We report experimental studies on small angle light scattering (SALS), and rheodielectric and electrorheological properties of a binary mixture of octyloxy cyanobiphenyl and hexyloxy cyanobiphenyl liquid crystals. The mixture exhibits nematic (N) to smectic-A (SmA) phase transitions, and then again to a reentrant nematic (N*) phase transition. Rapid shear thinning in the quenched samples in the low shear rate region in the N and SmA phases observed from SALS experiments is attributed to the realignment of the director within the domains. The domains are elongated along the shear direction at higher shear rates. The temperature variation of the effective viscosity and static dielectric constant reveals the changes in the director orientation across N-SmA-N* phase transitions. At a steady shear rate the effective viscosity increases with the electric field in all the phases and saturates at much higher fields. It also exhibits two anomalous peaks across N-SmA-N* phase transitions beyond a particular field. The shear modulus of the SmA phase in an intermediate field is significantly larger than that measured at both low and high fields. This enhanced viscoelasticity of the SmA phase is argued to originate from the increased dislocation density.

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I. INTRODUCTION

Liquid crystals are orientationally ordered fluids made of anisotropic organic molecules. They exhibit a variety of phase transitions owing to their molecular structures and shapes. Common mesophases exhibited by low molecular weight liquid crystals (LCs) are typically nematic (N), smectic-A (SmA) and cholesteric (N*). The flow properties of these LCs are very interesting and there are many theoretical and experimental studies on the flow viscosities [1–14]. Nematic liquid crystals (NLCs) in this respect are relatively simpler and have been investigated in detail [3]. The average alignment direction of the long axes of the molecules is called the director and is denoted by a dimensionless unit vector \( \mathbf{n} \). When the sample is sheared the director exhibits mainly three types of orientation with respect to the flow and the velocity gradient directions. Schematic representations of the director orientations in N as well as in SmA phases are shown in Fig. 1. The orientation of the director depends on the relative magnitude and sign of the two Leslie coefficients, \( \alpha_2 \) and \( \alpha_3 \). If both of these coefficients are negative the director aligns at an angle \( \theta = \tan^{-1} (\sqrt{2}/\sqrt{3}) \) with respect to the flow direction [4,15–17]. In this orientation the measured viscosity is \( \eta_2 \) (Miesowicz viscosity). Safinya et al. [13] reported that the director orientation changes with temperature in compounds exhibiting N-SmA phase transition. They showed theoretically and experimentally that \( \alpha_3 \) is renormalized (\( \alpha_3^R > 0 \)) due to the critical slowing down of the SmA order-parameter fluctuations in the N phase, and the ratio \( \alpha_2/\alpha_3 \) is negative [13,14]. As a result the director orientation changes from the flow direction to a neutral direction (x axis) as shown in Fig. 1(a). Later it was shown that in the case of freely flowing nematic liquid crystals the measured viscosity changes from \( \eta_2 \) to \( \eta_3 \) at a few degrees below the nematic-isotropic (NI) transition [18,19]. It suggests that just below the NI transition the director is oriented along the velocity direction (Fig. 1(b)) and changes its orientation to the neutral direction (as shown in Fig. 1(a)) as the temperature is reduced. Bhattacharya et al. measured flow viscosity in an oriented sample showing SmA-to-N* phase transition [20] and reported that the flow behavior of the N* phase is identical to that of the higher temperature nematic phase. Using synchrotron x-ray studies Safinya et al. [14] showed that several steady state structures appear in compounds exhibiting N-SmA transition due to the precessional motion of the director along the neutral direction [14] denoted by \( \alpha_0 \), \( \alpha_1 \), \( \alpha(b) \), and \( \alpha_c \). These structures are described by the equation of an ellipse: \( n_2(t)/n_2^0 + n_2^2(t)/n_3^2 = 1 \), where \( n_3(t) = n_3 > 0 \cos(\omega t) \) and \( n_2(t) = n_2 > 0 \sin(\omega t) \) are components of the director \( \mathbf{n}(t) = (n_3(t),n_2(t),n_1(t)) \). The angular frequency of the precessional motion is given by \( \omega_0 = \sqrt{\gamma^2(-\alpha^R_2 \alpha_3^2)/\gamma_1^2} \), where \( \alpha^R_2 \) is the renormalized Leslie coefficient, \( \gamma \) is the shear rate, and \( \gamma_1 = \alpha_3 - \alpha_0 \). These structures are physically interpreted as follows. In \( \alpha_0 \) structure, the precessional motion is anisotropic with larger amplitude in the y direction than in the z direction (\( n_2 > n_3 \)); in \( \alpha_1 \) structure, the isotropic precession occurs with equal amplitudes in both directions (\( n_2 = n_3 \)); in \( \alpha(b) \) structure, anisotropic precession occurs with lesser amplitude in the y direction than in the z direction (\( n_2 \ll n_3 \)); and in \( \alpha_c \) structure, anisotropic precession occurs with a very large amplitude in the z direction (\( n_2 \ll n_3 \)). Negita et al. [21] reported that the above structural features are also reflected in the rheodielectric measurements on octyloxy cyanobiphenyl (8CB) compound which exhibits N-SmA phase transition. Very recently we showed that the viscosity increases and the director orientation changes under the application of an external electric field when the temperature is reduced in octyloxy cyanobiphenyl (8OCB) [22]. The rheodi-electric measurements mostly provide overall information on the director orientation during the flow. However, small angle light scattering (SALS) measurements have the potential to infer the effect of domain shape and size on the rheological properties and such studies are meager in these materials. In addition, the flow behavior and hence the rheological
properties across the SmA-to-$N_R$ transition are very rare and interesting from a phase transition point of view.

In this paper we report SALS, rheodielectric, and electrorheological studies on a binary mixture of hexyloxy cyanobiphenyl (6OCB) and 8OCB and investigate the effect of an external ac electric field on the effective viscoelastic properties. We emphasize that the flow behavior and effect of presmectic fluctuations are similar in both $N$ and $N_R$ phases. The viscoelasticity in the SmA phase is dominated by dislocations and shows an interesting variation on the application of an external field.

II. EXPERIMENT

The compounds 8OCB and 6OCB were synthesized in our laboratory in Poland. 6OCB exhibits only the $N$ phase, while 8OCB exhibits both $N$ and SmA phases. A 60CB with 80CB mixture of 21.0 to 29.5 wt% exhibits the reentrant nematic ($N_R$) phase. There have been several studies on the phase transitions in these mixtures [23,24]. We have chosen a mixture of 27 wt% of 6OCB and 73 wt% of 8OCB that exhibits a reasonably wide temperature range (±10°C) of the SmA phase above the reentrant nematic phase. The mixture shows the following phase sequence as observed in a polarizing optical microscope on cooling: $N_R$ 32.4°C; SmA 43.2°C; $N$ 77.5°C. Rheological measurements were performed using a rheometer (Anton Paar MCR 501) in parallel plate geometry with a plate diameter of 50 mm. The parallel plate configuration was chosen for the simultaneous measurement of rheological and dielectric properties. The gap between the two parallel plates was 75 μm.

FIG. 1. (Color online) Schematic representation of the three fundamental director orientations in the $N$ and SmA phases under shear. The director orientations are along the $x$ (neutral), $y$ (velocity), and $z$ (velocity gradient) directions, denoted $a$, $b$, and $c$, respectively. Similar director orientation in the SmA phase is denoted by $a^\prime$, $b^\prime$, and $c^\prime$. Layer orientations in the SmA phase are shown by dotted lines. Miesowicz viscosities corresponding to each orientation in the $N$ phase are designated by $\eta_1$, $\eta_2$, and $\eta_3$, respectively.

III. RESULTS AND DISCUSSION

A. SALS measurements

We first present the variation of effective shear viscosity ($\eta_{ef}$) in a quenched sample with shear rate, in both $N$ and SmA phases (Fig. 4). In the $N$ phase $\eta_{ef}$ is very high (≈700 mPa s) in the low shear rate region (e.g., $\dot{\gamma} = 0.1$ s$^{-1}$) and exhibits strong shear thinning behavior. For example, it reduces to ≈35 mPa s at $\dot{\gamma} = 10$ s$^{-1}$. Beyond this shear rate $\eta_{ef}$ is constant and hence behaves like a Newtonian fluid. The shear rate dependent effective viscosity in the $N$ phase can be described using the
Very high shear rate) and the power-law index, respectively. viscosity ($\eta$) in $N$ ($T - T_{NI} = -30^\circ C$) and SmA phases ($T - T_{NI} = -43^\circ C$). The depolarized scattering patterns (HV) at some representative shear rates are shown in both the phases. The red arrow indicates the direction of shear. The upper and lower scattering patterns correspond to the SmA and $N$ phases, respectively. The continuous line is a best fit to Eq. (1).

We measured the temperature dependent effective viscosity ($\eta_{ef}$) at a steady shear rate ($\dot{\gamma} = 50 \text{ s}^{-1}$) and recorded the scattering patterns at some representative temperatures to investigate the domain structure. It was not possible to record SALS patterns above $T - T_{NI} = -15^\circ C$ due to the limitations of the associated temperature controller. In Fig. 5 we present the variation of $\eta_{ef}$ with temperature and a few SALS patterns. We find that $\eta_{ef}$ decreases in the $N$ phase just below the NI transition. This is due to the shear-induced alignment of the director along the shear direction as shown in Fig. 1(b). Below $T - T_{NI} = -4^\circ C$, $\eta_{ef}$ begins to increase, suggesting the presence of multiple shear thinning events.
onset of a mixed director orientation (i.e., \(a-b\) structure). The viscosity increases almost linearly up to \(T - T_{N\ell} \approx -25^\circ C\). A small slope change below this temperature, followed by a rapid increase of the viscosity in the SmA phase, is observed. Similar behavior of \(\eta_{\text{ef}}\) was also observed above the \(N\)-SmA phase transition in pure 8CB and 8OCB liquid crystals [21,22]. It was explained based on the occurrence of various structures, namely \(a_r, a(b), a_s,\) and \(a_m,\) that arise because of precessional motion of the director, discussed earlier. The scattering patterns at this shear rate (\(\gamma = 50\) s\(^{-1}\)) in the \(N\) phase (Fig. 5) are elongated perpendicular to the shear direction due to the deformation of domains, as explained previously. The orientation of the patterns at \(N\)-SmA and SmA-\(N_R\) transitions is noticeably different in the sense that the long axis of the ellipse is rotated by an angle \(\approx 45^\circ\) to the left side of the shear direction. This implies that the elongation directions of the domains are rotated by the same angle on the right side of the shear direction. It seems that the precessional motion of the director (as described by Safinya et al. [14]) also induces significant change in the microtexture of the sample. In the SmA phase the domains have \(c^\prime\) and \(a^\prime\) director orientation (Fig. 1), and the scattering pattern is almost circular (Fig. 5), suggesting that the shapes of the domains remain unaffected at this shear rate. This is also consistent with the observation in Fig. 4. In the \(N_R\) phase the viscosity decreases sharply and again the scattering pattern gets elongated perpendicular to the shear direction.

B. Rheodielectric and electrorheological measurements

To investigate the director orientation inside the domain we measured the effective dielectric constant (\(\epsilon_{\text{ef}}\)) simultaneously with the viscosity measurement as a function of temperature at various fields. First we show the electric field-dependent effective viscosity (\(\eta_{\text{ef}}\)) as a function of temperature in Fig. 6(a). Its behavior at a low field (i.e., \(0.8 \times 10^4\) V/m) was already discussed in Fig. 5 and is presented here again for the purpose of comparison with the data at higher field. At a fixed temperature in the \(N\) phase, \(\eta_{\text{ef}}\) increases with electric field and saturates beyond a threshold value (\(26.7 \times 10^4\) V/m).

The experimental data represented by star were measured without shear and at a field \(0.8 \times 10^4\) V/m. The frequency of the applied field is 3.11 kHz.

The anomalous behavior of \(\eta_{\text{ef}}\) across the \(N\)-SmA transition was also observed in a few liquid crystals and it was attributed to the significant contribution of the Leslie coefficient \(\alpha_1\) near the \(N\)-SmA transition [10,30]. Since the hydrodynamic theory of both the \(N\) and \(N_R\) phases is expected to be the same [20], the peak across the SmA-\(N_R\) transition could be due to the similar effect. Furthermore, it may be noted that both the peaks are asymmetric in shape with temperature and the second peak is relatively stronger than the first one. The origin of this asymmetry in not clear, however; the difference in the smectic short-range order in both \(N\) and \(N_R\) phases could be responsible.

The variation of \(\epsilon_{\text{ef}}\) that was measured simultaneously with the viscosity measurement is shown in Fig. 6(b). At zero shear rate and low field (\(0.8 \times 10^4\) V/m) in the \(N\) phase, \(\epsilon_{\text{ef}}\) is lower than in the I phase, suggesting that the parallel plate induces planar orientation of the director. Since the dielectric anisotropy (\(\Delta \epsilon = \epsilon_{\perp} - \epsilon_{\parallel}\)) of the mixture is positive [31] we essentially measure the perpendicular component, i.e., \(\epsilon_{\text{ef}} \approx \epsilon_{\parallel}\). In the SmA phase \(\epsilon_{\text{ef}}\) is comparatively lower than both the \(N\) and \(N_R\) phases, indicating a strong antiparallel correlation of the transverse component of the dipole moments in the SmA layers [32]. At the same field the temperature variation of \(\epsilon_{\text{ef}}\) is significantly different when the sample is subjected to a steady shear rate (\(\gamma = 50\) s\(^{-1}\)), especially below \(T - T_{NI} = -10^\circ C\). This is because of the orientational change of the director across the phase transitions. In the SmA phase \(\epsilon_{\text{ef}}\) is slightly larger than the values in both \(N\) and \(N_R\) phases due to the \(a-c^\prime\) orientation of SmA layers as described in Fig. 5. At an intermediate field (e.g., \(13.3 \times 10^4\) V/m), \(\epsilon_{\text{ef}}\) just below the NI transition is much larger than in the I phase and decreases gradually with decreasing temperature. Initially the director tends to orient along the field direction as \(\Delta \epsilon > 0\). On the other hand, due to the effect of shear and presmectic fluctuations it tends to be parallel to the shear plane with decreasing temperature. Thus, at every temperature the direction of director orientation is determined by these two competing force fields. When the electric field is increased.

FIG. 6. (Color online) (a) Variation of effective shear viscosity (\(\eta_{\text{ef}}\)) with temperature at various ac electric fields. All the data were collected at a steady shear rate (\(\gamma = 50\) s\(^{-1}\)). Inset: Suppression of peaks under strong electric fields. (b) Static dielectric constant at same shear rates and same electric fields as in (a). The dielectric data represented by star were measured without shear and at a field \(0.8 \times 10^4\) V/m. The frequency of the applied field is 3.11 kHz.
to $26.7 \times 10^4$ V/m, $\epsilon_{ef}$ is much higher and $\epsilon_{ef} \simeq \epsilon_{||}$ [33] and decreases gradually as the $N$-SmA transition is approached. In the SmA phase $\epsilon_{ef}$ again increases and reaches a maximum value ($\epsilon_{ef} \simeq 15$) which is slightly less than that measured in the $N$ phase (near the NI transition), suggesting that the layer orientation in this phase is almost $c$ type.

C. Field-dependent complex shear modulus measurements

The experimental results from the SALS measurement provided qualitative information about the microtexture, and the rheodielectric properties revealed the changes in the director orientation. In the phase diagram of this binary mixture the SmA phase is surrounded by the nematic phase [23] and has different types of defects (dislocations). We anticipated that the investigation on the shear modulus across the phase transitions could be interesting in the sense that the applied electric field can change the defect density. Hence we measured the storage and loss moduli ($G'$ and $G''$) as a function of temperature. In Fig. 7 we show the variation of $G'$ and $G''$ as a function of temperature at various applied electric fields. At a low field ($0.8 \times 10^4$ V/m) $G'$ and $G''$ are very small ($\approx 0.5$ Pa) in both $N$ and $N_R$ phases compared to the SmA phase ($\approx 20$ Pa). Both $G'$ and $G''$ increase in the SmA phase when the field is increased to $13.3 \times 10^4$ V/m and decrease again at much higher field ($66.7 \times 10^4$ V/m). For example, in the middle of the SmA phase (i.e., $T - T_{NI} = -42$°C) at a low field ($0.8 \times 10^4$ V/m), $G' \approx 20$ Pa and increases to $\approx 22.6$ Pa at a field $13.3 \times 10^4$ V/m and then decreases to a small value $\approx 4$ Pa beyond $226.7 \times 10^4$ V/m. Similar behavior with temperature and field is also observed in the case of $G''$.

To understand the temperature variation of $G'$ and $G''$ at various fields we simultaneously measured the effective dielectric constant ($\epsilon_{ef}$) across $N$-SmA-$N_R$ phase transitions at various ac electric fields at an angular frequency $\omega = 10$ rad/s and strain amplitude $\gamma = 0.05$. The frequency of the applied field is 3.11 kHz. Orientations of SmA layers with respect to field direction are shown schematically.

FIG. 7. (Color online) Variation of (a) storage modulus ($G'$) and (b) loss modulus ($G''$) across $N$-SmA-$N_R$ phase transitions at various ac electric fields at an angular frequency $\omega = 10$ rad/s and strain amplitude $\gamma = 0.05$.

FIG. 8. (Color online) Variation of effective dielectric constant ($\epsilon_{ef}$) across $N$-SmA-$N_R$ phase transitions at various ac electric fields at an angular frequency $\omega = 10$ rad/s and strain amplitude $\gamma = 0.05$.
than in the $N$ phase. The director orientation changes under the application of electric field as the temperature is reduced across $N$-Sm$A$-$N_R$ phase transitions. We presented possible layer orientations at various electric fields and showed that the zero-field viscoelasticity in the Sm$A$ phase is aided by the presence of dislocations, which disappear on application of strong external field.

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[33] We measured parallel ($\epsilon_{||}$) and perpendicular ($\epsilon_{\perp}$) components of the dielectric constant in planar and homeotropic cells as a function of temperature. We found $\epsilon_{\perp} \simeq 5.9$ and $\epsilon_{||} \simeq 16.5$ at $T - T_{NI} = -45^\circ C$. The subscripts refer to directions in relation to the director.