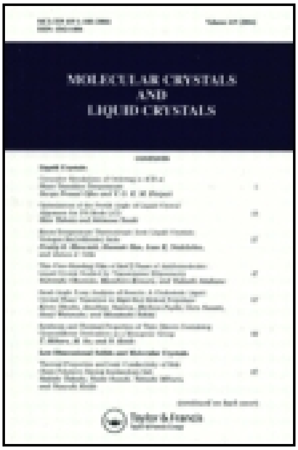

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Rheological Study on the Shear-Induced Structural Changes in Liquid Crystalline Phases of Octylcyanobiphenyl

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In the nematic (Ne) and the smectic A (SmA) phases of octylcyanobiphenyl (8CB), a steady shear flow induces various dynamical structures which do not appear in the absence of the shear flow. To make clear the relationship between these structures and the rheological properties, some rheological measurements, including the electrorheological (ER) effect, which is the effect of an electric field on rheology, are made. We find that the temperature dependence of the viscosity, the fluidity, and the ER effect show characteristic behaviors which can be understood on the basis of the reported shear-induced structures. These rheological properties are discussed in terms of the orientational changes of the director and/or the smectic layer and the critical effect of the Ne–SmA phase transition.

Keywords: rheology, viscosity, liquid crystal, nematic phase, smectic phase, phase transition, shear-induced structural change, electrorheological effect

INTRODUCTION

Rheological studies on various liquid crystalline phases have shown that characteristic rheological and electrorheological (ER) properties are observed depending on the respective orientational and/or positional orders of the director and the layer [1–3]. Of various liquid crystalline phases, rheological properties are well understood in the Ne phase [4–6]. In this phase, the steady-shear flow gives rise to a flow alignment of the director if

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the Leslie coefficients fulfill a condition of $\alpha_2/\alpha_3 > 0$; the director aligns in the shear plane containing the velocity ($\mathbf{v}$) and the velocity gradient ($\nabla\mathbf{v}$) directions, with the flow alignment angle θ given by $\tan^{-1}(\alpha_2/\alpha_3)$ [4,7]. Such a flow alignment is modified if an electric field is applied, making the viscosity increase or decrease depending on whether the dielectric anisotropy $\Delta\varepsilon$ is positive or negative [8–10]. The representative result for the former is 5CB [9] and for the latter MBBA [8]. These ER behaviors are understood to occur as a result of a field-induced orientational change of the director.

In the case that $\alpha_2/\alpha_3 < 0$, the flow alignment of the director is not possible since θ does not have a solution. For such a case, some theoretical [7,11–13] studies suggest that instead of the flow alignment a tumbling motion of the director occurs in the shear plane normal to the neutral axis, i.e., a plane composed of velocity and velocity-gradient directions. Experimentally, the tumbling motion of the director is ascertained in some transient stress measurements on 8CB [14,15], which undergoes the Ne–SmA phase transition and has a wide temperature region characterized by $\alpha_2/\alpha_3 < 0$ in the Ne phase [16]. From a structural study on 8CB [17] it is clarified that under a steady-shear flow a successive structural change occurs in the Ne and SmA phases as described below. In Figure 1, geometry specifying the direction of the shear deformation and three orientations of the director under a shear flow are given. In the temperature region where $\alpha_2/\alpha_3 < 0$, the director exhibits a precessional motion characterized by $n_y(t)^2/n_{y0}^2 + n_z(t)^2/n_{z0}^2 = 1$. Here, $n_y(t) = n_{y0}\cos(\omega_0 t)$ and

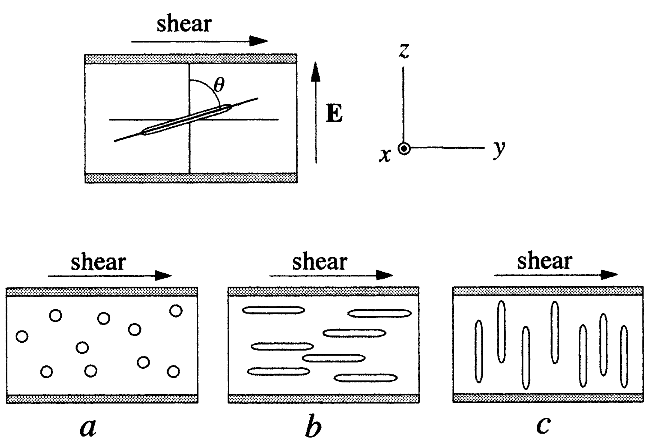
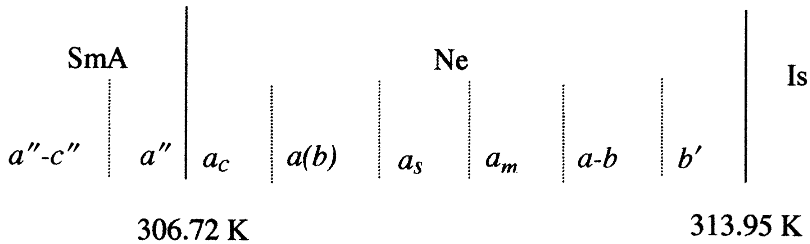


FIGURE 1 Coordinate system specifying the directions of the shear deformation, the electric field, and schematic structures (a, b, and c) under the shear deformation in Ne phase. In the SmA phase, a layer perpendicular to the director, which is not given in this figure, exists.

$n_z(t) = n_{z0}\sin(\omega_0 t)$ are y and z components of the director $\mathbf{n}(t)$ precessing about the x axis with an angular frequency of ω_0. The precessional motion changes its behavior with decreasing the temperature, and it is reported that the following structures are induced in the Ne and the SmA phases:



Of these structures, b', $a-b$, a_m, a_s, $a(b)$, and a_c are those in Ne phase and a'' and $a''-c''$ are those in SmA phase. In the Ne phase, α_2/α_3 is positive in the temperature region just below the Ne–Isotropic(Is) phase transition point, but becomes negative if the temperature is lowered toward the SmA–Ne phase transition point. In the temperature region of $\alpha_2/\alpha_3 > 0$, the structure is b' where the director aligns in the $y-z$ plane with its flow alignment angle specified by $\tan^{-1}(\alpha_2/\alpha_3)$. With decreasing temperature, $a-b, a_m, a_s, a(b)$, and a_c structures are successively induced. The $a-b$ structure is characterized by the coexistence of a and b structures. While in $a_m, a_s, a(b)$, and a_c structures, the mean direction of the director is along the x axis, and some elliptic or symmetric precessional motion of the director occurs with the amplitudes of the precessional motion, n_{y0} and n_{z0}, being different among them: $a_m, n_{y0} >> n_{z0}, a_s : n_{y0} = n_{z0}; a(b); n_{y0} < n_{z0}$; and $a_c, n_{y0} << n_{z0}$. In the SmA phase, the orientational order of the director is accompanied by a positional order of the layer perpendicular to the director, and following structures are induced by a shear deformation: a'', the director aligns along the x axis with a layer in $y-z$ plane; and $a''-c''$, a'' structure coexists with c'' structure in which the director aligns along the z axis with a layer in the xy plane. It is reported that the structural change from a'' to $a''-c''$ structure depends on the shear rate.

In our previous work [18], rheological properties of 8CB were studied, but it was not aimed to clarify the relationship between the shear-induced dynamical structures and the rheological properties. In the present study, precise measurements of the viscosity, rheology (shear stress versus shear rate), and ER effect are made as a function of temperature to make clear how the shear-induced structures mentioned above are responsible for the rheological properties. In temperature dependence of the viscosity, the shear stress versus shear rate relationship, and the ER effect, characteristic results which reflect the shear-induced structural changes are recognized. These results are discussed on the basis of the orientational changes of the director and/or the smectic layer and the critical effect of the Ne–SmA phase transition.

EXPERIMENTAL

The liquid crystal 8CB was obtained from Merck (Germany) and was used without further purification. The SmA–Ne and the Ne–Is phase transition points, which are determined from the temperature dependence of the viscosity, were 306.6 K and 313.5 K, respectively. The viscosity, the shear stress versus shear rate relationship, and the ER effect were measured with a viscometer of a concentric double cylinder type [19]. To observe the ER effect, high voltages of 200 Hz were applied to the gap (1 mm) between the inner and the outer cylinders to generate the electric field of a few kV mm^{-1} along the velocity gradient direction, i.e., perpendicular to the velocity (flow) direction. For supplying ac high voltages, a small ac voltage from an oscillator (1946, NF Electric Instruments, Japan) was amplified to a few kV with a high voltage amplifier (664, Trek KK, USA). In order to measure the temperature dependence of the rheological properties, the temperature of the sample was controlled to within ± 0.1 K using a heater and a thermocouple (chromel-constantan) attached on the outer cylinder. Throughout this article the amplitude of the ac electric field is expressed in rms.

RESULTS AND DISCUSSION

In Figure 2, temperature dependence of the viscosity measured at a shear rate of 527.2 s^{-1} is given. In this figure the temperature regions of the respective shear-induced structures are also specified. With decreasing temperature from the Is phase, the viscosity decreases and becomes temperature independent in the b' region. Such a behavior has been observed in other Ne liquid crystals characterized by $\alpha_2/\alpha_3 > 0$ [8,9], indicating that a flow alignment of the director occurs in the yz plane, with the flow alignment angle θ given by $\tan^{-1}(\alpha_2/\alpha_3)$. With further decrease in temperature, a monotonous increase of the viscosity is recognized in the $a-b$ region. Considering the well-known property that the viscosity of the a structure is higher than that of the b structure and that the observed viscosity at the

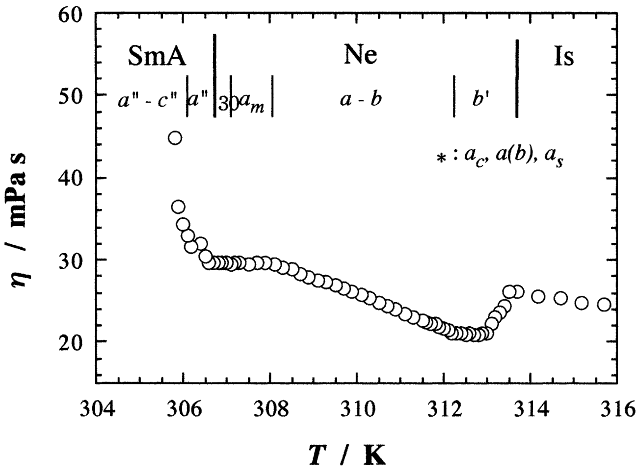


FIGURE 2 Temperature dependence of the viscosity (η) measured at a shear rate of $527.2\,s^{-1}$. Temperature regions of the respective phases and the shear-induced structures are also given.

lowest temperature end of the $a - b$ region is neary equal to the viscosity of the a structure [6], we can suggest that the fraction of the a structure monotonously increases with decrease in temperature. In the $a_m, a_s, a(b)$, and a_c regions, the viscosity is almost temperature independent, indicating that the viscosity is mainly governed by the mean orientation of the director, which is along the x axis, and is scarcely influenced by the change of the precessional motion. In the SmA phase, after a hump at the transition temperature from the a'' structure to the $a'' - c''$ structure the viscosity in the $a'' - c''$ region steeply increases with decrease in temperature.

In order to make clear the fluidity of each structure, shear stress versus shear rate relationship is measured at some temperatures. The result in the Ne phase is given in Figure 3 and that in SmA phase is given in Figure 4. Figure 3 shows that the shear stress is almost proportional to the shear rate without depending on the change of the structure, suggesting that the flow in the Ne phase is Newtonian and is not affected by the orientational change of the director and the difference in the precessional motion.

In the SmA phase, an interesting rheological property is observed, as depicted in Figure 4. As obvious from the result at 306.5 K, the flow is non-Newtonian at lower shear rates, but changes to Newtonian at higher shear rates. Such a fluidity change occurs at higher shear rates if the temperature is decreased. It is plausible to consider that in the a'' region the simple structure characterized by director aligning along the x-axis gives rise to a

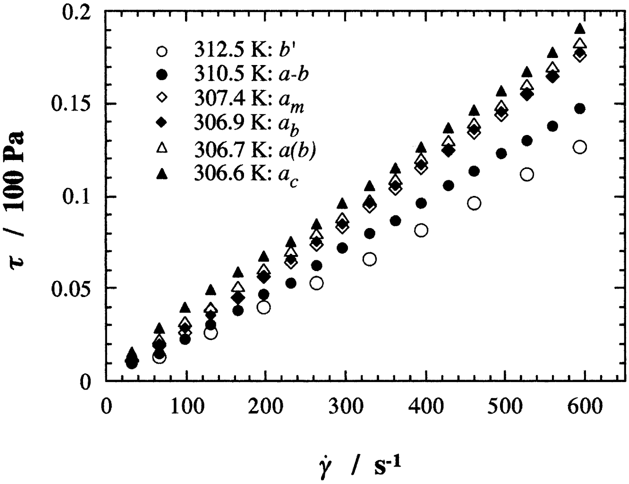


FIGURE 3 Shear stress (τ) versus shear rate ($\dot{\gamma}$) in the Ne phase.

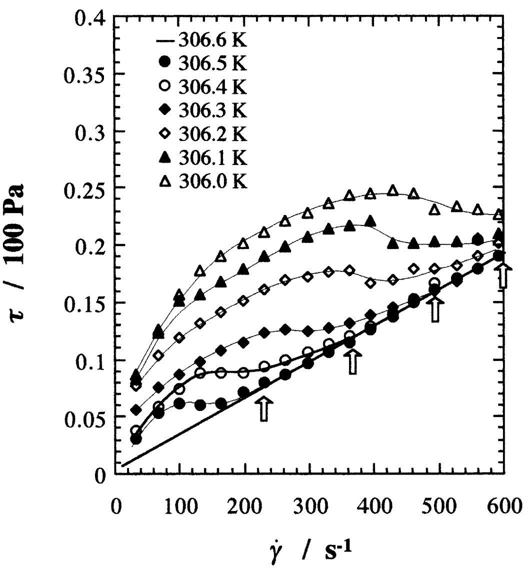


FIGURE 4 Shear stress (τ) versus shear rate ($\dot{\gamma}$) in the SmA phase. As a reference, Newtonian behavior at 306.6 K (Ne Phase) is given (straight line). Arrows specify the change from non-Newtonian to Newtonian flow.

Newtonian flow, but in the $a'' - c''$ region the coexistence of the a'' and the c'' structures leads to a non-Newtonian flow. The observed fluidity change can thus be understood to occur as a consequence of the structural change from the $a'' - c''$ to the a'' structure. To make clear the shear rate and the temperature dependence of the fluidity (structural) change, the shear rate at which the fluidity changes from non-Newtonian to Newtonian is plotted at each temperature in Figure 5. This figure shows that the shear-induced structural change from the $a'' - c''$ structure to the a'' structure is dependent on both the shear rate and the temperature. This diagram is almost consistent with that obtained from the X-ray measurement [17].

The rheological properties are modified if an electric field is applied. The results of such an ER effect in the Ne and the SmA phases are given in Figures 6 and 7, respectively. At 312.8 K (b' region), a monotonous increase of the viscosity is observed when the amplitude of the electric field along the z-axis is increased. This is interpreted to occur as a consequence of the field-induced orientational change of the director in the yz plane from the direction near the y-axis (b' structure) to the z-axis, in a similar manner to the case of 5CB [9]. If the temperature is decreased to $a - b, a_m, a_s, a(b)$, and a_c regions, a two-step increase of the shear stress is recognized. It is theoretically clarified that even in a condition of $\alpha_2/\alpha_3 < 0$, a flow alignment of the director is possible in the yz plane if an electric field exceeding a threshold magnitude is applied along the z-axis with the flow alignment angle given by $\tan\theta^{-1} = 1/2\{\Delta\varepsilon E_0^2/\alpha_3\dot{\gamma} - [(\Delta\varepsilon E_0^2/\alpha_3\dot{\gamma})^2 + 4\alpha_2/\alpha_3]^{1/2}\}$ [7,9]. Here $\Delta\varepsilon$ is the

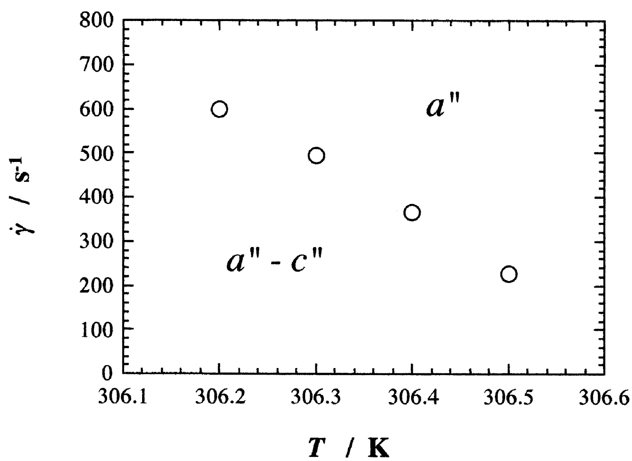


FIGURE 5 Shear rate ($\dot{\gamma}$) and temperature dependence of the structural change from the $a'' - c''$ to the a'' structure.

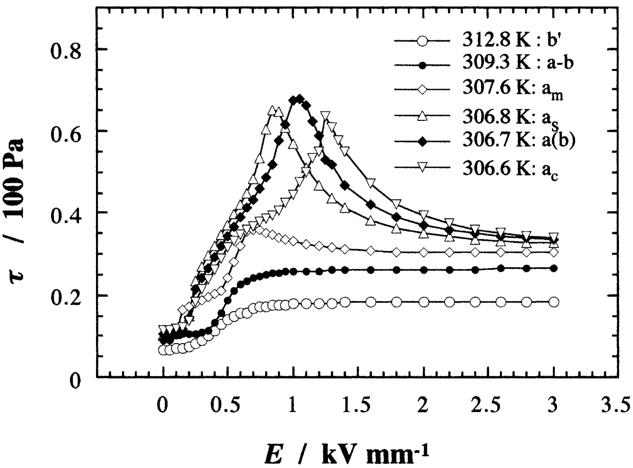


FIGURE 6 Electric field dependence of the shear stress (τ) in the Ne phase. Shear rate: $329.5\,s^{-1}$. Electric field frequency: 200 Hz.

dielectric anisotropy, E_0 the amplitude of the electric field, and $\dot{\gamma}$ the shear rate. This indicates that the second step at higher fields is due to the flow alignment of the director in the *yz* plane. The first step at lower fields can be understood as a step where the director along the *x*-axis, or

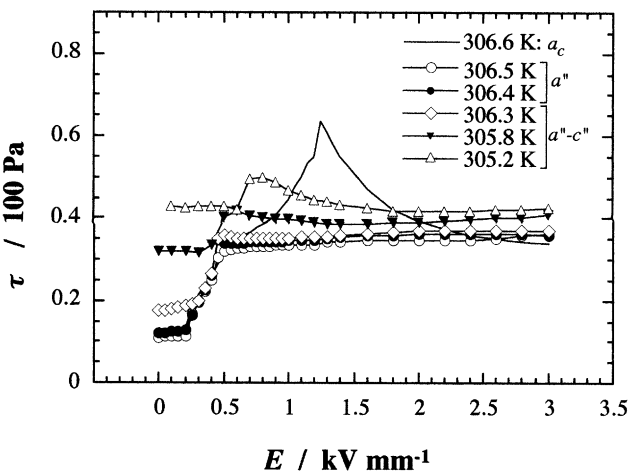


FIGURE 7 Electric field dependence of the shear stress (τ) in the SmA phase. The data at 306.6 K (Ne Phase) is given for comparison. Shear rate: $329.5\,s^{-1}$. Electric field frequency: 200 Hz.

precessing about the x axis, changes its direction toward the yz plane. In addition to the above-mentioned results, a peak is observed in the second-step region. The peak becomes apparent around 308 K and grows if the temperature is lowered to the Ne–SmA phase transition point, with its peak position shifting to higher electric fields. The appearance of such an anomalous peak can be explained in terms of the critical increase of the Leslie coefficient α_1 as has been already discussed in our previous work [18]. In the SmA phase, The ER effect dramatically changes (Figure 7); the shear-stress peak observed in the Ne phase completely disappears, as shown in the result at 306.5 K. This result indicates that the critical anomaly of α_1 observed in the Ne phase is not present in the SmA phase. The two-step increase of the shear stress observed in the Ne phase remains even in this phase, which can be understood as the same mechanism as that in the Ne phase.

The rheological properties in the liquid crystalline phases of 8CB can thus be consistently explained on the basis of the shear-induced structures suggested by the X-ray study and can be summarized as follows: (1) the temperature dependence of the viscosity is sensitive to the change of the mean direction of the director but not to the change of the precessional motion of the director; (2) the fluidity in the Ne phase is Newtonian without being affected by the precessional motion of the director; (3) the shear-induced structural change in the SmA phase is accompanied by a change of the fluidity and is dependent on shear rate and temperature; and (4) in the temperature region of $\alpha_2/\alpha_3 < 0$ (Ne phase) and SmA phase, the application of the electric field induces a two-step increase of the shear stress, which is characterized by the two-step orientational change of the director. In our recent rheological measurements on 8OCB(4-n-octyloxy-4′-cyanobiphenyl), which show the same phase sequence with 8CB, similar results are obtained in temperature-dependence of viscosity, fluidity, and ER effect. Thus we can suggest that the rheological properties obtained for 8CB are general properties of the liquid crystals exhibiting the Is–Ne–SmA phase sequence.

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