution of poly(\( \gamma \)-benzyl glutamate) PBG. In computing the free energy constants for PBT, \( n_c - n_0 \) was calculated from the relation

\[ n_c - n_0 = 1.0 \text{ (c/ml.g}^{-1}) \]  \hspace{1cm} (40)

given elsewhere [1] for a solution of PBT in methane sulfonic acid.

(a) Data for nematic solution of poly(\( \gamma \)-benzyl glutamate) in a mixed solvent (methylene chloride and dioxane) at a concentration just above the isotropic to nematic transition (\( w \approx 0.13 \)) [21].

(b) The solution of PBT in methane sulfonic acid discussed in the text.

(c) The viscosity determined from the steady stress for strain less than unity is entered, see the text.

The data in Table 2 for the PBT and PBG nematic solution are similar in that for both solutions \( K_1 \) is smaller than \( K_B \) or

![Figure 8](image-url)

Figure 8. Coherence times as a function of the modulus \( q \) of the scattering vector for several optical arrangements: \( G^{(2)}_{lL, 1}(q_L, q_T, T) \); \( 0 \); \( G^{(2)}_{hL, 2}(q_L, q_T, T) \); \( \star \); \( G^{(2)}_{hL, 1}(q_L, q_T, T) \); \( \oplus \); \( G^{(2)}_{hL, 1}(0, q_T, T, \Delta) \). The lines are drawn with slope -2, indicating the behavior for twist, splay and bend.

\[ K_s \] For the PBT solution, \( K_s \) is appreciably larger than \( K_B \). These features are in accord with some predictions based on molecular models which predict enhancement of \( K_s \) owing to chain-end concentration in splay modes [22]. The values of \( \eta_I \), etc. in Table 2 give \( \theta_0 \) equal to 22 deg and 4 deg for the PBT and PBG solutions, respectively. Use of Eq. (20) and the data on Table 2 give the estimate \( \eta_1 = -1.1 \eta_1 \) for the solution of PBT.
Table 2. Elastic and Viscosity Parameters for Nematic Solutions of Rodlike Polymers

<table>
<thead>
<tr>
<th>Mode</th>
<th>Parameter</th>
<th>PBG(a) Solution</th>
<th>PBT(b) Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Twist</td>
<td>$K_2/pN$</td>
<td>0.36</td>
<td>1.15</td>
</tr>
<tr>
<td>Splay</td>
<td>$K_1/pN$</td>
<td>4.1</td>
<td>18.2</td>
</tr>
<tr>
<td>Bend</td>
<td>$K_3/pN$</td>
<td>4.7</td>
<td>8.4</td>
</tr>
<tr>
<td>Twist</td>
<td>$\eta_1/Pa \cdot s$</td>
<td>3.47</td>
<td>220</td>
</tr>
<tr>
<td>Splay</td>
<td>$\eta_2/Pa \cdot s$</td>
<td>3.45</td>
<td>190</td>
</tr>
<tr>
<td>Bend</td>
<td>$\eta_3/Pa \cdot s$</td>
<td>0.02</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>$\eta_0/Pa \cdot s$</td>
<td>100</td>
<td></td>
</tr>
</tbody>
</table>

RHEOLOGICAL BEHAVIOR FOR RECENTLY SMALL STRAIN

As illustrated by the data in Fig. 1, frequently for nematic fluids $\eta_\kappa$ is found to increase without bound as $\kappa$ is decreased for small $\kappa$. Remarkably, in this range $R_\kappa$ is independent of $\kappa$ (i.e., $R_\kappa \approx R_0$). For $\eta_\kappa R_\kappa \approx 1$, $\eta_\kappa$ is about a constant $\eta_p$, independent of $\kappa$. For further increase in $\kappa$, both $\eta_\kappa$ and $R_\kappa$ decrease with increasing $\kappa$. These features are reproducible in that the same $\eta_\kappa$ and $R_\kappa$ are obtained with either increasing or decreasing $\kappa$.

The behavior at small $\kappa$ is similar to that described by Eq. (24) for $\eta_\kappa$ as a function of $\kappa$, suggesting a nonuniform flow pattern at low $\kappa$. The latter could result from the effects of a boundary layer created by adsorbed polymer on the rheometer plates, and the long orientational coherence lengths of the nematic fluid. The light scattering data discussed in the preceding section suggest that an adsorbed layer is important in determining the orientation of the director in the fluid at equilibrium. Although the cone-and-plate geometry has not been analyzed, results on several other geometries [16] suggest that $E_1 \approx 4\pi^2 h^2 \alpha/K_1$ for torsion between parallel plates with separation $h$ and radius $R$ ($h < < R$), and $E_1 \approx 4\pi^2 R^2 \theta^2/K_1$ for torsion between cone-and-plate with cone angle $\pi - \theta$ and radius $R$. For the data illustrated in Fig. 1, $0.1 < (\alpha/Pa) < 1$ for the range at low $\kappa$ of interest (i.e., $\eta_\kappa R_\kappa < 1$). For the rheometers used, $\theta = 0.035$ radian and $R = 2$ cm for the cone-and-plate geometry, and $h \approx 0.1$ cm and $R = 2$ cm in parallel plate geometry, so that for the relation $\alpha$ in Eq. 18, $E_1 > ca. 10^3$ in either case for the range studied with $\eta_\kappa R_\kappa > 1$. Calculations for the flow between parallel plates [16] predict that the boundary layer should be small, with minimal effect (e.g., $\eta_\kappa \approx \eta_0$) if $E_3 > ca. 10^3$, however, this depends somewhat on the orientation of the adsorbed layers relative to the flow direction. Nevertheless, it appears that the behavior for the nematic fluid exhibited in Fig. 1 for small $\kappa$ cannot be explained by application of Eq. (24).

Additional insight to the behavior at small $\kappa$ is afforded by experiments with a ramp strain (i.e., $\gamma(t) = \kappa t$). In this case one can examine the behavior at small strain for flow with small $\kappa$. The sample described in the preceding was investigated in torsional flow with a ramp strain history, i.e., the torsion angle $\phi(t) = \Omega t$. The transmission $T_+(t)$ with crossed polars was obtained as a function of $t$ for several $\Omega$ for flow between parallel discs ($h = 0.03$ cm); the polarizer was oriented at 45 deg. from the flow direction. The sample had a smooth texture at the inception of flow. The stress $\sigma(t)$ was measured for flow between cone-and-plate ($\theta = 0.035$ radians). Following onset of flow, $T_+(t)$ decreased monotonically with increasing $t$ and $\sigma(t)$ rapidly reached a constant value, see Fig. 9. For this flow, $E > 10^5$, so that at steady state the boundary layer would be expected to be very thin, and the measured viscosity may be $\eta_\kappa$ given by Eq. (20).

With Eq. (21), the data in Table 2 give an orientation angle $\theta_0 \approx 22$ deg. For the polarizer orientation specified,

$$T_+(t) = (1/2)[1 - \cos(4\beta(t))] \sin^2(\delta(t)/2)$$  \hspace{1cm} (41)

where $\beta(t)$ is the angle between the axis of the polarizer and the
unique axis \( (n_e) \) of the refractive index ellipsoid, and the retardation is given by

\[
\delta(t) = \frac{2\pi h\Delta n_{13}(t)}{\lambda}
\]

with \( \lambda \) the wavelength of the incident light in a vacuum. Thus, if the rodlike chains are oriented at angle \( \theta_0 \) to the flow direction in well-developed flow with negligible boundary layer, then instead of using \( n_e - n_0 \) given by Eq. (40) to compute \( \Delta n_{13} \), one would use \( |n_0^2 \sin^2 \theta_0 + n_e^2 \cos^2 \theta_0|^{-1/2} - n_0 \) with the result that \( \Delta n_{13} \) is reduced. This may be consistent with the decrease in \( T_+ (t) \) observed following onset of flow. However, in addition, an extinction cross should be observed. No such extinction cross was observed, indicating that the expected uniform orientation had not been achieved. (For these experiments the dichroic nature of the nematic PHT fluid is not relevant since the optical absorption is negligible for the 633 nm wavelength light used.) With isotropic solutions of PHT under similar condition [1], an extinction cross is observed along the polarizer and analyzer directions, and the retardation \( \delta \) increases monotonically with increasing \( \kappa \) until it reaches its limiting value \( 2\pi h(n_e - n_0)/\lambda \), and \( T_+ \propto \sin^2(\delta/2) \). Thus, for isotropic fluids, \( T_+ \) increases with increasing \( \kappa \) for small \( \kappa \).

As the strain \( \gamma \) exceeded about 1 to 2 in the flow with a ramp strain (independent of \( \kappa \) for small \( \kappa \)), the smooth texture was replaced by a mottled texture, resulting in substantial light scattering, and reduction of both \( T_+ \) and \( T_1 \) to very small values. In addition, the stress was observed to oscillate, finally coming to a new, higher steady-state value. Thus, if the flow for small \( \gamma \) may be interpreted to give \( \eta_0 \), then the final steady state flow gives \( \eta_e > \eta_0 \). The texture at steady-state flow under these conditions is similar to that obtained if flow is initiated with a mottled texture, such as that realized prior to annealing a newly formed nematic phase (e.g., as obtained by cooling an appropriate isotropic solution). The slow reduction in \( \eta_e \) for small \( \kappa \) shown in Fig. 1 for the nematic fluid corresponds to experiments on such a state. As \( \kappa \) is increased, \( \eta_e \) tends to reach a plateau value \( \eta_p \) for \( \kappa \approx [n_0 R_0]^{-1} \), with the texture returning to a more smooth appearance. For the solution discussed in the preceding, \( \eta_p \) approximates \( \eta_0 \) given by Eq. (25), but it is not known whether this correspondence is generally obtained. Nevertheless, according to the arguments given, it appears that \( \eta_e > \eta_0 \) for small \( \kappa \), so that it is not unreasonable for \( \eta_p \) to be near \( \eta_0 \) in general. However, the preferred orientation \( \theta_0 \) of the director with the flow direction may be closer to zero than to the orientation \( \theta_0 \) predicted by Eq. (21) for very slow flow (e.g., \( \theta_0 = 22 \) deg for the PHT solution studied). In that case, \( \eta_0 \) may be about equal to \( \eta_0 \). The observed mottled texture and consequent strong scattering may result from flow instabilities initiated by differences in the angle of adsorbed chains and those in flow as the latter tend toward a preferential orientation. Alternatively, the competition between orientation at the predicted slow flow orientation angle \( \theta_0 \) and an orientation angle closer to zero for the finite flow velocity may cause the instability.
The recoverable strain $\gamma_R(t)$ has been measured as a function of the time following cessation of steady flow in cone-and-plate rheometry [3]. As shown in Fig. 10, for shear rates such that $\eta_p R_0 \kappa \approx 1$, the data for $\gamma_R(t)/\alpha$ versus $t/\eta_p R_0$ are very similar to the corresponding curve for $R_0(t) = \gamma_R(t)/\alpha$ versus $t/\tau_c$ obtained for the linear viscoelastic behavior of isotropic solutions of PBT (e.g., a solution with slightly smaller concentration than the nematic fluid). The linear viscoelastic data can be represented in terms of a distribution of retardation times $\lambda_i$ by the expression

$$R_0 - R_0(t) = \Sigma R_i \exp(-t/\lambda_i).$$

(43)

The similarity of the reduced curves in Fig. 10 indicates that the spread of the distribution of the reduced retardation times, $\lambda_i/\tau_N$ and $\lambda_i/\tau_c$ for the nematic and isotropic fluids, respectively, are similar, where for the nematic fluid,

$$\tau_N = \eta_p R_0$$

(44)

plays the role of $\tau_c$ for the isotropic fluid.

The appearance of a recoverable strain following cessation of steady flow of a nematic fluid is not unique to solutions of PBT (or PPTA). For example, as shown in Fig. 11, such behavior is also observed with a nematic solution of poly $(\gamma$-benzyl glutamate), PGB [23,24]. In this case measurements [23] of $N^{(1)}_s$ revealed ranges of $\kappa$ for which $N^{(1)}_s < 0$; by contrast, $R_s > 0$ for all $\kappa$. The appearance of negative $N^{(1)}_s$ has been predicted for nematic fluids (flow with recently small strain), dependent on the viscosity coefficients $\alpha_i$ and the preferred orientation of an adsorbed layer [25]. For the data shown in Fig. 11, $\kappa$ is probably too large to give the true slow flow behavior, but perhaps the general feature predicted for $N^{(1)}_s$ may be valid if a preferred direction $\theta_0$ in slow flow is replaced by a preferred direction $\theta_s$, which decreases toward zero with increasing $\kappa$. In this case, the dependence of $N^{(1)}_s$ on $\kappa$ would be attributed to the coupling of $\theta_s$ with the preferred orientation at the boundary. According to

a treatment of Currie [25] based on the Leslie-Ericksen constitutive equation, for flow between parallel plates with recently small strain,

$$\nu^{(1)}_s / \alpha = \sin \theta_{AD} \cos \theta_{AD} \left( \alpha_1 + \eta_1 / \cos 2\theta_0 \right)$$

(45)

where $\theta_{AD}$ is the orientation of the adsorbed layer with respect to the flow direction. Since $\alpha_1 < 0$, this relation can give $N^{(1)}_s < 0$. If Eq. (45) is approximately valid for flow at larger $\kappa$, merely by replacement of $\theta_0$ by $\theta_s$, then it would be possible to transform from conditions with $N^{(1)}_s > 0$ to $N^{(1)}_s < 0$ as $\theta_s$ decreased toward zero with increasing $\kappa$.
RHEOLOGICAL BEHAVIOR FOR LARGER STRAIN RATES

As $\kappa$ is increased so that $\tau_N^* > 1$, the optical appearance becomes more like that of an isotropic rodlike solution in flow with $\tau_c^* > 1$. The birefringence increases, but unlike the behavior with isotropic fluids, large fluctuations of $\Delta n_{13}$ during flow restrict measurements of $T_\kappa$ see below. The stress is easily measured, without noticeable fluctuations.

The functions $\eta_\kappa$ and $R_\kappa$ both decrease with increasing $\kappa$ for $\tau_N^* > 1$. Consistent with the optical data, the decreasing $\eta_\kappa$ for $\eta_\kappa < \eta_0$ may be attributed to progressive increase in the local order parameter $S$, and with flow orientation angle $\theta_\kappa$ nearly zero, under the influence of flow with $\kappa > \tau_N^*$. Thus, in the first approximation, one might approximate $\eta_\kappa$ by use of Eq. (24-25), with $S$ an (unknown) function of $\kappa$. In this flow regime the isotropic and nematic fluids exhibit similar flow curves (i.e., $\eta_\kappa/\eta_0$ versus $\tau_c^*$ for the isotropic fluid or $\eta_\kappa/\eta_p$ versus $\tau_N^*$ for the nematic fluid), despite the dissimilarities in the magnitudes of $\eta_0$ and $\eta_p$ or the $R_\kappa$. Consequently, Eq. (5) is a useful representation for $\eta_\kappa/\eta_p$ versus $\tau_N^*$, and, for the PBT fluids studied, the properly normalized distribution of relaxation times obtained for the isotropic fluid may also be used for the nematic fluid of comparable $M_w$ (e.g., $\tau_c/\tau_N$ in the distribution for the isotropic is replaced by $\tau_c/\tau_N$ to obtain the distribution for the nematic).

During steady flow, $T_\kappa$ and $T_\parallel$ (measured with the polarizer at angle $\pi/4$ from the flow direction) are nearly equal, and tend to undergo nearly periodic fluctuations, with a mean that increases with $\kappa$; these fluctuations are not obtained with isotropic solutions of PBT for flow with $\tau_c^*$ comparable to $\tau_N^*$.

The fluctuations in $T_\kappa$ and $T_\parallel$ may be related to the appearance of the nonbirefringent bands noted above in the preparation of the monodomain of a PBT solution. According to a treatment by Marrucci [26] based on the Leslie-Ericksen constitutive equation, the unstable shear flow will be manifested as a periodic rotation of the director orientation between angle $\theta_0$ and $-\theta_0$, with the period $T$ of the oscillation being equal to $\pi(|\alpha_1|/|\alpha_2|)^{1/2}/\kappa$ if $|\alpha_3| < |\alpha_2|$. Such an effect would give rise to the observed behavior, but would not be expected for PBT...
solution if $\sigma_1$ and $\sigma_2$ have the values found from the light scattering studies since the latter lead to stable shear flow. The unstable flow might correspond to the predicted behavior using the values of $\sigma_2$ and $\sigma_3$ modified by the strong shear flow. In some cases, on cessation of flow $T_+$ increases to a very large value for a short time (ca. $\tau_N/100$) before decreasing to a very low value, nearly equal to the transmission for an isotropic state. Subsequently, $T_+$ increases slowly, in all cases eventually reaching a value near the initial value. The fluctuation in $T_+$ during flow and the behavior during relaxation on cessation of flow both indicate that the molecular alignment in flow may not be a simple uniaxial orientation at some angle $\theta_*$ relative to the flow direction. The dependence of $T_+$ on time at long time following cessation of flow is probably controlled principally by the return of the director field to the planar, twisted orientation obtained in the equilibrium quiescent fluid owing to the effects of the adsorbed layer of polymer. The small values of $T_+$ and $T_1$ observed for shorter time on cessation of flow could result from a texture with oscillations in the director orientation as a function of the position along the perpendicular to the surfaces (there could even be complete rotation of the director orientation). Thus, the sharp increase in $T_+$ with subsequent marked drop could be caused by momentary alignment of the optic axis along the former flow direction as the optic axis at each plane recoils from its direction in flow to a new direction in response to the viscoelastic memory of the fluid. Subsequently, this nonequilibrium texture gradually relaxes to the equilibrium texture prescribed by the orientation of chains adsorbed on the surfaces.

Following cessation of steady flow, the recoverable strain reaches its final value $\gamma_R$ at a time for which $T_+$ remains low. Consequently, quantitative explanation of the behavior for $R_*$ may be expected to be complex. The inherent time scale of the recovery is of order $\tau_N$, but for example, the dependence of $R_*/R_0$ on $\tau_N\ast$ cannot be represented by Eq (6). Neither is it known what relation might exist between $R_*$ and $N_\ast^{(1)}$.

The effects described in the preceding have obvious application in solution processing of nematic polymeric fluids to give preferred direction to the molecular chains. Both more systematic experiments and improved theoretical insights are needed to advance our understanding of the rheological behavior and our ability to manipulate the preferred direction of the nematic fluid with an applied stress. In particular, a constitutive equation is needed for a polymeric nematic fluid that includes memory effects, and questions of flow stability need further elucidation.

ACKNOWLEDGEMENT

This work described above was carried out under partial support from the Polymers Program, Division of Material Research, National Science Foundation, and the Materials Laboratory, Wright-Patterson Air Force Base. Certain of the rheological measurements were obtained by Mr. C. S. Kim.

REFERENCES