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Visco-elastic properties of reentrant nematic liquid crystalline mixtures

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The visco-elastic properties for binary mixtures of 4-*n*-hexyloxy-4'-cyanobiphenyl (6OCB) and 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB) are investigated in detail by a light scattering technique. The mixtures exhibit a reentrant nematic (RN) phase between the smectic A (SmA) and crystal phases in the range 22.0–29.5 wt % of 6OCB. The viscosity and the elastic constant increase with cooling in both the nematic and reentrant nematic phases. It is also found that the mixtures exhibit anomalously large values of viscosity and elastic constant near the phase transition, i.e. a pretransitional phenomenon can be observed. The activation energy for viscosity is smaller in the RN phase than in the ordinary nematic phase appearing at higher temperatures, while the normalized elastic constant (defined as the ratio of the elastic constant to the square of the dielectric anisotropy) is larger. Moreover, the visco-elastic behaviour depends on the specific time during which the sample has been kept in the SmA phase. These results confirm that the SmA phase has a strong influence on the formation of molecular aggregates, which plays an important role in the reentrant phenomenon of these systems.

1. Introduction

An unusual sequence of mesophases can be observed for certain weight fractions of binary liquid crystalline mixtures of 4-*n*-hexyloxy-4'-cyanobiphenyl (6OCB) and 4-*n*-octyloxy-4'-cyanobiphenyl (8OCB) [1]. Upon lowering the temperature, the mixtures undergo transitions to successive phases: isotropic (I), nematic (N), smectic A (SmA), and nematic again, followed by crystal (Cr). The lower temperature nematic phase is frequently termed the reentrant nematic (RN) phase in analogy to similar effects which have been observed in superconductors and helium. It has been reported that the RN phase exhibits no macroscopic difference from the ordinary high temperature N phase. Such an unusual phase formation was originally reported by Cladis for the binary mixture of *p*-[(*p*-hexyloxybenzylidene)amino]benzoinitride (HBAB) and *N*-*p*-cyanobenzylidene-*p*-*n*-octyloxyaniline (CBOOA) [2]. Since this first investigation, several binary mixtures have been found to exhibit a similar phase sequence. Moreover such sequences can be observed in some single-component systems on the application of pressure [3, 4].

Such reentrant phenomena have attracted much attention from researchers in the fields of physics, chemistry and materials science. However, the mechanism for the occurrence of the reentrant phenomena is still unclear,

whereas the phase transitional behaviour has been investigated in detail for birefringence [5] and heat capacity [6], in comparison with values obtained from empirical or theoretical models. Structural analyses by X-ray diffraction (XRD) have revealed that liquid crystalline molecules having a strong dipole moment at a chain end may aggregate antiparallel to each other to form dimers [1, 7, 8]. The XRD patterns in the vicinity of the N–SmA and SmA–RN transitions of such mixtures have suggested that the N and RN phases could be identical also on a microscopic scale [4]. The static and/or dynamic properties have been studied by using proton [9, 10], deuteron [11–14] and C¹³ [15] NMR, ESR [16, 17], and neutron scattering [18]. On the visco-elastic properties of such reentrant mixtures, a few studies have been reported, e.g. the rotational viscosity [19, 20] and the bend elastic constant [2].

Various theoretical models have been reported on the basis of competing interactions to account for the occurrence of reentrant phenomena in liquid crystals [4, 7, 21–25]. In particular, the interpretation of experimental data has been based on the coexistence of monomers and dimers. Recently a molecular field theory has been used to link the occurrence of reentrant phases to the concentration of dimers [26]. Furthermore a more compelling physical argument for reentrance in cyano compounds has been made on the basis of the spin-gas transition model [27]. An excellent review article has

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been published to give a recent summary of reentrant phenomena in liquid crystals from a physical perspective [28].

For the 6OCB–8OCB mixtures, there has been a high-resolution X-ray scattering study [7]. Moreover a birefringence study [5] suggests that N–SmA and SmA–RN phase transitions are identical in their characteristics. Conversely, weight fraction dependence of the viscosity and the activation energy suggests that the dynamics in the ordinary nematic phase is influenced by the smectic order fluctuations remnant in the system due to the underlying smectic phase, [20]; i.e. the RN phase could be dynamically different from the ordinary N phase.

This article presents the visco-elastic properties of a reentrant liquid crystal mixture, with a view to understanding the occurrence of the reentrant nematic phase. The visco-elastic constants were measured by the Rayleigh light scattering method. This method is based on the detection of small deformations of the director orientation caused by a cooperative motion of thermally fluctuating molecules [29–34]. Since the technique utilizes such small spontaneous deformations instead of rather large deformations induced by strong external fields such as electric or magnetic fields, we can disregard unnecessary components of director deformations, surface effects and complex flows accompanying the director reorientation. Therefore the values obtained may reflect the properties peculiar to the objective liquid crystal materials, and hence they can clarify the difference between the N and RN phases in detail.

2. Experimental

2.1. Preparation of sample cells

The liquid crystalline materials used in this experiment were two types of 4-alkoxy-4'-*n*-cyanobiphenyl abbreviated 6OCB and 8OCB. Both compounds were purchased from Merck Co., Ltd. and mixed at various concentrations (weight fractions) to form binary liquid crystalline systems.

The substrates used were ITO-coated glass slides that had been washed sequentially with acetone and pure water. For a homeotropic alignment cell the substrate surfaces were treated with a silane coupling agent AY-43-021 (Toray Dow Corning Silicone, Co., Ltd) which has a long alkyl chain, whereas for homogeneous alignment the surface was coated with Polyimide B (Nissan Chemicals, Co., Ltd) by the dip-coating method and rubbed with a cloth in one direction.

The liquid crystalline mixtures were assembled in sandwich-type cells constructed with the two surface-treated glass substrates and with two small pieces of polyester film of thickness 25 μm placed between the two substrates as spacer. Capillary action gave rise to a

spontaneous flow of the liquid crystal into the small space between two substrates, resulting in a sample cell with an appropriate alignment of liquid crystal molecules without air bubbles.

2.2. Measurements

The mesophase transition temperatures of the liquid crystalline mixtures were determined by optical microscopy with a Mettler FP82HT hot stage regulated by a Mettler FP80 controller. Phase assignments were made by microscopic observation of the optical textures obtained on cooling from the isotropic liquid.

Dielectric constants of the binary liquid crystals were measured at 1.0 kHz using a YHP-4192A Impedance Analyzer (Yokokawa Hewlett Packard, Co., Ltd); the parallel and perpendicular components of the dielectric constants were obtained from the capacitances of the homeotropically and homogeneously aligned cells, respectively. The amplitude of the applied electric field was regulated to be 12 kV m⁻¹.

For the determination of the visco-elastic constants we utilized the Rayleigh light scattering method [29–36]. The optical measurement system was similar to that used for previous studies [33, 35, 37] on the Rayleigh line intensity and the spectral width which is associated with the relaxation frequency. The light sources were the 448 nm line of an argon ion laser and the 633 nm line of a He-Ne laser. The signal scattered by the liquid crystal was detected with a photomultiplier. The data of the photoelectron pulses obtained were digitized and stored in the memory of a personal computer on the basis of the photon counting technique. All of the measurements were performed at a constant cooling rate.

The twist viscosity η_{twist} and elastic constant k_{22} were determined by the following method. The twist visco-elastic ratio, $k_{22}/\eta_{\text{twist}}$, can be determined from the relaxation frequency Γ of the depolarized Rayleigh line intensity from the homeotropic cell. Almost ideal homodyne detection can be achieved to measure the twist deformation mode by tilting the homeotropically-aligned cell with respect to the incident light around the axis perpendicular to the scattering plane. We chose a scattering geometry where the polar angle was 0°, the azimuthal angle -8° and the scattering angle 8° to determine the visco-elastic constants for twist deformation. Separation of the viscosity η_{twist} and elastic constant k_{22} from the relaxation frequency was achieved by application of an external electric field to the cell [31, 34],

$$\Gamma = \frac{k_{22} q_{\perp}^2}{\eta_{\text{twist}}} + \frac{\epsilon_0 \Delta\epsilon}{d^2 \eta_{\text{twist}}} V^2 \quad (1)$$

where q_{\perp} is the component of the scattering vector \mathbf{q} perpendicular to the director, ϵ_0 is the dielectric constant of vacuum, $\Delta\epsilon$ is the dielectric anisotropy of the

liquid crystalline mixture, d is the thickness and V is the applied voltage. The twist viscosity η_{twist} is equal to the rotational viscosity γ_1 , which can be expressed as the difference of the two components of Leslie coefficients, $\alpha_3 - \alpha_2$ [38].

3. Results and discussion

3.1. Phase diagram

The mixtures were miscible at any weight fractions. Figure 1 shows a phase diagram for the binary liquid crystal system of 6OCB and 8OCB. This diagram indicates that mixing of the two liquid crystals induces an RN phase at a weight fraction between 21.0 and 29.5 wt % of 6OCB. An SmA phase appears between the N and RN phases at a weight fraction below 29.5 wt % of 6OCB, while at a larger weight fraction of 6OCB the mixture exhibits only an ordinary N phase between the I and Cr phases. Below 21.0 wt % of 6OCB, no reentrant phenomenon was observed. This diagram is closely consistent with those observed by other researchers [5, 7, 20].

It should be noticed that the phase diagram might be incomplete in view of thermodynamics, because the observation for the phase diagram was performed in the time range of several hours. If the transitions or the phase separation occur slowly, the correct phase diagram may differ from our results. The properties of the RN phase have actually been varied depending on the cooling rate; details will be described in §3.6.

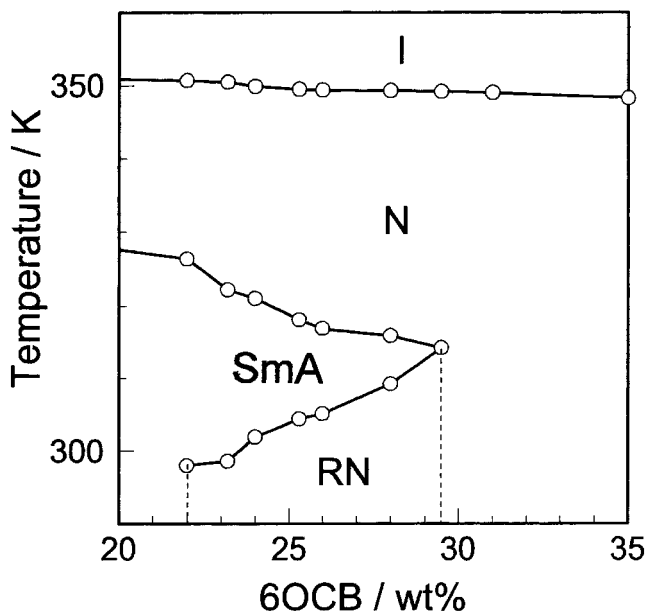


Figure 1. Phase diagram of the 6OCB–8OCB binary liquid crystal system: I, N, SmA and RN refer to the isotropic, ordinary nematic, smectic A and re-entrant nematic phases, respectively.

3.2. Dielectric properties

A higher weight fraction of 6OCB gave rise to a higher dielectric constant associated with a higher density of polar groups such as cyano groups, because the specific volume of 6OCB is smaller than that of 8OCB. Figure 2 shows the dielectric anisotropy $\Delta\epsilon$ of the LC mixtures. Open and closed symbols refer to the N phase and the SmA phase, respectively. The dielectric anisotropy also increases with an increase in weight fraction of 6OCB. It should be noted that there is no remarkable discontinuity in the dielectric anisotropy at the phase transition temperatures, although the birefringence exhibits a slight increase with cooling in the vicinity of the SmA–RN transition temperature [5].

3.3. Visco-elastic properties

Figure 3 shows the visco-elastic properties for the twist deformation as a function of temperature for various weight fractions of 6OCB. The visco-elastic ratios decrease with cooling both in the N and RN phases as shown in figure 3(a). The plots are lacking in some data in the SmA phase represented by arrows, because the twist deformation is reduced strongly in the SmA phase and therefore the intensity of the depolarized light scattered by the liquid crystal becomes very weak. On the other hand, the viscosity coefficients and elastic constants increase with cooling, being almost independent of the weight fraction at higher temperatures, as shown in figures 3(b) and 3(c). This behaviour might be associated with the fact that the N–I transitions for all the mixtures occur at almost the same temperature, as shown in figure 1.

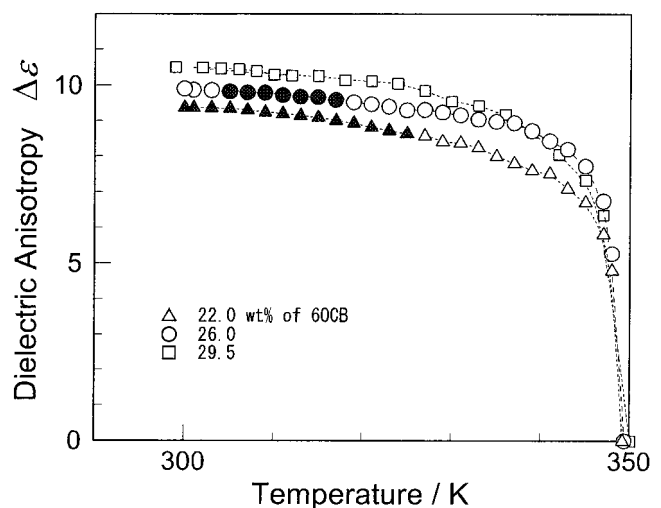


Figure 2. Dielectric anisotropy of the liquid crystalline mixtures as a function of temperature. Triangles, circles, and squares refer to the data for 22.0, 26.0, and 29.5 wt % of 6OCB, respectively. Open and closed symbols refer to the nematic and smectic phases, respectively.

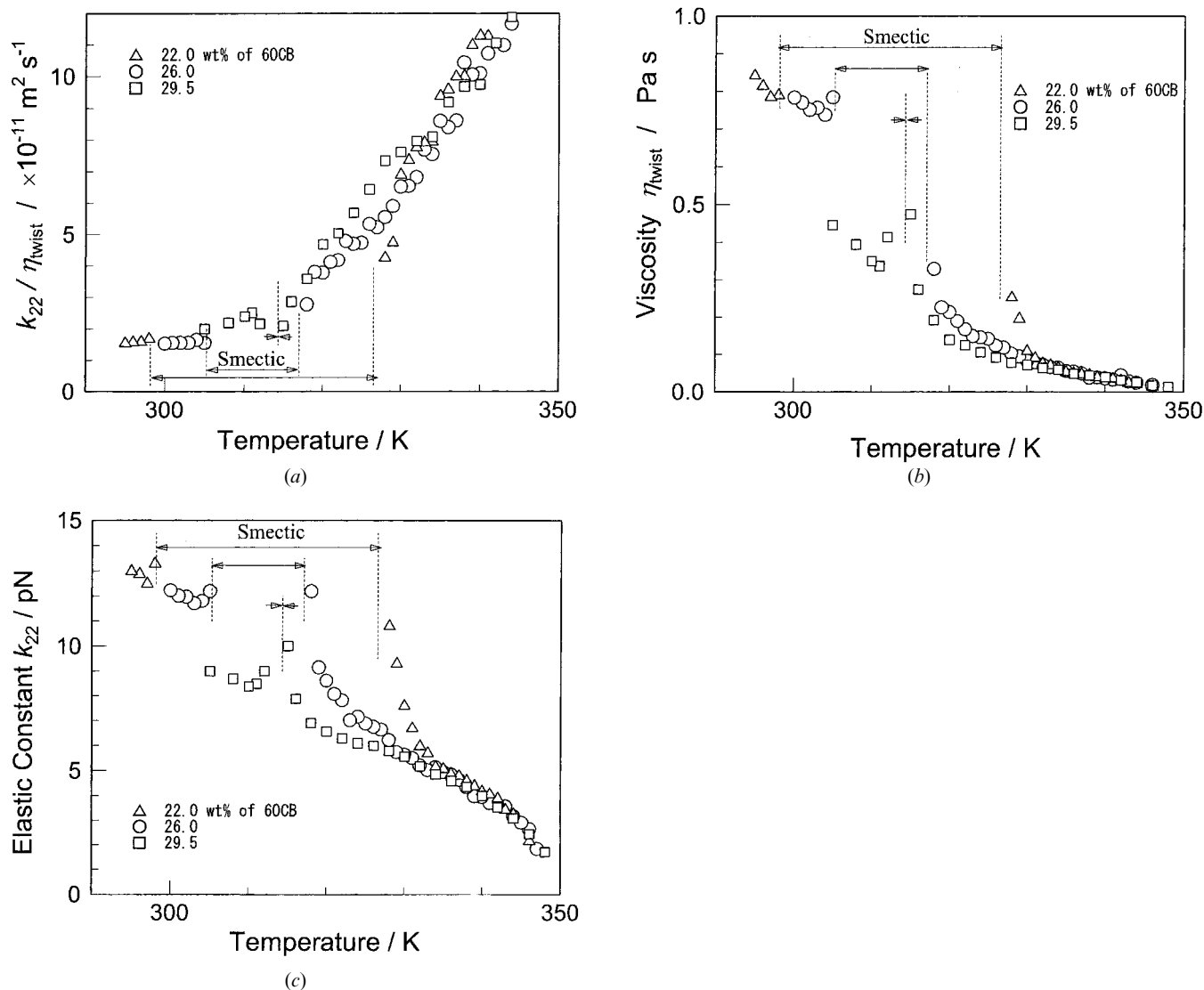


Figure 3. Visco-elastic properties of the mixture at various concentrations (a) visco-elastic ratio, (b) viscosity and (c) elastic constant. Triangles, circles, and squares refer to the data for 22.0, 26.0, and 29.5 wt % of 6OCB, respectively. The arrows indicate the smectic range.

It should be noted that both the viscosity and the elasticity show anomalous increases in the vicinity of the transition temperatures between the N and SmA phases. These increases can be associated with a pretransitional phenomenon in which a smectic-like order emerges in the nematic phase [30, 31]. Similar increases are observed in the SmA–RN transitions. The temperature at which such pretransitional behaviour begins is dependent on the weight fraction, as well as on the transition temperature. Consequently, the pretransitional region becomes wider as the weight fraction decreases. Such anomalous increases in the viscosity and elasticity can be interpreted as the formation of a locally layered structure. It is also

found that the pretransitional regions for the N–SmA transition are wider than those for the SmA–RN transitions.

3.4. Activation energy

In order to clarify the difference between the ordinary N phase and the RN phase, the activation energies were estimated from the temperature dependence of the viscosity coefficients. In general, viscosity is proportional to both S^n and $\exp(E_a/k_B T)$ [32], where S is the order parameter of director orientation, n is a constant, E_a is the activation energy, k_B is the Boltzmann constant and T is the temperature. The viscosities obtained for the

mixtures of the present study can be regarded as being independent of the order parameter except in the vicinity of the transition temperatures, where the order shows strong temperature dependence. The same result has been reported by Sailaja *et al.* [20]. Therefore we can estimate the activation energy from the slope in the plots of $\ln \eta_{\text{twist}}$ against the reciprocal temperature, namely the Arrhenius plots.

Figure 4 shows the activation energies thus obtained for the twist viscosity as a function of the weight fraction of 6OCB. The energies for the RN phase are smaller than those for the ordinary N phase and they approach each other with an increase in the weight fraction. It has been reported that liquid crystalline molecules having a strong polar group, such as cyano, tend to aggregate and to form dimers through an antiparallel coupling of their biphenyl moieties [32, 30]. This result indicates that the interaction between monomer molecules or that between dimer aggregates is weaker in the RN phase than in the ordinary N phase. It is consistent with the fact that dimerization results in a reduction in the apparent molecular dipole moment. For the ordinary N phase, the activation energy decreases with an increase in the 6OCB content, i.e. with a decrease in the average length of the molecules, while that for the RN phase is found to increase at about 30 wt % of 6OCB. This increase can be associated with the dependence of the dimer density on the 6OCB content [8].

3.5. Normalized elastic constant

In contrast to the viscosity coefficients, the elastic constants generally exhibit strong dependence on the

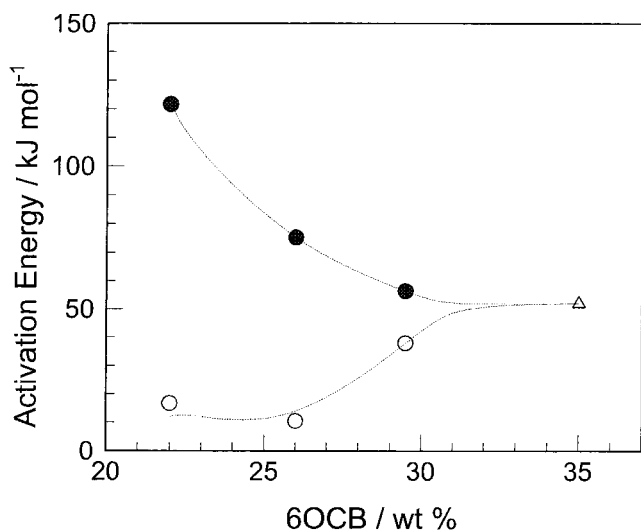


Figure 4. Activation energies for viscosity as a function of 6OCB concentration. Open and closed circles refer to the data for the reentrant and ordinary high temperature nematic phases, respectively. The 35.0 wt % mixture denoted by a triangle exhibits no reentrant phenomenon.

order parameter. In this section, we will try to eliminate the component of the order parameter from the elastic constant. By a theoretical consideration [32, 39] based on the Landau theory [40, 41], the twist elastic constant k_{22} can be given simply as:

$$k_{22} = 2L_1 S^2 \quad (2)$$

where L_1 is a constant associated with the elasticity.

As another property including the contribution of the order parameter S , we may consider the dielectric anisotropy $\Delta\epsilon$ which can be expressed as [30, 32, 42]:

$$\Delta\epsilon = \left(\frac{NhF}{\epsilon_0} \right) \left[\Delta\alpha - F \left(\frac{\mu^2}{2k_B T} \right) (1 - 3 \cos^2 \beta) \right] S \quad (3)$$

where N is the number of molecules per unit volume, h the cavity field factor, F the reaction field factor, $\Delta\alpha$ the polarizability anisotropy (the direction of maximum polarizability is assumed to be the long molecular axis). The permanent dipole moment μ is inclined at an angle β with respect to the molecular long axis.

Dividing the elastic constant k_{22} by the square of the dielectric anisotropy, $(\Delta\epsilon)^2$, we can obtain a parameter that should be independent of the order parameter S .

$$\frac{k_{22}}{(\Delta\epsilon)^2} = \frac{2L_1 \epsilon_0^2}{(NhF)^2 \left[\Delta\alpha - F \left(\frac{\mu^2}{2k_B T} \right) (1 - 3 \cos^2 \beta) \right]^2} \quad (4)$$

This ratio, which may be termed the normalized elastic constant, is associated with the size, the shape, the density, the dipole moment and the polarizability anisotropy of a unit molecular aggregate, in which separate motions of the component molecules are forbidden and all the molecules are in a single motion. The association of molecules generally gives rise to a decrease in the magnitude of the dipole moment and an increase in the anisotropy of the shape. Thus the normalized elastic constant becomes slightly larger with decreasing temperature, as expected from equation (4), because the temperature depending factor, $2k_B T$, should not vary widely in the narrow temperature range in the present study. Here it should be noted that the dielectric anisotropy itself, in fact exhibits no remarkable jump during the transitions as shown in figure 2, while the dipole moment should be reduced. This suggests that the increase in the order parameter can compensate for the depression of the dipole moment, to result in no remarkable change in the dielectric constant. On the other hand, for the birefringence, which is not associated with the dipole moment but with the order parameter, a discontinuity is found during the transition, as mentioned in §3.2.

Figure 5 shows the temperature dependence of the normalized elastic constant $k_{22}/(\Delta\varepsilon)^2$ for various weight fraction of 6OCB. The normalized elastic constants decrease with an increase in the weight fraction because 6OCB has the smaller specific volume which results in a higher density of polar groups than 8OCB, i.e. the effective dipole moment per unit volume increases. In addition, the contribution of the shape to elasticity should be taken into account. The twist elastic constants of the homologous series of cyanobiphenyl liquid crystals exhibit an increase with the length of alkyl chain [43, 44], if we disregard the odd–even effect. It has also been reported that $2L_1$, the factor for S^2 in equation (2), shows an increase with the alkyl chain length [43]. Hence we may consider that a larger amount of 6OCB gives rise to a shorter average length of alkyl chain and consequently results in a smaller elastic constant.

For the 35.0 wt % 6OCB mixture, the normalized elastic constant exhibits only a gradual increase with cooling, as expected from equation (4). Considering the fact that this weight fraction gives no RN phase, the properties of aggregates, such as their size, shape and dipole moment, would not vary much in the range of the present experimental temperatures. For the other weight fractions, only a small increase in the normalized elastic constants is observed within a higher temperature region as well as for the 35.0 wt % mixture. In comparison with the ordinary N phase, the normalized elastic constants exhibit rather large values in the RN phase. The difference in the normalized elastic constants between the N and RN phases decreases with increasing

the weight fraction, as well as the width of the pre-translational region. This result suggests that the increase may be attributed to the reduction of the effective dipole moment and the elongation of the apparent molecular length, accompanied by the formation of dimers or certain sizes of molecular aggregates.

3.6. Formation of molecular aggregates

Figure 6 shows the visco-elastic ratio of the 26.0 wt % mixture as a function of the specific time defined as the period of time during which the sample exhibits the SmA phase. The data points at each measurement temperature correspond to the average cooling rates in the SmA phase of 1.19, 0.33, and 0.13 K min⁻¹ from the left to the right. The decrease in the visco-elastic ratio with the specific time may be interpreted as the progress of the RN phase formation, because the RN phase shows a smaller value than the N phase, as shown in figure 3(a). Since the measurement temperature 305 K is just below the SmA–RN transition temperature, the additional aggregation in the RN phase is negligible. Therefore this tendency is attributed to preferential aggregation in the SmA phase. A similar tendency is observed for lower temperature, although the lower temperature affords the smaller visco-elastic ratio which could be associated with aggregation in the RN phase. The three curves would meet at about 3 h.

The gradual depression suggests that aggregation makes slow progress in the SmA phase, although the phase

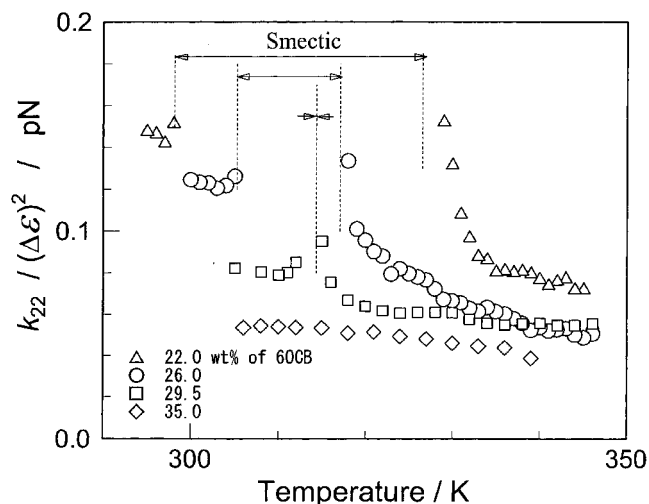


Figure 5. Normalized twist elastic constant $k_{22}/(\Delta\varepsilon)^2$ as a function of temperature. Triangles, circles, and squares refer to the data for 22.0, 26.0, and 29.5 wt % of 6OCB, respectively. It should be noted that the 35.0 wt % mixture denoted by diamonds exhibits no reentrant phenomenon. The arrows indicate the smectic range.

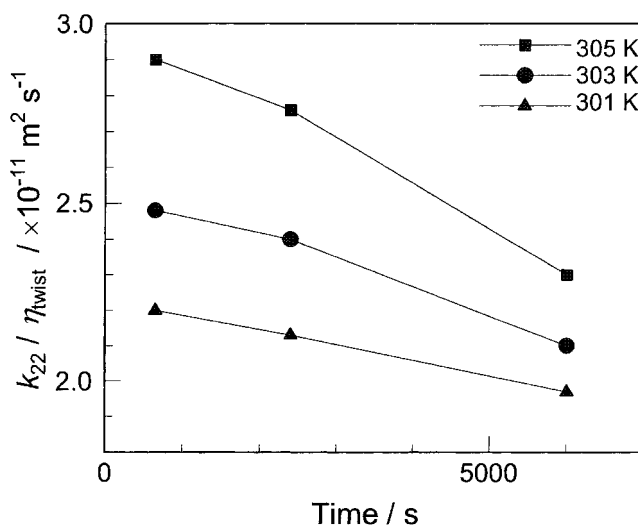


Figure 6. Visco-elastic ratio in the RN phase of the 26.0 wt % mixture as a function of the specific time during which the mixture exhibits the SmA phase. Solid triangles, circles, and squares refer to the data measured at 301, 303, and 305 K, respectively. The data points at each measurement temperature correspond to the average cooling rates in the SmA phase of 1.19, 0.33, and 0.13 K min⁻¹ from the left to the right.

transitions occurs rapidly. In addition, most dimerization has occurred preferentially in the ordinary N and SmA phases, and has already been complete before the SmA–RN transition. This could also be associated with the fact that the N–SmA transition appears with a wider pretransitional region than the SmA–RN transitions. These results lead to the conclusion that a layered structure in the smectic phase plays an important role in the association of molecules resulting in the RN phase.

4. Conclusions

The visco-elastic properties for binary mixtures of 6OCB–8OCB have been investigated by the light scattering technique. The mixtures exhibit the RN phase between the SmA and Cr phases in the range 22.0 to 29.5 wt % of 6OCB. The viscosity and the elastic constant increase with cooling, not only in the ordinary N phase but also in the RN phase. It is also found that the viscosity and elastic constant show an anomalous increase near the phase transition temperature, namely a pretransitional phenomenon. In the RN phase, the activation energy for viscosity is smaller than that observed in the ordinary N phase, while the normalized elastic constant, defined as the ratio of the elastic constant to the dielectric anisotropy, is larger. Moreover, the visco-elastic behaviour depends on the specific time during which the sample is kept in the SmA phase. These results confirm that the reentrant nematic phenomenon in the 6OCB–8OCB mixtures is triggered by the formation of molecular aggregates in the SmA phase.

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