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Rheology of nematic liquid crystals with highly polar molecules

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We report experimental studies on the rheology of a few nematic liquid crystals with highly polar molecules (CCH-7, PCH-7, CB-7). The selected molecules have the same alkyl chain (-C_7H_{15}) and cyano (-CN) end group. In the core part of the molecule, CCH-7 has two cyclohexane rings, PCH-7 has one cyclohexane and one aromatic ring, and CB-7 has two aromatic rings. Two viscosities were measured as a function of temperature, namely, η_2 (director parallel to the shear direction) and η_1 (director perpendicular to the shear direction). The orientation of the director was studied using small angle light scattering techniques. η_2 was measured in presheared sample, whereas the electrorheological technique was used to measure η_1. We show that both viscosities of the liquid crystals depend on the number of aromatic rings and Kirkwood correlation factor. The temperature dependent viscosities can be understood based on the intramolecular π-electron conjugation and intermolecular association of highly polar molecules.

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I. INTRODUCTION

The electrooptical response of liquid crystals depends on their physical properties, and they are related to the molecular structures [1–5]. A large number of liquid crystal compounds are used for various technological applications, and in many compounds the molecules have a highly polar cyano or nitro end group. In addition, polar molecules are more stable electrochemically and thermally. There are also some reports on new electrooptic effects in nematic liquid crystals with highly polar molecules [6]. Apart from applications, these compounds also exhibit several unusual features such as reentrant phase transitions, smectic-*A* polymorphism, nematic to nematic transition, and strong suppression of director fluctuation by fields [7–13]. When the nematic liquid crystals are sheared, they exhibit three different viscosities depending on the orientation of the director (the average molecular orientation direction) with respect to the flow and velocity gradient directions, and they are called Miesowicz viscosities [14]. A schematic representation of director orientation in calamitic nematic liquid crystals with respect to the shear direction and the corresponding viscosities are shown in Fig. 1. These viscosities can be expressed in terms of Leslie coefficients (α_1 to α_6), which are used to define the nematic stress tensor [15]. If both α_3 and α_2 are negative, the director aligns at an angle, $\theta = \tan^{-1}\sqrt{\alpha_2/\alpha_3}$ [16–20], and in this case the effective viscosity $\eta_{\mathrm{eff}} \simeq \eta_2$ (Fig. 1). The temperature dependent Miesowicz viscosities of nematic liquid crystals depend on the molecular structures and their intermolecular interactions [2,4,21]. There are a few studies on these viscosity coefficients of nematic liquid crystals with polar molecules [22–24], but there is no systematic investigation of the structural correlation to the Miesowicz viscosities. In this paper, we report on the measurement of temperature variation of two Miesowicz viscosities (η_1 and η_2) of a few low molecular weight nematic liquid crystals with highly polar molecules and a generic chemical structure. Our results reveal the effect of the antiparallel correlation of dipoles and π-electron conjugation of neighboring molecules on the viscosity.

II. EXPERIMENT

We have chosen the following compounds: 4-(*n*-heptyl)-4′-cyanobiphenyl (CB-7), *trans*-4-(4-heptyl-cyclohexyl)-benzonitrile (PCH-7), and *trans*,*trans*-4-*n*-heptyl-4′-cyanobicyclohexane (CCH-7), which have a generic molecular structure. The lengths and widths of all the molecules are almost the same [25]. The chemical structures and phase transition temperatures are shown in Fig. 2. They are low molecular weight nematic liquid crystals and have a generic chemical structure in the sense that all the compounds have the same alkyl chain (-C_7H_{15}) and cyano end group (-CN). There is a systematic variation of structure in the molecular cores; that is, CCH-7 and CB-7 are composed of bicyclohexane and biphenyl, respectively, whereas PCH-7 has one phenyl and one cyclohexane ring. The dielectric anisotropy of all the compounds is positive (see below), i.e., $\Delta\epsilon = \epsilon_{||} - \epsilon_{\perp} > 0$, where the subscripts refer to the directions in relation to the director. Some physical properties, such as dielectric constants, diamagnetic susceptibility, and elastic constants, have already been studied [22,25].

Viscosity measurements were made using a rheometer (Anton Paar MCR 501). Both parallel plate and cone-plate systems induce planar alignment of the director [26], and no additional alignment layer was used. We used cone-plate system with a diameter of 50 mm and a cone angle of 1° to measure η_2 and parallel plate geometry with a plate diameter of 50 mm to measure η_1. In the latter, the cell gap was taken as 75 μm, and an electric field was applied between the bottom and the top plates by using a low friction spring wire [26,27]. The temperature of the sample was controlled by a Peltier temperature controller with an accuracy of 0.1 °C. The heater and the measuring system was kept inside a protective cover for the uniformity of the sample temperature, and no measurable temperature gradient was observed. Calibration of the temperature controller was checked by measuring the rheological properties of some standard liquid crystals. All the measurements were made upon cooling the sample from

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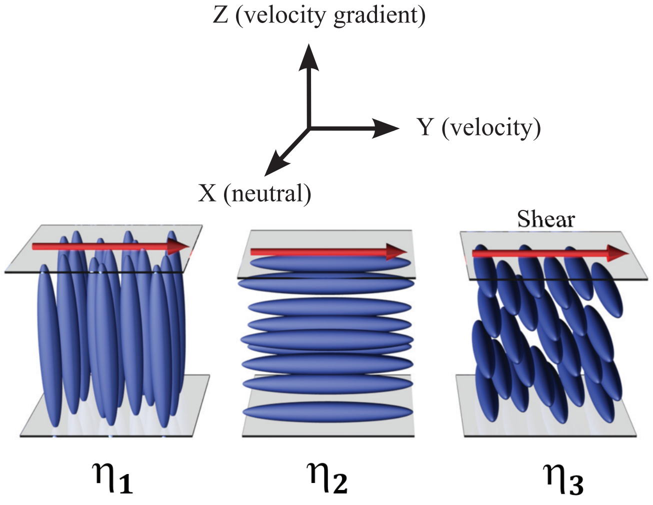

FIG. 1. (Color online) Schematic representation of the three fundamental director orientations of nematic liquid crystals with respect to the shear direction. Miesowicz viscosities corresponding to each orientations are designated by η_1, η_2, and η_3, respectively.

the isotropic phase. To measure electric field dependent viscosity, we used a signal generator (Tektronix AFG3102) and a high voltage amplifier (TEGAM). The frequency of the sinusoidal voltage was 3.11 KHz. The Fréedericksz threshold voltage for the nematic liquid crystal is given by $V_{th} = \sqrt{K_{11}/\epsilon_o \Delta\epsilon}$, where K_{11} is the splay elastic constant [3]. Since the dielectric anisotropy for the present samples is positive and the average molecular orientation is parallel to the direction of the shear, the measured viscosity below V_{th} is η_2. When the applied voltage $V > V_{th}$, the director changes orientation and becomes perpendicular to the shear direction, and we essentially measure η_1. The dielectric anisotropy and birefringence were measured by using a photoelastic modulator, He-Ne laser, and an LCR meter [28–30]. For small angle light scattering measurement a polarized diode laser of 658 nm was directed to the sample. An analyzer, crossed with respect to the polarizer, and a focusing lens adjusted to observe the scattering pattern on the screen were used. A CCD camera was used to record the image at various shear rates [27].

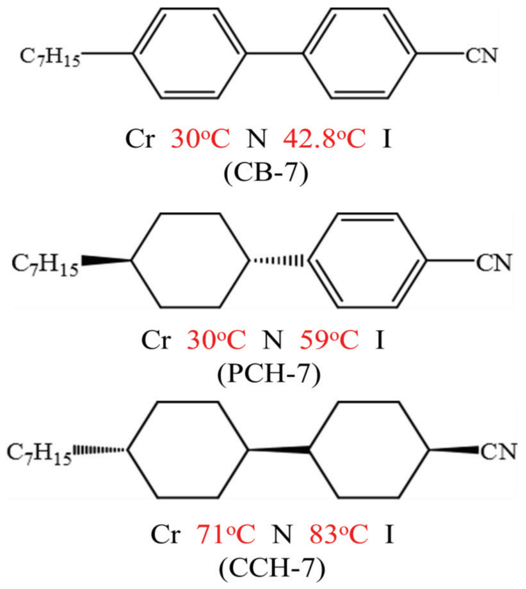

FIG. 2. (Color online) Chemical structures of CB-7, PCH-7, and CCH-7 liquid crystals and their phase transition temperatures.

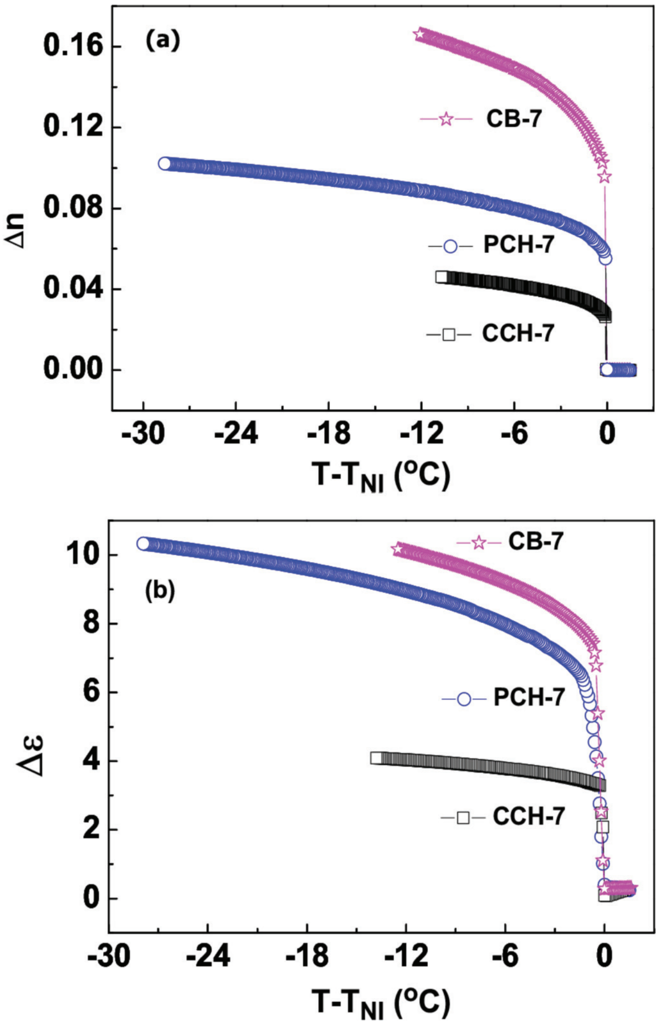

FIG. 3. (Color online) Variation of (a) birefringence Δn and (b) dielectric anisotropy $\Delta\epsilon$ with shifted temperature of CB-7 (open stars), PCH-7 (open circles), and CCH-7 (open squares) liquid crystals. The dielectric constants are measured at a frequency of 4.11 kHz. Cell thickness is 5 μm.

III. RESULTS AND DISCUSSION

First, we present and discuss some nonrheological properties such as the temperature variation of the birefringence Δn and dielectric anisotropy $\Delta\epsilon$ of the compounds in Fig. 3. These properties are essential for understanding the rheological properties discussed in the later sections. We observe that Δn of CB-7 is larger than PCH-7 and CCH-7 [Fig. 3(a)]. For example, at a fixed temperature ($T - T_{NI} = -10$ °C) $\Delta n_{CCH-7} = 0.046$, $\Delta n_{PCH-7} = 0.086$, and $\Delta n_{CB-7} = 0.016$. Thus, merely from the molecular structure point of view (Fig. 2), the replacement of a cyclohexane

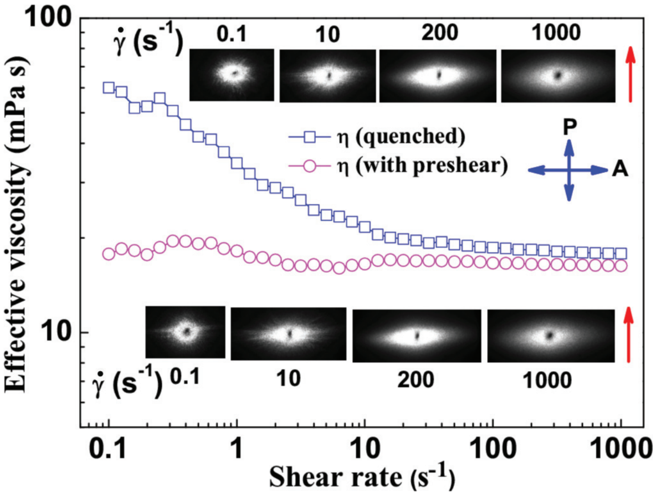

FIG. 4. (Color online) Variation of the effective viscosity as a function of shear rate in the nematic phase of CB-7 in quenched (open squares) and presheared (open circles) samples at 35 °C. P and A are the polarizer and analyzer. Red arrows indicate the direction of shear.

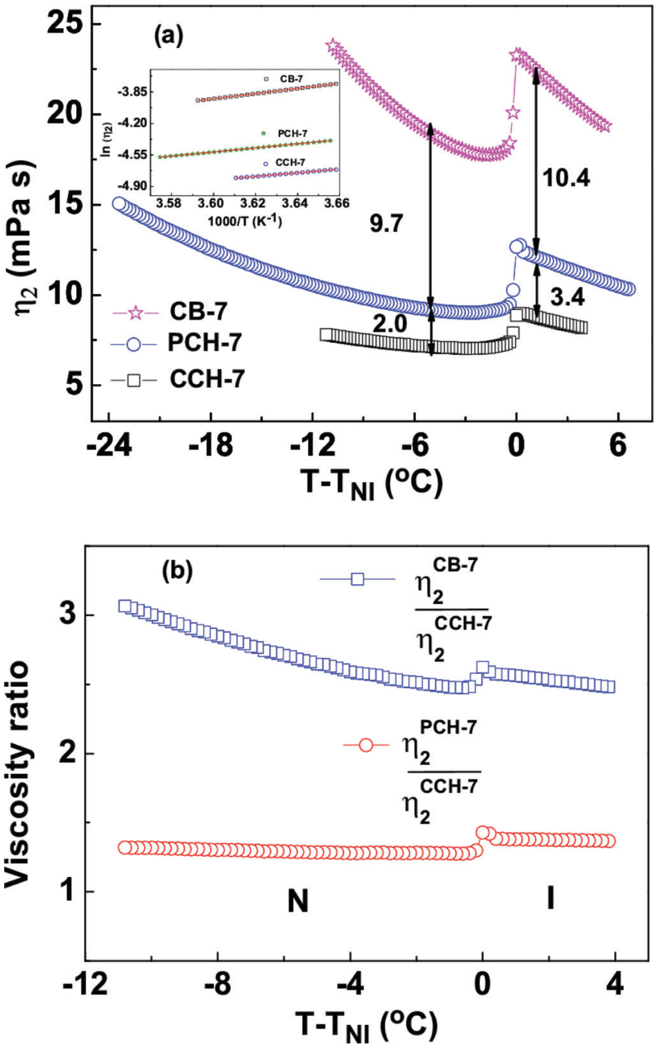

FIG. 5. (Color online) (a) Variation of η_2 as a function of shifted temperature at a fixed shear rate, $\dot{\gamma} = 50$ s^{-1}. The inset shows the variation of the logarithm of η_2 with the inverse of temperature in the isotropic phase. The solid lines are the best fit to the Arrhenius equation. (b) Comparison (ratio) of η_2 of CB-7 and PCH-7 with respect to that of CCH-7.

by an aromatic ring increases Δn by an amount of $\simeq$0.04. This is expected as the intramolecular conjugation length increases from CCH-7 to CB-7. The temperature variation of dielectric anisotropy $\Delta\epsilon$ is shown in Fig. 3(b). We observe similar behavior in the sense that $\Delta\epsilon$ also increases as we go from CCH-7 to CB-7. For example, at a fixed temperature ($T - T_{NI} = -10\,^{\circ}$C) $\Delta\epsilon_{CCH-7} = 4$, $\Delta\epsilon_{PCH-7} = 8.7$, and $\Delta\epsilon_{CB-7} = 9.9$. However, the relative difference of the dielectric anisotropy between two successive compounds is not regular. For example, at the same temperature, $\Delta\epsilon_{PCH-7} - \Delta\epsilon_{CCH-7} = 4.7$ and $\Delta\epsilon_{CB-7} - \Delta\epsilon_{PCH-7} = 1.2$. Although the dipolar group is the same (-CN), the contribution of the polarizability anisotropy is very different due to the different intramolecular conjugation lengths.

To show the effect of shear on the nematic phase, we provide representative rheology plus small angle light scattering (rheo-SALS) data for CB-7. We measured the effective viscosity as a function of the shear rate $\dot{\gamma}$ in the quenched (isotropic to 35 °C) and in the presheared samples (Fig. 4). It is observed that in the quenched sample, viscosity is high at lower shear rates ($<$10 s^{-1}) and shows strong shear thinning behavior at higher shear rates. When the sample is presheared at 500 s^{-1} for about 10 min, the viscosity is constant and does not depend on the shear rate. In fact, beyond $\dot{\gamma} = 50$ s^{-1}, the effective viscosities are almost comparable. The light scattering patterns in two cases in the low shear range are slightly different. For example, in the quenched sample, at $\dot{\gamma} = 0.1$ s^{-1}, the scattering pattern is almost circular. This indicates that in the quenched sample, at the low shear rate, there is a spatial variation of the director which gives polydomain textures. At higher shear rates the circular patterns get elongated perpendicular to the shear direction, and the viscosity shows shear thinning behavior. Since SALS measures the image in the **q** space. The scattering pattern suggests that the polydomain textures are elongated parallel to the shear direction. This enforces realignment of the director along the shear direction. In the presheared sample the scattering pattern at $\dot{\gamma} = 0.1$ s^{-1} is slightly elongated, suggesting that the director is already aligned along the shear direction. The scattering patterns in both cases are almost similar beyond $\dot{\gamma} = 10$ s^{-1}, suggesting that the effective viscosity at a higher shear rate is equal to η_2 (i.e., $\eta_{\text{eff}} \simeq \eta_2$).

In Fig. 5(a), the variation of η_2 of CB-7, PCH-7, and CCH-7 is shown as a function of temperature. The isotropic viscosity η_{iso} of CB-7 is much larger than that of PCH-7 and CCH-7, and they vary in the increasing order, $\eta_{\text{iso}}^{CB-7} > \eta_{\text{iso}}^{PCH-7} > \eta_{\text{iso}}^{CCH-7}$. In addition, η_{iso} increases as the temperature is reduced, and an abrupt decrease is observed at the nematic-isotropic (NI) transition temperature. The temperature dependent η_{iso} of all the compounds increase linearly, and we fitted to the Arrhenius equation, $\eta_{\text{iso}} = \eta_o \exp(-E_a/kT)$, where η_o is the preexponential factor and E_a is the activation energy of the isotropic viscosity. The logarithm of viscosity is plotted against inverse temperature in the inset of Fig. 5(a), and the activation

TABLE I. Molecular weight M, birefringence Δn, dielectric anisotropy $\Delta\epsilon$, activation energy E_a, dipole moment μ, and Kirkwood correlation factor g [25]. Both Δn and $\Delta\epsilon$ are taken from Fig. 3 at $T - T_{NI} = -10\,^\circ\mathrm{C}$.

	Compound		
	CCH-7	PCH-7	CB-7
M	289.5	283.45	277.40
Δn	0.046	0.086	0.161
$\Delta\epsilon$	4.0	8.7	9.9
E_a (eV)	0.17	0.2	0.24
μ (D)	3.5	4.4	4.7
g	0.70	0.60	0.50

energies are listed in the Table I. We notice that they increase in the following order: $E_a^{CB-7} > E_a^{PCH-7} > E_a^{CCH-7}$. The increase of activation energy is an indicator of increasing intermolecular interaction in the isotropic phase. It should be reemphasized that CCH-7 has no aromatic ring, PCH-7 has one aromatic ring, and CB-7 has two aromatic rings. The increase of the number of aromatic rings can enhance the π-π interaction of aromatic cores (π-electron conjugation) among neighboring molecules, and hence a stronger intermolecular interaction is expected. Thus the increase in isotropic viscosity in compounds having phenyl rings can be attributed to the effect of enhanced π-electron conjugation compared to compounds with cyclohexane because in the latter there is no π-electron at the core.

In the nematic phase, at a fixed temperature, η_2 also increases in the same order, i.e., $\eta_2^{CB-7} > \eta_2^{PCH-7} > \eta_2^{CCH-7}$ [Fig. 5(a)]. Further, it is interesting to note that the relative differences among the viscosities of CCH-7, PCH-7, and CB-7 are reduced in the nematic phase compared to those in the isotropic phase. For example, at $T - T_{NI} = -1\,^\circ\mathrm{C}$, $\eta_{\mathrm{iso}}^{PCH-7} - \eta_{\mathrm{iso}}^{CCH-7} = 3.4$ mPa s and $\eta_{\mathrm{iso}}^{CB-7} - \eta_{\mathrm{iso}}^{PCH-7} = 10.4$ mPa s. In the nematic phase, for example, at $T - T_{NI} = -5\,^\circ\mathrm{C}$, $\eta_2^{PCH-7} - \eta_2^{CCH-7} = 2$ mPa s and $\eta_2^{CB-7} - \eta_2^{PCH-7} = 9.7$ mPa s. We compare η_2 of CB-7 and PCH-7 with respect to CCH-7 and show their temperature variation in Fig. 5(b). It is noticed that $\eta_2^{CB-7}/\eta_2^{CCH-7}$ is much larger than (almost double) $\eta_2^{PCH-7}/\eta_2^{CCH-7}$, and the former increases with decreasing temperature. This suggests that the viscosity enhancement is not linear with the number of aromatic rings (replacing cyclohexane rings), keeping the other parts of the molecule same. The molecular weights of the compounds are slightly different (Table I) and hence are not expected to contribute very much to the viscosity. On the other hand, the NI phase transition temperatures are very different ($T_{NI}^{CCH-7} > T_{NI}^{PCH-7} > T_{NI}^{CB-7}$), which will have a significant effect on the viscosity in the sense that the viscosity is lower at higher temperature. Nevertheless, the large differences in η_2 among the compounds and their temperature dependence cannot be accounted for based on this fact alone. To understand this, we present some useful data in Table I, i.e., the birefringence Δn, dielectric anisotropy $\Delta\epsilon$, dipole moment μ, and Kirkwood correlation factor g,

$$g = (\mu_{\mathrm{eff}}/\mu)^2, \tag{1}$$

where μ_{eff} is the effective dipole moment as calculated from the Kirkwood-Froehlich equation [31] using dielectric data and μ is the dipole moment of a single molecule. Both Δn and $\Delta\epsilon$ are positive and increase from CCH-7 to CB-7 as expected because aromatic rings contribute more to the birefringence than cyclohexanes, as discussed earlier. The dipole moment μ of the molecules obtained from Ref. [25] varies in the order $\mu^{CB-7} > \mu^{PCH-7} > \mu^{CCH-7}$. It should be mentioned (Fig. 2) that the charge separations of the molecules in the ground state are very different [25]. For example, the conjugation between the two aromatic rings in CB-7 is only partial because the torsional angle between the planes in the ground state is about 35°. The cyano group is conjugated with one aromatic ring in PCH-7 and unconjugated in the case of CCH-7; hence there is no delocalization of the electrons, and as a result there is a systematic variation in the dipole moments (see Table I). This gives rise to molecular association, which is usually measured in terms of the Kirkwood correlation factor.

The Kirkwood correlation factors of these compounds were measured by Schad and Osman just above the NI transition temperature [25]. They are presented in Table I for comparative discussion. g less than 1 for all compounds suggests the existence of antiparallel correlation of the molecular dipoles even in the isotropic phase. In addition, we notice that $g^{CB-7} < g^{PCH-7} < g^{CCH-7}$. This suggests that the strength of the antiparallel correlation of dipoles is stronger in CB-7 than in both PCH-7 and CCH-7. In the nematic phase the density increases, the decrease of intermolecular distance, and the antiparallel correlation is even stronger, which is reflected in terms of a reduction of the average dielectric constant $[\bar{\epsilon} = (\epsilon_{||} + 2\epsilon_{\perp})/3]$ [25]. In addition to that causes π-electron conjugation of the aromatic rings of neighboring molecules. In the case of CB-7, due to the effect of intermolecular π-electron conjugation and dipolar antiparallel correlation, the molecules behave like a dimer because of almost complete overlap of the aromatic rings, whereas CCH-7 behaves like a monomer due to the lack of π-electron conjugation [2]. Thus the relative reduction of η_2 in the nematic phase compared to the isotropic viscosity η_{iso} can be attributed to the molecular association due to the antiparallel correlation of dipoles and intermolecular π-electron conjugation.

To measure η_1, first, we measured the electric field dependent viscosity at a fixed temperature in the nematic phase [Fig. 6(a)]. It is observed that the effective viscosity increases with applied electric field for all the samples and saturates beyond about 80×10^4 V/m. Since the dielectric anisotropy is positive (i.e., $\Delta\epsilon > 0$), beyond the Fréedericksz threshold field the director tends to orient along the electric field direction. However, the shear field tends to align the director along the shear direction. Thus there is a competing effect of these two force fields on the director orientation. However, at a steady shear rate, if the electric field is strong enough the director is finally orientated along the electric field direction. As a result the equilibrium orientation of the director is perpendicular to the shear direction. Thus, essentially, we measure η_1 at high electric field ($>80 \times 10^4$ V/m). In Fig. 6(b), we show the variation of η_1 as a function of temperature for all the compounds. We notice that apart from a sharp increase at the nematic-isotropic transition, η_1 increases almost linearly as the temperature is reduced for all the compounds.

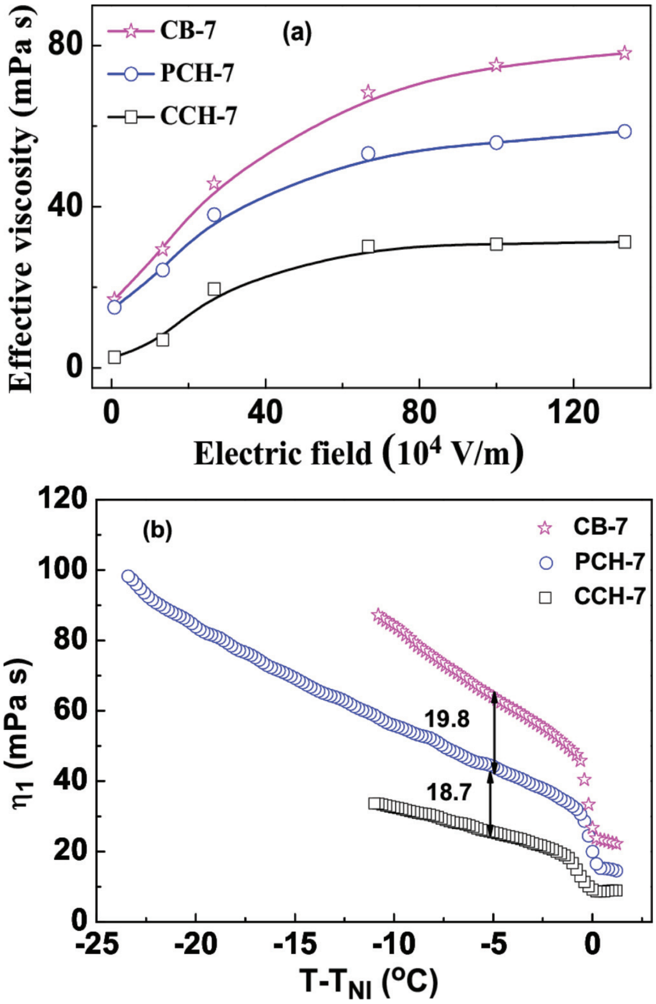

FIG. 6. (Color online) (a) Variation of effective viscosity η_{eff} at a fixed shear rate, $\dot{\gamma} = 50\ \text{s}^{-1}$, as a function of applied field at a frequency of 3.11 kHz. At high field (beyond about 80×10^4 V/m) $\eta_{\text{eff}} = \eta_1$. (b) Variation of η_1 as a function of shifted temperature and a fixed electric field of 133×10^4 V/m ($\dot{\gamma} = 50\ \text{s}^{-1}$).

At a fixed temperature, in all the compounds, $\eta_1 > \eta_2$, as expected. In the nematic phase, the relative differences of η_1 among the compounds are almost comparable. For example, at $T - T_{NI} = -5\,^\circ\text{C}$, $\eta_1^{PCH-7} - \eta_1^{CCH-7} = 18.7$ mPa s, and $\eta_1^{CB-7} - \eta_1^{PCH-7} = 19.8$ mPa s. The viscosity anisotropy $\Delta\eta$ ($= \eta_1 - \eta_2$) obtained from Figs. 5(a) and 6(b) is presented in Table II. It is noticed that $\Delta\eta$ increases almost linearly with Δn from CCH-7 to CB-7. As far as the molecular structure is concerned (Fig. 2), it seems that replacing a cyclohexane by an aromatic ring increases $\Delta\eta$ by 15 to 20 mPa s. In the case of η_2 the director is parallel, and in the case of η_1, the director is perpendicular to the shear direction. In the rheometer, the bottom plate is fixed, and the top plate is rotating; hence the velocity gradient decreases from top to bottom. From the microscopic point of view this will cause a net downward flow of momentum per unit time and area which is proportional to the viscous frictional force. The frictional force depends on molecular associations, which are due to the intermolecular conjugation and permanent dipole moment. Thus the molecular associations contribute not only to the dielectric and optical properties but also to the Miesowicz viscosities.

TABLE II. Viscosity anisotropy $\Delta\eta$ ($= \eta_1 - \eta_2$) obtained from Figs. 5(a) and 6(b) at $T - T_{NI} = -10\,^\circ\text{C}$.

	Compound		
	CCH-7	PCH-7	CB-7
$\Delta\eta$ (mPa s)	25	45	62

IV. CONCLUSIONS

We have measured the temperature dependence of two Miesowicz viscosities (η_1 and η_2) for a few highly polar nematic liquid crystals with a systematic variation in the molecular structure. We showed that nematic compounds with more aromatic rings and a lower Kirkwood correlation factor have larger viscosities. A low Kirkwood correlation factor is an indication of a strong antiparallel correlation of the dipoles. The temperature variation of η_2 reveals strong intermolecular associations that result from both the π-electron conjugation of neighboring molecules and the antiparallel correlation of molecular dipoles. Compared to molecular associations, the intramolecular conjugation length seems to be more significant in determining η_1. Finally, our measurements established that apart from the optical and dielectric properties, molecular associations of highly polar molecules in nematic liquid crystals significantly affect the rheological properties.

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