1692 *Macromolecules* **2000,** *33,* 1692−1697

Twist Viscosity of a Side-Chain Liquid-Crystalline Polysiloxane Dissolved in a Tumbling Nematic Solvent

Pei-Yuan Liu, Alex M. Jamieson,* and Ning Yao

Department of Macromolecular Science, Case Western Reserve University, Cleveland, Ohio 44106-7202

Received October 4, 1999; Revised Manuscript Received January 4, 2000

ABSTRACT: The dynamics of the twist distortion was characterized by electric-field-dependent dynamic light scattering (EFDLS) for a dilute solution of a side-chain liquid crystalline polysiloxane (SCLCP) dissolved in the tumbling nematic solvent, 4′-octyl-4-cyanobiphenyl (8CB). The results show a decrease in twist relaxation rate on dissolution of the SCLCP due to a large increase in twist viscosity $\delta\gamma_1$ with negligible change in twist elastic constant K_{22}. By comparing the twist viscosity values, $\gamma_1 = \alpha_3 - \alpha_2$, with previous measurements of the strain periodicity of oscillations in the shear stress transients due to director tumbling, $\gamma_p = (\pi/\delta_p)(1 + \delta_p^2)$, where $\delta_p = (-\alpha_3/\alpha_2)^{1/2}$, we further investigate the corresponding changes in Leslie viscosities, $\delta\alpha_2$ and $\delta\alpha_3$. The results indicate that $\delta\alpha_2$ and $\delta\alpha_3$ have opposite signs. These observations, together with literature data on the electrorheological behavior of these solutions, can be self-consistently described by a hydrodynamic model of the viscous dissipation by Brochard, modified through inclusion of an additional dissipation process which derives from an elastic torque between director rotation and LCP orientation.

Introduction

As for isotropic solutions, a large increase in the viscosity of a nematic solvent is expected on dissolution of a liquid crystal polymer (LCP) due to the fact that the polymer chain occupies a large hydrodynamic volume in the nematic.[1] It is further anticipated that the rheology will be a sensitive function of the LCP molecular architecture, since the chain conformation of an LCP in the nematic state is anisotropic to a degree which depends on the architecture. The latter fact has been confirmed via small-angle X-ray scattering (SAXS)[2−4] and small-angle neutron scattering (SANS)[5,6] measurements of the radii of gyration, $R_{g\perp}$ and $R_{g\parallel}$, perpendicular and parallel to the nematic director, respectively. Specifically, the conformation of main-chain LCP is highly prolate ($R_{g\parallel} > R_{g\perp}$)[5] whereas that of a side-chain LCP is quasi-spherical and can be weakly prolate[2−4] or oblate ($R_{g\perp} > R_{g\parallel}$),[6] depending on the polymer backbone flexibility, molecular weight, and spacer length and on whether the polymer exhibits a smectic phase.

Brochard[1] has carried out a molecular hydrodynamic analysis of the effect of a dissolved polymer on the viscosities of a nematic solvent. Several interesting predictions were made. For example, expressions were formulated[1] for the increments in the rotational and irrotational torque coefficients $\delta\gamma_1$ and $\delta\gamma_2$, which determine the response of the director to the applied shear, in terms of the conformational relaxation time, τ_R, and the rms end-to-end distances parallel and perpendicular, respectively, to the nematic director, $R_\parallel$ and $R_\perp$

$$\delta\gamma_1 = \left(\frac{ckT}{N}\right)\tau_R \frac{(R_\perp^{\,2} - R_\parallel^{\,2})^2}{R_\perp^{\,2} R_\parallel^{\,2}} \qquad (1)$$

$$\delta\gamma_2 = \left(\frac{ckT}{N}\right)\tau_R \frac{(R_\perp^{\,4} - R_\parallel^{\,4})}{R_\perp^{\,2} R_\parallel^{\,2}} \qquad (2)$$

where c is the LCP concentration, k is Boltzmann's constant, T is the absolute temperature, and N is the degree of polymerization of the LCP. Using the relationships connecting the torque coefficients to the Leslie rotational viscosities,[7,8] α_3 and α_2, viz. $\gamma_1 = \alpha_3 - \alpha_2$, and $\gamma_2 = \alpha_3 + \alpha_2$, respectively, we obtain the following expressions for the Leslie viscosity increments:

$$\delta\alpha_2 = \left(\frac{ckT}{N}\right)\tau_R \left(\frac{R_\perp^{\,2} - R_\parallel^{\,2}}{R_\perp^{\,2}}\right) \qquad (3)$$

$$\delta\alpha_3 = \left(\frac{ckT}{N}\right)\tau_R \left(\frac{R_\perp^{\,2} - R_\parallel^{\,2}}{R_\parallel^{\,2}}\right) \qquad (4)$$

The orientational response of the nematic director is principally determined[7,9] by the signs of α_2 and α_3. When $\alpha_2\alpha_3 > 0$, a flow-aligning response is observed, i.e., the director tends to align at an angle close to the flow direction; if $\alpha_2\alpha_3 < 0$, tumbling flow is observed, and the director rotates continuously in flow. Since α_2 is generally negative for nematics, the response of the shear stress is determined by the sign of α_3. Thus, eq 4 of Brochard predicts that, if $R_\perp > R_\parallel$, dissolution of a side-chain LCP in a flow-aligning nematic solvent ($\alpha_2\alpha_3 > 0$) changes the rheology to director-tumbling ($\alpha_2\alpha_3 < 0$). Conversely, eq 4 predicts that a main-chain LCP dissolved in a director-tumbling nematic ($\alpha_2\alpha_3 < 0$) suppresses the tumbling behavior and induces a flow-aligning response ($\alpha_2\alpha_3 > 0$) when $R_\parallel > R_\perp$.[8] Each of these predictions has been confirmed by experimental analysis of the stress transients produced by small shear deformations of nematic monodomains.[8,10−12] However, analysis of the stress transients from tumbling mixtures of side-chain LCPs indicates a discrepancy when compared with the theoretical predictions of the Brochard model.[8,10,11] In the experiments, the results indicate $\delta\alpha_2 < 0$ and $\delta\alpha_3 > 0$, whereas Brochard[1] predicts $\delta\alpha_2 > 0$ and $\delta\alpha_3 > 0$.

The analysis of Brochard[1] also considered the Miesowicz viscosities η_a, η_b, and η_c, where the director is fixed, respectively, along the vorticity axis, in the flow direc-

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* To whom all correspondence should be addressed.

10.1021/ma991666k CCC: $19.00

tion, and along the shear gradient. Specifically, for the viscosity increments $\delta\eta_c$ and $\delta\eta_b$, Brochard deduced

$$\delta\eta_b = \left(\frac{ckT}{N}\right)\tau_R\left(\frac{{R_\perp}^2}{{R_\parallel}^2}\right) \quad (5)$$

$$\delta\eta_c = \left(\frac{ckT}{N}\right)\tau_R\left(\frac{{R_\parallel}^2}{{R_\perp}^2}\right) \quad (6)$$

From these equations, a second interesting prediction relates to the ratio of $\delta\eta_c$ to $\delta\eta_b$:

$$\left(\frac{\delta\eta_c}{\delta\eta_b}\right) = \left(\frac{R_\parallel}{R_\perp}\right)^4 \quad (7)$$

For a nematic solvent with positive dielectric anisotropy, this prediction can be tested by analysis of the change in electrorheological (ER) response under the assumption that the apparent viscosity with the field on (η_{on}) is equal to η_c, and that with the field off (η_{off}) is equal to η_b.[13,14] Consistent with eq 7, on dissolving a main-chain LCP ($R_\parallel > R_\perp$), we observed a large increase in the ER effect, $\delta\eta_{on} \gg \delta\eta_{off}$, whereas, on dissolving a side-chain LCP ($R_\parallel \approx R_\perp$), the change in the ER effect is small, $\delta\eta_{on} \approx \delta\eta_{off}$.[14,15] In the latter case, however, a second discrepancy[11] between theoretical and experiment was observed. Specifically, solutions of side-chain LCPs which exhibit a flow aligning-to-tumbling transition and, according to eq 4, should therefore have an oblate conformation ($R_\parallel/R_\perp < 1$), exhibit an ER response which requires, via eq 7, a prolate conformation ($R_\parallel/R_\perp > 1$).

The origin of these discrepancies appears to reside in the fact that, for a liquid crystal polymer in a nematic solvent, because of the interaction between the mesogens on the LCP and the solvent, rotation of the director is accompanied by distortion of the backbone. Thus, it is necessary to refine the hydrodynamic theory of Brochard[1] by introducing an additional torque on the director, $\delta\Gamma^{el}$, owing to the elastic coupling between director rotation and LCP backbone:[11,16]

$$\Delta\Gamma^{el} = \delta\gamma_1^{el}\frac{d\vec{n}}{dt} = \left(\frac{ckT}{N}\tau_R\right)\frac{d\vec{n}}{dt} \quad (8)$$

The additional torque generates an extra increment in the twist viscosity, γ_1^{el}, and hence this analysis[11] leads to a modified version of the Brochard expression for the twist viscosity increment:

$$\delta\gamma_I^{modified} = \delta\gamma_I^{Brochard} + \delta\gamma_1^{el} = \left(\frac{ckT}{N}\right)\tau_R\left[\frac{(R_\perp^2 - R_\parallel^2)^2}{R_\perp^2\,R_\parallel^2} + 1\right] \quad (9)$$

Since $\alpha_2 = {}^1/_2(\gamma_2 - \gamma_1)$ and $\alpha_3 = {}^1/_2(\gamma_2 + \gamma_1)$,[7,8] it follows further that

$$\delta\alpha_2 = \left(\frac{ckT}{N}\right)\tau_R\left(\frac{1}{2} - \frac{{R_\parallel}^2}{{R_\perp}^2}\right) \quad (10)$$

$$\delta\alpha_3 = \left(\frac{ckT}{N}\right)\tau_R\left(\frac{{R_\perp}^2}{{R_\parallel}^2} - \frac{1}{2}\right) \quad (11)$$

Consistent with our observations on nematic solutions of side-chain LCPs, eqs 10 and 11 predict that $\delta\alpha_3$ is positive, but $\delta\alpha_2$ remains negative when $R_\parallel \approx R_\perp$. Moreover, the predictions of Brochard for the Miesowicz viscosity increments, $\delta\eta_c$ and $\delta\eta_b$, remain unchanged because the director is not allowed to rotate, and therefore it becomes possible to have $\delta\alpha_3 > 0$ when $\delta\eta_c > \delta\eta_b$.

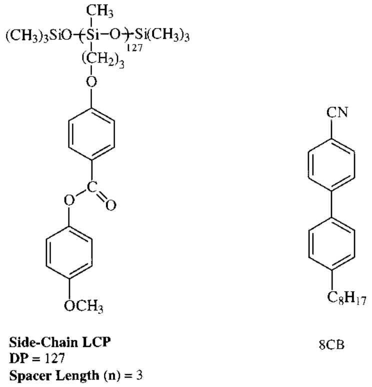

Figure 1. Chemical structures of the side-chain LCP and 8CB.

Recently, two additional sets of experimental evidence were obtained which support our modification of the Brochard theory. First, using electric-field-dependent dynamic light scattering (EFDLS), the twist viscosity increment ($\delta\gamma_1$) of dilute solutions of side-chain liquid-crystalline polysiloxanes in a flow-aligning nematic solvent (5OCB) was found to be large ($\sim ckT/N)\tau_R$, consistent with eq 9, rather than close to zero, as predicted by eq 1.[17] Second, the rheology of monodomain solutions of side-chain polysiloxane LCPs in the tumbling solvent 8CB was investigated.[18] A change in periodicity of the stress transients was observed following dissolution of the LCP, whose magnitude is in quantitative agreement with the modified theory.

In this paper, we determine for the first time the change in twist viscosity, $\delta\gamma_1$, of side-chain polysiloxanes in the tumbling nematic solvent 8CB. The unique aspect of the present work is that, since both solution and solvent exhibit tumbling rheology, it is possible to combine the twist viscosity data, γ_1, with earlier measurements of the strain periodicity of stress oscillations of shear stress transients, γ_p, and obtain particularly clear-cut estimates of the corresponding increments in the Leslie viscosities, $\delta\alpha_2$ and $\delta\alpha_3$. This enables a more direct test of experimental observation vs theoretical prediction. These results are further utilized in combination with previous determinations[18] of the change in Miesowicz viscosity, $\delta\eta_c$, to yield new estimates of the increment in Miesowicz viscosity $\delta\eta_b$, via the Parodi relation. The effect of temperature on the various viscosity coefficient increments is studied and discussed. We demonstrate that the Brochard theory,[1] as modified by Yao and Jamieson,[11] can provide an accurate interpretation of all four viscosity increments.

Experimental Section

Materials. The low molar mass nematic liquid crystal solvent 4′-octyl-4-cyanobiphenyl (8CB, T_{SN} = 33.3 °C and T_{NI} = 39.8 °C) used in this study was purchased from Aldrich Chemical Co. The side-chain LCP (DP = 127) was synthesized via hydrosilylation reaction between a mesogenic group 4-[(allyloxy)benzoy]-4′-methoxylphenyl and poly(methylhydrosiloxane).[15] The chemical structures of 8CB and the side-chain LCP are schematized in Figure 1.

A small amount of the polymer (0.02 g/mL) in 8CB was heated at a temperature above its clearing transition and ultrasonically agitated to make a homogeneous, miscible mixture. Equilibration was continued at least 24 h until complete dissolution in the isotropic state occurred. Homeotropic monodomains, in which the average molecular orientation of the director is perpendicular to the glass surfaces, were formed between ITO conductive glass slides coated with 0.35 wt % solution of lecithin in ethanol, purchased from Sigma Chemical Co. The thickness of the scattering cell was controlled by 12.5 μm Mylar spacers, and the cells were sealed with epoxy resin (DEVCON). The sample cell thickness was measured by interferometry[19,20] with values accurate to within 1%. Cells were filled with an isotropic mixture at a temperature around 50 °C via capillary action on a hot stage. A Carl Zeiss optical polarizing microscope equipped with a Mettler FP82HT hot stage and a Mettler FP90 central processor was used to evaluate the homogeneity and the homeotropic alignment of the specimens and to determine the smectic to nematic transition temperatures, T_{SN} and the nematic to isotropic transition temperatures, T_{NI}, of the samples at a cooling rate of 2 °C/min. For example, the T_{NI} of the mixture refers to the lower bound of the narrow biphasic region. Typically, the transition zone for the SCLCP/nematic mixture was in a range of 1−2 °C. The T_{NI} value of the mixture was found to be slightly higher than that of 8CB (ca. 0.4 °C). Also, the refractive index of the SCLCP mixture was assumed to be equal to that of pure 8CB since the polymer concentrations utilized are very dilute.[17]

Freedericksz Transition Measurement. The dielectric anisotropy, $\Delta\epsilon$ ($=\epsilon_{\parallel} - \epsilon_{\perp}$), and the threshold voltage, V_{th}, of the LCP samples were determined via the Freedericksz transition technique. This method also yields a determination of the splay elastic constant, K_{11}, and is described in detail elsewhere.[21,22] Essentially, this measurement involves monitoring the capacitance of a planar monodomain while an increasing 50 Hz AC bias voltage (V_{b}) is applied. A three-terminal-arrangement with guard electrodes was used to eliminate edge effects. K_{11} can be calculated via following expression:[21]

$$V_{\mathrm{th}}^{\,2} = \frac{K_{11}\pi^2}{\epsilon_0\Delta\epsilon} \tag{12}$$

The value of $\epsilon_{\perp}$ was measured at zero field for a planar monodomain, neglecting the capacitance contribution from the polyimide, and the value of $\epsilon_{\parallel}$ was determined by measuring the capacitance of the homeotropic cell in the presence of a 7 V bias voltage (at 3000 Hz AC frequency). The details of the method are given elsewhere.[22,23]

Electric-Field-Dependent Dynamic Light Scattering (EFDLS). The methodological and analytical procedures for the determination of viscoelastic parameters via the application of dynamic light scattering can be found in detail elsewhere.[24−27] Dynamic light scattering measurements in the homodyne mode were performed using a photon correlation spectrometer comprising a 15 mW He−Ne laser and a Brookhaven Instruments BI-2030AT 264-channel digital correlator at temperatures measured in a range 35−39 °C in steps of 1 °C. Homeotropic samples were prepared between two glass slides, and positioned in a refractive index-matching bath containing *tert*-butylbenzene, controlled to an accuracy of ±0.1 °C, using a custom-designed micromanipulator which enables a small adjustment to keep the scattering volume in the focal plane of the collecting lens. The incoming laser beam is normal to the cell surface so that the director is parallel to the incident wave vector. The incident light is polarized perpendicular to the scattering plane, and depolarized scattering is detected with a polarizer oriented in the scattering plane. For this scattering geometry, theory indicates[23,24] that, at small scattering angles, scattering from a pure twist distortion is observed, with a negligible contribution from the bend mode because of the large value of the ratio $q_{\perp}^{2}/q_{\parallel}^{2}$, where $q_{\parallel}$ and $q_{\perp}$ are, respectively, the components of the scattering vector parallel and perpendicular to the director. EFDLS measurements were typically made at a scattering angle of 18° in the laboratory frame for which the contribution of the bend mode to the relaxation rate of the bend-twist mode 2, Γ_2, is comparable to experimental error, i.e., about 2%.[23,24]

Table 1. Dielectric Anisotropies ($\Delta\epsilon$), Threshold Voltages (V_{th}), and Splay Elastic Constants (K_{11}) of Pure 8CB and the SCLCP/8CB Solution (c = 0.02 g/mL)

	$\Delta\epsilon \pm 3\%$		$V_{\mathrm{th}} \pm 2\%$		$(K_{11} \pm 5\%) \times 10^{-8}$ (dyne)	
temp (°C)	8CB	SCLCP/8CB	8CB	SCLCP/8CB	8CB	SCLCP/8CB
35	8.88	8.09	0.88	0.85	61.69 (60.00)	52.44
36	8.51	7.81	0.85	0.81	55.16 (54.00)	45.97
37	8.14	7.52	0.82	0.78	49.10 (47.00)	41.04
38	7.78	7.15	0.78	0.75	42.46 (40.00)	36.08
39	6.97	6.35	0.71	0.69	31.52 (29.56)	27.12

Individual values of the twist viscosity coefficient (γ_1) and elastic constant (K_{22}) were acquired by carrying out the EFDLS measurement at small angles in the presence of an electric field parallel to the director. The EFDLS decay rate[25,26] is

$$\Gamma_2(q) = \frac{K_{22}q_{\perp}^{\;2}}{\gamma_1} + \frac{\epsilon_0\Delta\epsilon\left(\frac{V}{d}\right)^2}{\gamma_1} \tag{13}$$

with

$$q_{\perp} = \left(\frac{2\pi n_{\mathrm{e}}}{\lambda}\right)\sin\theta_0$$

where $q_{\perp}$ is the scattering vector perpendicular to the nematic director, ϵ_0 is the electric permittivity in a vacuum, $\Delta\epsilon$ is the dielectric anisotropy of the liquid crystalline solution, V is the applied voltage across the sample cell, d is the cell thickness, n_{e} is the temperature-dependent extraordinary refractive index of the nematic, λ is the wavelength of incident light in a vacuum (632.8 nm), θ_0 refers to the scattering angle inside the nematic sample and can be calculated by Snell's law, viz., $n_{\mathrm{e}}\sin\theta_0 = n_{\mathrm{T}}\sin\theta_{\mathrm{lab}}$, where n_{T} is the refractive index of *tert*-butylbenzene, used as a matching liquid, and θ_{lab} is the scattering angle in the laboratory frame, i.e., the angle between the transmitted laser beam and the photomultiplier tube. In EFDLS measurements, the depolarized intensity correlation functions of each specimen were obtained by photon correlation analysis with each level of AC electric field applied by a Hewlett-Packard audio frequency generator model 200CDR at 3000 Hz. Further details of the experimental method can be found elsewhere.[23,28] Measurements were made on a 0.02 g/mL solution, which falls in the region where the viscosity is linearly dependent on LCP concentration.[15]

Results and Discussion

We report here measurements of the mean twist relaxation rates of light scattered by a dilute nematic solution of SCLCP in 8CB, based on single-exponential fits to the EFDLS autocorrelation function, determined in the twist scattering configuration described above. To apply eq 13, we first determined values of the dielectric anisotropy, $\Delta\epsilon$, and the threshold voltage, V_{th}, from Freederickz transition measurements for pure 8CB as well as for the SCLCP/8CB solutions, as listed in Table 1. From this table, it is evident that the polymer solution has slightly lower $\Delta\epsilon$ values than that of pure 8CB at each temperature in the nematic state, in agreement with previous studies,[22] indicating that dissolution of LCP in the nematic matrix leads to a decrease in local orientational order. Moreover, $\Delta\epsilon$ decreases with an increase of temperature for both pure 8CB and SCLCP/8CB solutions, which reflects a corresponding decrease in the nematic order parameter.[27]

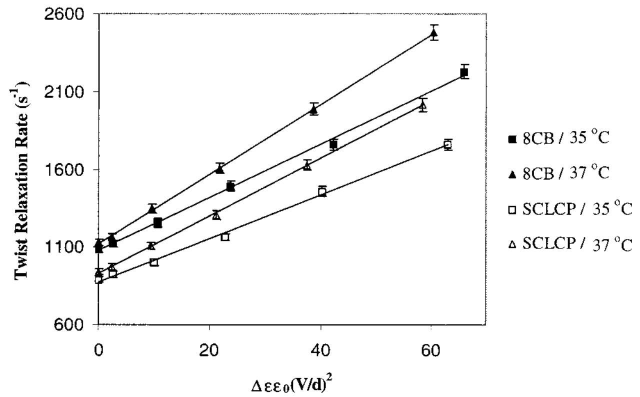

Figure 2. Electric field dependence of the twist relaxation rates for pure 8CB and the SCLCP/8CB solution (c = 0.02 g/mL) at 35 and 37 °C.

Table 2. Twist Viscosity, γ_1, Twist Elastic Constant, K_{22}, and Stress Oscillation Periodicity, γ_p, of Pure 8CB and the SCLCP/8CB Solution (c = 0.02 g/mL)

	$\gamma_1 \pm 2\%$ (poise)		$(K_{22} \pm 2\%) \times 10^{-8}$ (dyne)		$\gamma_p{}^a$ (strain units)	
temp (°C)	8CB	SCLCP/ 8CB	8CB	SCLCP/ 8CB	8CB	SCLCP/ 8CB
35	0.59	0.72	30.5	30.3	9.81	7.46
36	0.49	0.61	26.3	26.3	12.10	7.80
37	0.45	0.54	24.2	24.4	15.12	8.20
38	0.39	0.47	21.0	20.9	19.15	8.47
39	0.31	0.37	17.0	16.9	-	8.80

[a] Data taken from ref 18.

From the measured $\Delta\epsilon$ and V_{th} values, the splay elastic constants, K_{11}, can be calculated using eq 12, and are also listed in Table 1. The measured K_{11} values agree well with the earlier study of Bradshaw[29] on pure 8CB (values shown in parentheses). K_{11} decreases only very slightly with dissolution of the side-chain liquid-crystalline polysiloxane at each temperature, in agreement with literature observation in other solvents[17,22,24] and with data which show that the elastic constants are similar for the pure solvents and the pure polymers.[30]

Figure 2 shows a plot of the twist relaxation rate Γ_2 of pure 8CB and a SCLCP/8CB solution against the field parameter $\epsilon_0\Delta\epsilon(V/d)^2$ at two temperatures, together with a least-squares fits to eq 13. The values of γ_1 and K_{22} can be obtained, respectively, from the inverse slope and the intercept, corresponding to the zero-field decay rate, and are listed in Table 2. For pure 8CB, our experimental values for γ_1 and K_{22} are consistent with literature values.[8,31] Moreover, it is evident from Table 2 that, in agreement with previous observations,[17,24,32] the major contribution to the decrease in relaxation rate of the twist mode on dissolution of a SCLCP comes from a combination of a large increase in γ_1 with a negligible change in K_{22}. In Figure 3 the twist viscosity of the SCLCP/8CB solution, together with that of pure 8CB, is plotted as a function of temperature. It is further shown in Figure 3 that the twist viscosity increment $\delta\gamma_1 = \gamma_1(\text{solution}) - \gamma_1(\text{solvent})$ increases slightly at lower temperatures which, as we will see later, primarily reflects an increase in the conformational relaxation time τ_R, cf., eq 1.

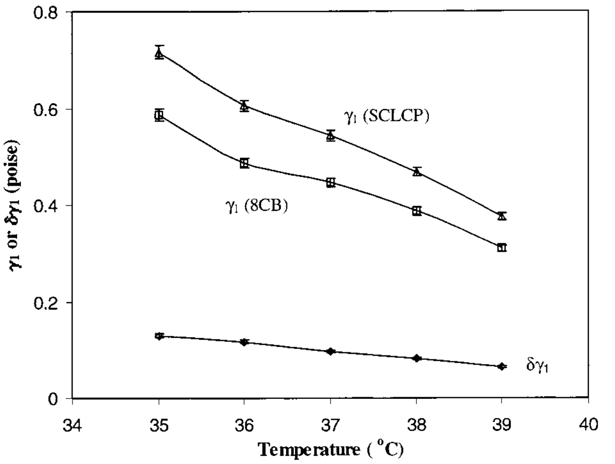

Figure 3. Temperature dependence of the values of γ_1 and $\delta\gamma_1$ of pure 8CB and the SCLCP/8CB solution (c = 0.02 g/mL).

As noted earlier, the rheological flow behavior of a monodomain nematic is determined mainly by α_2 and α_3. Unfortunately, the sign and magnitude of α_2 and α_3 cannot be accurately measured by DLS measurements.[8,24] As demonstrated in earlier work,[8,11,18,33] measurements of the oscillatory stress transient, combined with an independent measurement of the twist viscosity γ_1 or the Miesowicz viscosity η_c, can generate values of α_2 and α_3 with reasonable precision. In the present paper, we obtain values of α_2 and α_3 by combining twist viscosity values, $\gamma_1 = \alpha_3 - \alpha_2$, with values of the strain periodicity of the oscillatory stress transients, γ_p, taken from the recent study of Yao et al.[18] and also listed in Table 2 for convenience. Note, from Table 2, that the temperature dependence of the γ_p of pure 8CB is much stronger than that of the polymer mixture, reflecting the different origin of the tumbling behavior, viz., the occurrence of presmectic fluctuations for pure 8CB, vs the contribution of the polymer for the SCLCP/8CB solution.[18] We utilize the following expression which relates γ_p to the Leslie viscosities[34]

$$\gamma_p = \frac{\pi(1 + \delta_p{}^2)}{\delta_p} \tag{14}$$

where $\delta_p = (-\alpha_3/\alpha_2)^{0.5}$. In addition, from these results for α_2 and α_3, together with previous ER measurements[18] of the Miesowicz viscosity η_c, we can obtain new estimates for the small Miesowicz viscosity η_b, by employing the Parodi relation:[35]

$$\alpha_2 + \alpha_3 = \eta_b - \eta_c \tag{15}$$

Since this procedure can be carried out in the tumbling flow regime for both SCLCP/8CB solutions and for the pure solvent, we are able to determine in a straightforward way accurate estimates of the viscosity increments $\delta\alpha_2$, $\delta\alpha_3$, $\delta\eta_b$, and $\delta\eta_c$.

Table 3 shows values of the ratio α_3/α_2 for 8CB and the SCLCP/8CB solution deduced from γ_p in the earlier work.[18] Combining values of the twist viscosity $\gamma_1 = \alpha_3 - \alpha_2$ from Table 2 with the data on α_3/α_2 from Table 3, we determine via eq 14 the individual values of α_2 and α_3. Then, applying the Parodi relation (eq 15) and combining the results on α_2 and α_3 with η_c data from earlier ER experiments,[18] we obtain the values of η_b for pure 8CB and the SCLCP/8CB mixture. From these results, we determine the values of the viscosity increments $\delta\alpha_2$, $\delta\alpha_3$, $\delta\eta_b$, and $\delta\eta_c$ for the SCLCP/8CB solution shown in Table 3.

It remains to compare these experimental results vs the theoretical predictions of the Brochard model, in its modified form embodied in eqs 9, 10, and 11, together

Table 3. Leslie and Miesowicz Viscosity Coefficients and the Ratio α_3/α_2 of Pure 8CB and the Values of the Ratio α_3/α_2 Associated with the Viscosity Increments $\Delta\alpha_2$, $\Delta\alpha_3$, $\delta\eta_b$, and $\delta\eta_c$ of the SCLCP/8CBCB Solution (Unit = Poise)

	8CB					SCLCP/8CB				
temp (°C)	$(\alpha_3/\alpha_2)^a \pm 3\%$	$\alpha_2 \pm 2\%$	$\alpha_3 \pm 2\%$	$\eta_c{}^b \pm 1\%$	$\eta_b \pm 3\%$	$(\alpha_3/\alpha_2)^a \pm 3\%$	$\delta\alpha_2$	$\delta\alpha_3 \pm 3\%$	$\delta\eta_c{}^b \pm 15\%$	$\delta\eta_b \pm 12\%$
35	−0.131	−0.518	0.068	0.810	0.360	−0.299	−0.034 ± 0.015	0.097	0.095	0.158
36	−0.078	−0.452	0.035	0.770	0.353	−0.255	−0.030 ± 0.013	0.088	0.075	0.133
37	−0.047	−0.427	0.020	0.725	0.319	−0.217	−0.020 ± 0.012	0.077	0.070	0.127
38	−0.028	−0.376	0.011	0.670	0.305	−0.197	−0.015 ± 0.011	0.066	0.075	0.126
39	−	−0.310	-7.7×10^{-5}	0.613	0.303	−0.176	−0.009 ± 0.009	0.056	0.072	0.120

[a] These results were derived from data of stress oscillation periodicity, taken from ref 18. [b] These results were derived from ER measurements, taken from ref 18.

Table 4. Chain Anisotropy ($R_\|/R_\perp$) and the Ratio $\Delta\alpha_3/\Delta\alpha_2$ of the SCLCP/8CB Solution (c = 0.02 g/mL)

temp (°C)	$(R_\|/R_\perp)^a$ ± 5%	Brochard model $(\delta\alpha_2/\delta\alpha_3)^b$ ± 10%	modified model $(\delta\alpha_2/\delta\alpha_3)^c$ ± 14%	exptl results[d] $\delta\alpha_2/\delta\alpha_3$ ± 64%
35	0.88	0.774	−0.347	−0.351
36	0.87	0.752	−0.303	−0.341
37	0.86	0.742	−0.285	−0.260
38	0.88	0.772	−0.341	−0.227
39	0.88	0.776	−0.349	−0.161

[a] Equation 7. [b] Data calculated from the ratio of eq 3 to eq 4. [c] Equation 16. [d] The values were derived from Table 3.

with eqs 2, 5, 6, and 7 of the original theory. To accomplish this, we employ eq 7 to estimate the chain anisotropy $R_\|/R_\perp$ for the SCLCP/8CB solution from the $\delta\eta_b$ and $\delta\eta_c$ data and use these $R_\|/R_\perp$ values to predict values of $\delta\alpha_2$ and $\delta\alpha_3$ for comparison with our present results. Specifically, we consider values of the ratio $\delta\alpha_2/\delta\alpha_3$. Combination of eqs 10 and 11 of the modified Brochard theory[18] leads to

$$\left(\frac{\delta\alpha_2}{\delta\alpha_3}\right)^{\text{modified}} = \left(\frac{1}{2} - \frac{R_\|^{\,2}}{R_\perp^{\,2}}\right) \Big/ \left(\frac{R_\perp^{\,2}}{R_\|^{\,2}} - \frac{1}{2}\right) \qquad (16)$$

From the values of $\delta\eta_b$ and $\delta\eta_c$ listed in Table 3, using eq 7, we can determine the values of $R_\|/R_\perp$ tabulated in Table 4 which indicate that the side-chain polysiloxane LCP with DP = 127 has a slightly oblate conformation ($R_\| < R_\perp$) over the entire nematic temperature region. This is consistent with earlier results for this SCLCP specimen in the flow-aligning solvent, 5OCB.[15,17] Using these results, we compute values of the ratio $\delta\alpha_2/\delta\alpha_3$ via eq 16, which are also shown in Table 4, together with the experimental values computed from Table 3. Table 4 indicates that the experimental $\delta\alpha_2/\delta\alpha_3$ are negative, reflecting that $\delta\alpha_2$ and $\delta\alpha_3$ have the opposite signs, i.e., $\delta\alpha_2 < 0$ and $\delta\alpha_3 > 0$, and consistent with our previous studies.[8,10,11] Comparing the experimental results with those calculated from $R_\|/R_\perp$ via eq 16, it is clearly evident from Table 4, and plotted in Figure 4, that the modified hydrodynamic model is in good agreement with the experimental results over the nematic temperature range. It is further apparent, from eqs 9−11, that, knowing $R_\|/R_\perp$, we can determine the conformational relaxation time, τ_R. This enables a quantitative test of the consistency of the theory by comparing values of τ_R determined from the $\delta\gamma_1$ data vs those obtained from the $\delta\eta_c$ results. The temperature dependence of the two sets of τ_R values is shown in Figure 5 and exhibit good agreement with each other. A small but significant deviation between experiment and theory appears to occur near the clearing temperature in both Figure 4 and Figure 5, the nature of which is not clear. This may indicate a need for further refinement of the theory. However, we note that the data at T = 39 °C fall in the flow-aligning regime of the solvent 8CB and hence were derived by curve-fitting the stress overshoot of the solvent.

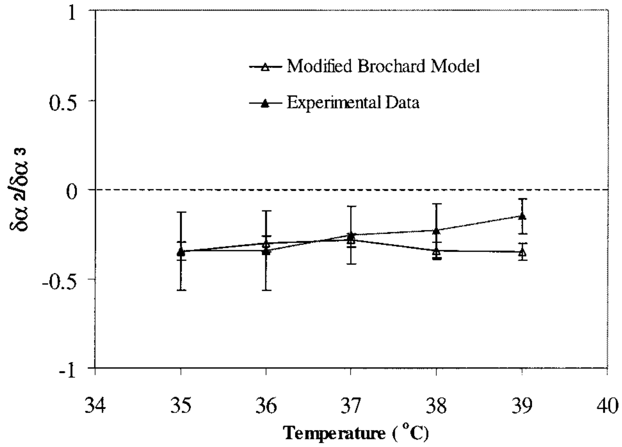

Figure 4. Temperature dependence of $\delta\alpha_2/\delta\alpha_3$ of a 0.02 g/mL SCLCP/8CB solution.

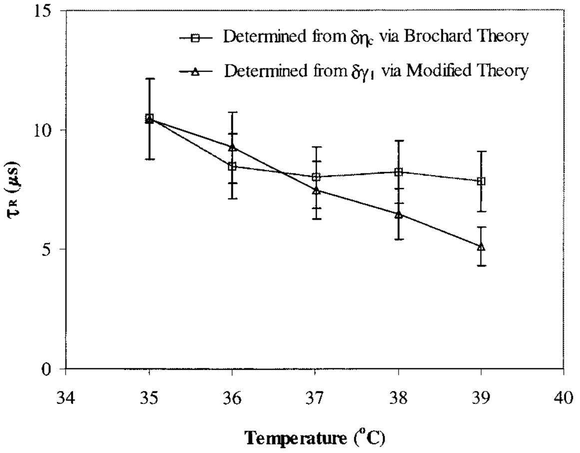

Figure 5. Temperature dependence of the τ_R of a 0.02 g/mL SCLCP/8CB solution.

Conclusions

Electric-field-dependent dynamic light scattering (EFDLS) was used to determine the increment in twist viscosity of a miscible nematic solution of a side-chain liquid crystal polysiloxane (SCLCP) in 8CB. The results show that dissolution of the SCLCP leads to a substantial increase in the twist viscosity increment $\delta\gamma_1$. By combination of $\delta\gamma_1$ values with data on the strain periodicity (γ_p) of stress oscillations in shear deformation of nematic monodomains, the Leslie viscosity increments, $\delta\alpha_3$ and $\delta\alpha_2$, were estimated, and they indicate that $\delta\alpha_3 > 0$ and $\delta\alpha_2 < 0$. Use of these results, together with values of the increment in Miesowicz viscosity, $\delta\eta_c$, from electrorheological measurements and application of the Parodi relation, yields values of $\delta\eta_b$ from which we deduce that the chain conformation of the SCLCP is slightly oblate in 8CB. All of these results are found to be in good agreement with a modified version of the Brochard hydrodynamic model, in which an additional viscous dissipation mechanism is included, postulated to arise from an elastic torque between director rotation and LCP orientation.

Acknowledgment. We are grateful to the National Science Foundation Science and Technology Center, ALCOM, for support of this work through award No. DMR 89-20147. We also thank Mr. Doug Bryant at Kent State University for preparation of ITO-coated and polyimide glass slides.

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MA991666K