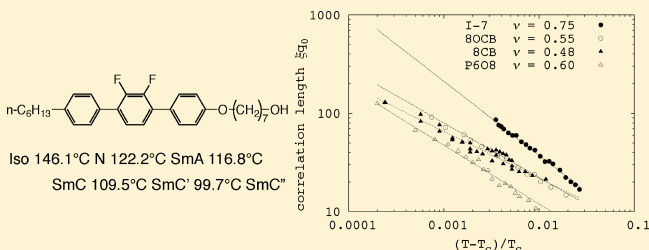


Anomaly of Pretransitional Behavior at the Nematic–Smectic-A Phase Transition of Amphiphilic Liquid Crystals with a Hydrophilic Group

Yasuhiro Kimoto,[†] Ayumi Nishizawa,[‡] Yoichi Takanishi,^{*,†} Atsushi Yoshizawa,[‡] and Jun Yamamoto[†][†]Department of Physics, Graduate School of Science, Kyoto University, Kitashirakawa Oiwake-cho, Sakyo-ku, Kyoto 606-8562, Japan[‡]Department of Frontier Materials Chemistry, Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, 036-8561, Japan

ABSTRACT: In order to clarify the origin of the X-ray diffraction peak corresponding to the smectic-like layer ordering appearing even in the nematic phase over a wide temperature range above the nematic–smectic A (NA) phase transition in liquid crystal (LC) molecules with a hydroxy group, we investigated the critical behavior of bend elastic constants and the correlation length of the smectic-like ordering in the N phase. It is found that cybotactic clusters with the transient layer ordering grow up extremely even far above the NA phase transition, and the critical exponent of the correlation length of the cybotactic clusters is estimated anomalously larger than that of conventional LC materials. Furthermore, we measured diffusion constants parallel and perpendicular to the director in the N phase, and concluded that cybotactic clusters with the smectic layer ordering create a finite potential barrier to prevent diffusion of the molecules parallel to the director as well as the true smectic A layer structure.



INTRODUCTION

The nematic to Smectic-A (NA) phase transition has been extensively studied as a simple model of one-dimensional positional order–disorder phase transition of soft matters. In the N phase just above the NA transition point, it is known that the X-ray diffraction peak corresponding to the smectic-like layer ordering appears.^{1–4} This phenomenon is caused by the emergence of the temporal (fluctuating/transient) microscopic smectic-like layer ordering (called a cybotactic cluster⁵).

Yoshizawa et al.⁶ reported the synthesis and phase behavior in a novel liquid crystal molecule with a hydroxyl group at the end part, 4-[4-(7-hydroxyheptyloxy)phenyl]-1-(4-hexylphenyl)-2,3-difluorobenzene (I-7), as shown in Figure 1, and found that

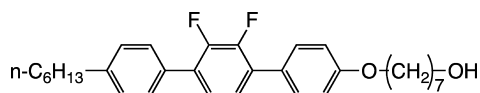


Figure 1. Chemical structure of I-7.

the X-ray diffraction peak appears over 10 K above the NA phase transition point. It is assumed that this is likely to be caused by cybotactic clusters existing and growing over a wide temperature range in the N phase, but it is still an open question whether such a cluster is formed over 10 K. In this paper, to verify the formation of the cluster in detail and figure out the effect of this cluster on the physical properties in the N phase, we performed the following experiments: First, to discuss the effect of clusters on the critical behavior around the NA transition, we investigated the temperature dependence of a

bend elastic constant K_{33} using the Freedericksz transition. Second, to find out about the formation of cybotactic clusters in detail, we carried out a small-angle X-ray diffraction measurement with high resolution, and the correlation length as a function of temperature was discussed. Furthermore, to clarify the effect of cybotactic clusters on the dynamics in the N phase, we also discussed the anisotropy of diffusion constants in the N and SmA phases using a fluorescent diffusion measurement.

EXPERIMENTAL SECTION

The sample used was 4-[4-(7-hydroxyheptyloxy)phenyl]-1-(4-hexylphenyl)-2,3-difluorobenzene (I-7), and the chemical structure and the phase sequence were referred to in ref 6. For each experiment, the phase transition temperature from N to SmA was confirmed from the texture because it sometimes depends on the sample preparation and used electric furnaces. Because I-7 has negative dielectric anisotropy, we used homeotropically aligned cells for measuring the bend elastic constant K_{33} . Prepared sample cells were 12 μm thick glass sandwich cells coated with an ITO electrode. For homeotropic alignment, polyimide (Nissan Chemical Industry, LTD., RN1211) was spin-coated on the ITO surface. To measure K_{33} , we measured the optical transmittance under the application of an AC electric field of 1000 Hz with various amplitudes, and determined the threshold voltages of the

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Freedericksz transition, which is proportional to the square root of K_{33} , using a polarization microscope (Olympus, BX51) and a photo sensor (New Focus Inc., Large-Area Visible Photo receiver, model 2031). Furthermore, in order to determine K_{33} , the temperature dependence of $\Delta\epsilon$ was measured from the frequency dispersion of capacitance of 12 μm thick planar and homeotropic cells using a LCR meter (HIOKI, LCR HiTESTER 3532-50).

For the discussion about the layer ordering of clusters, the X-ray experiments were carried out using an X-ray diffractometer (Rigaku Corp., MicroMax-007HF; $\lambda = 1.54 \text{ \AA}$) equipped with a handmade hot stage and a temperature-control processor. Each sample was put on a convex lens and oriented perpendicular to the surface of the lens, the temperature of which was controlled to within $\pm 0.1^\circ\text{C}$. X-rays were generated at 45 kV and 20 mA and its resolution was $4.14 \times 10^{-3} \text{ \AA}^{-1}$ (FWHM) in the vertical direction, which is determined from the diffraction results of standard sample (Ag Behenate). This resolution is narrow enough to obtain a correlation length less than 1500 \AA . Each diffraction pattern was obtained using the two-dimensional detector which combines an image intensifier (Hamamatsu) and a cooled CCD camera (Hamamatsu, C9299-001). For comparison, we also measured the diffraction in the N phase of 8CB (4-octyl-4'-cyanobiphenyl; I 39.7°C N 30.7°C SmA 21°C Cr), 8OCB (4-octyloxy-4'-cyanobiphenyl; I 81.3°C N 67.6°C SmA 33.8°C Cr), and P6O8 (2-(4-hexyloxyphenyl)-5-octylpyrimidine; I 66°C N 57.7°C SmA 45.9°C SmC 26°C Cr).

For the investigation of the anisotropic diffusion behavior, we have developed an original technique based on the enhancement effect on fluorescent emission of the LC molecules induced by the irradiation of the strong UV laser. Some LC molecules such as I-7 and a series of cyanobiphenyls absorb UV light and exhibit fluorescence.^{7,8} LC molecules were inserted in 12 μm thick planar aligned cells coated with rubbed polyimide (JSR, AL1254). First, by irradiation of a UV laser beam with a wavelength of 349 nm (Spectra-physics Corp., Explorer OEM) through a pinhole during 30 s, the LC molecules in the irradiated area are locally excited (0.03 mm in diameter). In this process, it is considered that excited LC molecules are temporally changed as their fluorescent ability increases. Afterward, by the irradiation of all of the sample cells (more than 1 cm^2) with weak UV light of a Hg lamp (350–385 nm), the LC molecules exhibit fluorescence, and the fluorescent intensity at the narrow irradiation area by UV laser is higher than that at other regions. Later, this brighter region is expanded during the gradual decrease in fluorescent intensities due to the two-dimensionally translational diffusion of the excited LC molecules. By measuring the time evolution of the fluorescent intensity of LC molecules, we determined the diffusion constants D_{\parallel} and D_{\perp} which are diffusion constants parallel and perpendicular to the director in the plane of cell substrates.

Analyzing the time evolution of the expansion of the fluorescence intensity profiles in the direction parallel and perpendicular to the director detected by a cooled CCD camera (Andor Technology PLC, Andor Luca S), we obtained the diffusion constants along each direction. The principle of the measurement has an analogy to the fluorescence photo-bleaching recovery spectroscopy.⁹

RESULTS AND DISCUSSION

Figure 2 shows the temperature dependence of the bend elastic constant K_{33} determined from the following equation:

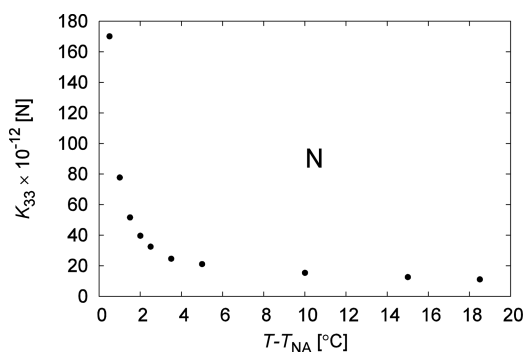


Figure 2. Temperature dependence of the bend elastic constant (K_{33}) of I-7. K_{33} diverges to the NA transition point ($T_{NA} = 398 \text{ K}$).

$$K_{33} = \Delta\epsilon \left(\frac{V_c}{\pi} \right)^2 \quad (1)$$

Here V_c is a threshold voltage of the Freedericksz transition of homeotropic cells and $\Delta\epsilon$ is the dielectric anisotropy. Threshold voltage related to the bend elastic constant K_{33} diverges up to the NA transition temperature. Although X-ray diffraction peaks corresponding to the short-range positional order or the smectic-like layer ordering were already observed at 10 K above the NA transition mentioned later, abnormal behavior for the threshold voltage was not observed. Hence, it is found that no macroscopic static layer structure is formed in the N phase of I-7, and it is reasonable to consider that the X-ray diffraction peak in the N phase comes from the dynamic microscopic layer structure, i.e., a cybotactic cluster.^{5,10–12}

Cybotactic clusters appear as a pretransitional effect of transient manifestation of the smectic layer order in the N phase, and those clusters should have only the short-range correlation of the layer ordering. Hence, we analyzed the correlation length from the X-ray diffraction peaks. The correlation length along the layer normal (ξ) was determined by fitting the X-ray diffraction profiles using the Orstein–Zernicke equation (Lorentzian form)

$$\sigma(q) = \frac{\sigma_0}{1 + \xi^2(q - q_0)^2} \quad (2)$$

in which σ_0 and q_0 are the peak height and the peak position of wavenumber q , respectively. If it is supposed that the correlation length ξ diverges to the NA transition point, ξ is determined by the following equation:

$$\xi(T) = A \left(\frac{T - T_c}{T_c} \right)^{-\nu} \quad (3)$$

Here T_c is the critical temperature of the NA transition, A is a coefficient constant, and ν is the critical exponent. Figure 3 shows the temperature dependence of the correlation length ξ in the layer normal direction of I-7. For comparison, we also measured the correlation length in the N phase of the other three compounds with the N–SmA phase sequence and they are superimposed in Figure 3. It is found that I-7 has the longer correlation length, which indicates that the size of cybotactic clusters of I-7 is larger than that of other compounds, and the

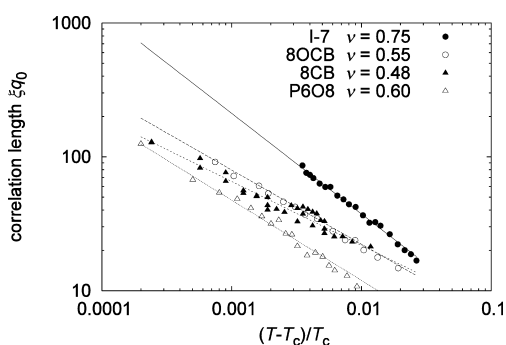


Figure 3. Longitudinal correlation lengths of the layer ordering as a function of the reduced temperatures of eq 3, and fitted values of ν of each compound are written in the inset.

critical exponent ν obtained from eq 2 of I-7 in the N phase is also larger than that of the other compounds, which is qualitatively consistent with those obtained from the K_{33} measurement. Moreover, ΔT ($=T_{NA} - T_c$) of I-7 is 1.5 K, which is much larger than that of other compounds (8OCB, $\Delta T = 0.26$ K; 8CB, $\Delta T = 0.23$ K; P6O8, $\Delta T = 0.1$ K). This result suggests that the NA phase transition in I-7 is first-order-like, though the transition enthalpy at the NA transition was hardly observed.⁶

Figures 4 and 5 show the diffusion constants in the N and SmA phases of 8OCB and I-7, respectively. The temperature

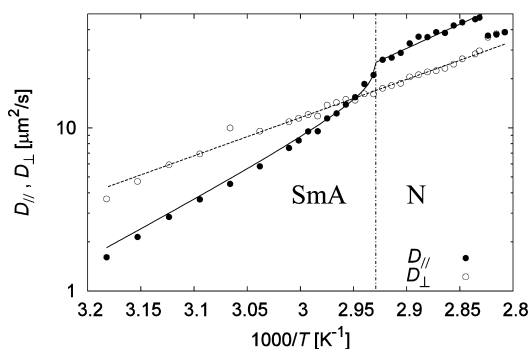


Figure 4. Diffusion constants as a function of temperature in the isotropic, nematic (N), and Smectic-A (SmA) phase of 8OCB. The solid and dotted lines are fitting results obtained from eqs 4 and 6 in the N and SmA phases, respectively. T_{NA} determined by texture observation is indicated by a dashed line.

dependence of diffusion constants $D_{||}$ and D_{\perp} obeys the Arrhenius type equation in the N phase. However, previous works report the anomalous temperature dependence of interlayer translational diffusion constant $D_{||}$ in the SmA phase, because the periodic potential along the smectic director emerges and it creates a potential barrier for the translational diffusion of LC molecules across the layers.^{13,14} Thus, we can define the constants with the following equations:¹⁴

$$D_{||}(T) = D_{||\infty} \exp\left(\frac{-E_{||}}{RT}\right) [I_0(\text{Step}[T_{01}]V_1/2RT)]^{-2} \quad (4)$$

$$V_1(T) = V_0(1 - T/T_0)^p \quad (5)$$

$$D_{\perp}(T) = D_{\perp\infty} \exp\left(\frac{-E_{\perp}}{RT}\right) \quad (6)$$

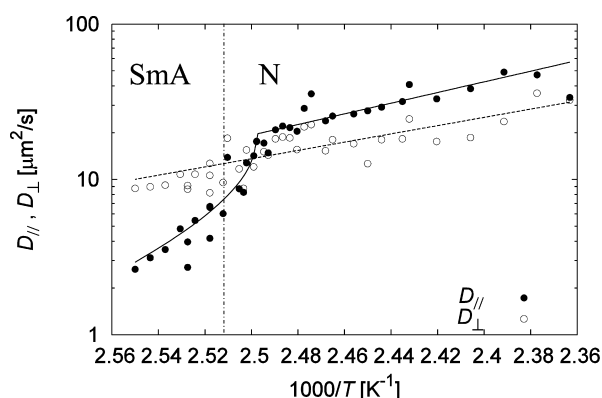


Figure 5. Diffusion constants as a function of temperature in the isotropic, nematic (N), and Smectic-A (SmA) phase of I-7. The solid and dotted lines are fitting results obtained from eqs 4 and 6 in the N and SmA phases, respectively. T_{NA} determined by texture observation is indicated by a dashed line.

Here $E_{||}$ and E_{\perp} are the Arrhenius activation parameters for diffusion in the direction parallel and perpendicular to the director, respectively, and T_{01} and T_0 are the critical temperature near the NA transition point. $\text{Step}[T_{01}]$ is a step function such that $\text{Step}[T_{01}] = 0$ over T_{01} and $\text{Step}[T_{01}] = 1$ below T_{01} . I_0 is the modified Bessel function of the first kind and zero order. V_0 and p are phenomenological parameters which determine the intensity of the potential barrier. This time, the fitting was performed under the condition $T_{01} = T_0$. In the SmA phase, $D_{||}$ of both of the compounds becomes smaller than D_{\perp} because the layer ordering suppresses the molecular diffusion along the layer normal. A remarkable point is the crossover temperature T_0 at which $D_{||}$ and D_{\perp} are the same. In 8OCB, T_0 is 341.2 K and it is closely in agreement with the NA transition point ($T_{NA} = 341.1$ K). On the other hand, in I-7, T_0 is 400.3 K, and it is 2 K higher than the NA transition point ($T_{NA} = 398.1$ K). This means that $D_{||}$ of I-7 already decreases in the N phase near the NA transition point, suggesting that cybotactic clusters greatly affect the diffusion parallel to the director; i.e., the microscopic layer structure of clusters creates a potential barrier for the cross-layer component $D_{||}$ as well as the SmA layer structure.

At present, it is not yet clear why cybotactic clusters are generated in the higher temperature region in the N phase of I-7. It might be possible that the intermolecular hydrogen bonding of hydroxyl groups is related to the cluster formation, and now we are investigating the IR spectrum peaks assigned as the vibration mode of hydroxy groups as a function of temperature.

In summary, we investigated the behavior of physical properties in the N phase of liquid crystals with a hydroxy group such as bend elasticity, the correlation length of the smectic-like ordering, and diffusive anisotropy, in order to clarify the origin of the X-ray diffraction peak corresponding to the smectic-like layer ordering appearing over a wide temperature range above the NA phase transition. It is found that I-7 forms giant cybotactic clusters from the higher temperature region in the N phase, although the bend elastic constant is diverged up to the NA transition as observed in normal compounds with N–SmA phase sequence. Moreover, we also concluded that clusters with the smectic layer ordering create a potential barrier for the cross-layer component $D_{||}$ as well as the SmA layer structure, and that the generation of

cybotactic clusters affects not only the static structure but also the dynamics in the N phase.

AUTHOR INFORMATION

Notes

The authors declare no competing financial interest.

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