

**The effect of the confinement in
nano-micelles on the liquid
crystalline order**

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Main Papers:

- (1) S. Bono, Y. Takanishi and J. Yamamoto, “Isotropic-to-nematic phase transition of liquid crystals confined in nanoemulsion droplets” *Europhys. Lett.*, **109**, 26004 (2015)
- (2) S. Bono, Y. Takanishi and J. Yamamoto, “The effect of the layer order on the mobility of mesogenic molecules in the SmA-liquid crystalline nanoemulsion” *Europhys. Lett.* Submitted

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- (3) S. Bono, M. Yokoyama, Y. Takanishi and J. Yamamoto, “The effect of the liquid-crystalline order on releasing dye molecules from liquid-crystalline nano-emulsions” *Mol. Cryst. Liq. Cryst.*, **610**, 157 (2015)

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Chapter I Introduction

Confinement can change the physical nature of “soft matter” such as liquid crystals (LCs), colloidal suspensions, surfactants and polymers [1-6]. In particular, the effect of surface is important in the confined geometry because interaction between surface and soft matter becomes dominant. The effect of the confinement on the LC order is attractive because the effect of surface eventually changes physical properties of LCs owing to the intrinsic softness of LCs. LCs have physical character between liquid and crystal, and therefore, orientational and translational orders are important for the physics of LCs [7-19]. For example, orientational order of LCs induced at surface permeates over the distance of several ten nanometers [7-9].

Recently, studies of the confinement effect on the phase transition behavior were reported [10-19]. According to these studies, the effect of the confinement not merely induces (or suppresses) the LC order monotonously but can change the order of the phase transition behavior. In consequence, novel LC structure appears in some cases [10-13, 20]. In addition, the dynamic properties are also affected by the confinement [21-25]. For example, short wavelength-fluctuations, which are hidden by long wave length-fluctuation in the bulk state, become dominant in the dynamics of LCs in the confined system. However, experimental difficulty prevents us from investigating the effect of the three-dimensional confinement on the LC order.

In this paper, in order to construct such a three-dimensional confinement system, we fabricated liquid crystalline nano-micelles (LCNMs) and then, we investigated the effect of the three-dimensional confinement on the structure and the dynamics of LCs. First, we investigate the isotropic-nematic (N) phase transition of LCs confined in nano-micelles. Then, we study the dynamics of N-LCs confined in nano-micelles. Second, we fabricate smectic A (SmA)-LCNMs and investigate the SmA-N phase transition of LCs confined in nano-micelles. Finally, we construct the method to estimate the mobility of LCs in nano-micelles so that we investigate the effect of the layer order on the mobility of LCs in nano-micelles.

1.1 Effects of the confinement on nematic liquid crystals

1.1.1 Nematic-isotropic phase transition

A schematic image of the nematic (N) liquid crystals (LCs) and the isotropic (Iso) liquid is shown in Fig.1.1 [26, 27]. N-LCs have the orientational order, that is, anisotropic distribution of the molecular long axis. However, N-LCs do not have long-range translational order. The direction along which the molecular long axis aligns is called ‘director’ which is represented by the unit vector $\mathbf{n}$. The orientational order of N-LCs are characterized by the following tensor order parameter,

$$Q_{\alpha\beta} = \frac{S}{2}(3n_{\alpha}n_{\beta} - \delta_{\alpha\beta}), \quad (1.1.1)$$

where S is a scalar order parameter corresponding to the anisotropy of the distribution of the molecular long axis. Usually, N-LCs melts into Iso liquid which has no orientational order ($S=0$) on heating [26, 27]. The N-Iso phase transition in the bulk state is characterized by following phenomenological free energy,

$$f_{\text{NI}} = \frac{3A}{4}S^2 - \frac{B}{4}S^3 + \frac{9C}{16}S^4, \quad (1.1.2)$$

where A , B and C are material constants. Since eq.1.1.2 includes cubic term of S , the N-Iso phase transition in the bulk state is first order transition.

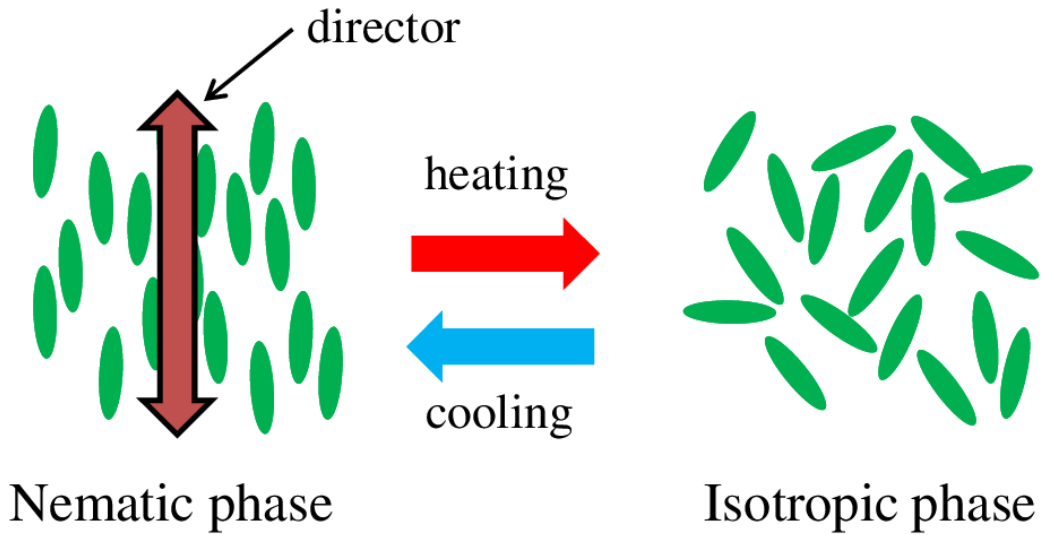


Fig.1.1 The schematic images of the N-LCs, the Iso liquid and the N-Iso phase transition.

1.1.2 Effects of the confinement on the nematic-isotropic phase transition

The effect of confinement in nanometer-sized containers can change the nature of N-LCs. For example, the N-Iso phase transition behavior of LCs confined in nanometer-sized containers has

been studied experimentally [8-13, 28] and theoretically [7, 14-16, 29-31]. One of the most important origins of the confinement effect is the interaction between LCs and a surface. The free energy of the interaction between LCs and a surface can be represented phenomenologically as follows,

$$f_s = -\frac{wS}{2}[3(\mathbf{n} \cdot \mathbf{v})^2 - 1], \quad (1.1.3)$$

where w is the strength of the surface interaction strength, and $\mathbf{v}$ is easy axis along which director tends to align at surface [14]. Finite orientational order is induced at a surface because of the surface interaction. Since surface area increases as the region of confinement decreases, the effect of the surface, which induces the orientational order, is important in the confined LC system.

The effect of the confinement between two plates on the orientational order was theoretically studied by Sheng [7, 30]. Then, it was reported that the surface-induced order remains over several ten nanometers from surface even though temperature is higher than the N-Iso phase transition temperature in the bulk state. Moreover, the discontinuous behavior of the first-order N-Iso phase transition is replaced by continuous behavior.

The effect of the confinement was also investigated experimentally [8,9, 14-16, 28]. Recently, Kityk *et al.*, investigated experimentally the N-Iso phase transition of LCs two-dimensionally confined in the silica nano-channels with the diameter of 10 nm and the length of 300 μm as shown in inset of Fig.1.2 (c) [10]. They measured birefringence in order to estimate the orientational order parameter. Birefringence is proportional to the scalar order parameter [32]. Birefringences of 7CB (Fig.1.2 (a)) and 8CB (Fig.1.2 (b)) in the bulk state discontinuously changes at $\sim 42^\circ\text{C}$ and $\sim 41^\circ\text{C}$, respectively, which indicates the N-Iso phase transition is weak first order phase transition. On the other hand, in the silica channels the discontinuous transition is replaced by continuous transition as Figs.1.2 (c) and (d). Then, the paranematic phase which connects continuously the N and the Iso phases appears as the inset of Fig.1.2 (c). In order to evaluate the strength of the surface interaction, they analyzed experimental data using the phenomenological model proposed by Kutnjak, Kralj, Lahajnar and Zumer (KKLZ model) [14-16]. However, in previous work, the confinement is two-dimensional, at most, and hence the macroscopic N order remains along one dimension. For example, in the case of the silica channel confinement, the N order is not restricted along the cylindrical axis of silica channels.

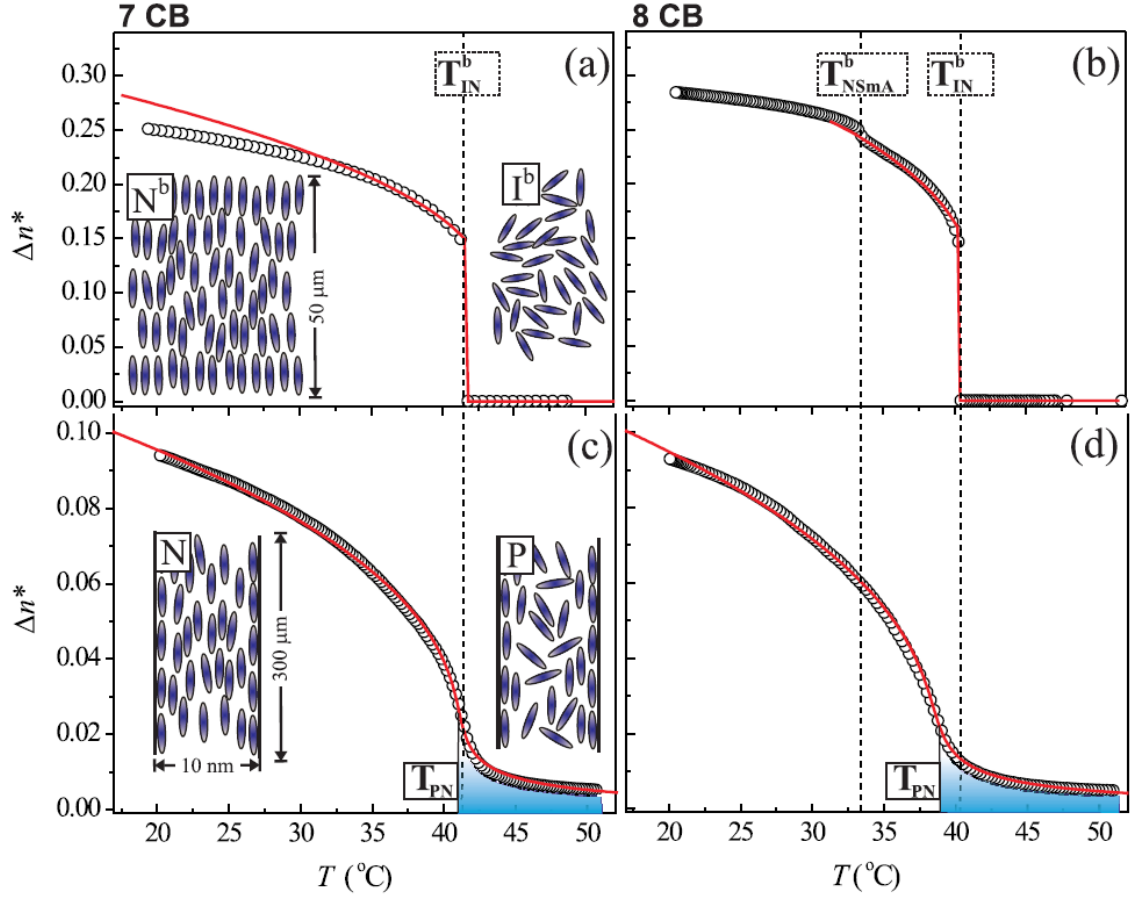


Fig.1.2 The temperature dependence of birefringence of 7CB in the bulk state (a), that in silica channels (c), that of 8CB in the bulk state (b) and that in the silica channels (d) [10]: The red lines indicate the fitting results on the basis of KKLZ model [14-16]. The inset of (a) indicates the schematic images of the N phase (N^b) and the Iso phase in the bulk state (I^b). The inset of (c) indicates the paranematic phase (P) and the N phase (N) in the silica channel. “Reprinted figure with permission from A. V. Kityk, M. Wolff, K. Knorr, D. Morineau, R. Lefort and P. Huber. *Phys. Rev. Lett.*, **101**, 187801 (2008). Copyright (2008) by the American Physical Society.”

1.1.3 Effects of the confinement on the orientational fluctuation of nematic liquid crystals

The orientational motion of director of N-LCs is attractive from the point of view of not only application of display industry [33-34] but also fundamental physics [21-25, 36-38]. The characteristic time to restore distorted director to a uniform state, τ , is determined by the balance between elastic force and viscous force as following dispersion relation [26, 39],

$$\tau \sim \frac{\gamma}{Kq^2}, \quad (1.1.4)$$

where γ , K and $1/q$ are the rotational viscosity, the elastic constant and the length scale of distortion (Fig.1.3), respectively. Eq.1.1.4 indicates that the characteristic time of fluctuation with short

wavelength is faster than that with long wavelength.

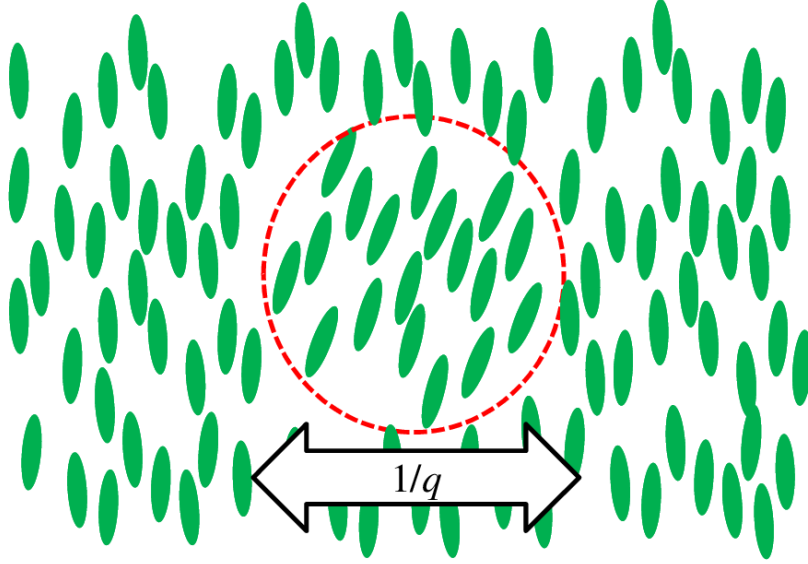


Fig1.3 The schematic image of the distortion with length scale of $1/q$.

The frustration between microscopic anisotropy and macroscopic isotropy is one of the most attractive topics in the frustrated system [36-38]. In such a frustrated system, LCs have microscopic anisotropy together with macroscopic isotropy. For example, the transparent N phase, in which inverse micelles disperse in N-LC solvent, has local orientational order [36]. However, since inverse micelles force the director of N-LCs to be deformed, in macroscopic length scale (typically the wavelength of visible light), the transparent N phase is isotropic. Yamamoto *et al.* observed the fluctuation of the local orientational order in spite of macroscopic isotropy [36].

Hyper-swollen B4 phase is one of the most interesting systems in which confinement affects the dynamics of N-LCs. In the hyper-swollen B4 phase, helical nanofilaments disperse in N-LCs as shown in Fig.1.4 [21, 40]. Helical nanofilaments are twisted layer structure made of bend-core-LCs like the B2 phase with size of several ten nano-meters [42, 42]. N-LCs are confined between helical nanofilaments with the average spacing, D_c . Since the orientational motion of director of N-LCs at the helical nanofilament interface is anchored, the fluctuation whose wavelength is longer than D_c is suppressed. Thus, the slow dynamics of N-LCs in the hyper swollen B4 phase is removed owing to the effect of the confinement, and as a result, the only fast dynamics of short wavelength-fluctuation remains [21].

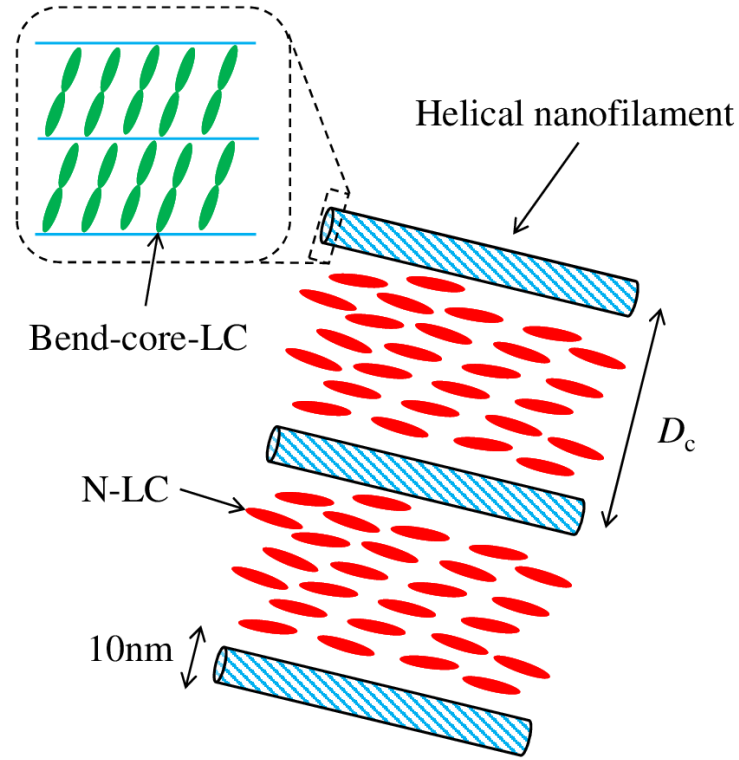


Fig.1.4 The schematic image of the hyper-swollen B4 phase [21].

The dynamics of LCs in the Blue phase is also affected by the confinement. The Blue phase appears within the narrow temperature range ($\sim 1^\circ\text{C}$) between the chiral N phase and the Iso phase [37, 43-45]. The Blue phase has lattice structure made of the double twist cylinders as Fig.1.5 (a), together with disclination lines Fig.1.5 (b) [37]. Since the diameter of double twist cylinders is several hundred nanometers, the Blue phase LCs reflects visible light corresponding to the lattice-spacing. The Blue phase is stabilized by the frustration between chiral force and inconsistency of symmetry, that is, the double twist chiral N-LCs cannot fill up the three-dimensional space without disclination. Then, the loss of free energy caused by the disclination line destabilizes the Blue phase. Recently, Kikuchi *et al.*, succeeded in stabilizing the Blue phase over a temperature range of more than 60°C by introducing polymers to disclination lines by polymeric chains.

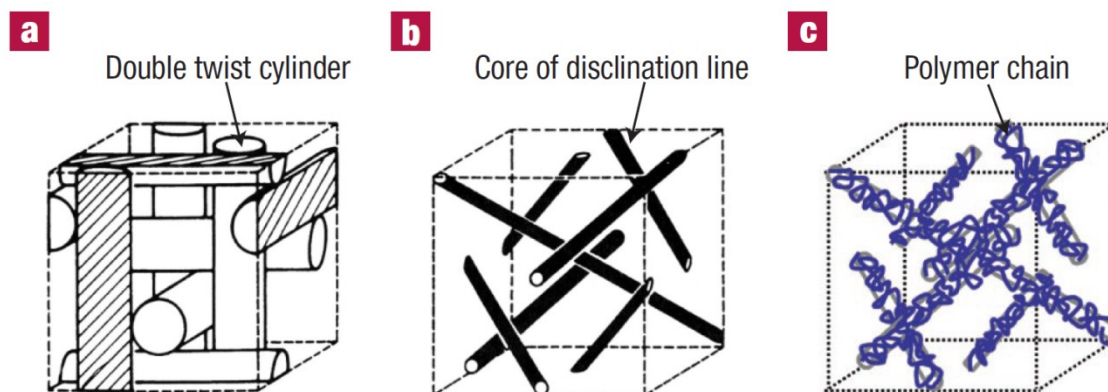


Fig.1.5 The schematic images of the Blue phase: (a) and (b) show double twist cylinders and disclination lines, respectively. (c) shows polymer chains which stabilize the Blue phase [37]. Reprinted by permission from Macmillan Publishers Ltd: [*Nat. Mater.*], advanced online publication, (doi: 10.1038/nmat712) Copyright (2002).

N-LC molecules in the double twist cylinders are confined between the disclination lines. Then, the director of the N-LC is anchored at the surface of double twist cylinder. Thus, the deformation of the director of the N-LC with longer wavelength than the diameter of double twist cylinder cannot be excited by thermal fluctuation. As a result, short-wavelength deformation, which is restored to the equilibrium state faster, remains. Actually, the relaxation time of the Blue phase LCs is ten-times faster than that of N-LCs.

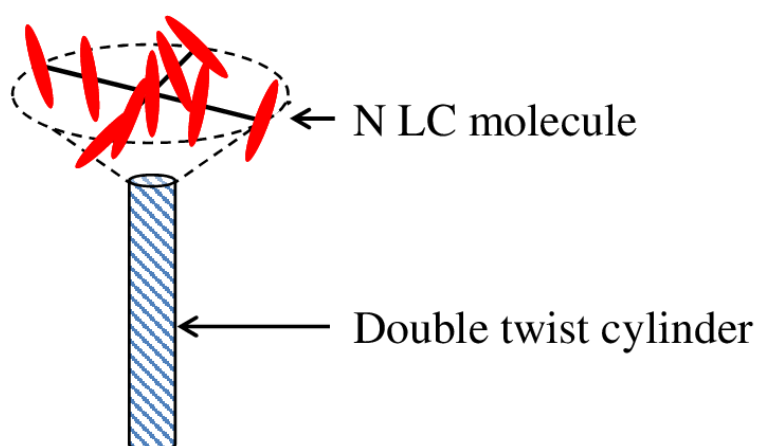


Fig.1.6 The schematic image of a double twist cylinder: N-LC molecules in the double twist cylinder. The rotation of the director of N LCs from one end to another is 90° , that is, the director rotates from 45° to -45° .

1.2 Effects of the confinement on smectic A liquid crystals

1.2.1 Smectic A-nematic phase transition

Smectic A (SmA)-LCs have one-dimensional translational order, which is called layer order, together with two-dimensional fluidity in the layer plane as shown in Fig.1.7 [26, 27]. The layer order of SmA-LCs is characterized by the following complex order parameter,

$$\psi = \eta \exp(i\phi), \quad (1.2.1)$$

where ϕ corresponds to the layer spacing. On the other hand, η is scalar order parameter of the layer order. Generally, the SmA-N phase transition is second order phase transition. Thus, the layer order with finite correlation length in the N phase appears, and the correlation length continuously diverges toward the SmA-N phase transition temperature on cooling. Generally, the diffusion constant of LCs in SmA phase along the layer-normal direction ($D_{\parallel}$) is suppressed rather than that in layer plane ($D_{\perp}$) because of the existence of the layer order [46-48]. Additionally, since LCs in the N phase do not have the macroscopic layer order, $D_{\parallel}$ of LCs in the N phase is larger than that in the SmA phase [46-48].

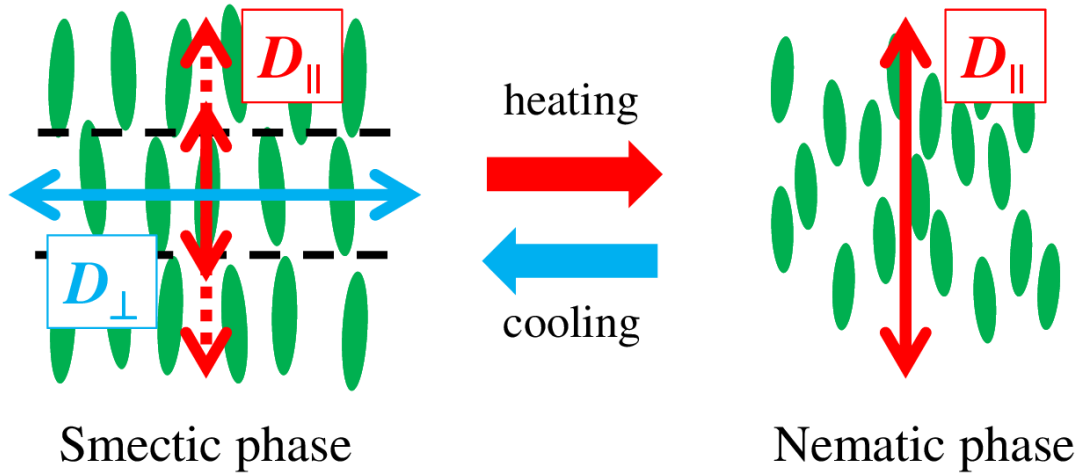


Fig.1.7 The schematic images of the SmA-LCs and the SmA-N phase transition: $D_{\parallel}$ and $D_{\perp}$ are diffusion constants of LCs along layer normal direction and in the layer plane, respectively.

1.2.2 Effects of the confinement on the smectic A-nematic phase transition

The confinement changes the physical nature of SmA-LCs such as the SmA-N phase transition behavior [49-57] and the layer structure [49-53]. For example, calorimetric studies of the effect of the confinement in controlled-pore matrices on the SmA-N phase transition were reported [15, 54]. Kutnjak *et al.* found that anomalous behavior of specific heat at the SmA-N phase transition is suppressed and becomes gradually rounded as the mean pore size decreases [15]. Furthermore, it was reported that elastic deformation due to the geometry of the confinement decreases the SmA-N

phase transition temperature [15].

X-ray scattering studies of the SmA-N phase transition behavior of LCs confined in silica aerogel were reported by Bellini *et al.* [17-19]. The surface of the silica aerogel imposes quenched disordering on LCs. As a result, the orientation of LCs at surface becomes random. Fig.1.8 (A) shows temperature dependence of the correlation length of the layer order of LCs confined in silica aerogel, ξ , as blue, red and green markers [19]. ϕ is a silica volume fraction, and thus, mean pore size of silica aerogel becomes smaller as ϕ increases. It was revealed that ξ does not diverge at the SmA-N phase transition temperature in the bulk state, $T_{\text{SmA-N}}^{\text{bulk}}$ which was shown in Fig1.8 (A) as a red dashed line. Moreover, ξ continuously develops over the temperature range of 10 °C below $T_{\text{SmA-N}}^{\text{bulk}}$ on cooling. At low temperature, ξ eventually saturates at a constant value which depends on the ϕ . Fig.1.8 (B) shows temperature dependence of the X-ray susceptibility of LCs confined in silica aerogel, χ , and the inset shows ξ dependence of χ . Clearly, χ is proportional to the square of ξ , which indicates a critical behavior of fluctuations near the second order phase transition. According to Bellini, this behavior indicates that LCs confined in aerogel is in the pretransitional region.

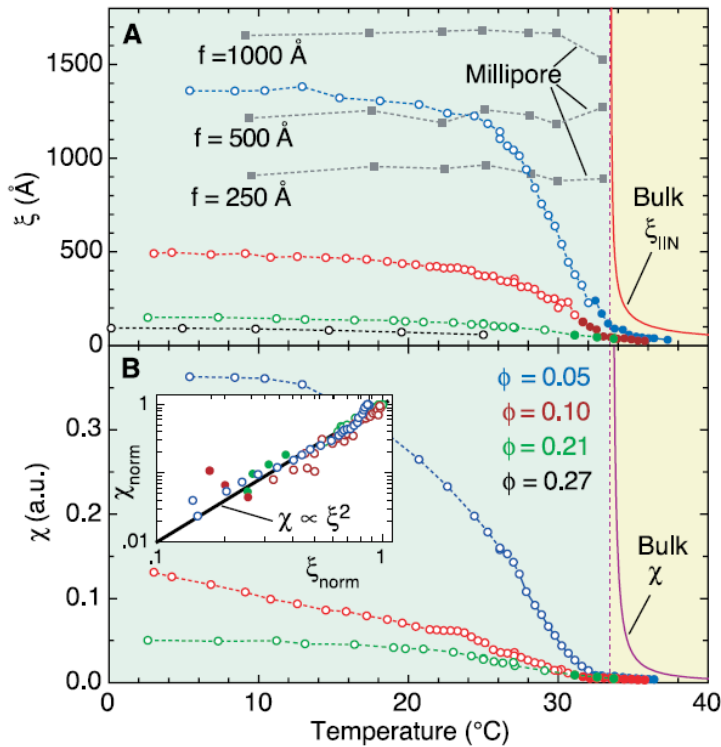


Fig.1.8 (A) Temperature dependence of the correlation length of the layer order of LCs confined in silica aerogels (blue, red and green markers) [19]. (B) shows temperature dependence of the X-ray susceptibility of LCs confined in silica aerogel, χ , and the inset shows the ξ dependence of χ .“ From [T. Bellini, L. Radzihovsky, J. Toner and N. A. Clark, *Science*, **294**, 1074 (2001)]. Reprinted with permission from American Association for the Advancement of Science.

1.3 Liquid crystals three-dimensionally confined in nano-micelles

1.3.1 Polymeric micelles

Polymeric micelles are made of amphiphilic diblock copolymers which are synthesized by combining hydrophilic and hydrophobic polymers chemically [58-65]. If the concentration of the amphiphilic copolymers in water increases, the amphiphilic copolymers form the self-assembling polymeric micelles. The core and shell parts of polymeric micelles are occupied by hydrophobic and hydrophilic chains, respectively, which is called “core-shell structure” as shown in Fig.1.9 [61-65].

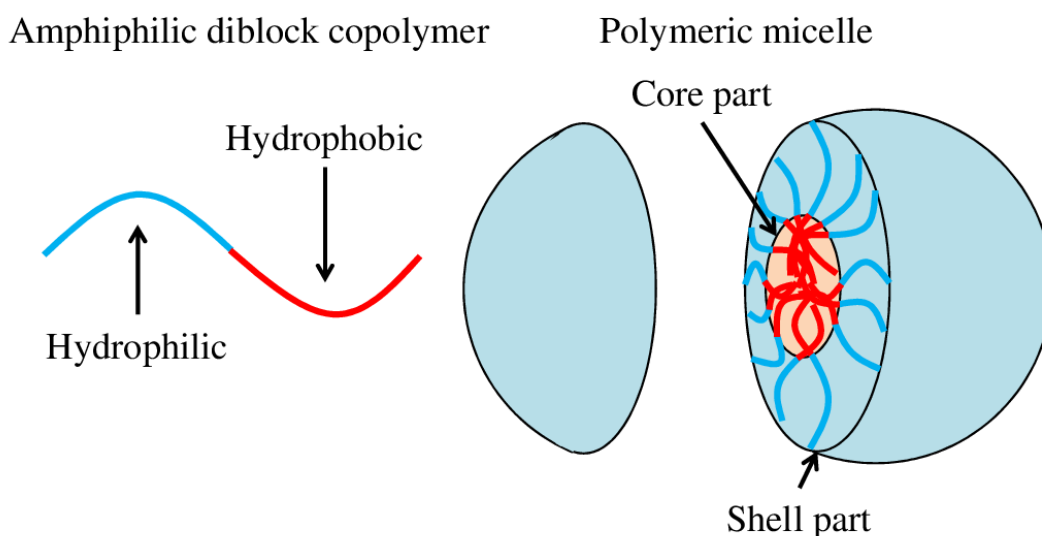


Fig.1.9 The schematic images of an amphiphilic diblock copolymer and a polymeric micelle.

Recently, Nishihara *et al.* synthesized a LC amphiphilic diblock copolymer, PEG-*b*-P(AzoPyl), in order to make a temperature-responsive polymeric micelle [66]. Fig.1.10 shows the structural formula of PEG-*b*-P(AzoPyl). The side chains of the hydrophobic parts of PEG-*b*-P(AzoPyl) are mesogenic groups. Nishihara *et al.* made LC polymeric micelles by using PEG-*b*-P(AzoPyl), and then, investigated the existence of LC phase transition by using differential scanning calorimetry technic. As a result, they found the endothermic and exothermic peaks, which may correspond to the LC phase transition of mesogenic side chains.

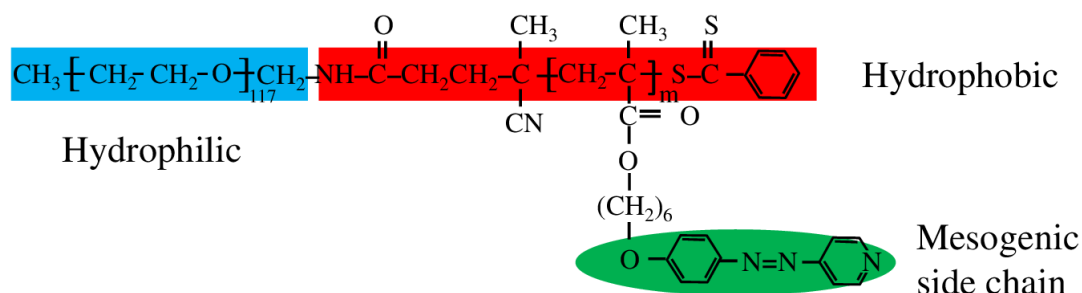


Fig.1.10 The structural formula of the LC diblock copolymer, PEG-b-P(AzoPyl), synthesized by Nishihara *et al.* [66].

1.3.2 Liquid crystalline nano-micelles

We have succeeded in fabricating liquid crystalline nano-micelles (LCNMs) by introducing LC molecules into the hydrophobic core part of nano-micelles as shown in Fig.1.11 [67, 68]. In such a LCNM system, the diblock copolymers work as surfactants, and as a result, the shell and core parts of nano-micelles are occupied by surfactants and LCs, respectively. The typical size of LCNMs is several hundred nanometers. LCNMs are expected to be convenient system for the investigation of the confinement effects on the LC order for following reasons.

First, LCs are three-dimensionally confined in the core parts of nano-micelles. Maximum dimensions of the confinement of previous studies are two dimensions such as silica nano-channels and bicontinuous matrices [10-19]. The effect of the confinement in nano-micelles is expected to be stronger than that of previous studies because surface area per unit volume in three-dimensionally confined geometry is larger than that in two-dimensionally confined geometry.

Second, we can control the size of the confinement. LC polymeric micelles mentioned in the section 1.3.1 are composed of water and LC amphiphilic diblock copolymers. On the other hand, our LCNMs are composed of water, surfactants and LCs. Thus, the size of micelles, that is, the size of confinement can be controlled by changing the weight ratio of LCs to surfactant as we will mention in the section 2.2.

Finally, the concentration of impurities in LCs decreases. The back bone polymer of the LC amphiphilic diblock copolymer must mix LCs confined in the core parts of LC polymeric micelles. On the other hand, in a LCNM system, the core parts of nano-micelles are occupied by LCs. Although a small amount of hydrophobic part of surfactant should mix with LCs in the core parts of nano-micelles, the concentration of impurities in the core parts of LCNMs is expected to be less than that of LC polymeric micelles.

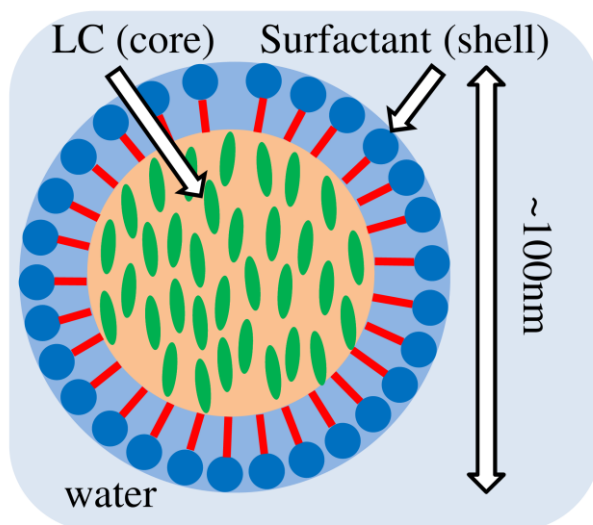


Fig.1.11 The schematic image of a LCNM dispersing in water [67, 68]. The core and shell parts of a nano-micelle are occupied by LCs and surfactants, respectively. The typical size of LCNMs is several hundred nanometers.

In the chapter III, we will fabricate SmA-LCNMs in which SmA-LCs are confined into the hydrophobic core parts of nano-micelles. As we will mention in the section 1.2.1, the diffusion of SmA-LCs along the layer normal direction is suppressed rather than that in layer plane by the layer order. If the alignment of LCs is homeotropic (the layer is parallel to surface of nano-micelles), an onion like structure appears as shown in Fig.1.12.

Multi-lamellar vesicles have an onion like structure of bilayers as shown in Fig.1.12. The inside and outside of a bilayer are occupied by hydrophobic parts of the phospholipid and hydrophilic parts, respectively. Solvents such as water are put between bilayers. Additional molecules introduced in the center of vesicles are held because inside and outside of vesicles are completely separated by bilayers [69-71]. Therefore, vesicles are used as a drug carrier which can hold drug molecules [72, 73].

If SmA-LCNMs have the onion like structure, SmA-LCNMs are also expected to be able to hold drug molecules. Furthermore, the layer order is expected to disappear above the SmA-N phase transition temperature, which indicates that the onion like structure disappears. Since such a SmA-LCNM can release drug molecules loaded in the core part by means of temperature-change via the SmA-N phase transition, we believe that the SmA-LCNM is one of the most promising drug carriers in drug delivery system [74-77]. For this reason, it is important to reveal the layer structure of LCs in the core parts of nano-micelles and to investigate the mobility of LCs confined in the core parts of nano-micelles.

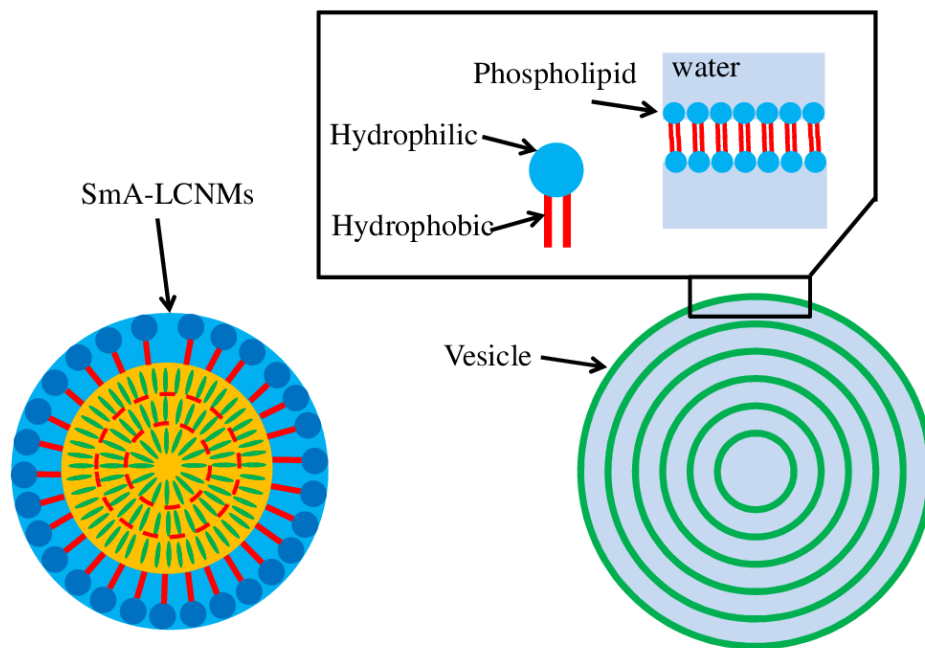


Fig.1.12 Schematic images of a SmA-LCNM and a multi-lamellar vesicle [69-71]: The core part of the SmA-LCNM is occupied by SmA-LCs. The multi-lamellar vesicle has an onion-like structure composed of bilayer of phospholipids and water. Inside and outside of bilayer are occupied by hydrophobic and hydrophilic parts of phospholipids, respectively.

1.4 The purposes and the construction of this paper

As we have mentioned in the sections 1.1 and 1.2, the confinement effect changes the physical properties of liquid crystals (LCs) from that in the bulk state. However, experimental difficulty has prevented us from investigating the effect of the three-dimensional confinement on LCs. As mentioned in the section 1.3, liquid crystalline nano-micelles (LCNMs) enable us to construct the experimental system in which we can investigate the effect of the three-dimensional confinement. In this paper, we fabricated nematic (N)- and smectic A (SmA)-LCNMs and investigated the effect of the three-dimensional confinement into nano-micelles on the LC order.

In the chapter II, we fabricated the N-LCNMs, and we investigated the N-Iso phase transition and orientational fluctuation of LCs confined in the core parts of nano-micelles. First, we controlled the hydrodynamic radii of nano-micelles by changing the weight ratio of LCs to surfactants, and then, we estimated the radii from the relaxation times of autocorrelation functions measured by the polarized dynamic light scattering experiment. Second, we used the depolarized light scattering technique to measure the scalar order parameter of LCs three-dimensionally confined in the nanometer-scale region, and we investigated the effect of the three-dimensional confinement on the N-Iso phase transition behavior. Finally, we studied the confinement effect on the orientational fluctuation of N-LCs by using the depolarized dynamic light scattering.

In the chapter III, we fabricated the SmA-LCNMs, and we investigated the SmA-N phase transition and the mobility of LCs confined in nano-micelles. First, we performed the synchrotron X-ray scattering in order to confirm the layer order of LCs confined in the core parts of nano-micelles. Second, we investigated the effect of the confinement in nano-micelles on the SmA-N phase transition on the basis of critical behavior of the correlation length of the layer order. Third, we studied the mixing process of LC molecules between SmA- and N-LCNMs in order to estimate the mobility of LC molecules in the core parts of nano-micelles, and we investigated the effect of the layer order on the mobility of LCs confined in nano-micelles. Finally, we performed time-resolved synchrotron X-ray diffraction measurement in order to investigate the structural change in the layer structure during the mixing process.

Chapter II Orientational order of liquid crystals confined in the core parts of nano-micelles

The effect of the confinement in nanometer-sized containers can change the phase behavior of liquid crystals (LCs) [10-16, 28-31]. It was reported that the surface-induced order and the quenched disordering in the nanometer-scale silica channel [10-13] and in bicontinuous porous media [14-16] can change the isotropic-nematic (N) phase transition behavior from that in the bulk state. However, in previous works, the confinement is two-dimensional, at most, and hence the macroscopic orientational order should remain along one dimension.

In this chapter, first, we fabricated N-liquid crystalline nano-micelles (LCNMs) by introducing N-LCs into the core parts of nano-micelles. The samples which were used for fabrication of LCNMs were shown in the section 2.1. Second, we controlled the radii of LCNMs by changing the weight ratio of N-LCs to surfactant polymers, and the radii of LCNMs are determined by using polarized dynamic light scattering technique in the section 2.2. Third, we investigated the effect of the three-dimensional confinement on the N-Iso phase transition by using the depolarized light scattering technique in the section 2.3. Finally, we investigated the confinement effect on the orientational fluctuation of N-LCs in the core parts of nano-emulsions in the section 2.4.

2.1 Nematic liquid crystalline nano-micelles

We fabricated nematic (N)-liquid crystalline nano-micelles (LCNMs). In this section, we show the samples which were used in order to fabricate LCNMs. Then, we explain the way to fabricate LCNMs. Finally, we performed the differential scanning calorimetry measurement in order to investigate the thermodynamic properties of surfactants and LCNMs.

2.1.1 Samples

2.1.1.1 Sample preparation

In this section, we used N-LCs, 5CB and 7CB. The structural formulae of 5CB and 7CB are shown in Fig.2.1. The N-isotropic (Iso) phase transition temperatures of 5CB and 7CB in the bulk state are 35.0 °C and 42.8 °C, respectively. We used an amphiphilic diblock copolymer, Poly(ethylene oxide-b-6-[4'-cyanobiphenyl-4-yloxy]hexyl methacrylate) (PEO-PLC, Polymer Source Inc.). PEO-PLC has hydrophobic mesogenic side chains together with a hydrophilic PEO chain as shown in Fig.2.2.

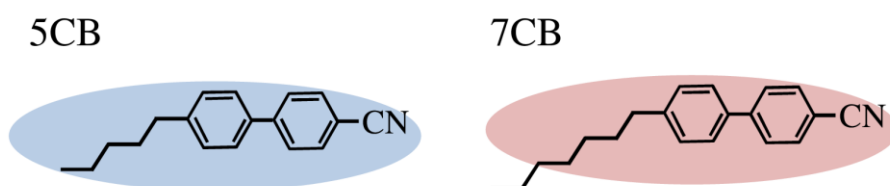


Fig.2.1 The structural formulae of 5CB and 7CB.

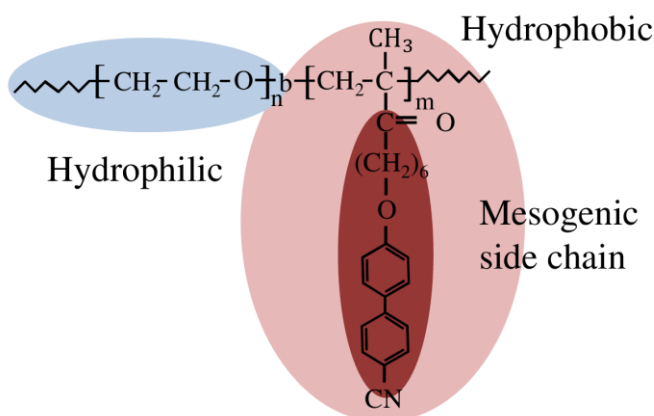


Fig.2.2 The structural formula of the Poly(ethylene oxide-b-6-[4'-cyanobiphenyl-4-yloxy]hexyl methacrylate) (PEO-PLC).

2.1.1.2 Emulsification

We got the N-LCNMs in the following way [67, 68]. PEO-PLCs and N-LCs are mixed with proper mixing ratio in acetone. We removed acetone by evaporation, and added water into this mixture. After the sonication for more than 2 hours at 60 °C, we purified this solution with a 1 μm diameter syringe filter.

2.1.2 Differential Scanning Calorimetry (DSC)

In order to confirm the phase series of PEO-PLC in the bulk state, we performed DSC measurement. We used micro-DSCIII (SETARAM Inc.). Fig.2.3 shows the temperature dependence of heat flow of PEO-PLC. PEO-PLC has the peak of heat flow at 49 °C on heating. This peak indicates the crystal-Iso phase transition of PEO-PLC on heating. On the other hand, the peak is observed at 28 °C on cooling. The integrated value of the peak of heat flow on cooling is close to that on heating. Thus, the peak on cooling also indicates the crystal-Iso phase transition of PEG-PLC. The difference in temperature dependence between on heating and on cooling originates from super cooling of PEO-PLC. Note that PEO-PLC has no LC phase even though PEO-PLC has mesogenic side chains.

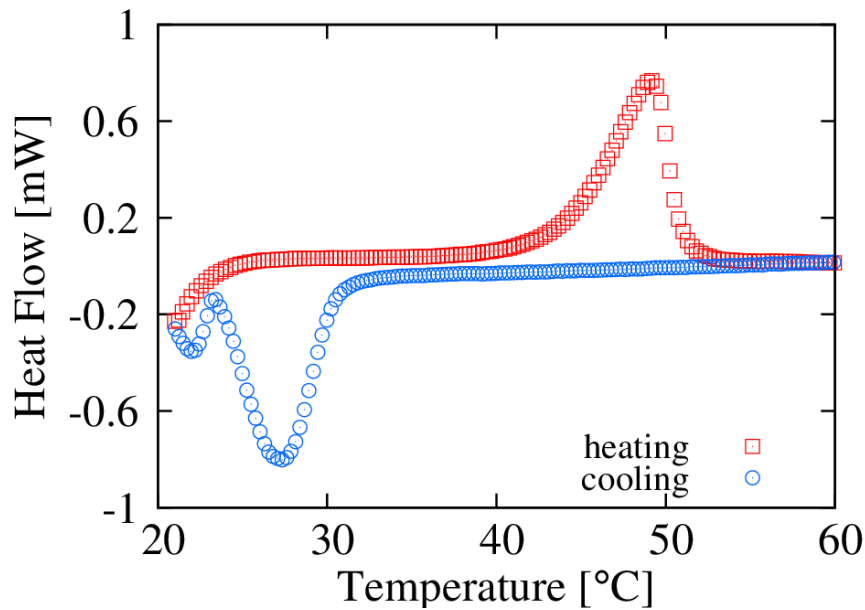


Fig.2.3 The temperature dependence of heat flow of PEO-PLC in the bulk state.

In order to confirm the phase transition of N-LCs confined in the core parts of nano-micelles, we performed the DSC measurement. We made 5CB- and 7CB-NMs by introducing the 5CB and 7CB in the core parts of nano-micelles, respectively.

Fig.2.4 shows the temperature dependence of the heat flow of the 5CB-NMs and that of

7CB-NMs. 5CB-NMs absorb heat at 34.0 °C, which is close to the N-Iso phase transition temperature of 5CB in the bulk state (~35 °C). Therefore, it is suggested that the endothermic peak corresponds to the N-Iso phase transition of 5CB-NMs. On the other hand, 7CB-NMs absorb heat at higher temperature which is close to the N-Iso phase transition temperature of 7CB in the bulk state (~42.8 °C). Thus, it is revealed that LCNMs exhibit the N-Iso phase transition near the N-Iso phase transition temperature of the N-LCs in the bulk state.

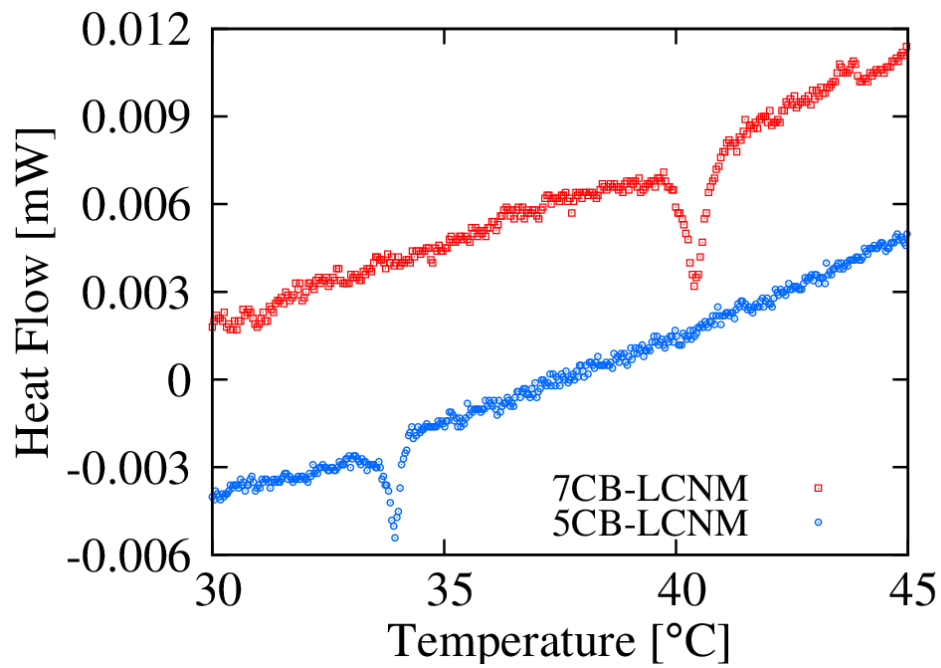


Fig.2.4 The temperature dependence of the heat flow of the 5CB-NMs and that of 7CB-NMs.

2.2 Size of nematic liquid crystalline nano-micelles

In this section, we controlled the radii of liquid crystalline nano-micelles (LCNMs) by changing the weight ratio of nematic (N)-LCs to surfactant. Micelles are usually consisted of water and a surfactant. On the other hand, LCNMs are consisted of water, a surfactant and LCs. Therefore, we can change the ratio of LCs to surfactants. If the LCs simply swell the core parts of nano-micelles, the radius is expected to increase as the ratio of LCs to surfactants increases. We introduced the simple theoretical model dealing with radii of LCNMs. Then, we performed the dynamic light scattering experiment, and determined the hydrodynamic radius as a function of the weight ratio of LCs to surfactants. We compared the experimental results with theoretical prediction in order to confirm the validity of our model.

2.2.1 Theoretical model

In this section, we used 7CB (Fig.2.1) as N-LCs. In LCNMs, the core part is filled with 7CB while the shell part is filled with PEO-PLC because 7CB and PEO-PLC are hydrophobic and amphiphilic, respectively. We constructed the theoretical model dealing with the radii as a function of the weight ratio of 7CB to PEO-PLC, α ($=w_{7CB}/w_{PEO-PLC}$, where w_{7CB} and $w_{PEO-PLC}$ are the weight of 7CB and PEO-PLC, respectively) with two hypotheses: I) 7CB in the core part and PEO-PLC in the shell part are completely separated, II) density of

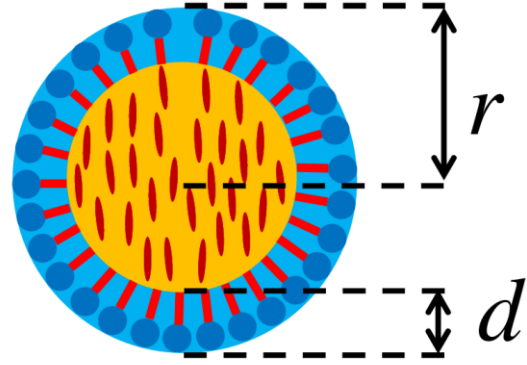


Fig.2.5 Schematic image of LCNMs: the core part and the shell part are filled with 7CB and PEG-PLC, respectively. r and d are the radius and the shell thickness, respectively.

7CB, ρ_{7CB} , PEO-PLC, $\rho_{PEO-PLC}$ and the thickness of shell parts, d are independent of the weight ratio α . Since we assumed hypothesis I), the volume of the core part V_{core} and the shell part V_{shell} are given as follows:

$$V_{core} = w_{7CB} / \rho_{7CB}, \quad (2.2.1)$$

$$V_{shell} = w_{PEO-PLC} / \rho_{PEO-PLC}. \quad (2.2.2)$$

For the geometrical reason (Fig.(2.5)), V_{core} and V_{shell} are given as follows:

$$V_{core} = \frac{4\pi}{3}(r-d)^3, \quad (2.2.3)$$

$$V_{shell} = \frac{4\pi}{3}\{r^3 - (r-d)^3\}. \quad (2.2.4)$$

Here, r is the radius of a LCNM. We can obtain the relation between α and r as follows:

$$r = \frac{(1 + \gamma\alpha)^{1/3}}{(1 + \gamma\alpha)^{1/3} - (\gamma\alpha)^{1/3}} d, \quad (2.2.5)$$

where γ is the density ratio of $\rho_{\text{PEO-PLC}}$ to ρ_{7CB} . If hypothesis II) is correct, γ and d are independent of α , and it is revealed that r monotonically increases with increasing α . Fig. 2.6 shows α dependence of r . Here, we assume that $\gamma=0.5$ and $d=100$ nm. For $\alpha>0.1$, r linearly increases with increasing α .

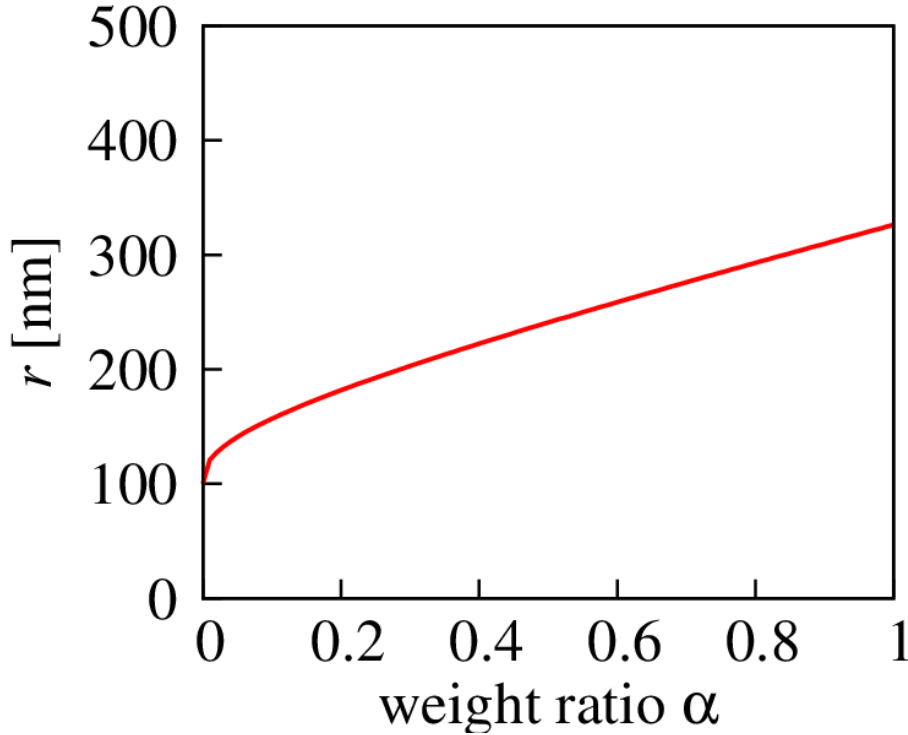


Fig. 2.6 Weight ratio, α dependence of the radius of LCNMs, r . Here, we assume that $\gamma=0.5$ and $d=100$ nm.

2.2.2 Dynamic light scattering

2.2.2.1 Experimental setup

In order to estimate the hydrodynamic radius of LCNMs, we performed the dynamic light scattering (DLS) experiment in which we measured autocorrelation function of the intensity of polarized (VV) scattered light. Fig.2.7 shows the schematic experimental setup of DLS measurement. The wave length of incident beam is 532 nm. The direct beam is scattered by sample, and the scattered beam is detected by PMT. The intensity correlation function is calculated by the ALV-5000 correlator. By changing the angle of the $\lambda/2$ wave plate, we can select the VV component of scattered light. We enclosed the sample into quartz cell whose thickness is about 1 mm, and then set the cell on the temperature-controlled holder.

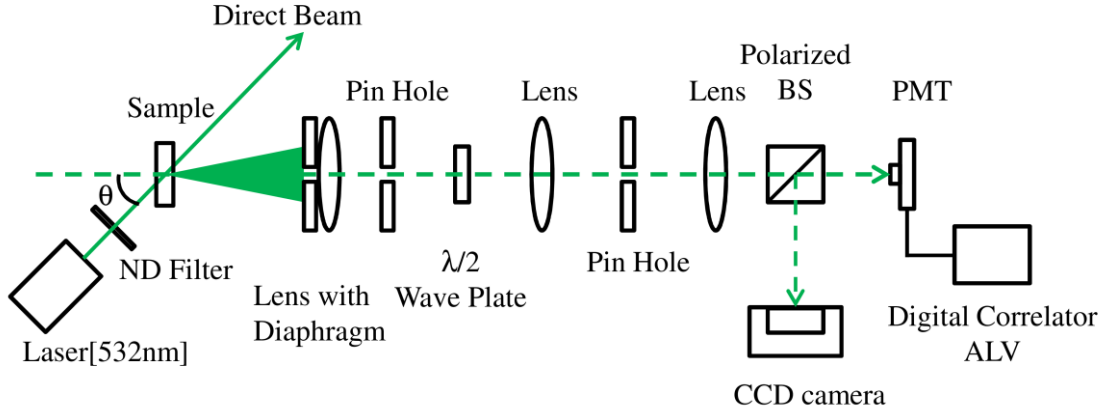


Fig.2.7 The schematic setup of the DLS measurement.

The laser and the sample holder are placed on a rotational stage. Thus, we can control the scattering angle, θ which is defined as the angle between direct and scattering lights. In particular, we set θ over the range $18^\circ < \theta < 39^\circ$. Fig.2.8 shows the relation between the scattering angle and the scattering vector, $\mathbf{q}$ defined as $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$, where $\mathbf{k}_i$ and $\mathbf{k}_f$ are the wave vectors of the incident light and the scattering light, respectively. We can change the magnitude of the scattering vector $q = |\mathbf{q}|$ from $4.93 \times 10^6 \text{ m}^{-1}$ ($\theta = 18^\circ$) to $1.05 \times 10^7 \text{ m}^{-1}$ ($\theta = 39^\circ$).

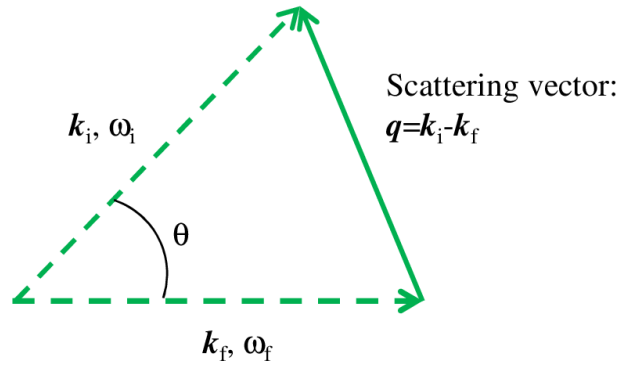


Fig.2.8 The schematic image of relation between the scattering angle and the scattering vector.

In the homodyne method, the autocorrelation function of the intensity of scattered light, $I_2(t) = \langle E(0)E^*(0)E(t)E^*(t) \rangle$, is obtained. On the other hand, in heterodyne method the autocorrelation function of the electric field, $I_1(t) = \langle E(0)E^*(t) \rangle$, is obtained [78]. Forth moment can be represented by second moment as follows.

$$\langle x_1 x_2 x_3 x_4 \rangle = \langle x_1 x_2 \rangle \langle x_3 x_4 \rangle + \langle x_1 x_3 \rangle \langle x_2 x_4 \rangle + \langle x_1 x_4 \rangle \langle x_2 x_3 \rangle. \quad (2.2.6)$$

Considering that $\langle E(0)E(t) \rangle$ and $\langle E^*(0)E^*(t) \rangle$ are equal to zero, the relation between $I_1(t)$ and $I_2(t)$ is described as shown below.

$$I_2(t) = |I_1(0)|^2 + |I_1(t)|^2. \quad (2.2.7)$$

2.2.2.2 Theory of polarized light scattering [78]

The incident light of the ideal light scattering experiment is a plane wave. Thus, incident electric field, $\mathbf{E}_{\text{in}}$, is represented as follows.

$$\mathbf{E}_{\text{in}}(\mathbf{r}, t) = \mathbf{n}_i E_0 \exp(i[\mathbf{k}_i \cdot \mathbf{r} - \omega_i t]),$$

where $\mathbf{n}_i$, E_0 and ω_i are the polarization, the amplitude of the plane wave and the circular frequency of incident beam, respectively. $\mathbf{E}_{\text{in}}$ is scattered by the contrast of the dielectric constant between water and LCNMs. Since LCNMs exhibit the thermally excited Brownian motions in water, the distribution of the dielectric constant temporally fluctuates. The local dielectric tensor, $\boldsymbol{\varepsilon}(\mathbf{r}, t)$, is represented by mean dielectric constant, ε_0 , and deviation from it, $\delta\boldsymbol{\varepsilon}(\mathbf{r}, t)$, as follows.

$$\boldsymbol{\varepsilon}(\mathbf{r}, t) = \varepsilon_0 \mathbf{I} + \delta\boldsymbol{\varepsilon}(\mathbf{r}, t), \quad (2.2.8)$$

where $\mathbf{I}$ is the unit matrix. The scattered electric field, E_s , far from sample, R ($\gg 1$), is represented as follows.

$$E_s(R, t) = \frac{E_0}{4\pi R \varepsilon_0} \exp(ik_f R) \int_V d^3r (\mathbf{n}_f \cdot \mathbf{k}_f \times [\mathbf{k}_f \times \{\delta\boldsymbol{\varepsilon}(\mathbf{r}, t) \cdot \mathbf{n}_i\}]) \exp(i[\mathbf{q} \cdot \mathbf{r} - \omega_i t]), \quad (2.2.9)$$

where $\mathbf{n}_f$ and $\mathbf{k}_f$ are the direction of polarizer and the wave vector of the scattering light, respectively. $\mathbf{q} = \mathbf{k}_i - \mathbf{k}_f$ is the scattering vector. In the case of LCNMs, we can assume that the wave length of the incident light is identical with that of the scattering light, ($|\mathbf{k}_i| \approx |\mathbf{k}_f|$). Thus, the magnitude of the scattering vector, q ($=|\mathbf{q}|$), is approximated as follows (Fig.2.8).

$$q \approx 2k_i \sin\left(\frac{\theta}{2}\right) = \frac{4\pi n}{\lambda_i} \sin\left(\frac{\theta}{2}\right), \quad (2.2.10)$$

where n is the refractive index. The Fourier transformation of $\delta\boldsymbol{\varepsilon}(\mathbf{r}, t)$ is defined as follows.

$$\delta\boldsymbol{\varepsilon}(\mathbf{q}, t) = \int_V d^3r \delta\boldsymbol{\varepsilon}(\mathbf{r}, t) \exp(i\mathbf{q} \cdot \mathbf{r}), \quad (2.2.11)$$

$$\delta\varepsilon_{\text{if}}(\mathbf{q}, t) = \mathbf{n}_f \cdot \delta\boldsymbol{\varepsilon}(\mathbf{q}, t) \cdot \mathbf{n}_i. \quad (2.2.12)$$

By using above equations, the scattered electric field, $E_s(R, t)$, is represented as follows.

$$\begin{aligned} E_s(R, t) &= \frac{E_0}{4\pi R \varepsilon_0} \exp\{i(k_f R - \omega_i t)\} (\mathbf{n}_f \cdot \{\mathbf{k}_f \times \mathbf{k}_f \times [\delta\boldsymbol{\varepsilon}(\mathbf{q}, t) \cdot \mathbf{n}_i]\}) \\ &= \frac{k_f^2 E_0}{4\pi R \varepsilon_0} \exp\{i(k_f R - \omega_i t)\} \delta\varepsilon_{\text{if}}(\mathbf{q}, t). \end{aligned} \quad (2.2.13)$$

Therefore, the autocorrelation function of electric field, $I_1(q, t)$, is described as shown below.

$$\langle E_s^*(R,t)E_s(R,0) \rangle = \frac{k_f^2 E_0}{16\pi^2 R^2 \epsilon_0^2} \langle \delta\epsilon_{if}(\mathbf{q},0)\delta\epsilon_{if}(\mathbf{q},t) \rangle. \quad (2.2.14)$$

We consider the system in which optically isotropic molecules dispersing in solvent. Dipole moment induced by the incident light is $\boldsymbol{\mu}=\boldsymbol{\alpha}\cdot\mathbf{E}$, where $\boldsymbol{\alpha}$ is a polarizability tensor. Since we assumed that molecules are isotropic, $\boldsymbol{\alpha}$ is represented as follows.

$$\alpha_{\alpha\beta} = \alpha \delta_{\alpha\beta}. \quad (2.2.15)$$

The scattered electric field at a detector is proportional to $\alpha^j \exp(i\mathbf{q}\cdot\mathbf{r}_j)$, where α^j and $\mathbf{r}_j$ are the polarizability tensor and the center of gravity of j th molecule, respectively. Since we can neglect multiple scattering in the dilute system, total scattered electric field, E_s , is described as shown below.

$$E_s = \sum_j b_j(t) \alpha_{if}^j(t) \exp(i\mathbf{q}\cdot\mathbf{r}_j(t)), \quad (2.2.16)$$

$$\alpha_{if} = \mathbf{n}_i \cdot \boldsymbol{\alpha} \cdot \mathbf{n}_f = \alpha (n_i)_\alpha (n_f)_\beta, \quad (2.2.17)$$

$$b_j(t) = \begin{cases} 1 & j \in V \\ 0 & j \notin V \end{cases}, \quad (2.2.18)$$

$$N(t) = \sum_j b_j(t), \quad (2.2.19)$$

where $N(t)$ is the total number of scattering molecules in the scattering volume, V . Since α is independent of time, the autocorrelation function of the scattered electric field is proportional to $F_1(\mathbf{q},t)$, where

$$F_1(\mathbf{q},t) = \langle \psi^*(\mathbf{q},t)\psi(\mathbf{q},t) \rangle = \left\langle \sum_j b_j(0)b_j(t) \exp[i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))] \right\rangle, \quad (2.2.20)$$

$$\psi(\mathbf{q},t) = \sum_j b_j \exp(i\mathbf{q}\cdot\mathbf{r}_j(t)). \quad (2.2.21)$$

In order to estimate the contribution of each term in eq.2.2.20, we discuss their characteristic time scale of the relaxation of eq.2.2.20. Only molecules in the scattering volume can contribute to $F_1(\mathbf{q},t)$. Thus, $b_j(0)=1$. The time scale for variation of $b_j(0)b_j(t)$, τ_b , is the time taken by j th molecule to move the characteristic distance L ($L^3 \sim V$). Therefore, τ_b is represented as follows.

$$\tau_b = \frac{L^2}{D}, \quad (2.2.22)$$

where D is the diffusion constant. On the other hand, $\exp[i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))]$ changes if the distance $(\mathbf{r}_j(t)-\mathbf{r}_j(0))$ becomes comparable length to q^{-1} ($q \sim 10^5 \text{ cm}^{-1}$). Thus, the time scale for variation of $\exp[i\mathbf{q}\cdot(\mathbf{r}_j(t)-\mathbf{r}_j(0))]$, τ_q , is described as shown below.

$$\tau_q = \frac{1}{q^2 D}. \quad (2.2.23)$$

The ratio of τ_b to τ_q is as follows,

$$\frac{\tau_b}{\tau_q} = (q^2 L)^2 \sim 10^6. \quad (2.2.24)$$

As a result, it is revealed that the time scale for variation of $b_j(0)b_j(t)$ is slower than that of $\exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))]$. Thus, we can regard $b_j(0)b_j(t)$ as $b_j(0)b_j(0)(=b_j(0))$. Considering $b_j(0)$ is independent of $\exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))]$, we got following equation.

$$\begin{aligned} F_1(\mathbf{q}, t) &= \left\langle \sum_j b_j(0) \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \right\rangle \\ &= \langle N \rangle F_s(\mathbf{q}, t), \end{aligned} \quad (2.2.25)$$

$$F_s(\mathbf{q}, t) = \left\langle \exp[i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \right\rangle. \quad (2.2.26)$$

$F_s(\mathbf{q}, t)$ is the self-intermediate scattering function. The Fourier transformation of $F_s(\mathbf{q}, t)$ is identical with the probability distribution function, $G_s(\mathbf{R}, t)$,

$$\begin{aligned} G_s(\mathbf{R}, t) &= \left\langle \delta(\mathbf{R} - [\mathbf{r}_j(t) - \mathbf{r}_j(0)]) \right\rangle \\ &= (2\pi)^{-3} \int d^3q F_s(\mathbf{q}, t) \exp(-i\mathbf{q} \cdot \mathbf{R}). \end{aligned} \quad (2.2.27)$$

In a LCNM system, $G_s(\mathbf{R}, t)$ is the solution of the diffusion equation,

$$\frac{\partial}{\partial t} G_s(\mathbf{R}, t) = D \nabla^2 G_s(\mathbf{R}, t). \quad (2.2.28)$$

We substituted eq.2.2.26 and eq.2.2.27 for eq.2.2.28, and obtained the following equation,

$$\frac{\partial}{\partial t} F_s(\mathbf{q}, t) = -q^2 D F_s(\mathbf{q}, t). \quad (2.2.29)$$

Since $F_s(\mathbf{q}, 0)=1$, the self-intermediate scattering function is an exponential relaxation function.

$$\begin{aligned} F_s(\mathbf{q}, t) &= \exp(-q^2 D t) \\ &= \exp\left(-\frac{t}{\tau_q}\right), \end{aligned} \quad (2.2.30)$$

where $\tau_q=(q^2 D)^{-1}$ is the relaxation time defined in eq.2.2.23. The autocorrelation function of the scattered electric field is proportional to $F_s(\mathbf{q}, t)$. In homodyne method, we measure the autocorrelation function of the scattered light intensity, $F_2(\mathbf{q}, t)$.

$$F_2(\mathbf{q}, t) = \langle N \rangle^2 + \langle N \rangle^2 \exp(-2q^2 D t). \quad (2.2.31)$$

Then, according to the Einstein-Stokes relation [78], the diffusion constant is related to the

hydrodynamic radius of LCNMs, r' .

$$D = \frac{k_B T}{6\pi\eta r'}, \quad (2.2.32)$$

where η is the viscosity constant of water. Therefore, we can estimate r' from the relaxation time of the autocorrelation function of the VV light scattering intensity.

2.2.2.3 Results and discussions

Fig.2.9 shows the typical data of the normalized autocorrelation function of the VV light scattering intensity of LCNMs as open squares. The weight ratio α and scattering angle θ are 0.8 and 24° (which corresponds to $q=6.55 \times 10^{-3} \text{ nm}^{-1}$), respectively. We fitted the experimental results using following function based on eq.2.2.30.

$$f(x) = A_0 \exp\left(-2\left(\frac{t}{\tau}\right)^\beta\right), \quad (2.2.33)$$

where β is a stretch parameter, which represents the degree of dispersity of the radius of LCNMs and we showed fitting results as dashed line in Fig.2.9. When β is equal to 1, radius distribution of LCNMs is monodisperse, and it has polydispersity when β is less than 1. Obtained fitting value are $\tau=24 \text{ ms}$, $\beta=0.84$ and $A_0=0.957$.

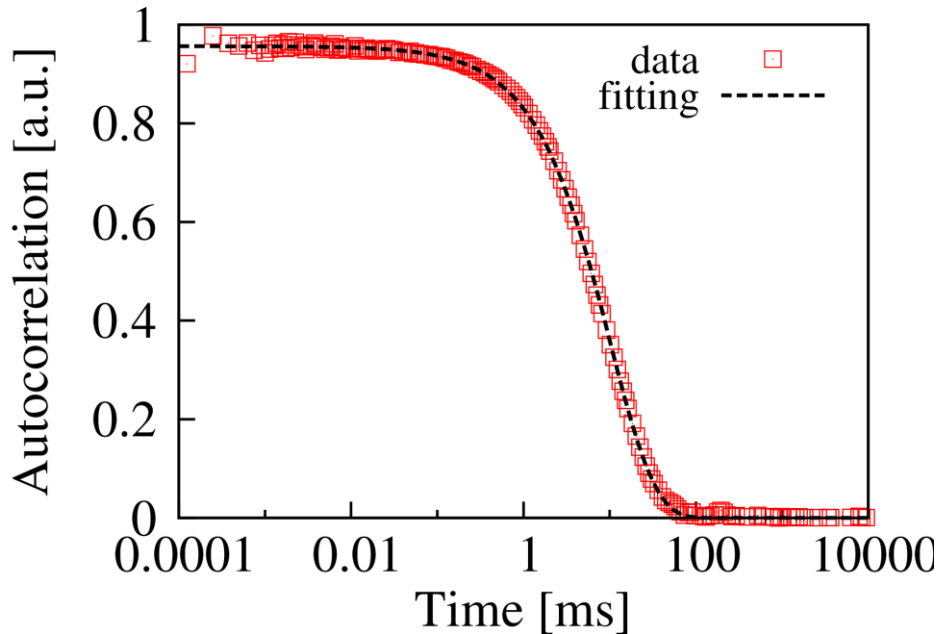


Fig.2.9 Autocorrelation function of the VV light scattering intensity: The open squares and dashed line represent the experimental data and fitting curve, respectively. The weight ratio α of LCNMs is 0.80 wt%. The scattering angle and wave number are 24° and $6.55 \times 10^{-3} \text{ nm}^{-1}$, respectively. Obtained fitting values are $\tau=24 \text{ ms}$, $\beta=0.84$ and $A_0=0.957$.

We measured the autocorrelation functions at various temperatures. Then, we estimated the hydrodynamic radius, r' from the relaxation time obtained by fitting with eq.2.2.32. We used temperature dependence of the viscosity of water, η reported by Ref.79. Fig.2.10 shows temperature dependence of the hydrodynamic radius of LCNMs. The scattering angle θ and weight ratio α are 24° ($q=6.55 \times 10^6 \text{ m}^{-1}$) and 0.80, respectively. It is revealed that r' is independent of temperature. The average value of r' is 319 nm and standard deviation is 15.1 nm.

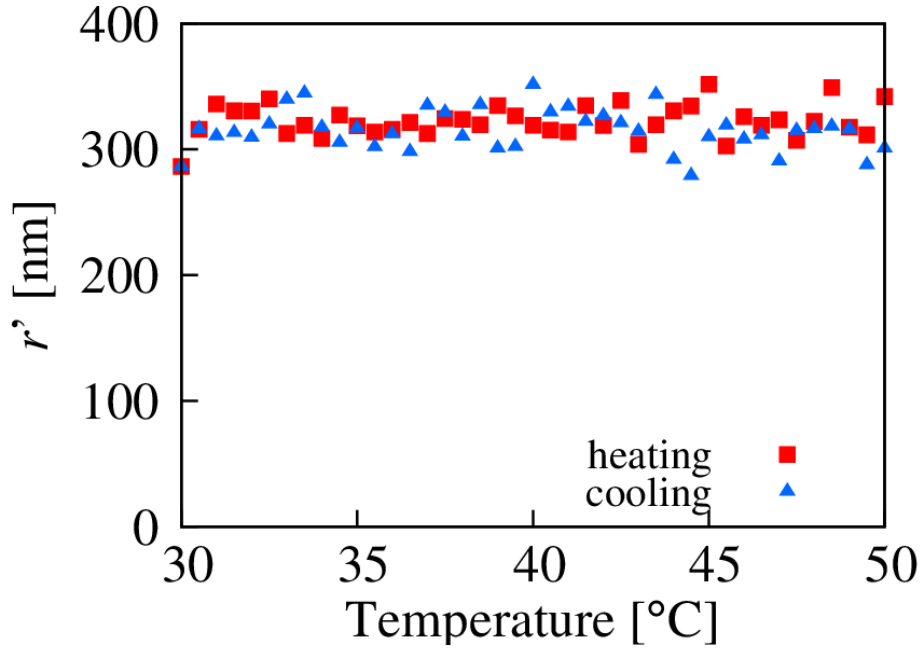


Fig.2.10 shows temperature dependence of the hydrodynamic radius of LCNMs. The scattering angle θ and weight ratio α are 24° ($q=6.5 \times 10^6 \text{ m}^{-1}$) and 0.80, respectively.

Fig.2.11 shows the q^{-2} dependence of τ at 30°C . According to eq.2.2.23, τ is expected to be proportional to q^{-2} [39]. Thus we fitted experimental data using the following dispersion relation.

$$\tau = A + \frac{1}{D} \times q^{-2}, \quad (2.2.34)$$

where D and A are the diffusion constant in eq.2.2.23 and a fitting parameter, respectively. The experimental results are well fitted by the dispersion relation eq.2.2.34. It is revealed that A and $1/D$ are -1.82 ms and $12.2 \times 10^{14} \text{ ms m}^{-2}$, respectively. The hydrodynamic radius r' was estimated to be 346 nm.

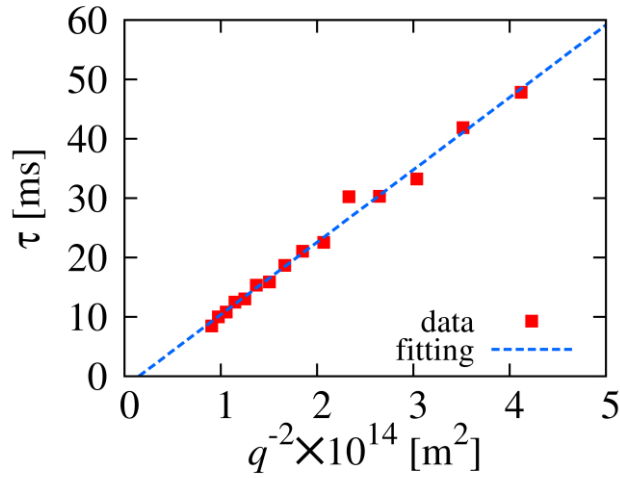


Fig.2.11 q^{-2} dependence of τ at 30 °C. We fitted the experimental data with eq.2.2.34. A and $1/D$ are -1.82 ms and 12.2×10^{14} ms m^{-2} , respectively.

Fig.2.12 shows the hydrodynamic radius r^* as a function of the weight ratio α . The broken blue line indicates the vest fit by eq.2.2.5. If we assume that the shell thickness, d , is independent of α , micelles can be swollen by the increase in 7CB in accordance with the simple dilution law (eq.2.2.5). Thus, we can control the radius of LCNMs by the weight ratio α . The shell thickness d is estimated as 57.93 ± 15.88 nm. Since the fitting line obtained from eq.2.2.5 agrees with experimental result, it is suggested that almost all 7CB molecules are confined in the hydrophobic core.

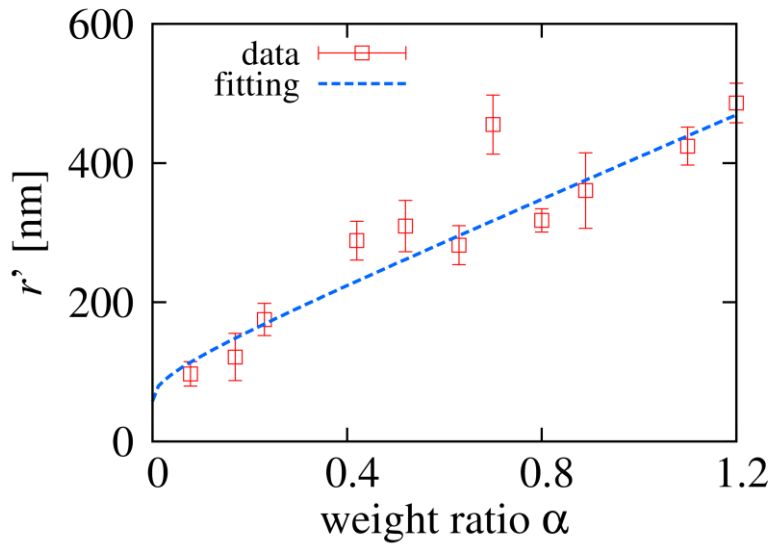


Fig.2.12 The weight ratio, α , dependence of the hydrodynamic radius of LCNMs, r^* . the open square symbols show the hydrodynamic radius of LCNMs as a function of the weight ratio, and the broken line indicate the best-fitting curve calculated by eq.2.2.5.

2.2.3 Summary

We succeeded in fabricating LCNMs by introducing N-LCs into the hydrophobic core parts. In VV DLS experiment, we measured the autocorrelation function of the scattered light intensity. In order to obtain the relaxation time of translational diffusion, we fitted the autocorrelation function by a single exponential function. Then, we estimated the hydrodynamic radius of LCNMs from the relaxation time within Einstein-Stokes relation. It was revealed that the radius of LCNMs becomes larger as the weight ratio of N-LCs increases. In order to analyze the behavior of the hydrodynamic radius, we constructed the simple model with assumption that micelles can be swollen by the increase in N-LCs in accordance with the simple dilution law. As a result, it was revealed that hydrodynamic radius obtained by DLS is well fitted by our simple model. Therefore, we concluded that N-LCs are completely confined in the core parts of nano-micelles, and the hydrodynamic radii of LCNMs can be controlled by changing the weight ratio of LCs to surfactant.

2.3 Phase transition of confined liquid crystals

We succeeded in fabricating nematic (N)-liquid crystalline nano-micelles (LCNMs) by introducing N-LCs into the hydrophobic core parts. The diameter of LCNMs is of the order of several hundred nanometers. Moreover, radii of LCNMs can be controlled by changing the weight ratio of LCs to surfactant. In this section, we studied the orientational order of LCs three-dimensionally confined in the nanometer-scale region by using light scattering technique. In particular, we investigated the effect of three-dimensional confinement on the isotropic (Iso)-N phase transition.

2.3.1 Light scattering

2.3.1.1 Experimental setup

We performed light scattering experiment using the same equipment as that used in the section 2.2.2.1. In this section, we used the depolarized (VH) geometry in which the polarization of the incident beam is perpendicular to that of analyzer. In this experiment, we measured the mean intensity of the scattered light.

2.3.1.2 Theory of depolarized light scattering

According to the theory of light scattering from a small nematic droplet [80], the mean VH light scattering intensity, I_{VH} , reflects the orientational order of N-LCs in the core parts of nano-micelles. In this section, we deal the detail of this theory.

The incident light is scattered by a nematic droplet in isotropic solvent. The dielectric constant of the isotropic solvent is ϵ_m . For the situation in which the size of the nematic droplet is close to the wave length, we can use the Rayleigh Gans approximation (RGA). Dipole moment, $\mathbf{P}_s(\mathbf{r}_m)$, induced by the incident light at the distance from the center of the droplet, $\mathbf{r}_m$, is represented as follows.

$$\mathbf{P}_s(\mathbf{r}_m) = \epsilon_0 \epsilon_m [\boldsymbol{\epsilon}_r(\mathbf{r}_m) - \mathbf{I}] \mathbf{E}(\mathbf{r}_m),$$

where $\mathbf{E}(\mathbf{r}_m)$ is the electric field at $\mathbf{r}_m$. $\boldsymbol{\epsilon}_r(\mathbf{r}_m) = \boldsymbol{\epsilon}'/\epsilon_m$ is the tensor defined by the ratio of the dielectric constant of LCs to that of isotropic solvent as follows.

$$\boldsymbol{\epsilon}_r = \frac{1}{\epsilon_m} \begin{pmatrix} \epsilon_{\perp} & 0 & 0 \\ 0 & \epsilon_{\perp} & 0 \\ 0 & 0 & \epsilon_{\parallel} \end{pmatrix}, \quad (2.3.1)$$

where $\epsilon_{\perp}$ and $\epsilon_{\parallel}$ are the eigenvalues perpendicular and parallel to molecular long axis, respectively. The scattered electric field far from the drop ($kr \gg 1$) is described as shown below.

$$\mathbf{E}_s = \mathbf{f}(\mathbf{k}, \mathbf{k}') \frac{\exp(ikr)}{r}, \quad (2.3.2)$$

$$f(\mathbf{k}, \mathbf{k}') = -\frac{1}{4\pi} \int dV \mathbf{k} \times \mathbf{k}' \times \{[\boldsymbol{\varepsilon}_r(\mathbf{r}_m) - \mathbf{I}] \cdot \mathbf{E}(\mathbf{k}, \mathbf{r}_n)\} \exp(-i\mathbf{k}' \cdot \mathbf{r}_n). \quad (2.3.3)$$

Here, $f(\mathbf{k}, \mathbf{k}')$ is the amplitude of the scattering electric field, where $\mathbf{k}$ and $\mathbf{k}'$ are the scattering vectors of the incident and the scattering light, respectively. The amplitude of $\mathbf{k}$ equals that of $\mathbf{k}'$ as shown follows.

$$|\mathbf{k}| = |\mathbf{k}'| = \frac{2\pi n_m}{\lambda}, \quad (2.3.4)$$

where λ is the wave length. In RGA, the incident light, $\mathbf{E}(\mathbf{r}_m)$, is regarded as the plane wave.

$$\mathbf{E}(\mathbf{k}, \mathbf{r}_n) = \mathbf{E}_0 \exp(i\mathbf{k} \cdot \mathbf{r}_n). \quad (2.3.5)$$

We substituted eq.2.3.5 for eq.2.3.3, and obtained the following equation,

$$f(\mathbf{k}, \mathbf{k}') = \frac{1}{4\pi} V k^2 E_0 \{ \mathbf{D} \mathbf{e} - \mathbf{i}' [\mathbf{i}' \cdot (\mathbf{D} \mathbf{e})] \}, \quad (2.3.6)$$

$$\mathbf{D} = \frac{1}{V} \int dV (\boldsymbol{\varepsilon}_r - \mathbf{I}) \exp(-i\mathbf{k}_s \cdot \mathbf{r}_n), \quad (2.3.7)$$

where $\mathbf{i} = \mathbf{k}/k$, $\mathbf{i}' = \mathbf{k}'/k'$ and $\mathbf{e} = \mathbf{E}_0/E_0$ are the unit wave vector of incident, scattering light and polarization, respectively. $\mathbf{D}$ is the Fourier transformation of $(\boldsymbol{\varepsilon}_r - \mathbf{I})$, and $\mathbf{k}_s = \mathbf{k}' - \mathbf{k}$ is the scattering vector in eq.2.2.10. In order to distinguish anisotropic part from isotropic part, we introduced ζ and η as follows,

$$\zeta = \varepsilon_r - 1, \quad (2.3.8)$$

$$\eta = \frac{\varepsilon_{\parallel} - \varepsilon_{\perp}}{3\varepsilon_m}, \quad (2.3.9)$$

where $\varepsilon_r = 1/3 \text{Tr}(\boldsymbol{\varepsilon}_r)$ is mean dielectric constant. By using ζ and η , $(\boldsymbol{\varepsilon}_r - \mathbf{I})$ is represented as follow.

$$\boldsymbol{\varepsilon}_r - \mathbf{I} = \zeta \mathbf{I} + \eta \mathbf{Q}(\phi_n, \theta_n) \boldsymbol{\beta}_0 \mathbf{Q}(\phi_n, \theta_n)^{-1}, \quad (2.3.10)$$

$$\boldsymbol{\beta}_0 = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 2 \end{pmatrix}, \quad (2.3.11)$$

where $\mathbf{Q}(\phi_n, \theta_n)$ is the transfer matrix from the laboratory frame to nematic frame in which z axis is parallel to the molecular long axis. In cylindrical coordinates (k_{sp}, ϕ_s, k_{sz}) , $\mathbf{D}$ is represented by eq.2.3.8 and eq.2.3.9 as follows.

$$\mathbf{D} = \mathbf{I} \zeta u(k_s R) + \eta \sum_{j=0, \pm 1, \pm 2} \boldsymbol{\beta}_j v_j(k_{sp}, \phi_s, k_{sz}), \quad (2.3.12)$$

$$\boldsymbol{\beta}_{+1} = \begin{pmatrix} 0 & 0 & 1 \\ 0 & 0 & 0 \\ 1 & 0 & 0 \end{pmatrix}, \quad \boldsymbol{\beta}_{-1} = -\begin{pmatrix} 0 & 0 & 0 \\ 0 & 0 & 1 \\ 0 & 1 & 0 \end{pmatrix}, \quad \boldsymbol{\beta}_{+2} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad \boldsymbol{\beta}_{-2} = -\begin{pmatrix} 0 & 1 & 0 \\ 1 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}, \quad (2.3.13)$$

$$u(k_s R) = \frac{3}{(Rk_s)^3} [\sin(Rk_s) - Rk_s \cos(Rk_s)], \quad (2.3.14)$$

$$v_0(Rk_{sp}, Rk_{sz}) = \frac{4\pi}{V} \int_0^R \int_0^{\rho(z)} d\rho_n dz_n (1 - \frac{3}{2} \sin^2 \theta_n) J_0(k_{sp} \rho_n) \cos(k_{sz} z_n) \rho_n, \quad (2.3.15)$$

$$v_{\pm 1}(Rk_{sp}, \phi_s, Rk_{sz}) = -\frac{4\pi}{V} \left\{ \frac{\cos \phi_s}{\sin \phi_s} \right\} \int_0^R \int_0^{\rho(z)} d\rho_n dz_n \sin(2\theta_n) J_1(k_{sp} \rho_n) \sin(k_{sz} z_n) \rho_n, \quad (2.3.16)$$

$$v_{\pm 2}(Rk_{sp}, \phi_s, Rk_{sz}) = -\frac{4\pi}{V} \left\{ \frac{\cos 2\phi_s}{\sin 2\phi_s} \right\} \int_0^R \int_0^{\rho(z)} d\rho_n dz_n \sin^2 \theta_n J_2(k_{sp} \rho_n) \cos(k_{sz} z_n) \rho_n, \quad (2.3.17)$$

where J_0 , J_1 and J_2 are Bessel functions. The terms of ζ and η in eq.2.3.12 are diagonal and off-diagonal element of dielectric tensor, respectively. We separated scattered electric field into the components in scattering plane, $E_{s\parallel}$, and perpendicular to this plane, $E_{s\perp}$.

$$\begin{pmatrix} E_{s\parallel} \\ E_{s\perp} \end{pmatrix} = \frac{Vk^2 E_0}{4\pi} \frac{\exp(ikr)}{r} \begin{pmatrix} \mathbf{i}_{\parallel} \cdot (D\mathbf{e}) \\ \mathbf{i}_{\perp} \cdot (D\mathbf{e}) \end{pmatrix} = \begin{pmatrix} S_{\parallel\parallel} & S_{\parallel\perp} \\ S_{\perp\parallel} & S_{\perp\perp} \end{pmatrix} \begin{pmatrix} \mathbf{e} \cdot \mathbf{i}_{\parallel} \\ \mathbf{e} \cdot \mathbf{i}_{\perp} \end{pmatrix} E_0 \frac{\exp(ikr)}{kr}, \quad (2.3.18)$$

where $\mathbf{i}_{\perp}$ and $\mathbf{i}_{\parallel}$ are the unit vectors perpendicular and parallel to the scattering plane, respectively. S are van Hulst's scattering matrices,

$$S_{ps} = \frac{(kR)^3}{3} [\zeta(\mathbf{i}_p \cdot \mathbf{i}_s) u + \eta \sum_j \mathbf{i}_p \cdot (\boldsymbol{\beta}_j \mathbf{i}_s) v_j]. \quad (2.3.19)$$

Here, indices (p and s) take $\parallel$ or $\perp$. In our experiment, that is, VH geometry, p and s are $\perp$ and $\parallel$, respectively. Thus, the light scattering intensity, I_{VH}^{th} , is calculated as follows.

$$I_{VH}^{\text{th}} = \frac{\eta^2}{(kr)^2} \left| B_2 \sin^2 \alpha - B_3 \cos^2 \alpha + \frac{1}{2} (B_1 - B_4) \sin 2\alpha \right|^2, \quad (2.3.20)$$

$$B_1 = \sum_j \mathbf{i}_{\parallel} \cdot (\boldsymbol{\beta}_j \mathbf{i}_{\parallel}) v_j, \quad B_2 = \sum_j \mathbf{i}_{\parallel} \cdot (\boldsymbol{\beta}_j \mathbf{i}_{\perp}) v_j, \\ B_3 = \sum_j \mathbf{i}_{\perp} \cdot (\boldsymbol{\beta}_j \mathbf{i}_{\parallel}) v_j, \quad B_4 = \sum_j \mathbf{i}_{\perp} \cdot (\boldsymbol{\beta}_j \mathbf{i}_{\perp}) v_j. \quad (2.3.21)$$

Since LCNMs are uniformly dispersed in water and exhibit the thermally excited rotational Brownian motions, the director of nematic LCs is perfectly random. Therefore, the light scattering intensity obtained by experiment, I_{VH} , can be calculated by integrating I_{VH}^{th} over the angle between

the director of LCs and the scattering vector,

$$I_{\text{VH}} = \int I_{\text{VH}}^{\text{th}} d\alpha d\theta d\gamma$$

$$= \text{const} \times \eta^2. \quad (2.3.22)$$

Since η is proportional to the anisotropy of dielectric constants ($\epsilon_{\parallel} - \epsilon_{\perp}$), I_{VH} is proportional to $(\epsilon_{\parallel} - \epsilon_{\perp})^2$. As a good approximation, the scalar order parameter S is proportional to the birefringence, $\Delta n (= n_e - n_o$, where n_o and n_e are the ordinary and extraordinary refractive indices, respectively) [32]. Since the temperature dependence of $(\epsilon_{\parallel} - \epsilon_{\perp})$ is stronger than that of the average dielectric constant, $1/3((\epsilon_{\parallel} + 2\epsilon_{\perp}))$, the order parameter is approximately proportional to the dielectric anisotropy $(\epsilon_{\parallel} - \epsilon_{\perp})$. Therefore, we can introduce the relation between I_{VH} and $S(T)$ is approximated as follows,

$$I_{\text{VH}} \propto S(T)^2. \quad (2.3.23)$$

2.3.1.3 Results and discussions

Fig.2.13 shows temperature dependence of the VH light scattering intensity, I_{VH} , in mixtures with $\alpha=1.2$ and 0.17. The light scattering intensity in the mixture with $\alpha=1.2$ ($r'=480$ nm) abruptly decreases at 40.5 °C on heating. This temperature is close to the N-Iso phase transition temperature of the 7CB in the bulk state $T_{\text{IN}}^{\text{b}}=42$ °C. Considering that I_{VH} is quadratically proportional to the orientational order parameter, S , this abrupt change is ascribed to the N-Iso phase transition. In contrast, I_{VH} of the mixture with $\alpha=0.17$ ($r'=130$ nm) gradually decreases but does not attain to zero even at temperature higher than T_{IN}^{b} . It was suggested that the order of the phase transition behavior changes from the first order to the biased second order. This result is consistent with the phase transition behavior of the LCs confined into parallel silica channels with 10 nm diameter reported by Kityk *et al.* [10].

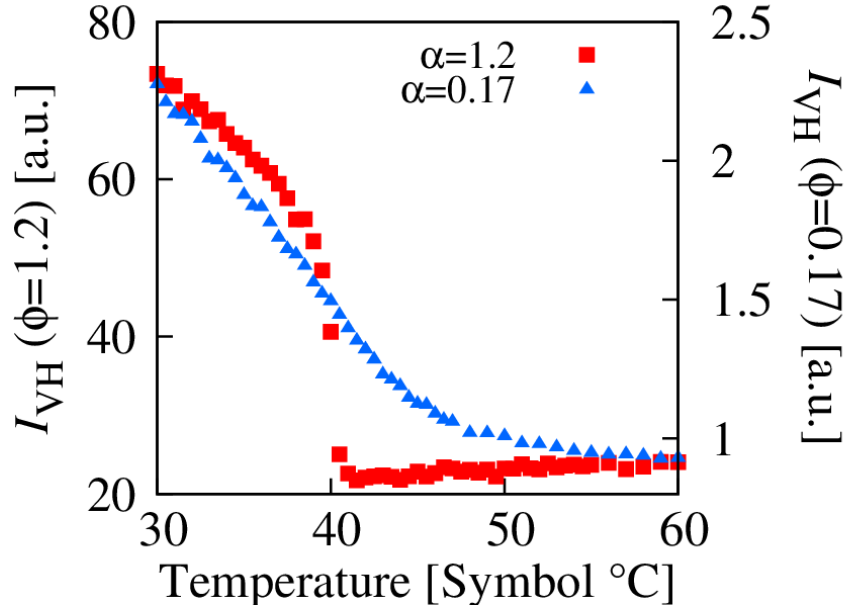


Fig.2.13 Temperature dependence of the light scattering intensity, I_{VH} , in mixtures with $\alpha=1.2$ and 0.17 .

2.3.2 Theoretical analysis

2.3.2.1 KKLZ model [10, 14-16]

We analyzed the behavior of $I_{VH}(T)$ based on the Kutnjak, Kralj, Lahajnar and Zumer (KKLZ) model. The KKLZ model includes the surface interaction, and so it is suitable to deal with the N-Iso phase transition of LCs confined in nanometer scale region. In KKLZ model, the free energy, F , is described by homogeneous (f_h), elastic (f_e), gradient (f_{grad}), Gaussian curvature (f_{gauss}) and surface (f_s) terms as follow,

$$F = \int d^3r (f_h + f_e + f_{grad} + f_{gauss}) + \int d^2r f_s, \quad (2.3.24)$$

$$f_h = A_0(T - T_*)S^2 - bS^3 + cS^4, \quad (2.3.25)$$

$$f_e = \frac{K_{11}}{2}(\text{div}\mathbf{n})^2 + \frac{K_{22}}{2}(\mathbf{n} \times \text{curl}\mathbf{n})^2 + \frac{K_{33}}{2}(\mathbf{n} \cdot \text{curl}\mathbf{n})^2, \quad (2.3.26)$$

$$f_{grad} = -\frac{L}{2}(\text{grad}S)^2, \quad (2.3.27)$$

$$f_{gauss} = -\frac{K_{24}}{2}\text{div}(\mathbf{n} \times \text{curl}\mathbf{n} + \mathbf{n}\text{div}\mathbf{n}), \quad (2.3.28)$$

$$f_s = (-W_1S\left(\frac{3(\mathbf{n} \cdot \mathbf{e})^2 - 1}{2}\right) + W_2S^2), \quad (2.3.29)$$

where A_0 , b and c are phenomenological parameters dealing with the N-Iso phase transition. K s and L are the elastic constants of the director, $\mathbf{n}$, and that of the orientational order parameter, S , respectively. W_1 and W_2 are the surface interaction strength of ordering and that of disordering, respectively. The W_1 term induces S at surface, and the W_2 term disturbs S at surface. The director tends to align along the direction of $\mathbf{e}$ at surface. We can obtain the dimensionless free energy density, g , by calculating eq.2.3.24 with the following hypotheses: I) elastic constants, K and L , are proportional to S^2 [81, 82], II) the variation in S is restricted within the distance, ξ_n , from the core of a defect, III) the director, $\mathbf{n}$, is independent of S . g is represented as follows,

$$g = t_{\text{eff}} q^2 - 2q^3 + q^4 - \sigma q, \quad (2.3.30)$$

$$t_{\text{eff}} = \tau + \kappa, \quad (2.3.31)$$

$$\tau = \frac{T - T_*}{T_{\text{IN}} - T_*}, \quad (2.3.32)$$

$$\kappa = \frac{\xi_n^2}{2\xi_d^2} + \frac{\xi_n^2}{R\xi_n(T)} - \frac{\xi_n^2}{Rd_e^{(2)}} + t_{\text{def}}, \quad (2.3.33)$$

$$\sigma = \frac{\xi_n^2}{Rd_e^{(1)}}, \quad (2.3.34)$$

where t_{eff} and σ are the effective temperature and the coefficient which reflects the strength of surface induced order, respectively. S_0 is the order parameter at the N-Iso phase transition temperature, T_{IN} . $d_e^{(1)} = W_1/LS_0$ and $d_e^{(2)} = W_2/L$ are the penetration lengths of surface alignment and surface disorder in eq.2.3.29, respectively. $q = S/S_0$ is the normalized orientational order parameter. t_{def} originates from f_{grad} . κ is the coefficient which reflects quenched disordering due to surface irregularity and elastic distortion induced by geometry. κ simply shifts the phase transition temperature. In the KKLZ model, the fourth term in eq.2.3.30 was contributed by the surface free energy (the fourth in eq.2.3.24), and hence it was obtained by dividing the integrated surface free energy by volume. Thus, the coefficient σ is inversely proportional to the system size (eq.2.3.34). In the case of the bulk state, that is, $\sigma = \kappa = 0$, the dimensionless free energy is identical with that in the Landau-de Gennes (LdG) model.

In order to obtain q which minimizes g , we calculated eq.2.3.30 numerically using Newton's method. Fig.2.14 shows t_{eff} dependence of q . q discontinuously changes at the N-Iso phase transition temperature for $\sigma < 0.5$. However, discontinuous behavior of the N-Iso phase transition changes to continuous behavior for $\sigma \geq \sigma_c = 0.5$.

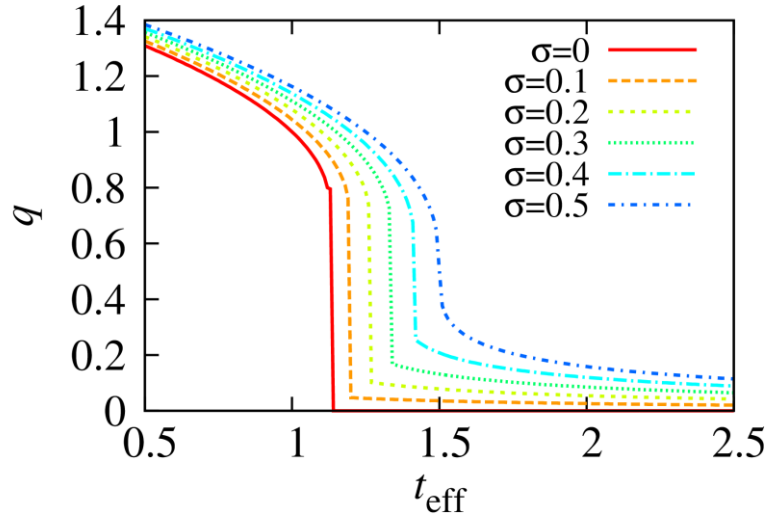


Fig.2.14 The effective temperature, t_{eff} , dependence of the normalized order parameter, q .

2.3.2.2 Preparation for theoretical analysis

$I_{\text{VH}}(T)$ includes finite and constant background above the N-Iso phase transition temperature (Fig.2.13). This origin should be the multiple scattering and the anisotropic shape of the nano-micelles. Fig 2.15 shows the temperature dependence of the VH light scattering intensity in the mixture of $\alpha=0$. Since this sample (PEO-PLC micelles) does not include 7CB, PEO-PLC micelles should not exhibit N phase. However, PEO-PLC micelles have the finite VH light scattering intensity which is independent of temperature. Thus, PEO-PLC also constantly contributes to $I_{\text{VH}}(T)$.

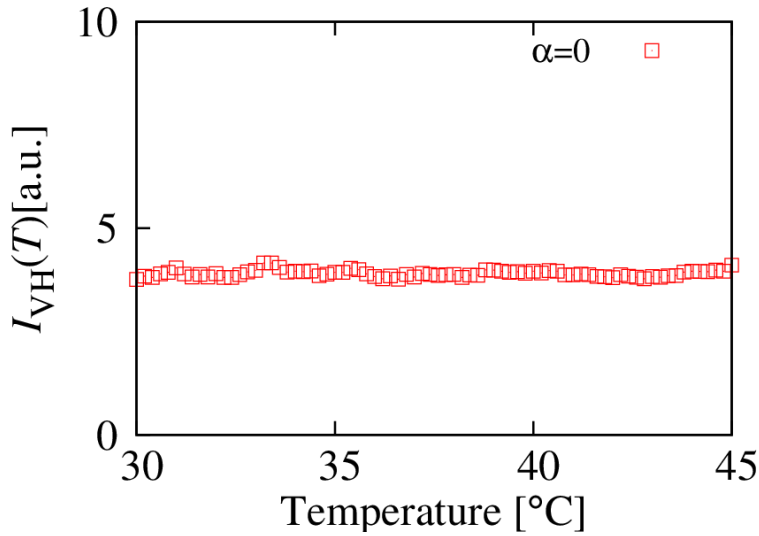


Fig 2.15 The temperature dependence of the light scattering intensity in the mixture of $\alpha=0$.

In order to distinguish the contribution of the orientational order of LCs in the core parts of nano-micelles from background, we normalized $I_{\text{VH}}(T)$, and then we obtained the square root of the normalized light scattering intensity, $i(t)$ as follows.

$$i(T) = \sqrt{\frac{I_{\text{VH}}}{I_{\text{min}}} - 1}, \quad (2.3.35)$$

where I_{min} reflects the constant component of the VH light scattering intensity.

2.3.2.3 Theoretical analysis within the KKLZ model

Fig2.16 shows temperature dependence of $i(T)$ of LCNMs in the mixture with $\alpha=1.2$ and 0.17 as square and circle symbols, respectively. We analyzed $i(T)$ whose $\alpha=1.2$ using the LdG free energy, that is, we set $\sigma=\kappa=0$ in eq.2.3.30. In the LdG theory, temperature dependence of the orientational order parameter is represented as follows.

$$q(T) = \frac{3 + \sqrt{9 - 8\tau}}{4} \quad (T < T_{\text{IN}}) \quad (2.3.36)$$

$$q(T) = 0 \quad (T > T_{\text{IN}}) \quad (2.3.37)$$

The broken red line in Fig.2.16 indicates the best-fitting curve calculated by eq.2.3.36 and eq.2.3.37. The experimental result was well fitted within the LdG theory described by eq.2.3.36 and eq.2.3.37. It is revealed that $T_{\text{IN}}=40.5$ °C and $T^*=36.5$ °C by fitting.

For $\alpha=0.17$, we fitted $i(T)$ using the orientational order parameter minimizing the free energy density (eq.2.3.30) and the relationship between S and I_{VH} eq.2.3.35. In particular, we performed fitting as following process [12].

- (1) We set parameters T_{IN} , κ and σ in eq.2.3.30 at random. For these parameters, we calculated the $q(T)$ which minimizes the free energy density (eq.2.3.30) by Newton's method.
- (2) The deviation of the calculated $q(T)$ from the experimental data was calculated.
- (3) We changes the set of parameters (T_{IN} , κ and σ in eq.2.3.30) at random.
- (4) We minimized the deviation by repeating process (1)-(3).

The dotted blue line in Fig.2.16 indicates the best-fitting curve calculated by eq.2.3.30. The fitting parameters σ and κ in the KKLZ model are 2.1 and 1.7, respectively. σ of LCNMs is larger than the reported value of σ_{silica} (0.71-1.15) in the silica channel system [10-13], though the confinement size of LCNMs (~100 nm) is larger than that of silica channel (~10 nm). Thus, this strong effect of confinement is intrinsically caused by the fact that surface area in three-dimensionally confined system is larger than that in the two-dimensionally confined system with constant volume.

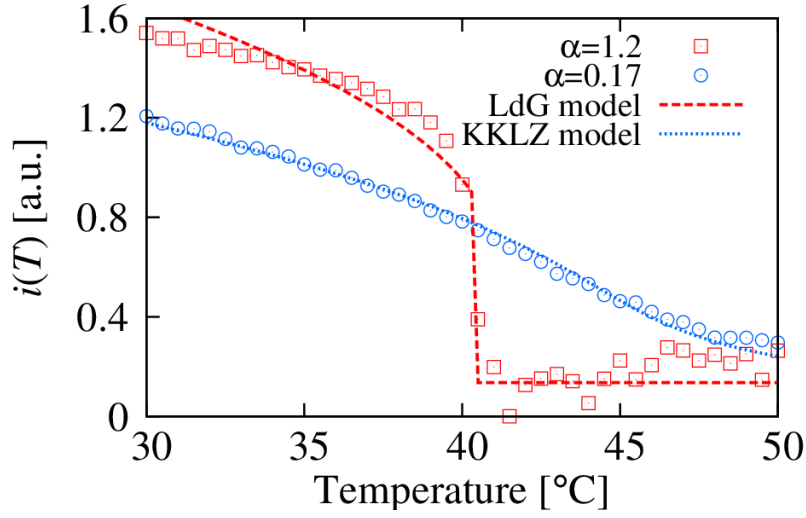


Fig.2.16 Temperature dependence of the square root of the normalized scattered light intensity. Square and circle symbols show the intensities of LCNM whose α are 1.2 and 0.17, respectively. Dashed red and dotted blue lines are fitting results obtained by LdG model and KKLZ model, respectively.

We controlled the hydrodynamic radius, r' , by changing α as shown in Fig.(2.12). Then, we fitted $i(T)$ by eq.2.3.20 in order to determine σ for each r' . Fig.2.17 shows σ as a function of the core-size of LCNMs, $r'-d$, where d is the shell thickness of LCNMs. We used the value of d obtained in the section 2.2.2.3 ($d \sim 57.93$ nm). σ increases with decreasing core-size. According to the KKLZ model, σ is inversely proportional to the system size. Thus, the behavior observed by our experiment qualitatively agrees with the KKLZ model.

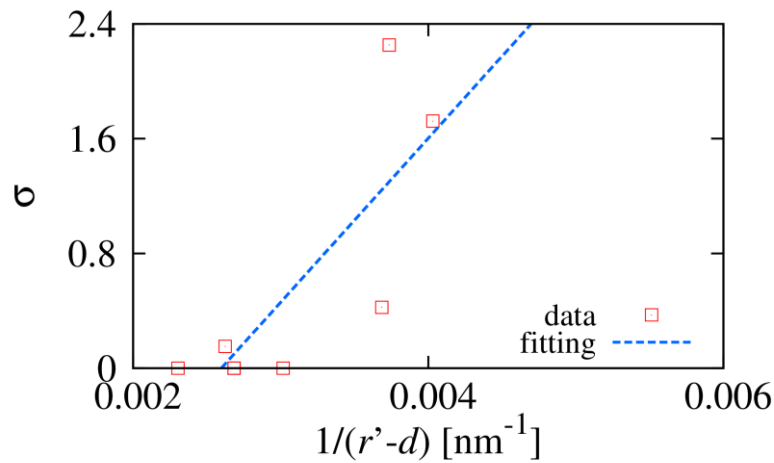


Fig.2.17 σ as a function of the core-size of LCNMs, $r'-d$, where d is the shell thickness of LCNMs.

2.3.3 Summary

We measured the mean VH light scattering intensity, and investigated the phase transition behavior of N-LCs confined in the core parts of nano-micelles. The VH light scattering intensity, which is reflected in the dielectric anisotropy originating from the orientational order, decreases on heating. Moreover, the N-Iso phase transition behavior of N-LCs confined in the hydrophobic core parts changes from first order, which is the same behavior as that in the bulk state, to second order with decreasing radius of LCNMs. We estimated the strength of surface interaction, σ , within the KKLZ model. The behavior of σ observed by our experiment qualitatively agrees with the KKLZ model. Therefore, it was suggested that the three-dimensional nanometer-scale confinement effect changes the order of the N-Iso phase transition.

2.4 Dynamics of liquid crystal confined in nano-micelles

Nematic (N)-liquid crystalline nano-micelles (LCNMs) have the orientational order in their core parts. Then, in the section 2.3, it was revealed that the orientational order is strongly affected by the confinement. It is expected that the confinement change the nature of the director fluctuation of N-LCs. Generally, the characteristic time-scale of the rotational motion of the director of LCs in confined geometries is faster than that in the bulk state [21, 37, 38, 43]. For example, the rotational motion of the Blue phase is ten-times faster than that of N-LCs because LCs are confined in a lattice whose size is several hundred nano-meters [43-45]. Thus, we expect the confinement into nano-micelles to cause the fast response of the rotational motion of director.

In this section, we introduced the theory of the depolarized (VH) dynamic light scattering (DLS) experiment in section 2.4.1. Then, we performed the VH DLS experiment, and measured the autocorrelation function. We identified relaxation mode of the autocorrelation function. We measured the relaxation time as a function of the size of confinement, and investigated the effect of confinement on the dynamics of LCs confined in nano-micelles.

2.4.1 Theory of depolarized dynamic light scattering experiment

We performed the VH DLS measurement. In the VH DLS measurement, we measured the autocorrelation function of the intensity of light scattered by optical anisotropy. It is expected that LCNMs have two kinds of anisotropic motions, that is, the rotational diffusion of LCNMs and the orientational fluctuation of the director of N-LCs in the core parts of nano-micelles. Thus, we introduce the theory of the VH DLS experiment dealing with the rotational diffusion of LCNMs and the orientational fluctuation of the director of N-LCs.

2.4.1.1 Rotational diffusion of an optically anisotropic particle [78]

Electric field scattered by an optically anisotropic particle is represented as eq.2.2.13. Thus, the autocorrelation function, $I^{(1)}(t)$, is described as shown below,

$$I_{\text{VH}}^{(1)}(\mathbf{q}, t) = \sum_{j=1}^N \left\langle \alpha_{\text{if}}^j(0) \alpha_{\text{if}}^j(t) \exp(i\mathbf{q} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)]) \right\rangle, \quad (2.4.1)$$

$$\alpha_{\text{if}} = \mathbf{n}_f \cdot \boldsymbol{\alpha} \cdot \mathbf{n}_i.$$

If we assume that the rotation is statistically independent of translation, we can separate the rotational term in eq.2.4.1, $\alpha_{\text{if}}^j(0) \alpha_{\text{if}}^j(t)$, and translational term, $\exp(i\mathbf{q} \cdot [\mathbf{r}_j(t) - \mathbf{r}_j(0)])$. Then, each LCNM can be regarded as statistical equivalent. Thus, the autocorrelation function (eq.2.4.1) is approximated as follows.

$$I^{(1)}(\mathbf{q}, t) = \langle N \rangle \langle \alpha_{\text{if}}(0) \alpha_{\text{if}}(t) \rangle F_s(\mathbf{q}, t), \quad (2.4.2)$$

where $\langle N \rangle$ is the mean number of LCNMs in scattering volume. $F_s(\mathbf{q}, t)$ is the contribution of

translational diffusion in eq.2.2.30. $\langle \alpha_{if}(0)\alpha_{if}(t) \rangle$ includes the information of the $\alpha_{\alpha\beta}$ component of a polarizability tensor in the laboratory frame. Since LCNMs exhibit the rotational Brownian motions, α_{if} changes temporally.

LCNMs are optically anisotropic due to the orientational order of N-LCs, which have cylindrical symmetry. Thus, we assumed that LCNMs also have cylindrical symmetry. The polarizability tensor of LCNMs, α , in the molecular frame is represented as follows.

$$\alpha = \begin{pmatrix} \alpha_{\parallel} & 0 & 0 \\ 0 & \alpha_{\perp} & 0 \\ 0 & 0 & \alpha_{\perp} \end{pmatrix}, \quad (2.4.3)$$

where $\alpha_{\parallel}$ and $\alpha_{\perp}$ are the polarizabilities parallel and perpendicular to the molecular long axis, respectively. Fig.2.18 shows the molecular and the laboratory frames. The molecular and the laboratory frames are specified by $x'y'z'$ and xyz coordinates, respectively. x' axis is parallel to the molecular long axis of N-LCs, which is specified (θ, ϕ) in Fig.2.18. y' axis is in the plane defined by x' axis and z axis. $\mathbf{k}_i$ and $\mathbf{k}_f$ are the wave vector of the incident and the scattering light, respectively. The direction of $\mathbf{k}_f$ is parallel to the x axis, and $\mathbf{k}_i$ is in the x - y plane. In this geometry, $\mathbf{n}_i$ and $\mathbf{n}_f$ are parallel to the z and the y axis, respectively. Therefore, $I_{\text{VH}}^{(1)}$ is represented as follows.

$$I_{\text{VH}}^{(1)}(\mathbf{q}, t) = \langle N \rangle \langle \alpha_{zy}(0) \alpha_{zy}(t) \rangle F_S(\mathbf{q}, t), \quad (2.4.4)$$

$$\begin{aligned} \alpha_{zy} &= (\cos \theta, \sin \theta, 0) \begin{pmatrix} \alpha_{\parallel} & 0 & 0 \\ 0 & \alpha_{\perp} & 0 \\ 0 & 0 & \alpha_{\perp} \end{pmatrix} \begin{pmatrix} \sin \theta \sin \phi \\ -\cos \theta \sin \phi \\ -\cos \phi \end{pmatrix} \\ &= (\alpha_{\parallel} - \alpha_{\perp}) \sin \theta \cos \theta \sin \phi \\ &= i \left(\frac{2\pi}{15} \right)^{1/2} \beta [Y_{2,1}(\theta, \phi) + Y_{2,-1}(\theta, \phi)], \end{aligned} \quad (2.4.5)$$

where β is the anisotropy of the polarizability ($=\alpha_{\parallel}-\alpha_{\perp}$), and $Y_{2,\pm 1}(\theta, \phi) = \mp \sqrt{15/8\pi} \sin \theta \cos \theta \exp(\pm i\phi)$ are spherical harmonic functions. We substituted eq.2.4.5 for eq.2.4.4, and then we obtained the autocorrelation function.

$$I_{\text{VH}}^{\alpha}(\mathbf{q}, t) = \langle N \rangle \frac{2\pi}{15} \beta^2 [F_{1,1}^{(2)}(t) + F_{1,-1}^{(2)}(t) + F_{-1,1}^{(2)}(t) + F_{-1,-1}^{(2)}(t)] F_S(\mathbf{q}, t), \quad (2.4.6)$$

$$F_{m,m'}^{(2)}(t) = \langle Y_{2,m'}^*(\theta(0), \phi(0)) Y_{2,m}(\theta(t), \phi(t)) \rangle. \quad (2.4.7)$$

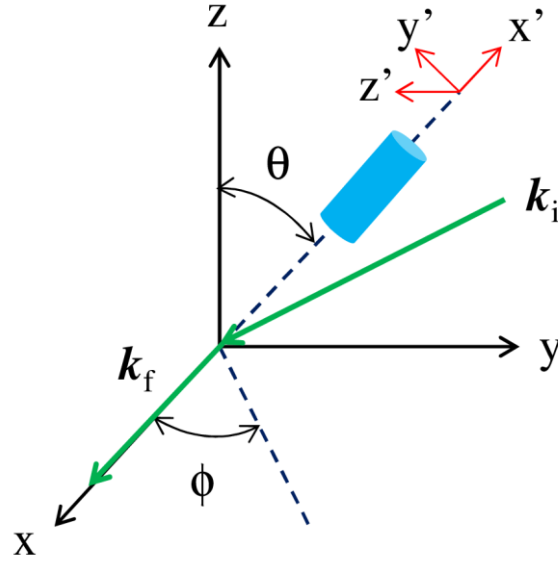


Fig.2.18 The molecular and the laboratory frames. The molecular and the laboratory frames are specified by $x'y'z'$ and xyz coordinates, respectively.

In order to calculate the autocorrelation function of LCNMs represented as eq.2.4.6, we considered the motion of the unit vector $\mathbf{u}(\theta, \phi)$ which is parallel to the cylindrically symmetric axis. Since LCNMs exhibit the rotational Brownian motion, $\mathbf{u}(\theta, \phi)$ also exhibit the rotational Brownian motion on the unit spherical surface. Thus, we consider the diffusion equation of $\mathbf{u}(\theta, \phi)$ as shown below.

$$\frac{\partial c(\mathbf{u}, t)}{\partial t} = -\Theta \hat{I}^2 c(\mathbf{u}, t), \quad (2.4.8)$$

$$-\hat{I}^2 = \frac{1}{\sin^2 \theta} \left[\sin \theta \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right], \quad (2.4.9)$$

where $c(\mathbf{u}, t)$ is the probability density of $\mathbf{u}$ at time t . Θ is the rotational diffusion constant. Since $c(\mathbf{u}, t)$ is the probability transition from an initial direction, $\mathbf{u}_0$, to $\mathbf{u}$, $F_{m,m'}^{(2)}(t)$ is represented as shown below.

$$F_{m,m'}^{(2)}(t) = \int d^2 u_0 \int d^2 u Y_{2,m}(\mathbf{u}) c(\mathbf{u}, t) p(\mathbf{u}_0) Y_{2,m'}^*(\mathbf{u}_0), \quad (2.4.10)$$

where $p(\mathbf{u}_0)$ is the distribution function of the direction LCNMs at the initial state. Since the initial direction of LCNMs is $\mathbf{u}_0$, the probability of $\mathbf{u}$ at $t=0$, $c(\mathbf{u}, 0)$ is described as below.

$$c(\mathbf{u}, 0) = \delta(\mathbf{u} - \mathbf{u}_0) = \sum_{l,m} Y_{l,m}(\mathbf{u}_0) Y_{l,m}^*(\mathbf{u}). \quad (2.4.11)$$

The eigenvalues of $\hat{I}^2$ are spherical harmonic functions as follows.

$$\hat{I}^2 Y_{l,m}(\mathbf{u}) = l(l+1)Y_{l,m}(\mathbf{u}) \quad l = 0, 1, 2, \dots \infty \quad (2.4.12)$$

Therefore, we can resolve the diffusion equation (eq.2.4.12) as follows.

$$c(\mathbf{u}, t) = \sum_{l,m} \exp(-l(l+1)\Theta t) Y_{l,m}^*(\mathbf{u}) Y_{l,m}(\mathbf{u}_0). \quad (2.4.13)$$

We got the following autocorrelation function of the rotational diffusion of nano-micelles, $I_{\text{VH}}^{(1)}(\mathbf{q}, t)$ by substituting eq.2.4.13 for eq.2.4.6.

$$I_{\text{VH}}^{(1)}(\mathbf{q}, t) = \langle N \rangle \frac{1}{15} \beta^2 \exp\left[-\frac{t}{\tau_{\text{rot}}}\right], \quad (2.4.14)$$

$$\tau_{\text{rot}} = \frac{1}{6\Theta + q^2 D}, \quad (2.4.15)$$

where τ_{rot} is the relaxation time of the rotational diffusion of nano-micelles.

2.4.1.2 Orientational fluctuation of the director of nematic liquid crystals [26, 39]

The fluctuation of the dielectric constant, $\delta\epsilon(r, t)$, causes the change in the scattered electric field, $E_S(R, t)$, as represented in eq.2.2.13. Since the fluctuation of the order parameter, S , is so small that we can neglect it, we consider the orientational fluctuation of the director, $\mathbf{n}$.

$$\mathbf{n} = \mathbf{n}_0 + \delta\mathbf{n}, \quad (2.4.16)$$

where $\mathbf{n}_0$ is the mean direction and $\delta\mathbf{n}$ is the deviation of $\mathbf{n}$ from $\mathbf{n}_0$. Since $\mathbf{n}_0$ is independent of time, only $\delta\mathbf{n}$ contributes to temporal change in $\mathbf{n}$. We defined $\delta\mathbf{n}$ in the geometry shown in Fig.2.19 as follows.

$$\delta\mathbf{n} = \delta n_1 \mathbf{e}_1 + \delta n_2 \mathbf{e}_2, \quad (2.4.17)$$

where $\mathbf{e}_1$ and $\mathbf{e}_2$ are basis vectors. The local dielectric tensor of N-LCs, $\boldsymbol{\epsilon}$, is represented by $\mathbf{n}$ as follows.

$$\epsilon_{\alpha\beta} = \epsilon_{\perp} \delta_{\alpha\beta} + \epsilon_a n_{\alpha} n_{\beta}, \quad (2.4.18)$$

where $\epsilon_a = \epsilon_{\parallel} - \epsilon_{\perp}$ is the dielectric anisotropy. $\delta\epsilon_{\text{if}}(\mathbf{q}, t)$, which contributes to the temporal change in $E_S(R, t)$, is described as follows.

$$\delta\epsilon_{\text{if}}(\mathbf{q}, t) = \epsilon_a \sum_{j=1,2} \{(\mathbf{i} \cdot \mathbf{n}_0)(\mathbf{f} \cdot \mathbf{e}_j) + (\mathbf{f} \cdot \mathbf{n}_0)(\mathbf{i} \cdot \mathbf{e}_j)\} \delta n_j(\mathbf{q}, t). \quad (2.4.19)$$

We substituted $\delta\epsilon_{\text{if}}(\mathbf{q}, t)$ for eq.2.2.14, and obtained the autocorrelation function of the orientational fluctuation of N-LCs, $I^{(1)}(\mathbf{q}, t)$ as follows.

$$I^{(1)}(\mathbf{q}, t) = \left(\frac{k^2 \epsilon_a}{4\pi} \right)^2 \sum_{j=1,2} \{(\mathbf{i} \cdot \mathbf{n}_0)(\mathbf{f} \cdot \mathbf{e}_j) + (\mathbf{f} \cdot \mathbf{n}_0)(\mathbf{i} \cdot \mathbf{e}_j)\} \langle \delta n_j(\mathbf{q}, 0) \delta n_j^*(\mathbf{q}, t) \rangle. \quad (2.4.20)$$

$I^{(1)}(\mathbf{q}, t)$ has time dependent through $\langle \delta n_j(\mathbf{q}, 0) \delta n_j^*(\mathbf{q}, t) \rangle$. Therefore, we calculated the dynamics of

$\delta n_j(\mathbf{q}, t)$. The deformation of the director as $\mathbf{n}_0 \rightarrow \mathbf{n} + \mathbf{n}_0$ increases free energy, δf_e , in eq.2.3.26. δf_e is represented as follows.

$$\int \delta f_e dV = \frac{1}{2V} \sum_{\mathbf{q}} \sum_{j=1,2} (K_j q_{\perp}^2 + K_3 q_z^2) |\delta n_j(\mathbf{q}, t)|^2, \quad (2.4.21)$$

where K_i is the Frank elastic constants. The wave vector, $\mathbf{q}$, is $\mathbf{q}_z + \mathbf{q}_{\perp}$ in Fig.2.19. The motion equation of the director is presented as follows.

$$-\frac{\partial \delta f_e}{\partial \delta n_{\alpha}(\mathbf{r})} = \gamma_1 \frac{d \delta n_{\alpha}(\mathbf{r})}{dt}, \quad (2.4.22)$$

where γ_1 is the rotational viscosity constant. Fourier transformation of eq.2.4.22 was performed. Then, we got the motion equation of $\delta n(\mathbf{q})$ as follows.

$$\gamma_1 \frac{d \delta n_j(\mathbf{q}, t)}{dt} = -(K_j q_z^2 + K_3 q_z^2) \delta n_j(\mathbf{q}, t), \quad (2.4.23)$$

$$\delta n_j(\mathbf{q}, t) = \exp\left(-\frac{t}{\tau_{LC,j}(\mathbf{q})}\right), \quad (2.4.24)$$

$$\tau_{LC,j}(\mathbf{q}) = \frac{\gamma_1}{K_j q_{\perp}^2 + K_3 q_z^2}, \quad (2.4.25)$$

where τ_j is the relaxation time of the orientational fluctuation of N-LCs. We substituted eq.2.4.24 for eq.2.4.20, and then we obtained the autocorrelation function.

$$I^{(1)}(\mathbf{q}, t) \propto \exp\left(-\frac{t}{\tau_j(\mathbf{q})}\right). \quad (2.4.26)$$

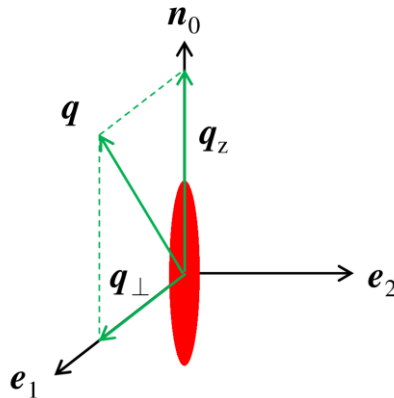


Fig.2.19 The geometry of the basis vectors, $\mathbf{e}_1$ and $\mathbf{e}_2$. $\mathbf{e}_1$, $\mathbf{e}_2$ and $\mathbf{n}_0$ are perpendicular to each other. $\mathbf{e}_1$ is in the plane defined by $\mathbf{n}_0$ and $\mathbf{q}$, where $\mathbf{q}$ is the wave vector. $\mathbf{q}_z$ and $\mathbf{q}_{\perp}$ are parallel to $\mathbf{n}_0$ and $\mathbf{e}_1$, respectively.

2.4.1.3 Fitting function of the autocorrelation function

We got the autocorrelation functions of the rotational diffusion of nano-micelles (eq.2.4.14) and the orientational fluctuation of N-LCs (eq.2.4.26). The dynamics of LCNMs in the VH light scattering experiment arises from both of the rotational diffusion of nano-micelles and the orientational fluctuation of N-LCs. Thus, we used the following fitting functions.

$$I_{\text{VH}}^{(1)}(\mathbf{q}, t) = A_{\text{LC}} \exp\left(-\frac{t}{\tau_{\text{LC}}}\right) + A_{\text{rot}} \exp\left(-\frac{t}{\tau_{\text{rot}}}\right), \quad (2.4.27)$$

$$\begin{aligned} g_2(\mathbf{q}, t) &= I_{\text{VH}}^{(2)}(\mathbf{q}, t) - |I_{\text{VH}}^{(1)}(\mathbf{q}, 0)|^2 \\ &= A_{\text{LC}}^2 \exp\left(-\frac{2t}{\tau_{\text{LC}}}\right) + A_{\text{LC}} A_{\text{rot}} \exp\left(-\left(\frac{1}{\tau_{\text{LC}}} + \frac{1}{\tau_{\text{rot}}}\right)t\right) + A_{\text{rot}}^2 \exp\left(-\frac{2t}{\tau_{\text{rot}}}\right), \end{aligned} \quad (2.4.28)$$

where $I_{\text{VH}}^{(1)}$ and $I_{\text{VH}}^{(2)}$ are the autocorrelation function of the heterodyne and the homodyne method, respectively. Fig.2.20 shows $g_2(\mathbf{q}, t) = I_{\text{VH}}^{(2)}(\mathbf{q}, t) - |I_{\text{VH}}^{(1)}(\mathbf{q}, 0)|^2$. The first, second and third terms of eq.2.4.28 are also showed in Fig.2.20. We set $A_{\text{LC}} = A_{\text{rot}}$, $\tau_{\text{LC}} = 0.1$ ms and $\tau_{\text{rot}} = 10$ ms.

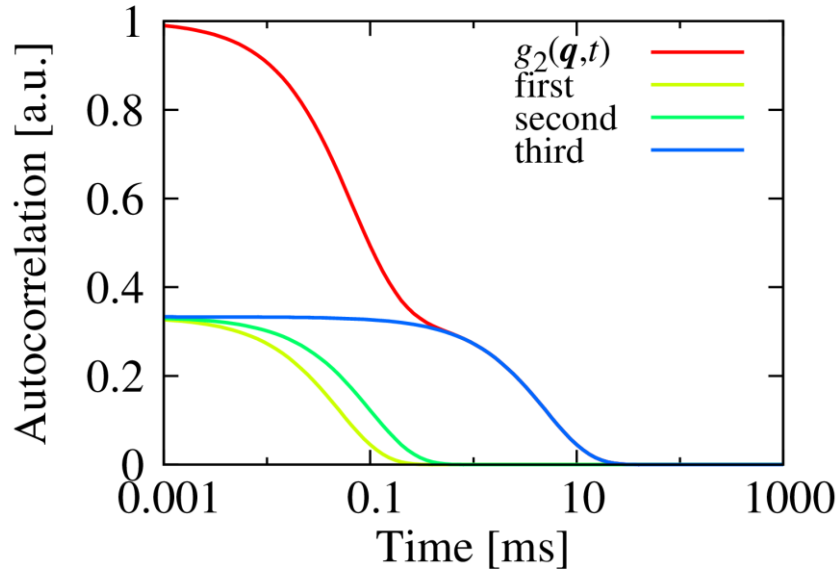


Fig.2.20 shows $g_2(\mathbf{q}, t) = I_{\text{VH}}^{(2)}(\mathbf{q}, t) - |I_{\text{VH}}^{(1)}(\mathbf{q}, 0)|^2$, the first, second and third terms of eq.2.4.28.

2.4.2 Depolarized dynamic light scattering experiment

2.4.2.1 Identification of the relaxation mode

Fig.2.21 shows the autocorrelation function of LCNMs at 30 °C. The weight ratio of 7CB to PEO-PLC, α , is 0.28. We fitted the experimental data using the following function.

$$f(t) = A \exp \left(-2 \left(\frac{t}{\tau_{LC}} \right)^\beta \right) + B \exp \left(-2 \frac{t}{\tau_{rot}} \right). \quad (2.4.29)$$

The fitting result is shown in Fig.2.21. Fitting parameters τ_{LC} , τ_{rot} , β , A and B are 0.030 ms, 14.9 ms, 0.41, 0.65 and 0.16, respectively. Here, we ignored the second term of eq.2.4.28 and added stretch parameter, β , to the first term of eq.2.4.29 because of the following reasons.

(1) The relaxation time of the rotational diffusion of nano-micelles differs from that of the orientational fluctuation of N-LCs. In particular, obtained τ_{LC} (=0.030 ms) is faster than τ_{rot} (=14.9 ms). Thus, the second term of eq.2.4.28 can be renormalized into the first term because the relaxation time of the second term of eq.2.4.28 is close to τ_{LC} as shown in Fig.2.20.

(2) According to the elastic theory of N-LCs as shown in eq.2.4.25, the relaxation time depends on the angle between the wave vector of the incident light and the mean direction of the director, $\mathbf{n}_0$, that is, relaxation time depends on the scattering geometry. Since the distribution of the direction of N-LCs in nano-micelles is random, the relaxation time of the orientational fluctuation of N-LCs in the core parts of nano-micelles can be obtained by the convolution of the multiple modes. Therefore, the autocorrelation function of director fluctuation must be stretched. In order to describe this stretch, we used the stretch parameter β .

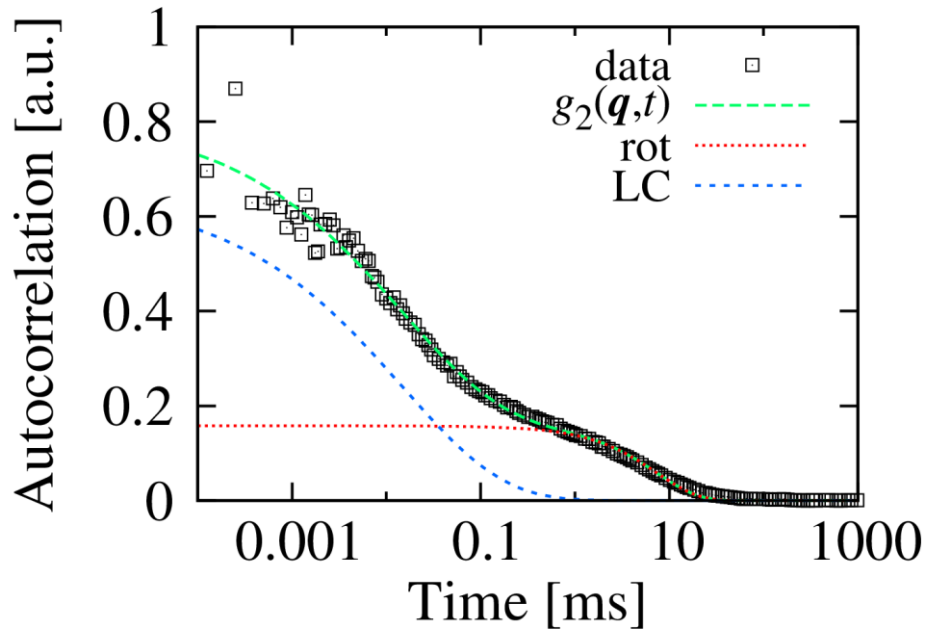


Fig.2.21 The autocorrelation function of LCNMs at 30 °C. The weight ratio of 7CB to PEO-PLC, α , is 0.28. The green line is the fitting result of eq.2.4.29. The red (rot) and blue (LC) lines are the first and second term in eq.2.4.29, respectively.

Fig.2.22 shows the autocorrelation function of 7CB in the bulk state. We measured the autocorrelation function at 30 °C with $1/q=2.0\times 10^{-7}$ m. Here, we used the geometry in which $\mathbf{q}$ is parallel to $\mathbf{n}_0$ so that $1/\tau=\gamma_1/q^2K_3$. We fitted the experimental result using as stretched exponential function, $A \exp(-2(t/\tau)^\beta)$, and then the fitting result is indicated as a blue line. The relaxation time of 7CB in the bulk state is determined to 0.17 ms. Since τ_{LC} in Fig.2.21 is close to the relaxation time of 7CB in the bulk state, it is suggested that fast mode of the autocorrelation function, $g_2(\mathbf{q},t)$, arises from the orientational fluctuation of N-LCs.

On the other hand, the relaxation time of the rotational diffusion of nano-micelles is represented by eq.2.4.15. It is difficult to obtain the rotational diffusion constant, Θ , in eq.2.4.15. However, it is expected that the time scale of the rotational motion is close to that of the translational motion because both of the translational and the rotational motion correspond to the motion of nano-micelles. The slower relaxation time τ_{rot} (~ 10 ms) in Fig.2.21 is close to the relaxation time of the translational diffusion (~ 9.3 ms) which was obtained by the polarized DLS experiment (§2.2.2). Therefore, we concluded that the slow relaxation mode of the autocorrelation function arises from the rotational diffusion of nano-micelles.

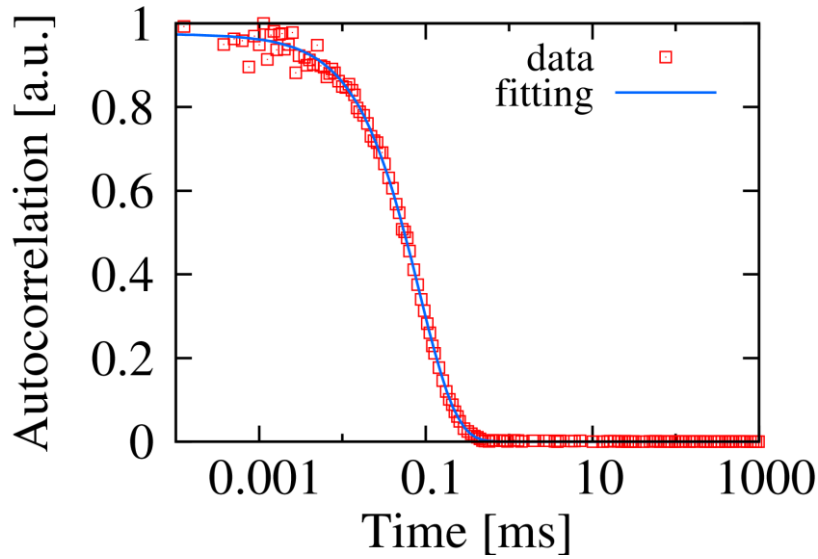


Fig.2.22 The autocorrelation function of 7CB in the bulk state. Temperature is 30 °C, and $1/q=2.0\times 10^{-7}$ m. The line is the fitting result by $A \exp(-2(t/\tau)^\beta)$. Fitting parameters, A , τ and β are 0.97, 0.17 ms and 0.97, respectively.

2.4.2.2 The effect of confinement on the orientational fluctuation

We can control the scattering angle θ as shown in Fig.2.8. Fig.2.23 shows θ dependence of the autocorrelation function at 30 °C with $\alpha=0.078$. The relaxation mode of the orientational fluctuation of N-LCs (fast relaxation) is independent of the scattering angle. On the other hand, the relaxation

mode of the rotational diffusion of nano-micelles (slow relaxation) becomes fast with increasing θ .

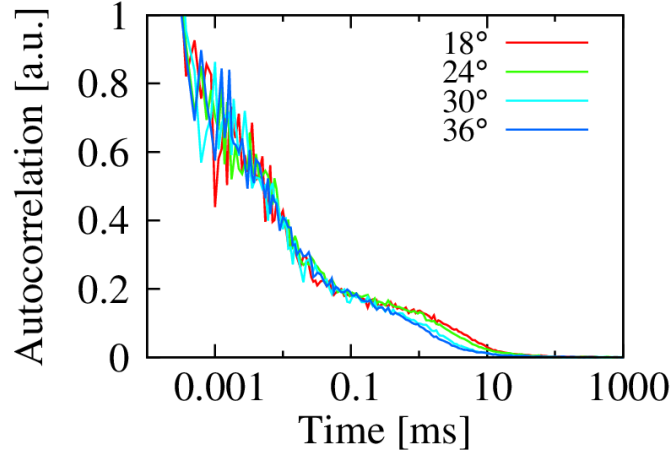


Fig.2.23 The scattering angle dependence of the autocorrelation function at 30 °C with $\alpha=0.078$.

We fitted the autocorrelation function at 30 °C with $\alpha=0.078$ by eq.2.4.29 and estimated the relaxation times. Fig.2.24 shows the scattering vector dependence of the relaxation times of the rotational diffusion and the orientational fluctuation. We fitted the relaxation time using the following function.

$$\log(\tau) = \alpha \times \log(q) + \log(\tau_0), \quad (2.4.30)$$

where α and $\log(\tau_0)$ are fitting parameters. The fitting results are shown in Fig.2.24. The relaxation time of the rotational fluctuation on nano-micelles is proportional to $1/q^2$, which agrees with theoretical prediction represented by eq.2.4.15. The relaxation time of the orientational fluctuation of N-LCs is expected to be proportional to $1/q^2$ as indicated in eq.2.4.25. However, the relaxation time of the orientational fluctuation of N-LCs is independent of q . This is considered to be caused by the confinement effect on dynamics of N-LCs.

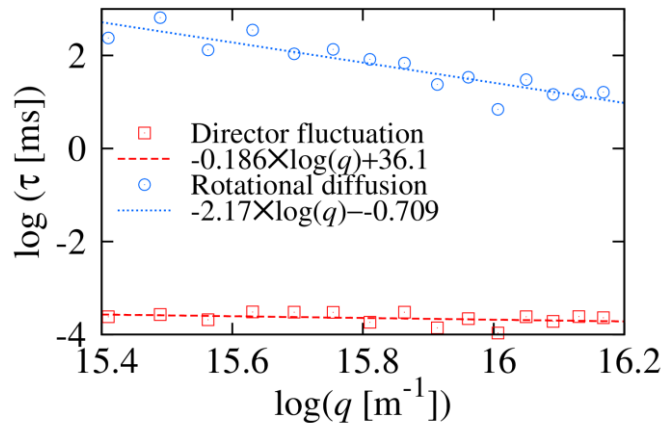


Fig.2.24 The scattering vector dependence of the relaxation times of the rotational diffusion and the orientational fluctuation. The experimental results were fitted by eq.2.4.30.

In order to reveal the reason for independence of the relaxation time of the orientational fluctuation, we considered the effect of the confinement on the orientational fluctuation of N-LCs. If the wavelength of scattering vector ($1/q$) is shorter than the system size, the relaxation time will obey eq.2.4.25. In a LCNM system, N-LCs are confined in the core parts of nano-micelles. Therefore, long-wavelength fluctuation ($q < q_c$, where $1/q_c$ is the characteristic length of confinement) cannot be excited. In the case of LCNMs, q_c is determined by the diameter of the core parts of nano-micelles.

$$q_c = \frac{\pi}{2(r-d)}, \quad (2.4.31)$$

where r and d are the radius and the shell thickness of LCNMs in eq.2.2.5. Since the elastic energy caused by the orientational fluctuation decreases as the wavelength of the deformation decreases, longer-wavelength fluctuation is excited dominantly. Thus, the relaxation time is represented as follows.

$$\tau_c(q_c) = \frac{\gamma_1}{Kq_c^2}. \quad (2.4.32)$$

Fig.2.25 shows q_c dependence of the relaxation time of the director fluctuation of N-LCs confined in the core parts of nano-micelles at 34 °C. We fitted the experimental result using the following function.

$$\log(\tau_c) = A \times \log(q_c) + B. \quad (2.4.33)$$

The fitting result is shown in Fig.2.25. Obtained fitting value are $A = -1.65 \pm 0.43$ and $B = -7.96 \pm 1.62$. The experimental result is well fitted by eq.2.4.33. The inset of Fig.2.25 shows the temperature dependence of A , and A is independent of temperature. The mean value of A is -1.76 , which is close to the theoretical prediction (~ -2). Thus, it is suggested that the confinement suppresses the long wavelength fluctuation and extracts the short-wavelength fluctuation defined by characteristic length of confinement.

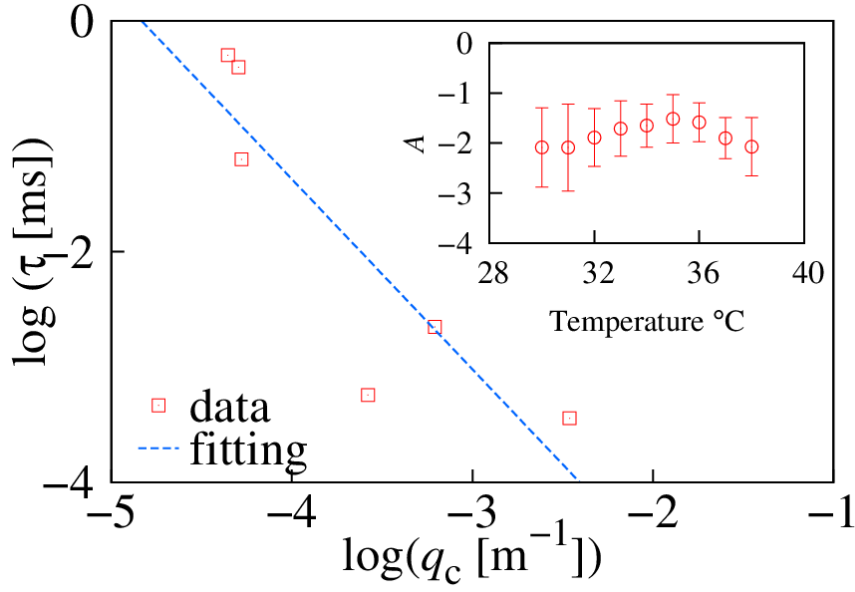


Fig.2.25 q_c dependence of the relaxation time of the director fluctuation at 34 °C. The dashed line is the fitting result by eq.2.4.33. Inset shows exponent A as a function of temperature.

2.4.3 Summary

We performed the VH DLS, and measured the autocorrelation function of LCNMs. We observed the autocorrelation function which has two relaxation modes. The fast and slow modes of the autocorrelation function are identified as the orientational fluctuation of N-LCs in the core of LCNMs and the rotational diffusion of nano-micelles, respectively. We measured the wavelength dependence of the relaxation times. Then, it is revealed that the relaxation time of the rotational diffusion of nano-micelles depends on the wavelength of scattering vector as predicted by theory of the rotational relaxation of an optically anisotropic particle. However, the relaxation time of the orientational fluctuation of N-LCs is independent of the wavelength of scattering vector. Since the relaxation time of the orientational fluctuation of N-LCs depends on the characteristic length of confinement, it is suggested that the maximum wavelength of the orientational fluctuation of N-LCs is restricted by the confinement.

Chapter III Smectic A liquid crystalline nano-micelles

In Chapter II, we fabricated the nematic (N)-liquid crystalline nano-micelles (LCNMs) with size of the several hundred nanometers. In such a N-LCNM system, the shell and core parts of nano-micelles are occupied by surfactants and N-LC molecules, respectively. LCNMs are convenient system for the investigation of confinement effect of the LC order because we can control the radius of the each micelle by changing the weight ratio of LCs to surfactants.

In this chapter, first, we fabricated smectic A (SmA)-LCNMs by using SmA-LCs whose physical properties in the bulk state were studied in the section 3.1. Second, we confirmed the layer order of LCs in the core parts of nano-micelles and investigated the effect of the confinement into nano-micelles on the SmA-N phase transition. Finally, we investigated the mobility of LC molecules in the core parts of nano-micelles by using the mixing process of LC molecules between the core parts of SmA- and N-LCNMs.

3.1 Physical property of smectic A liquid crystals in the bulk state

In next section 3.2, we will fabricate smectic A (SmA)-liquid crystalline nano-micelles (LCNMs), and we will investigate the confinement effect on the SmA-N phase transition. Therefore, the physical properties of SmA-LCs in the bulk state are important for the investigation of the confinement effect. Thus, in this section, we studied the physical properties of SmA-LCs in the bulk state, such as the SmA-N phase transition temperature and the layer spacing. In particular, in the section 3.3, we will investigate the mobility of LC molecules in the core parts of nano-micelles by using the mixing process between SmA- and N-LCNMs. Thus, it is important to study the physical properties of the mixture of SmA- and N-LCs in the bulk state.

3.1.1 Phase diagram

3.1.1.1 Experimental setup

a) Samples

We used three kinds of LCs, 8CB (SmA-32.5 °C-N-40.0 °C), 8OCB (SmA- 67.0 °C-N-80.0 °C-Iso) and 7CB (N- 42.8 °C-Iso), and their chemical structures and the phase sequences are shown in Fig.3.1. Mixing weight ratio of 7CB to 8CB was defined as ϕ .

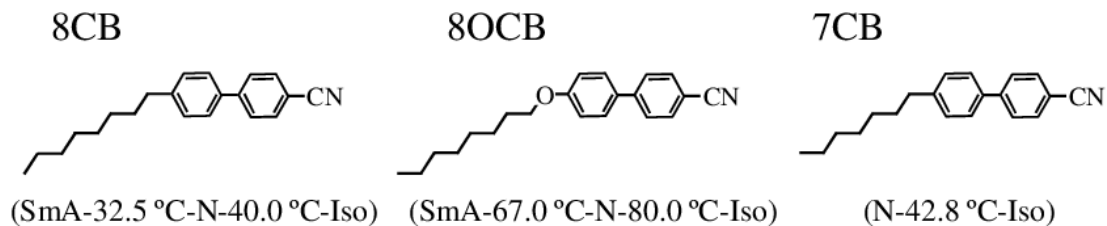


Fig.3.1 Chemical structures and the phase sequences of 8CB, 8OCB and 7CB.

b) Polarized microscope observation

We observed the textures of the LC mixture of 7CB and 8CB by the polarized microscope (BX51, OLYMPUS) in order to identify the mesogenic phases of the mixture. The LC mixtures were injected in the commercial glass sandwich cell with the thickness of 10 μm (EHC Co.). Observation was performed under the crossed nikols during the heating and cooling processes with the rate of 0.5 °C/min.

3.1.1.2 Results and discussions

Fig.3.2 shows the polarized microphotographs of the LC mixture of 8CB and 7CB with $\phi=10.2$ wt% at 30.5 °C (a), 38.0 °C (b) and 40.2 °C (c). The focal conic texture characteristic to the SmA phase is observed at 30.5 °C [83, 84]. At 38.0 °C, the focal conic texture disappears and the homogeneous alignment is observed (the N phase) (b). At 40.4 °C, the N phase has melted, and the

N droplets are dispersing in the Iso phase, which corresponds to the coexisting phase.



Fig.3.2 The polarized microscopic images of the LC mixture of 8CB and 7CB ($\phi=10.2$ wt%) at 30.5 °C (a), 38.0 °C (b) and 40.4 °C (c) on heating.

Fig.3.3 shows the binary phase diagram of 8CB and 7CB. The SmA-N phase transition temperature linearly decreases with increasing ϕ . This result indicates that the relative temperature, $\Delta T = T_{\text{SmA-N}} - T$, where $T_{\text{SmA-N}}$ is the SmA-N phase transition temperature, linearly decreases with increasing ϕ even if temperature is the same.

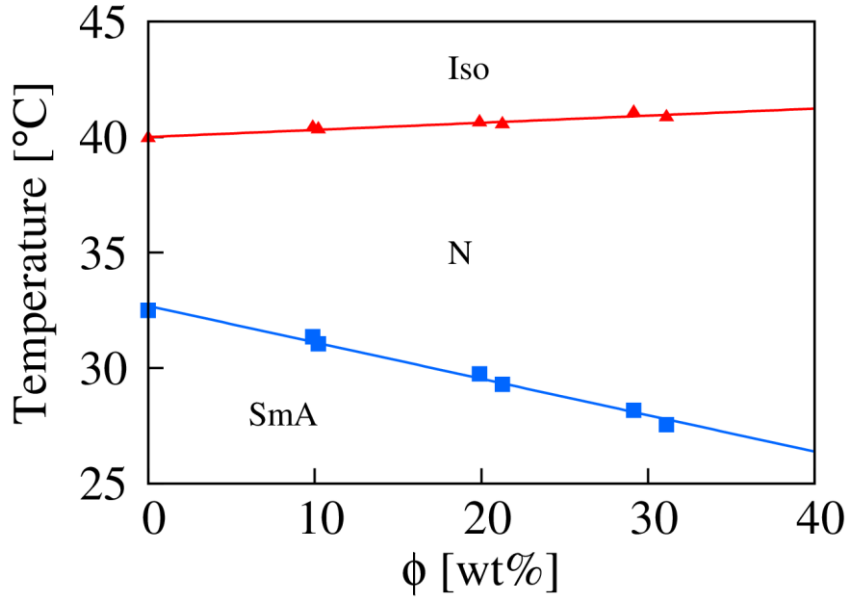


Fig.3.3 The binary phase diagram of 8CB and 7CB.

3.1.2 X-ray diffraction measurement

In the section 3.3.3, we will estimate the concentration of 7CB mixed with 8CB, ϕ , using the relation between the layer spacing and ϕ . For this reason, we studied the layer spacing of the LC mixture of 7CB and 8CB as a function of ϕ in this section.

3.1.2.1 Experimental set up

In order to investigate the layer structure of the LC mixture of 8CB and 7CB, we performed X-ray diffraction measurement by using the commercial X-ray generator (MicroMax-007HF, Rigaku Corp.). Samples were completely enclosed with a capillary with diameter of 1.5 mm. In this experiment, we performed the X-ray diffraction measurement in the following temperature range (Table 3.1).

ϕ [wt%]	T [°C]
0	30.0-34.0
9.9	29.0-32.8
19.9	29.5-32.0
29.1	27.5-30.2

Table 3.1 The temperature range of the X-ray diffraction measurement

3.1.2.2 Theory of X-ray diffraction

SmA-LCs have the one-dimensional translational order along the layer normal direction with the layer spacing, d . Since the SmA-N phase transition is generally the second order phase transition, LCs in the N phase have short-range smectic-like layer order near $T_{\text{SmA-N}}^{\text{bulk}}$ with the finite correlation length, ξ as shown in Fig.3.4. The correlation function of the molecular density, $\langle \rho(0)\rho(x) \rangle$ decays exponentially as follows,

$$\langle \rho(0)\rho(x) \rangle \sim \exp\left(-\frac{x}{\xi}\right). \quad (3.1.1)$$

In the bulk state, ξ of the cybotactic smectic layer order diverges toward $T_{\text{SmA-N}}^{\text{bulk}}$ on cooling. In X-ray diffraction (XRD) measurement, if LCs have the layer order, the XRD peak should be observed. Then, we can determine d and ξ by fitting the XRD peak using the following Lorentz function,

$$f(q) \propto \frac{1}{1 + \xi^2 (q - q_0)^2}, \quad (3.1.2)$$

where $q_0 = 2\pi/d$ corresponds to the wavenumber of the layer spacing.

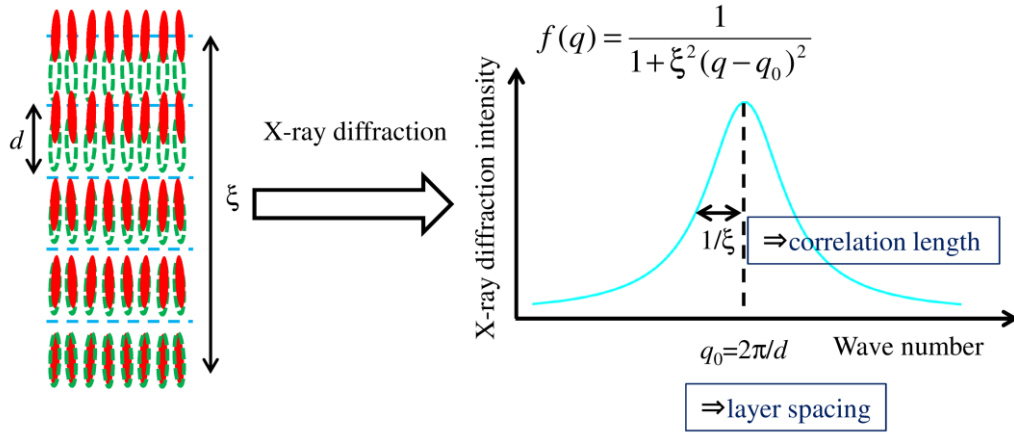


Fig.3.4 Schematic images of short-range layer order and X-ray diffraction peak. If the LCs have the layer order with layer spacing, d , and with the correlation length, ξ , corresponding X-ray diffraction peak should be observed.

3.1.2.3 Results and discussions

Fig. 3.5 (a) shows the X-ray diffraction profiles of the LC mixture of 8CB and 7CB with various mixing ratios. The position of the X-ray diffraction peak shifts toward higher wavenumber as ϕ increases, which indicates that the layer spacing shrinks. Considering the fact that the molecular length of 7CB is shorter than that of 8CB, the decrease in layer spacing is expected to be caused by the mixing of 7CB as shown in Fig. 3.5 (b). In order to determine the layer spacing, the experimental data were fitted by Lorentz function (eq.3.1.2) and then, the fitting results were superimposed in Fig.3.5.

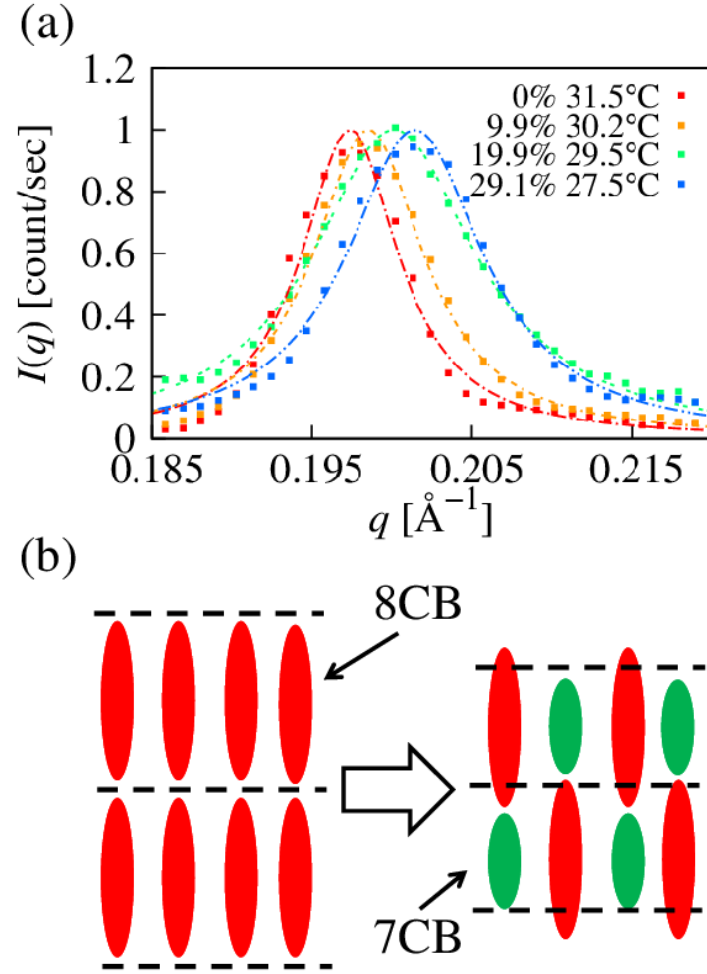


Fig. 3.5 (a) The X-ray diffraction profiles of the LC mixture of 8CB and 7CB with various mixing ratios. The lines indicate the fitting results by Lorentz function. (b) the schematic image of the shrinkage of the layer order due to the mixing of 7CB molecules.

We determined $d(q_0)$ from fitting results of eq.3.1.2. Fig.3.6 shows the ϕ dependence of d . Bars show the range of temperature dependence. d linearly decreases with increasing ϕ . In the section 3.3.3, we will use the relation between d and ϕ . For this reason, we fitted the experimental result by linear function, and then, we determined the relation between d and ϕ . Fitting result is shown in Fig.3.6 as a blue dashed line. We found that ϕ dependence of d is represented as follows,

$$d = -0.0201\phi + 31.75. \quad (3.1.3)$$

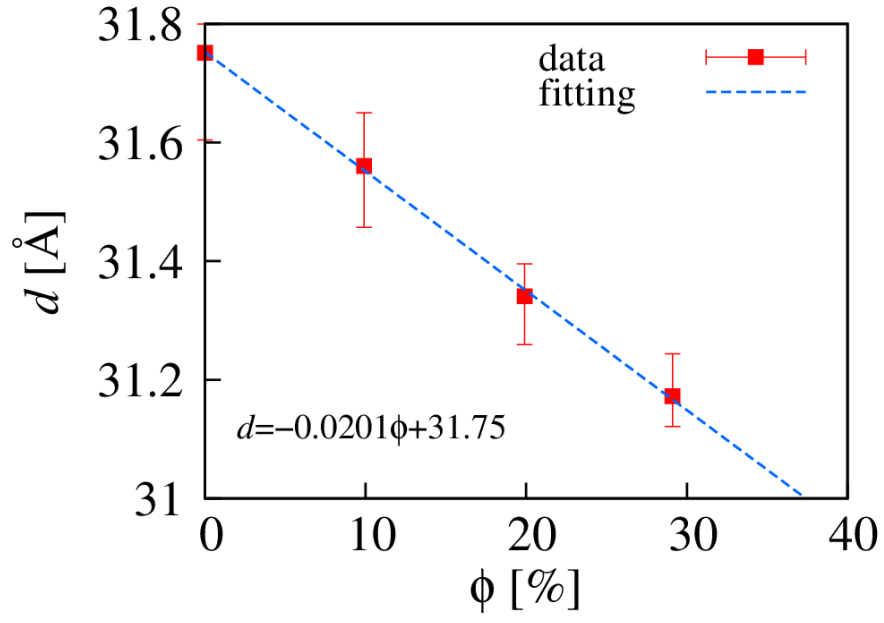


Fig.3.6 The ϕ dependence of the layer spacing, d . Bars show the range of temperature dependence. The blue line indicates fitting results by a linear function.

3.2 The layer structure of liquid crystals confined in the core part of nano-micelles

In this section, we tried to fabricate smectic A (SmA)-liquid crystalline nano-micelles (LCNMs) in which SmA-LCs are confined into the core parts of nano-micelles. SmA-LCs have the one-dimensional layer order together with two-dimensional fluidity. In order to confirm the existence of the layer order in the core parts of nano-micelles, we performed the synchrotron X-ray diffraction measurement. Then, we investigated the effect of the confinement into nano-micelles on the SmA-N phase transition by measuring the temperature dependence of the correlation length of the layer order (§3.2.1). In the sections 3.3.1 and 3.3.2 we will study the mixing process of LC molecules between the core parts of SmA- and N-LCNMs by using light scattering technique. Thus, it is worthwhile to study the optical properties of the N-LC-doped SmA-LCNMs which are fabricated by emulsifying the mixture of N- and SmA-LCs. For this reason, we performed the light scattering experiment in order to reveal the effect of mixing of N-LCs on the optical properties of SmA-LCNMs.

3.2.1 Synchrotron X-ray diffraction measurement

3.2.1.1 Experimental setup

In this section, we used 8CB whose structural formula was shown in Fig.3.1. We used Poly(ethylene oxide-b-6-[4'-cyanobiphenyl-4-yloxy]hexyl methacrylate) which was used in the chapter II. In order to obtain 8CB-NMs, we emulsified 8CB in the same way as we described in section 2.1.1.2. In order to confirm the existence of the layer order, we performed the synchrotron X-ray diffraction measurement at FSBL03XU of SPring-8 (Harima, Japan). We used an imaging plate (Rigaku, R-Axis VII) as a two-dimensional X-ray detector. Fig.3.7 shows the schematic experimental setup of the synchrotron X-ray diffraction measurement. The wavelength of incident X-ray and the distance from samples to the detector are 1 Å and 1.7 m, respectively. Exposure time was 180-480 sec. In order to prevent the evaporation of water, samples were completely enclosed with a capillary with diameter of 1.5 mm.

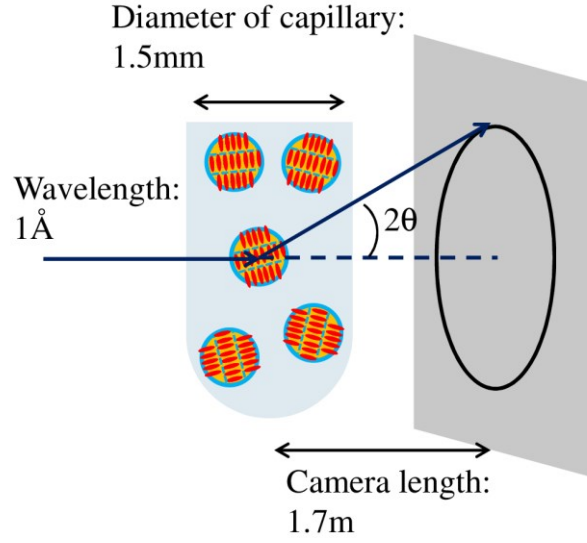


Fig.3.7 The schematic experimental setup of the synchrotron X-ray diffraction measurement.

3.2.1.2 Results and discussions

Fig.3.8 (a) shows the wavenumber, q , dependence of X-ray scattering intensities, $I(q)$, of 8CB-NMs at 26 °C and 36 °C with the radius of 270 nm. The X-ray diffraction peak is observed sufficiently below the SmA-N phase transition temperature in the bulk state, $T_{\text{SmA-N}}^{\text{bulk}}$, (26 °C), which indicates that 8CB-NMs have the layer order. On the other hand, this peak disappears sufficiently above $T_{\text{SmA-N}}^{\text{bulk}}$ (36 °C). Therefore, we confirmed the existence of the SmA-N phase transition in 8CB-NMs.

In order to remove $I_{\text{background}}$ which linearly decreases with increasing q , we normalized $I(q)$ as follows.

$$i(q) = \frac{I(q) - I_{\text{background}}}{I_0} = \frac{1}{1 + \xi^2 (q - q_0)^2}, \quad (3.2.1)$$

where I_0 is the peak intensity. Fig.3.8 (b) shows $i(q)$ of 8CB-NMs and that of 8CB in the bulk state at 26 °C. Both profiles were fitted by Lorentz function eq.3.2.1. Since the layer spacing of 8CB-NMs ($d \sim 31.8$ Å) is identical with that of 8CB in the bulk state, it is sure that the X-ray diffraction peak of 8CB-NMs originates from the layer structure formed by 8CB molecules in the core part of nano-micelles. On the other hand, the correlation length, $2\pi\xi$, of 8CB-NMs ($\sim 4.2 \times 10^3$ Å) was found to be shorter than that of 8CB in the bulk state ($\sim 1.2 \times 10^4$ Å, which is almost equivalent to the resolution of instruments).

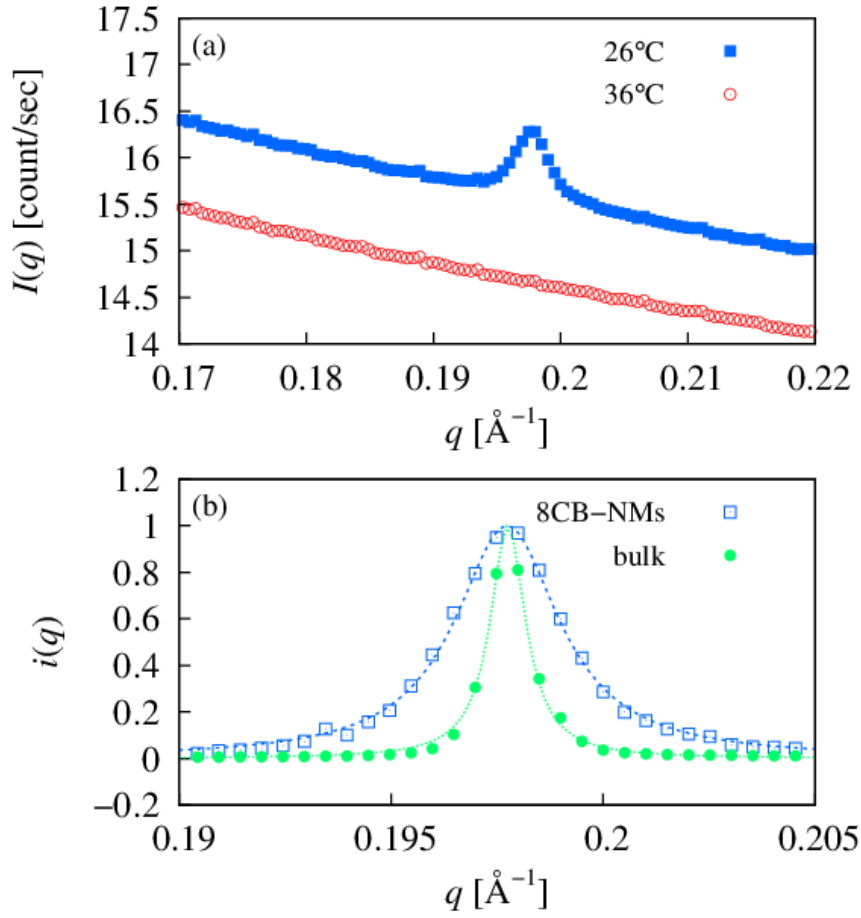


Fig.3.8 (a) q dependence of X-ray scattering intensities of 8CB-NMs at 26 °C and 36 °C. (b) The normalized X-ray profile of 8CB-NMs and 8CB in the bulk state. Dotted lines are fitting curves calculated by eq.3.1.2.

In order to clarify the reason $2\pi\xi$ in nano-micelles is shorter than that in the bulk state, we investigated the SmA-N phase transition behavior on the basis of the temperature dependence of $2\pi\xi$. Fig.3.9 shows temperature dependence of $2\pi\xi$ of 8CB-NMs whose radius is 425 nm and that of 8CB in the bulk state. In the bulk state, $2\pi\xi$ in the N phase continuously increases on cooling and diverges toward $T_{\text{SmA-N}}^{\text{bulk}}$. The dashed line indicates fitting by the power law, $(T - T_{\text{SmA-N}}^{\text{bulk}})^{-\nu}$. We assumed the critical exponent $\nu=0.48$ reported by Ref.46. The fitting yields that $T_{\text{SmA-N}}^{\text{bulk}}$ is 31.8 °C. $2\pi\xi$ of 8CB-NMs continuously increases on cooling from 32.0 °C to 30.5 °C in the same way as that of 8CB in the bulk state. However, $2\pi\xi$ of 8CB-NMs does not diverge at 30.5 °C, which is regarded as the SmA-N phase transition temperature ($T_{\text{SmA-N}}^{\text{LCNM}}$). Moreover, below $T_{\text{SmA-N}}^{\text{LCNM}}$, $2\pi\xi$ of 8CB-NMs is saturated and keeps constant value, which is shorter than that in the bulk state ($\sim 1.0 \times 10^4 \text{ \AA}$).

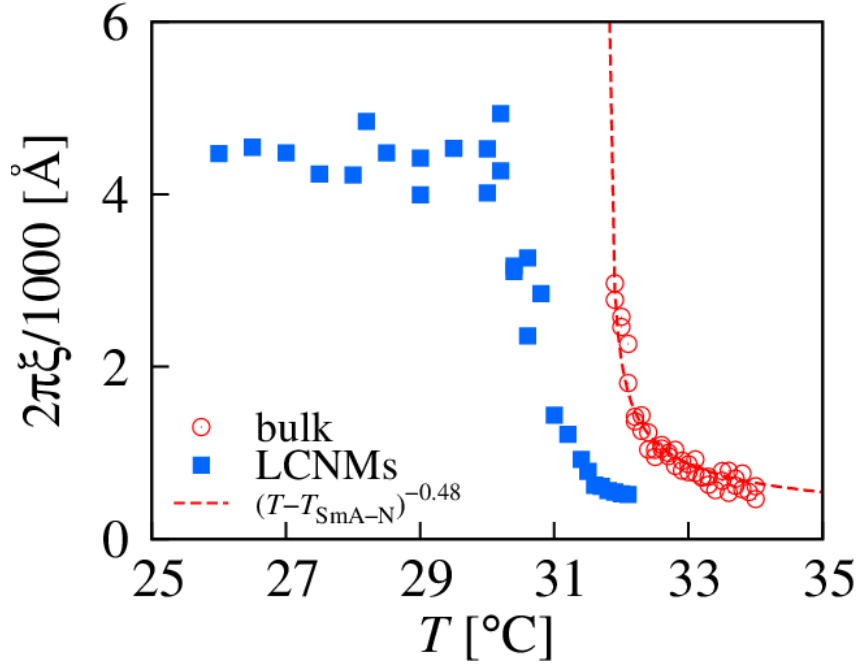


Fig.3.9 The temperature dependence of the correlation length of the layer order of 8CB-NMs whose radius is 425 nm and that of 8CB in the bulk state: The dashed line indicates the fitting results by $(T-T_{\text{SmA-N}})^{-0.48}$.

In order to clarify the origin of the saturation of the correlation length, we measured $2\pi\xi$ of 8CB-NMs as a function of the hydrodynamic diameter of nano-micelles, $2R$. We controlled $2R$ by changing the weight ratio of SmA-LCs to surfactants as we mentioned in the section 2.2 and we determined $2R$ by the polarized dynamic light scattering technic in the same way as the section 2.2.2.3. $2\pi\xi$ of 8CB-NMs is almost independent of temperature between 26 °C to 30 °C. Then, we defined the saturated $2\pi\xi$ as $2\pi\xi_s$. Fig.3.10 shows $2\pi\xi_s$ as a function of $2R$. The gray area indicates that $2\pi\xi_s$ is shorter than $2R$. It is evident that $2\pi\xi_s$ is always shorter than $2R$. The dotted line indicates that $2\pi\xi_s$ is equal to the diameter of the core parts of nano-micelles, $2(R-d)$, where d (~ 58 nm) is the shell thickness estimated in the section 2.2.2.3. $2\pi\xi_s$ continuously decreases as $2R$ decreases and is always close to $2(R-d)$. Thus, it can be concluded that the confinement into the core parts of nano-micelles suppresses $2\pi\xi$ below $T_{\text{SmA-N}}^{\text{LCNM}}$, though confinement does not affect the development of the layer order in the N phase under the condition that $2\pi\xi$ is shorter than $2(R-d)$. These results prove that the layer order is completely confined in the core parts of nano-micelles.

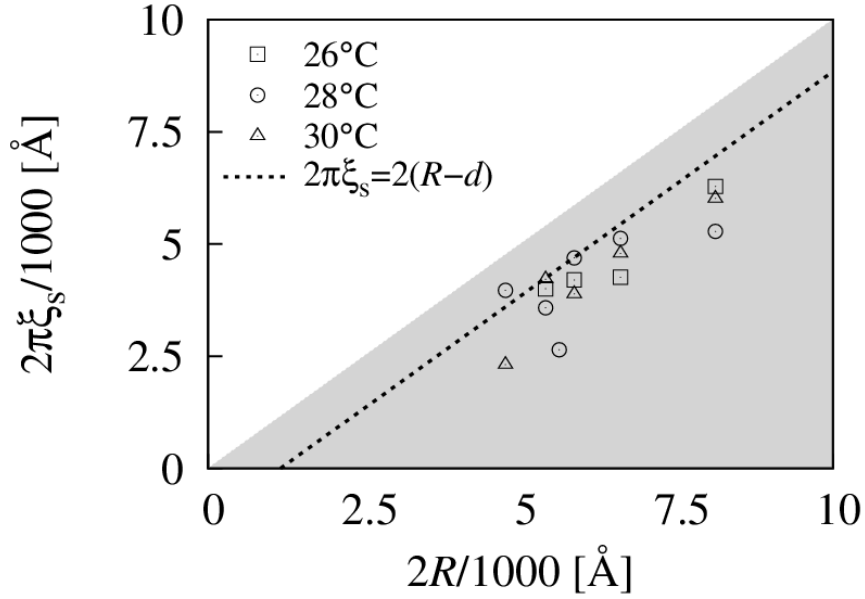


Fig.3.10 The saturated correlation length of the layer order of 8CB-NMs, $2\pi\xi_s$, as a function of the hydrodynamic diameter of nano-micelles, $2R$: The gray area indicates that $2\pi\xi_s$ is shorter than $2R$. The dotted line indicates that $2\pi\xi_s = 2(R-d)$.

3.2.2 Light scattering experiment

It was revealed that LC molecules in the core parts of nano-micelles have the layer order. Generally, the orientational fluctuation of the director of LCs in the SmA phase is suppressed rather than that in the N phase owing to the existence of the layer order. According to the theory of the light scattering [26, 85-87], the fluctuation of director generates the light scattering. Thus, we expected that the optical property of SmA-LCNMs differs from that of N-LCNMs because of the existence of the layer order. In this section, we investigated the SmA-N phase transition by the depolarized (VH) light scattering technique.

In the section 3.3, we will study the mixing process of LC molecules between the core parts of SmA- and N-LCNMs by using the VH light scattering technic. As we will describe in the section 3.3.1, 7CB (N) molecules permeate 8CB (SmA)-NMs during the mixing process, and 7CB and 8CB eventually mix uniformly in the core parts of nano-micelle. For this reason, it is worthwhile to study the optical properties of the LC mixture of 7CB and 8CB in the core parts of nano-micelles.

3.2.2.1 Experimental setup

In order to separate the effects of the layer order and simple temperature-change, we prepared SmA-LCNMs whose SmA-N phase transition temperatures are different from each other by using two kinds of LCs. One is pure 8CB and another is the mixture of 8CB and 8OCB. The SmA-N phase

transition temperature of 8OCB is higher than that of 8CB. Thus, the SmA-N phase transition temperature of LC mixture becomes higher than that of pure 8CB in the bulk state. On the other hand, in order to study the optical properties of the LC mixture of 8CB and 7CB in the core parts of nano-micelles, we fabricated 8CB+7CB-NMs. We got 8CB+7CB-NMs by emulsifying the LC mixture composed of 8CB and ϕ wt% of 7CB.

We used the same equipment as used in the section 2.2.2.1. In this section, we used the depolarized (VH) geometry as used in the section 2.3.1. Thus, we can observe the light scattering intensity caused by the dielectric anisotropy and the orientational fluctuation of the director. As in mentioned in the section 2.3.1.2, the contribution of the dielectric anisotropy to the VH light scattering intensity, $I_{\text{VH}}^{(\text{I})}$, is described as follows,

$$I_{\text{VH}}^{(\text{I})} \propto S(T)^2. \quad (3.2.2)$$

On the other hand, the fluctuation of director also contributes to I_{VH} . According to Ref.26, the contribution of the orientational fluctuation of the director of LCs in the N phase, $I_{\text{VH}}^{(\text{II})}$ is represented as follows,

$$I_{\text{VH}}^{(\text{II})} \propto S(T)^2 / K(T), \quad (3.2.3)$$

where $K(T)$ is the Frank elastic constant with the one constant approximation in eq.2.3.2.6. In the case of N-LCs, $K(T)$ is proportional to the square of $S(T)$ [81-82, 88]. Thus, $I_{\text{VH}}^{(\text{II})}$ is independent of temperature. However, according to Chu *et al.* [89, 90], the twist and bend elastic constants near the SmA-N phase transition temperature are renormalized as follows,

$$K = K_0 + \text{const.} \times \xi, \quad (3.2.4)$$

where ξ is the correlation length of the layer order. Since the SmA-N phase transition is second order phase transition, ξ divergently develops toward the SmA-N phase transition temperature. $I_{\text{VH}}^{(\text{II})}$ s of the twist and bend mode critically decreases toward SmA-N phase transition temperature because $I_{\text{VH}}^{(\text{II})}$ is inversely proportional to K . Although the contribution of the splay mode fluctuation remains in the SmA phase, $I_{\text{VH}}^{(\text{II})}$ is expected to decrease owing to the development of the correlation length of the layer order.

3.2.2.2 Results and discussions

Fig.3.11 shows the temperature dependence of the normalized light scattering intensity, i_{VH} , of 8CB-NMs as blue markers. i_{VH} was normalized so that maximum and minimum values become one and zero, respectively. i_{VH} of 8CB-NMs decreases on cooling below 32.4 °C which corresponds to the pretransitional region of the SmA-N phase transition in which ξ continuously diverges toward $T_{\text{SmA-N}}^{\text{LCNM}}$ (§.3.2.1.2). Since $S(T)$ should monotonously increase, $I_{\text{VH}}^{(\text{I})}$ (eq.3.2.2) does not decreases.

Thus, decrease in i_{VH} is expected to be reflected in the increase in ξ .

In order to confirm whether decrease in i_{VH} is caused by the increase in ξ , we compared the temperature dependence of i_{VH} of 8CB-NMs with that of 8CB+8OCB-NMs. The SmA-N phase transition temperature of 8CB+8OCB in the bulk state (~ 41.4 °C) is higher than that of 8CB (~ 32.5 °C). The temperature dependence of i_{VH} of 8CB+8OCB-NMs is shown in Fig.3.11 as red markers. The i_{VH} of 8CB+8OCB-NMs decreases in the temperature region from 39.6 °C to 38.0 °C with decreasing temperature. Compared with that of 8CB-NMs, the pretransitional region of 8CB+8OCB-NMs shifts toward higher temperature. Moreover, the temperature at which i_{VH} starts decreasing (~ 39.6 °C) is close to the SmA-N phase transition temperature of 8CB+8OCB in the bulk state. Therefore, we concluded that the decreasing behavior of i_{VH} on cooling is caused by the layer order.

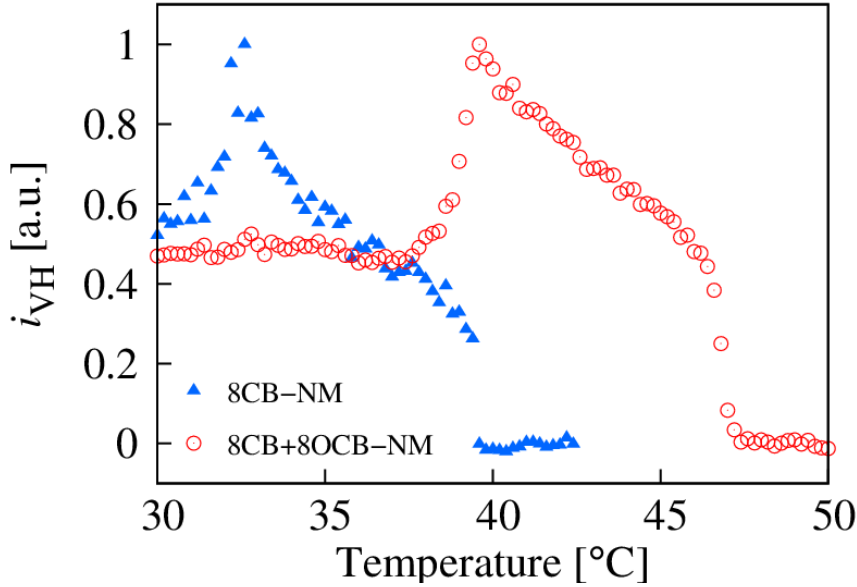


Fig.3.11 Temperature dependence of i_{VH} of 8CB-NMs (Blue markers) and that of 8CB+8OCB-NMs (Red markers): i_{VH} was normalized so that maximum and minimum values become one and zero, respectively.

In order to investigate the optical property of the LC mixture of 8CB and 7CB in the core parts of nano-micelles, we measured temperature dependence of i_{VH} of 8CB+7CB-NMs with various ϕ as shown in Fig.3.12. It is evident that the pretransitional region (the temperature-range in which i_{VH} decreases on cooling) shifts toward lower temperature with increasing ϕ . Considering the fact that the origin of decreasing behavior of i_{VH} on cooling is the development of ξ , this result indicates that the relative temperature, $\Delta T = T_{\text{SmA-N}} - T$, decreases with increasing ϕ because $T_{\text{SmA-N}}$ decreases.

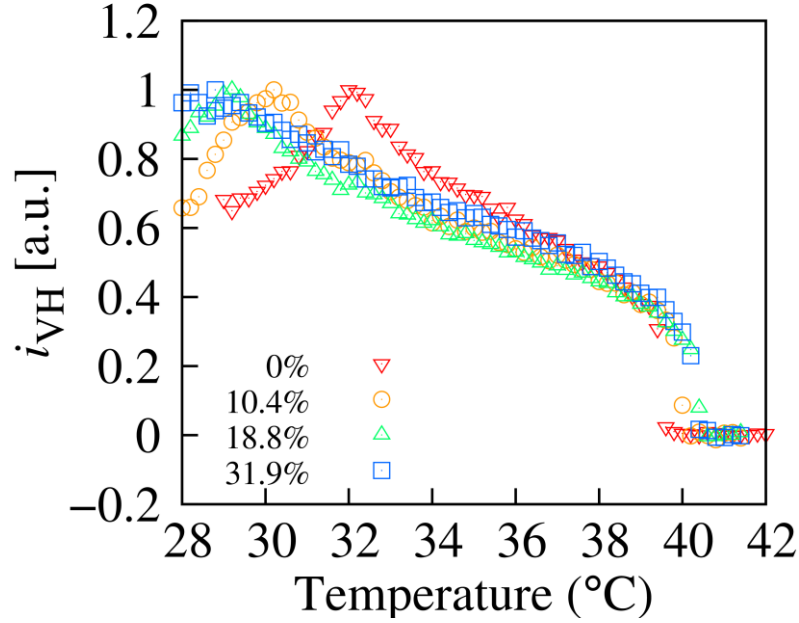


Fig.3.12 Temperature dependence of i_{VH} of 8CB+7CB-LCNMs with various mixing ratio of 7CB: i_{VH} was normalized so that maximum and minimum values become one and zero, respectively.

3.2.3 Summary

First, we confirmed that SmA-LCNMs have the layer order by synchrotron X-ray diffraction measurement. We observed the X-ray diffraction peak corresponding to the wavenumber of the layer spacing of SmA-LCs confined in the core parts of nano-micelles. This X-ray diffraction peak disappears sufficiently above the SmA-N phase transition temperature of LCs in the bulk state.

Second, we investigated the SmA-N phase transition of SmA-LCNMs on the basis of the temperature dependence of the correlation length of the layer order, ξ . Above $T_{\text{SmA-N}}^{\text{LCNM}}$, ξ develops on cooling in the same way as that in the bulk state. However, ξ is saturated below $T_{\text{SmA-N}}^{\text{LCNM}}$. Since the saturated correlation length, $2\pi\xi_s$, continuously decreases as $2R$ decreases, the saturation of ξ is surely caused by the confinement into the core parts of nano-micelles. This result provides that the layer order exists in the core parts of nano-micelles.

Finally, we studied the optical property of SmA-LCNMs by the light scattering experiment. It was revealed that the VH light scattering intensity decreases as temperature decreases in pretransitional region. Furthermore, it was revealed that the pretransitional region of 8CB+8OCB-NMs is higher than that of 8CB-NMs because the SmA-N phase transition temperature of 8CB+8OCB-NMs is higher than that of 8CB-NMs. Thus, we concluded that the development of ξ decreases the VH light scattering intensity. Additionally, we investigated the optical properties of LC mixture of 7CB and 8CB in the core parts of nano-micelles. Then, it was revealed that the relative temperature decreases as the concentration of N-LCs increases even if temperature is constant.

3.3 The mobility of liquid crystals in the core parts of nano-micelles

We succeeded in fabricating liquid crystalline nano-micelles (LCNMs) by introducing smectic A (SmA)-liquid crystals (LCs) into the hydrophobic core parts. In this section, we discuss the mobility of LC molecules in the core parts of nano-micelles by observing the mixing process of LC molecules between the core parts of SmA- and nematic (N)-LCNMs. Since SmA-LCs have one dimensional translational order along layer normal direction, the mobility of SmA-LC molecules in the core parts of nano-micelles is expected to be suppressed rather than that in the N phase. First, we explained the mixing process of LC molecules between the core parts of SmA- and N-LCNMs in the section 3.3.1. Second, we performed the time-resolved light scattering experiment and investigated the effect of the layer order on the mobility of LC molecules in the core parts of nano-micelles using the mixing process in the section 3.3.2. Third, we studied this mixing process by time-resolved synchrotron X-ray scattering experiment in the section 3.3.3. Finally, we summarized the effect of the layer order on the mobility of LC molecules in the core parts of nano-micelles.

3.3.1 Mixing process of liquid crystalline molecules between the core parts of nano-micelles

In order to estimate the mobility of LC molecules in the core parts of nano-micelles, we used the mixing process of LC molecules between core parts of SmA- and N-LCNMs. Fig.3.13 shows the schematic image of this mixing process. First, we fabricated 8CB-NMs (SmA-LCNMs) and 7CB-NMs (N-LCNMs), separately. Thus, the core parts of 8CB-NMs are occupied by pure 8CB just after mixing. After mixing 8CB- and 7CB-NMs, the concentrations of 8CB and 7CB in each micelle gradually change. When time passes sufficiently, the concentrations of 8CB and 7CB in each micelle are expected to become uniform by transporting each other. By measuring the time evolution of this mixing process, we can discuss the mobility of 8CB-NMs.

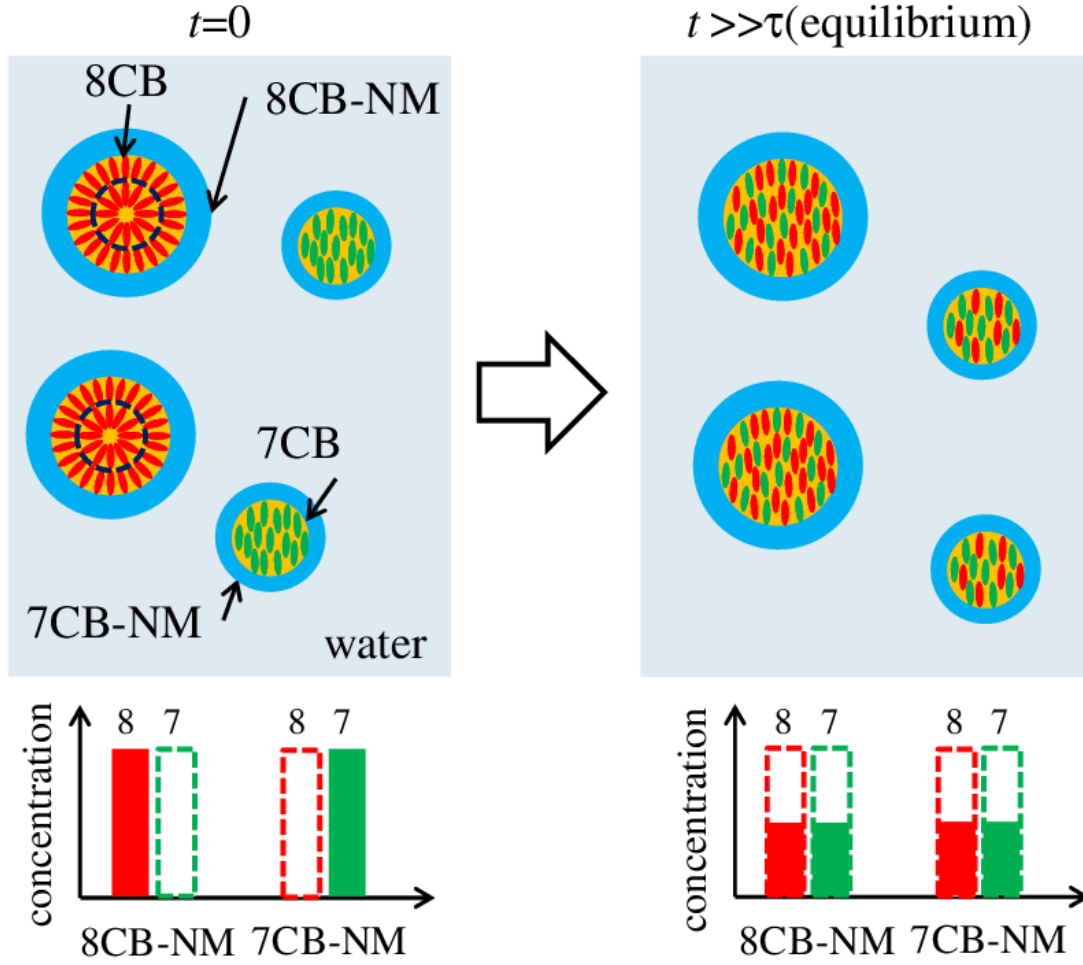


Fig.3.13 The schematic image of the mixing process of LC molecules between core parts of SmA- and N-LCNMs.

3.3.2 Time-resolved light scattering

In order to measure the mixing process experimentally, we performed the time-resolved depolarized (VH) light scattering experiment. After mixing of 7CB-NMs, we recorded the time evolution of VH light scattering intensity, $I_{VH}(t)$. As mentioned in the section 2.3.1.2 and the section 2.4.1.2, I_{VH} almost linearly increases with increasing temperature in pretransitional region because I_{VH} mainly originates from the orientational fluctuation which is strongly suppressed by the layer order. 7CB molecules permeate 8CB-NMs as time passes (Fig.3.14 red line), which decreases the SmA-N phase transition temperature, $T_{\text{SmA-N}}$. Then, I_{VH} increases because the relative temperature, $\Delta T (=T_{\text{SmA-N}} - T)$ decreases (Fig.3.14 blue line). In consequence, I_{VH} from 8CB-NMs gives us the information on the concentration of 7CB in the core parts of 8CB-NMs.

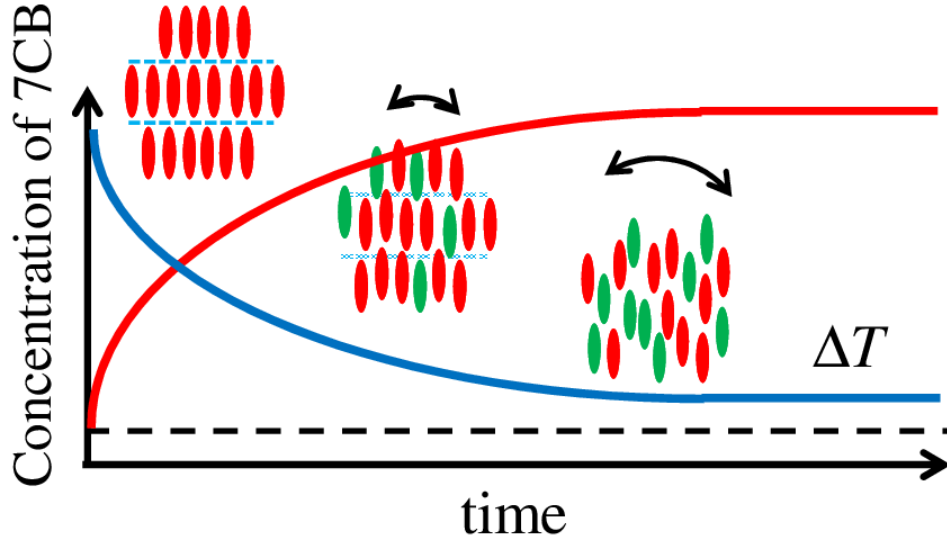


Fig.3.14 Schematic image of the time evolution of the concentration of 7CB in 8CB-NMs (Red line) and relative temperature (Blue line).

3.3.2.1 Experimental setup

In this section, we explain the procedure for measurement. First, we made large 8CB-NMs and small 7CB-NMs, separately. Generally, the I_{VH} in the N phase is larger than that in the SmA phase because the orientational fluctuation is larger in N phase [85-87, 89, 90]. Hence, in order to neglect the light scattered by 7CB-NMs, we made the size of 7CB-NM small. The typical value of the radii of 7CB-NM and 8CB-NM are 210 and 400 nm, respectively. Just after mixing 8CB- and 7CB-NMs, we measured $I_{VH}(t)$ using the same equipment as VH light scattering setup used in the section 2.2.2.1.

The time-resolved light scattering experiment was performed as follows. (I) We set a sample in the temperature-controlled stage which keeps the temperature of the sample constant. (II) After waiting Δt_{bef} , we measured the light scattering intensity for Δt_{mes} . (III) In order to record the data, we wait Δt_{aft} . By taking the average value of the recorded data, we can determine the mean intensity at time, $\Delta\tau(1) (= \Delta t_{bef} + \Delta t_{mes})$. We got the time evolution of the light scattering intensity by repeating processes (II) and (III). Typical values of Δt s are 40-60 sec. Here, we defined the normalized VH light scattering intensity, $i(t) = (I_{VH}(t) - I_{VH}(\infty)) / (I_{VH}(\infty) - I_{VH}(0))$, so that $i(t)$ increases from -1 to 0 as the concentration of 7CB increases, where $I_{VH}(0)$ and $I_{VH}(\infty)$ are the light scattering intensities at the initial and equilibrium states, respectively.

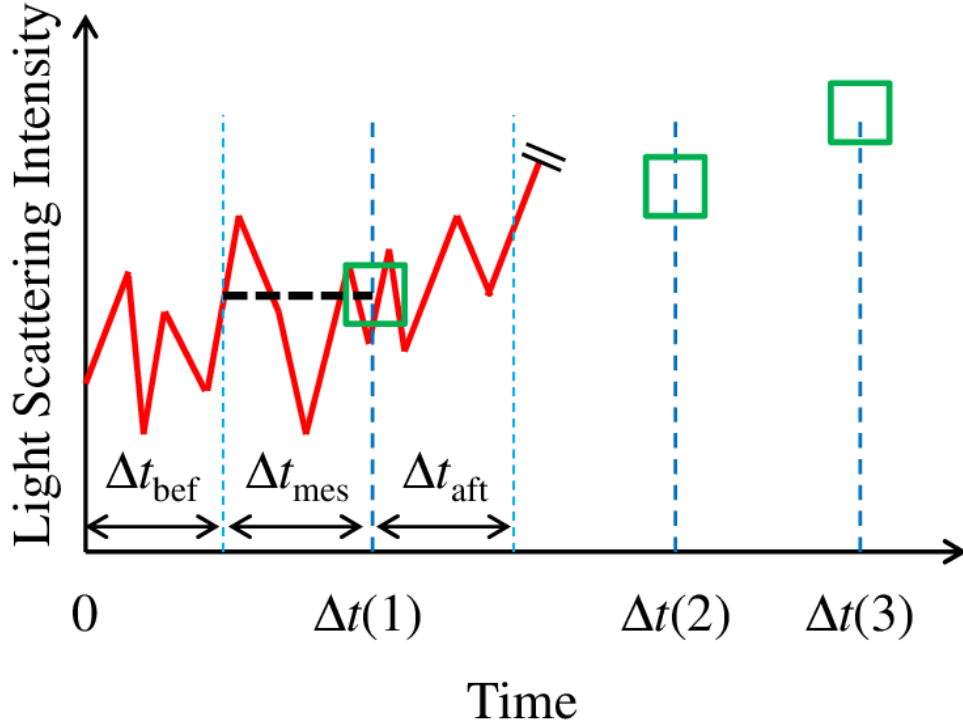


Fig.3.15 The schematic diagram of the time-resolved light scattering experiment.

3.3.2.2 Results and discussions

Fig.3.16 shows the time evolution of the normalized depolarized light scattering intensity, $i(t)$, during the mixing process of 8CB- and 7CB-NMs at 28 °C, 30 °C and 32 °C. Initial concentrations of 8CB- and 7CB-NMs are 0.12 wt% and 0.023 wt%, respectively. Then, the number density of 7CB-NMs is 1-2 times higher than that of 7CB-NMs. Just after mixing 7CB-NMs to 8CB-NM solution, $i(t)$ starts to increase and relaxed with the characteristic time τ , which indicates that the system becomes an equilibrium state. τ strongly depends on temperature and accelerates with increasing temperature. We fitted $i(t)$ using the following single exponential function,

$$i(t) = \frac{I_{\text{vh}}(t) - I_{\text{vh}}(\infty)}{I_{\text{vh}}(\infty) - I_{\text{vh}}(0)} = -\exp\left(-\frac{t}{\tau}\right). \quad (3.3.1)$$

As shown in Fig.3.16, obtained results were well fitted by eq.3.3.1, and τ s were estimated to 1.14 h at 28 °C, 0.52 h at 30 °C and 0.15 h at 32 °C. Fig.3.17 shows temperature dependence of $1/\tau$ in the mixing process of 8CB- and 7CB-NMs as blue squares.

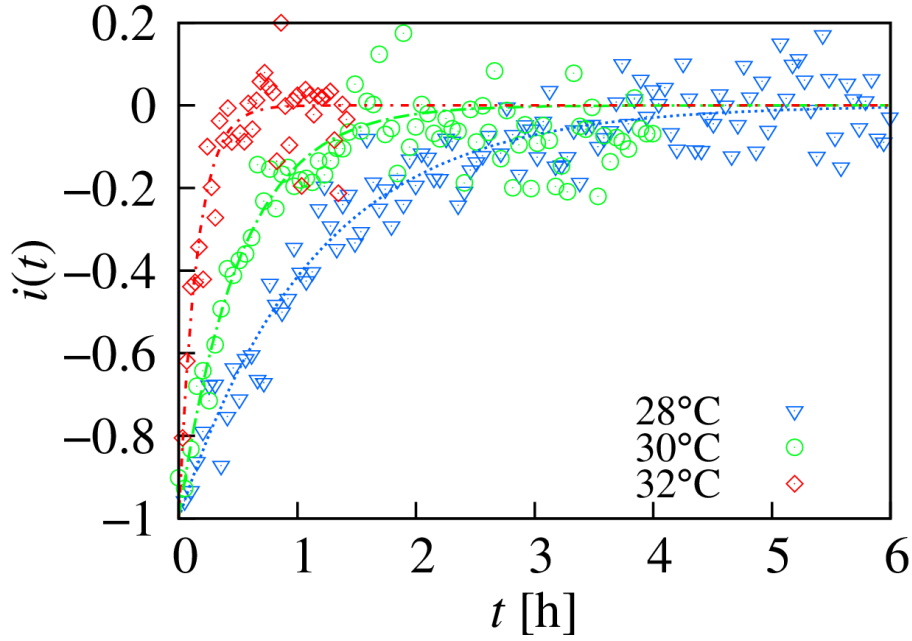


Fig.3.16 Time evolution of the normalized light scattering intensity $i(t)$ of the mixture of 8CB- and 7CB-NMs at 28 °C, 30 °C and 32 °C. Dotted and broken lines are fitting results by eq.3.3.1.

By contrast, above the temperature at which the layer order disappears the mixing process is so fast that we cannot observe the mixing process under our experimental resolution. Then, it is evident that τ in the SmA phase is quite slower than that in N phase. The slow mixing process is expected to be caused by the fact that the permeation of 7CB molecules into 8CB-NMs is suppressed by the existence of the layer order.

In order to confirm that the existence of the layer order is the origin of the slow mixing process, we modified the SmA-N phase transition temperature of SmA-LCNMs by addition of 8OCB into 8CB. As mentioned in the section 3.2.2.2, the SmA-N phase transition temperature of the LC mixture of 8CB and 8OCB is higher than that of pure 8CB.

We plotted temperature dependence of $1/\tau$ in the mixing process of 8CB+8OCB-NMs with 7CB-NMs in Fig.3.17 as red circles. The abrupt increase in $1/\tau$ of 8CB+8OCB-NMs is observed at higher temperature than that of 8CB-NMs. This result directly indicates that permeation of 7CB molecules is suppressed by the layer order. Additionally, according to Refs.46-47, the layer order suppresses the mobility of LC molecules along the layer-normal direction in the bulk state. Therefore, it is suggested that LC molecules align perpendicular to surface and form an onion-like stack of smectic layers in nano-micelles.

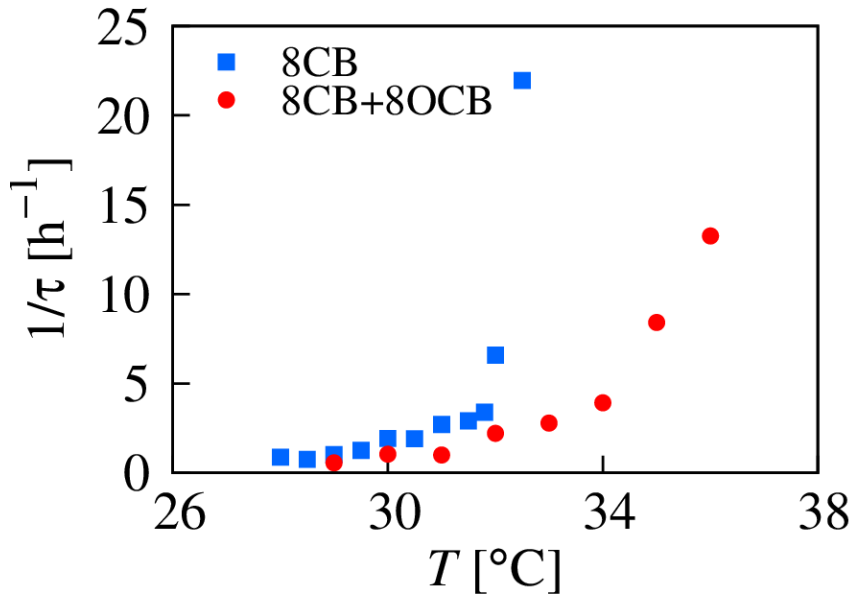


Fig.3.17 shows temperature dependence of $1/\tau$ in the mixing process of 8CB-NM (blue squares) and 8CB+8OCB-NMs (red circles) with 7CB-NM.

3.3.3 Time-resolved synchrotron X-ray scattering

In the section 3.3.2, we found that the existence of the layer order suppresses the permeation of N-LC molecules into SmA-LCNMs. In this section, in order to confirm that the layer order affects permeation of 7CB molecules in the core parts of 8CB-NMs, we also performed time-resolved synchrotron X-ray scattering experiment during the mixing process.

3.3.3.1 Experimental setup

We performed the synchrotron X-ray diffraction measurement at FSBL03XU of SPring-8 (Harima, Japan) in the same way as that in the section 3.2.1.1. In order to determine the time evolution of the layer structure during the mixing process, we performed the time-resolved synchrotron X-ray diffraction measurement as follows. First, we mixed 8CB- and 7CB-NMs so that the concentration of 7CB in all the amount of LCs is 16.3 wt%. Then, we stored the X-ray scattering intensity for 240 sec. In order to record the data and to initialize the imaging plate, we wait for about 160 sec. By repeating these processes, we obtained the time evolution of the X-ray scattering profile. In order to determine the layer spacing and the correlation length, we fitted the X-ray scattering profiles by Lorentz function in the same way as the section 3.1.2.2.

3.3.3.2 Results and discussions

Fig.3.18 shows the time evolution of the X-ray profile during the mixing process of 8CB- and 7CB-NMs. Lines are the fitting results by Lorentz function eq.3.1.2. It is confirmed that LC

molecules in the core parts of nano-micelles have the layer order even though time passes enough ($t=5.58$ h). Clearly, the center of the X-ray diffraction peak shifts toward higher wavenumber as time passes, which indicates that the layer spacing, $d=2\pi/q_0$, shrinks. Typical values of the layer spacing at 0.05 h and at 5.58 h are 31.65 Å and 31.43 Å, respectively. Since the molecular length of 7CB is shorter than that of 8CB, the continuous decrease in the layer spacing indicates that 7CB molecules continuously permeate 8CB-NMs. The width of the X-ray diffraction peak becomes wider as time passes, which indicates that the correlation length becomes shorter. The experiment in the section 3.2.1.2 yields that the decrease in the correlation length corresponds to the decrease in ΔT . Thus, our experimental result suggests ΔT continuously decreases owing to the mixing of 7CB.

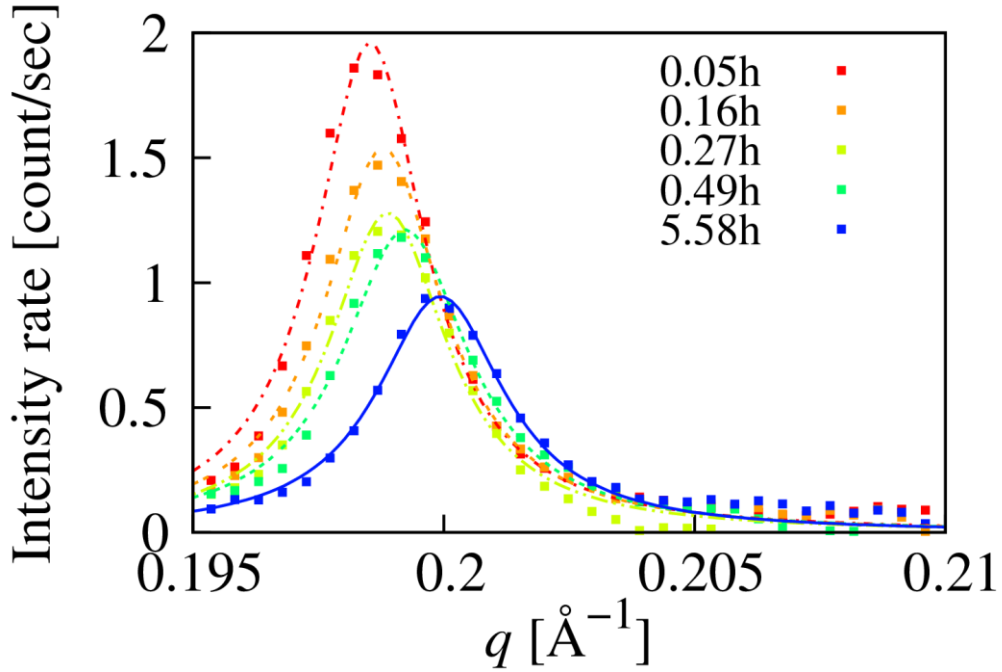


Fig.3.18 The time evolution of the X-ray diffraction profile: Lines are the fitting results by Lorentz function eq.3.1.2.

Fig.3.19 shows the time evolution of the layer spacing, d of 8CB-NMs after mixing of 7CB-NMs. In order to compare the time evolution of d with that of the normalized scattered light intensity, $-i(t)$, we showed $-i(t)$ of the same mixture. d continuously decreases as time passes as the similar way for the change in $-i(t)$. In order to determine the characteristic time of change in d , we fitted the experimental data using the following single exponential function,

$$d(t) = d_{\infty} - (d_{\infty} - d_0) \exp\left(-\frac{t}{\tau_d}\right), \quad (3.3.2)$$

where τ_d , d_0 and d_{∞} are the characteristic time of change in d , the layer spacing at $t=0$ and that at

equilibrium state, respectively. We showed the fitting result in Fig. 3.19 as a red dashed line. It is revealed that τ_d (~ 0.39 h) is almost consistent with the result obtained by light scattering experiment (~ 0.56 h). The results support that the layer order suppresses the permeation of N-LC molecules in nano-micelles.

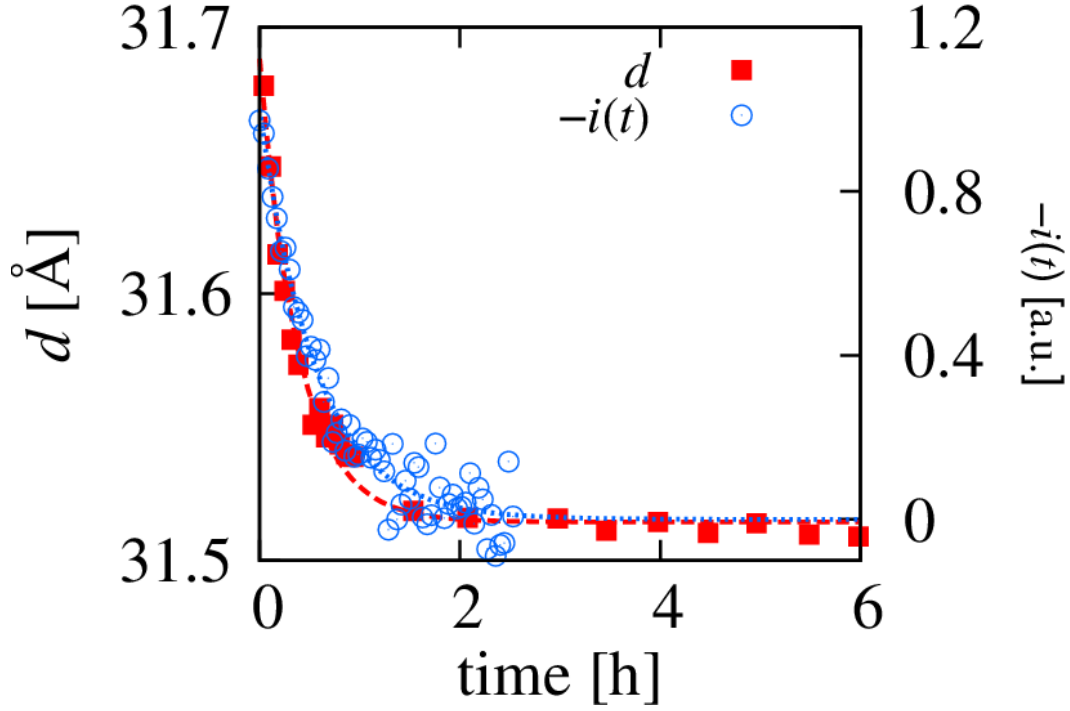


Fig.3.19 The time evolution of the layer spacing, d , and the normalized scattered light intensity, $-i(t)$, of the mixture of 8CB- and 7CB-NMs.

By using the relation between d and the concentration of 7CB in 8CB, ϕ (eq.3.1.3), we estimated ϕ from the experimental value of d . Fig.3.20 shows time evolution of ϕ of 8CB-NMs during the mixing process. Since we define $t=0$ as the time at which we start the X-ray scattering diffraction measurement, a small amount of 7CB had mixed. However, the value of ϕ is very small (~ 5.3 wt%). When time passes sufficiently, ϕ becomes 14.8 wt%. In this experiment, we added 7CB-NMs to 8CB-NMs so that the concentration of 7CB in all the amount of LCs is 18.1 wt%. Since ϕ at $t=\infty$ is close to 18.1 wt%, the 8CB and 7CB in the core part of each micelle are expected to mix uniformly. We succeeded in estimating the concentration of 7CB in 8CB-NMs quantitatively.

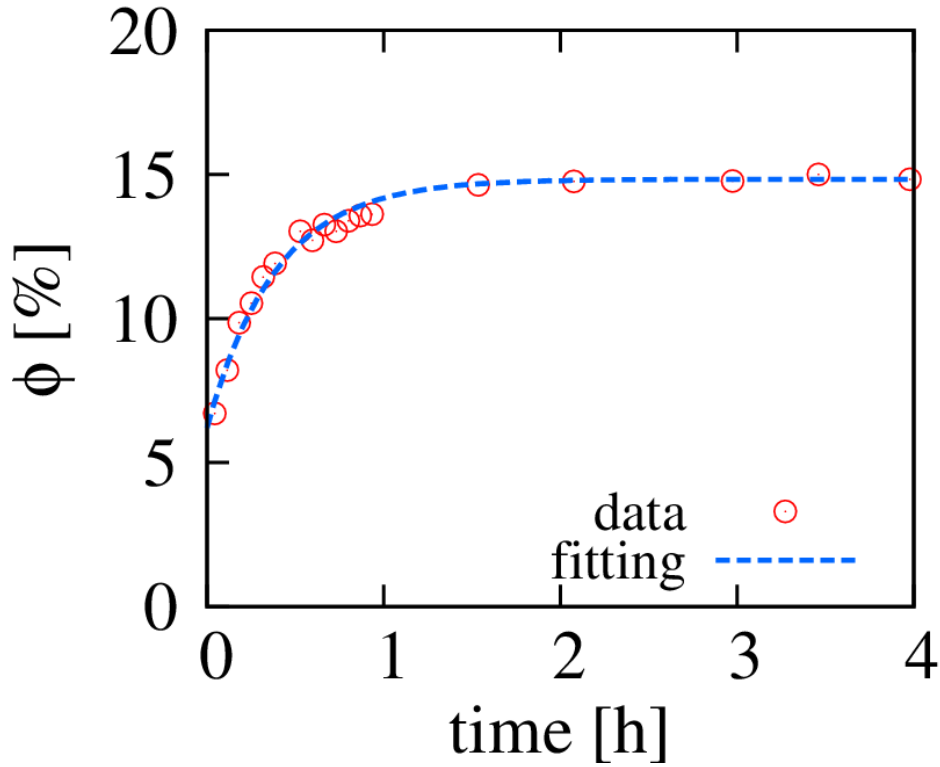


Fig.3.20 The time evolution of the concentration of 7CB in 8CB-NMs, ϕ : The blue dashed line is the fitting result obtained by eq.3.3.3.

3.3.4 Summary

In order to investigate the mobility of LC molecules in the core parts of nano-micelles, we used the mixing process of LC molecules between the core parts of SmA- and N-LCNMs. We performed depolarized light scattering experiment which enables us to measure the mixing process experimentally. As a result, we found that the mobility of LC molecules in the core parts of nano-micelles in the SmA phase is quite lower than that in the N phase. Additionally, the abrupt increase in the mobility of 8CB+8OCB-NMs whose SmA-N phase transition temperature is higher than that of 8CB-NMs were observed at higher temperature than that of 8CB-NMs. Therefore, we conclude that the layer order suppresses the mobility of LC molecules in the core parts of nano-micelles.

We investigated the change in the layer structure due to the mixing process of LC molecules. In the time-resolved synchrotron X-ray scattering, we found shrinkage in the layer spacing due to the permeation of 7CB molecules whose molecular length is shorter than that of 8CB. We quantitatively estimated the concentration of 7CB in 8CB-NMs on the basis of the relation between the layer spacing and the concentration of 7CB in the bulk state. As a result, it was revealed that 7CB molecules continuously permeate 8CB-NMs and, the concentrations of 8CB and 7CB in each

micelle become uniform when time passes sufficiently.

Chapter IV General conclusion

In this paper, we fabricated nematic (N)- and smectic A (SmA)-liquid crystalline nano-micelles (LCNMs) and investigated the effect of the confinement in nano-micelles on the LC order. In a LCNM system, LCs confined in the core parts of nano-micelles are strongly affected by the surface interaction. Therefore, the phase transition and dynamical properties of LCs in LCNMs differ from that in the bulk states.

In chapter II, we fabricated N-LCNMs and studied the confinement effect on the N-isotropic (Iso) phase transition and orientational fluctuation of N-LCs. First, we succeeded in controlling the radii of nano-micelles by changing the weight ratio of LCs to surfactants (§2.2). We measured the autocorrelation function in the polarized dynamic light scattering (DLS) experiment. Then, we estimated the hydrodynamic radii of nano-micelles from the relaxation times of autocorrelation functions using Einstein-Stokes relation. As a result, it was revealed that the radii of nano-micelles increase as the weight ratio of LCs to surfactants increases. We constructed the theoretical model in which the hydrophobic core parts of nano-micelles are simply swollen by LCs. Our theoretical model agrees with the experimental result. Therefore, we concluded that almost all LCs are confined in the hydrophobic core parts of nano-micelles.

Second, we investigated the N-Iso phase transition behavior of LCs three-dimensionally confined in the core parts of nano-micelles (§2.3). In order to estimate the scalar order parameter of LCs confined in the core parts of nano-micelles, we performed the depolarized (VH) light scattering experiment. In consequence, it was revealed that the phase transition behavior of LCs confined in nano-micelles with the large radius (~480 nm) is first order phase transition in the same way as that in the bulk state. By contrast, the phase transition behavior changes from the first order to the second order as the radius of nano-micelles becomes smaller (~130 nm). In addition, we analyzed the phase transition behavior on the basis of the Kutnjak, Kralj, Lahajnar and Zumer model which includes the effect of the surface interaction, and then, we estimated the strength of the surface interaction. As a result, we found that the strength of the surface interaction in our LCNM system is larger than the reported value of two-dimensional confinement system. Thus, we concluded that the strong effect of the confinement is caused by the fact that surface area per unit volume becomes large owing to three-dimensional confinement.

Third, we investigated the orientational fluctuation of N-LCs confined in the core parts of nano-micelles (§2.4). We measured autocorrelation functions of LCNMs by using the VH DLS technique. In consequence, it was revealed that LCNMs have two kinds of relaxation mode, that is fast and slow modes. Since the relaxation time of the fast mode is close to that of orientational fluctuation of N-LCs in the bulk state, we concluded that the fast mode originates from the

orientational fluctuation of N-LCs confined in the core parts of nano-micelles. On the other hand, the relaxation time of the slow mode is close to that of the translational diffusion of nano-micelles. Thus, we concluded the slow mode corresponds to the rotational diffusion of nano-micelles.

Finally, we studied the effect of the confinement on the orientational fluctuation of N-LCs (§2.4). We measured the relaxation time of the autocorrelation function of LCNMs as a function of the wave number of scattering vector by using the VH DLS technique. It was revealed that the relaxation time of rotational diffusion of nano-micelles follows the dispersion relation of the purely diffusive mode. By contrast, the relaxation time of the orientational fluctuation of N-LCs in the core parts of nano-micelles is independent of the wave number of the scattering vector. Then, we measured the relaxation time of the orientational fluctuation of N-LCs as a function of the size of the confinement. As a result, the relaxation time of the orientational fluctuation of N-LCs accelerates as the size of the confinement decreases. For these reasons, we concluded that the orientational fluctuation of N-LCs with long-wavelength is suppressed by the confinement and therefore, that with the short-wavelength corresponding to the size of the confinement becomes dominant.

In chapter III, we fabricated the SmA-LCNMs which have the layer order in their core parts and then, we studied the layer structure and the mobility of LC molecules in the core parts of nano-micelles. First, we performed the synchrotron X-ray diffraction measurement in order to confirm the layer order of LCs confined in the core parts of nano-micelles (§3.2.1). We analyzed the layer structure by analyzing X-ray diffraction peak. Since the X-ray diffraction peak is observed at the wave number corresponding to the layer spacing of SmA-LCs in the bulk state, it was confirmed that the X-ray diffraction peak of SmA-LCNMs originates from the layer structure of SmA-LCs introduced in the core parts of nano-micelles. Additionally, the correlation length of the layer order in the core parts of nano-micelles divergently increases on cooling in the N phase in the same way as the SmA-N phase transition behavior in the bulk state. However, the correlation length of the layer order in the core parts of nano-micelles in the SmA phase is shorter than that in the bulk state. In order to clarify the origin of the suppression on the correlation length of the layer order, we measured the saturated correlation length as a function of micellar size. Then, it was revealed that the saturated correlation length decreases as the micellar size decreases. Furthermore, the saturated correlation length is close to the diameter of the core parts of nano-micelles. Therefore, we concluded confinement in the core parts of nano-micelles suppresses the correlation length below the SmA-N phase transition temperature, though confinement does not affect the development of the layer order in the N phase under condition that the correlation length is shorter than the diameter of nano-micelles. Additionally, these results prove that the layer order is completely confined in the core parts of nano-micelles.

Second, we investigated the effect of the layer order on the mobility of LC molecules in the core parts of nano-micelles (§3.3). In the time-resolved light scattering experiment, the mixing process

was measured as change in the light scattering intensity. Then, we discussed the mobility on the basis of the characteristic time of mixing process. As a result, it was revealed that the mobility of LCs in the SmA phase is quite lower than that in the N phase. In order to confirm the effect of the layer order, we modified the SmA-N phase transition temperature and then, investigated the divergent behavior of the mobility of LC molecules. In consequence, the temperature toward which the mobility of LC molecules diverges shifts toward higher temperature. Therefore, we concluded that the layer order suppresses the permeation of N-LC molecules into SmA-LCNMs, and consequently, the mobility of LC molecules decreases.

Finally, we investigated the structural change in the layer order during the mixing process. We performed time-resolved synchrotron X-ray diffraction measurement in order to measure the change in the X ray diffraction peak which corresponds to the layer structure of LCs in the core parts of nano-micelles. Then, we found that the layer spacing becomes shorter continuously as mixing progresses, which indicates that the N-LCs continuously permeate SmA-LCNMs during mixing process. Furthermore, the characteristic time of change in the layer spacing is close to that of light scattering intensity. In addition, we estimated quantitatively the concentration of N-LCs in SmA-LCNMs by using the relation between the layer spacing and the concentration of N-LCs in the bulk state. As a result, it was confirmed that N- and SmA-LCs mixes uniformly at equilibrium state.

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