Experimental assessment of quasi-binary picture of thermotropics: Induced smectic A phase in 7CB–n-heptane system

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Quasi-binary (QB) picture of thermotropics, which regards a neat thermotropic liquid crystal as a binary system consisting of (semi)rigid core and molten alkyl chain, was assessed experimentally for the most famous (and representative) thermotropic mesogenic series *n*CB. By adding *n*-heptane as solvent, the smectic A phase was induced in 7CB–*n*-heptane system. Small angle x-ray diffraction showed that the QB picture holds not only in the phase behavior but also in the structure. It is suggested that the melting of 8CB and 9CB to isotropic liquid via smectic and nematic liquid crystals can be understood as a thermotropic–lyotropic crossover. © *2011 American Institute of Physics*. [doi:10.1063/1.3615491]

I. INTRODUCTION

Liquid crystals (LC) have usually been treated, from the point of view of basic research, while dividing them into two groups: thermotropic and lyotropic. The former results from the shape anisotropy of constituting particle and can be realized in neat systems in contrast to the latter arising from the micro phase separation in multicomponent systems. Indeed the nematic (N) LC can be modeled by rigid rods (or disks) according to Onsager's theory.[1] A more realistic model by Maier and Saupe[2] considers only anisotropic intermolecular interaction while neglecting the particle size. The introduction of molecular length (for rod) results in possible formation of smectic A (SmA) phase in addition to the N phase.[3] Results of molecular dynamics simulation on systems consisting of spherocylinders are essentially consistent with such understanding.[4]

The use of molecules with designed shape is currently an important strategy to construct intended (and/or unpredictable) aggregation structures such as cylinders (using a fan-shaped molecule). On the other hand, the utilization of amphiphilic mesogens has also become an important strategy to construct exotic aggregation structures. Since the aggregation structures thus formed usually exhibit micro phase separation, spatial arrangement of functionality specific to a component (such as conduction) can be controlled. Adequate combination of "thermotropy" and "lyotropy" is currently a standard methodology in LC chemistry.[5–7]

Apart from the recent intended introduction of amphiphilic nature into mesogenic molecules, most of classical mesogens such as 4-alkyl-4′-cyanobiphenyl (abbreviated as *n*CB, with *n* being the number of carbon atoms in the alkyl group) have long alkyl group(s) as terminal groups as shown in Fig. 1. Although the terminal chain was assumed to contribute essentially to the elongation of molecules by

McMillan,[3] developed later were some theories that take the chain flexibility into accounts.[8–15] These theories showed that the importance of entropic stabilization of LC phases. However, the experimental confirmation through the analyses of entropy itself were performed only recently.[16,17] Indeed, the molten state of chain in LC states were established through the analysis of absolute entropy for some mesogens showing cubic LC phases such as 4′-alkyloxy-3′-nitrobiphenyl carboxylic acid (ANBC(*n*), Fig. 1).[18–20] The most recent finding relevant to this issue is that the alkyl chain is already melted as in the isotropic liquid even in SmE phase, which is one of LC phases the closest to ordered crystal.[17] It is noted that according to the theories considering the chain flexibility,[8–14] the tendency is predicted towards the segregation of the core and chain due to the difference in molecular dynamics.

In ANBC(*n*), the molten alkyl chains behave such as a solvent in lyotropic systems as evidenced by the close similarity of the LC phase diagram between the neat systems (against chain length *n*) and binary systems mixed with *n*-alkane.[21,22] On the basis of this finding, one of the present authors proposed the quasi-binary (QB) picture of thermotropics consisting of mesogens having long alkyl group(s).[23] The QB picture treats a thermotropic LC as a binary mixture of (semi)rigid cores and molten chains. The QB picture has been very useful in understanding cubic phases of ANBC(*n*).[16,24] Yoneya *et al.*[25] independently applied a model of micro phase separation to cubic mesogens, which was based on their amphiphilic nature and had originally been developed for melts of amphiphilic block copolymers.[26]

Although the validity and usefulness of the QB picture are certain in a limited class of mesogens such as ANBC(*n*), the range of its applicability has not yet been studied. If the QB picture holds in a reasonably wide range of mesogens, it puts a possibility to (re)organize the unified view over thermotropics and lyotropics in the field of LC research. More precisely, a new axis "thermotropic–lyotropic" can be introduced though the quantitative measure is hard to define.

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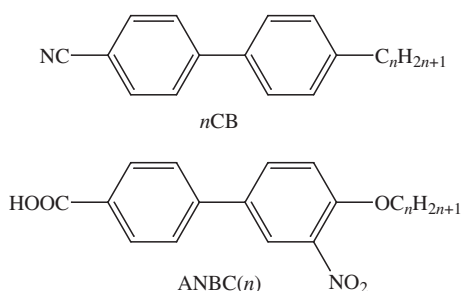
FIG. 1. Molecular structures of *n*CB and ANBC(*n*).

Historically, the view of "lyotropic" nature for the formation of smectic phases is not quite new.[27–30] Guillon *et al.*[29,30] reported some experimental works showing that the core and flexible chains segregated though weakly. However, they did not intend to use the view for controlling a whole phase diagram against the chain length. It is, therefore, still interesting to widen objects of the QB picture. The present paper reports the experimental result on 7CB.

7CB is a member of *n*CB, which is one of the most representative rod-like mesogens[31] exhibiting much simpler LCs than ANBC(*n*). Short chain *n*CB ($n \leq 7$) exhibits only the N phase in between an ordered crystal and isotropic liquid while *n*CB with a long chain ($n \geq 10$) exhibits only the SmA phase. Both N and SmA phases appear in 8CB and 9CB in this order upon heating. The structure of SmA phase in *n*CB was the object of extensive studies, because the layer spacing is significantly larger than the length of molecules with the fully extended alkyl chain, in contrast to the "ideal" SmA phase naively expected for a system of hard rod-like objects.[4] This discrepancy was resolved by assuming interdigitated bilayers. Namely, the rigid molecular cores (biphenyl moiety and cyano [CN] group) are assumed to aggregate themselves through strong interaction between the cyano groups. Leadbetter *et al.*[32] later proposed a realistic model of the molecular packing in SmA phase of 8CB through a densitometric study. This model was further supported by the detailed analysis of x-ray diffraction pattern.[33] Interestingly, the local aggregation structure (as expressed in terms of the ratio between the molecular length and the average repeat distance between molecules) was reported to remain the same even in the N phase of 5CB and 7CB.[34] This puts a question whether the appearance of the SmA phase upon chain elongation in the neat system results not from the enhancement of shape anisotropy in accordance with the phase diagram of hard objects,[4] but from the enhanced segregation of the core and chain. This paper describes the results of experimental study on phase behavior of the binary system between 7CB and *n*-heptane. *n*-Heptane (C_7H_{16}) was chosen as a real solvent consisting of only alkyl chains because the good miscibility was expected due to matching in the length of chain.

It is noted that there are many papers reporting results of the experiments on *n*CB–*n*-alkane systems.[35–40] Indeed, a literature claiming the induction of SmA phase in 7CB-*n*-octane system exists.[36] Although a similar phase diagram to that obtained in this study was obtained as compared in Fig. 3, the identification of the induced phase is insufficient. On the other hand, most papers treated alkane as a minor component that

affects the relative stability of fluid phases. Only a little attention has been paid for the lyotropic aspect of the system for the whole phase diagram. This paper will demonstrate the importance of the view point of "thermotropic–lyotropic" crossover especially for the melting process of neat 8CB and 9CB.

II. EXPERIMENTAL

Commercial chemicals (7CB [> 97%], 8CB [> 97%], and *n*-heptane [> 99%]) were purchased from Wako Chemicals and used without further purification. Composition of binary mixture was first determined by gravimetrically for differential scanning calorimetry (DSC) after confirming the loss of *n*-heptane being less than 0.1% during the sample preparation. For other experiments, the composition was deduced from the phase diagram determined by DSC, because the transition temperature to isotropic liquid was a steep continuous function of composition.

The composition of binary mixtures between 7CB and *n*-heptane is expressed by the number of effective paraffinic carbon atoms per molecule (or effective chain length) n^* throughout the paper for the sake of easy comparison with the neat system. The n^* is calculated as[21]

$$n^* = 7 + \frac{7x}{1-x}, \tag{1}$$

where x is the mole fraction of *n*-heptane in a binary mixture. The first "7" of the right side comes from the number of carbon atoms in an alkyl (heptyl) group attached to a 7CB molecule whereas "7" in the numerator of the second term from *n*-heptane. It is emphasized that the validity of the use of n^* is the subject of this study, though it is also evident that it will not work in the region $x \approx 1$.

The phase diagram of 7CB–*n*-heptane system was determined using a commercial DSC apparatus (TA Instruments, Q200). The samples were sealed into sealable sample pans (PerkinElmer). The mass of samples (ranged from 2 to 9 mg) were weighed using an ultra micro balance (Mettler-Toledo, XP2U). The mixture was kept for 1 min at temperatures of the isotropic liquid state to achieve homogeneous mixing prior to experiments. DSC experiments were done at a temperature ramp rate of 5 K min^{-1} or 1 K min^{-1}.

Texture of binary mixture was observed using a polarizing microscope (Olympus, BX50) under crossed Nicole condition. The sample was sandwiched between glasses coated with polyvinyl alcohol. The thickness of the sample was ∼0.20 mm. As the composition varied during sample preparation due to the vaporization of *n*-heptane, it was deduced from the transition temperature to isotropic liquid state on the basis of the phase diagram determined by DSC. Observation was performed with a temperature ramp rate of 2 K min^{-1} using a hot stage (Linkam, LK-600PM).

Small angle x-ray diffraction was performed to ensure the appearance of SmA phase in the binary system. Each sample was sandwiched between Kapton films with thickness of 7.5 μm. The thickness of the sample was ∼0.45 mm. The composition was deduced from the transition temperature to isotropic liquid state by polarizing optical microscopic observation on the basis of the phase diagram determined
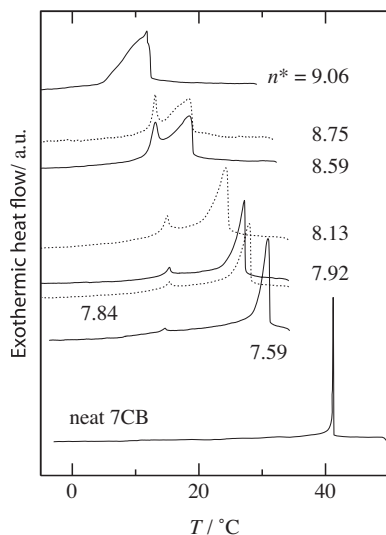
FIG. 2. Representative DSC traces in cooling runs for the neat 7CB and mixtures in 7CB–n-heptane system. Traces are placed vertically in accordance with the effective alkyl chain length (n^*), and scaled to the amount of 7CB in each sample.

by DSC. The diffraction experiments were performed at λ = 1.5405 Å (Cu$K_{\alpha 1}$) using a laboratory diffractometer (Rigaku, Nano-Viewer) equipped with a rotating copper anode with 40 kV and 30 mA. Incident x-ray was normal to the Kapton films of sandwiched sample. The camera length (450 mm) was calibrated using (100) diffraction of the standard silver behenate (Gem Dugout). Measurements were performed at constant temperature within 0.5 K, which was achieved using the same hot stage as that used in the polarizing optical microscopy.

III. RESULTS AND DISCUSSION

A. Phase diagram

DSC experiments were performed for 14 compositions in the range $0 \leq n^* \leq 14.82$. Typical DSC traces in cooling runs
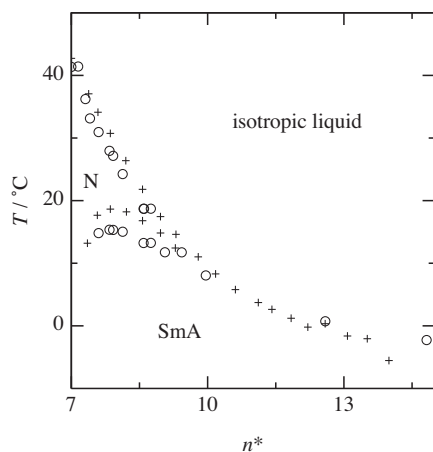

FIG. 3. Phase diagram of 7CB–n-heptane (open circle) in cooling and 7CB–n-octane (plus sign, data taken from the literature (Ref. 36)). Isotropic liquid and LC phases below 11.8 $^\circ$C (eutectic point) are thermodynamically metastable in 7CB–n-heptane system.

from the isotropic liquid are shown in Fig. 2. The DSC results were mutually consistent between the heating and cooling runs without notable supercooling unless the sample was cooled down to low temperatures at which 7CB crystallizes.

There is an unidentified anomaly in DSC traces for $7.59 \leq n^* \leq 8.75$ around 18 $^\circ$C. This strongly implies that an unidentified phase is newly induced by the addition of n-heptane. The boundaries in the phase diagram can easily be identified by collecting the temperatures of anomalies in DSC traces as shown in Fig. 3. On the basis of its topology (i.e., thermodynamic consistency), the regions of isotropic liquid and N phase (and also of pure crystal of 7CB) are determined. The phase boundary between the N phase and isotropic liquid is smooth with rather large dependence against n^*. This is the basis for the use of this phase diagram in the determination of n^* for samples in experiments of polarizing microscopy and small angle x-ray diffraction.

The phase appeared in the binary mixture was identified by polarizing microscopic observation. The textures observed for the sample with $n^* = 7.9$ are shown in Fig. 4. The schlieren texture characteristic to N phase can be identified in the texture observed at 23.3 $^\circ$C shown in Fig. 4(a), in accordance with the phase diagram (Fig. 3). On the other hand,
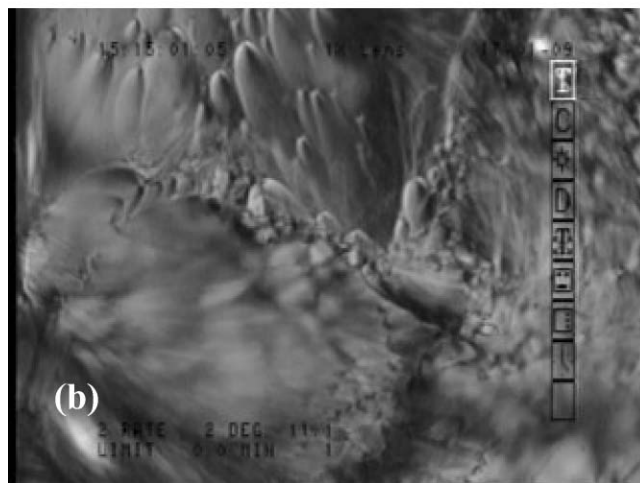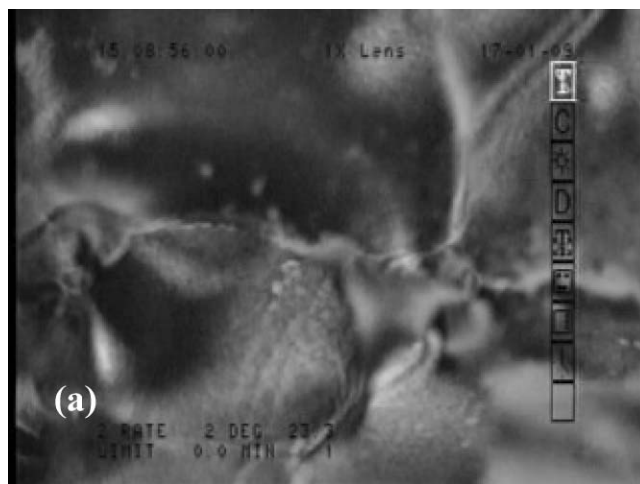

FIG. 4. Textures observed for the binary mixture ($n^* = 7.9$) in polarizing microscopy showing the schlieren texture characteristic to N phase at T = 23.3 $^\circ$C (a) and focal conic one of SmA phase at $T = 11.1$ $^\circ$C (b).
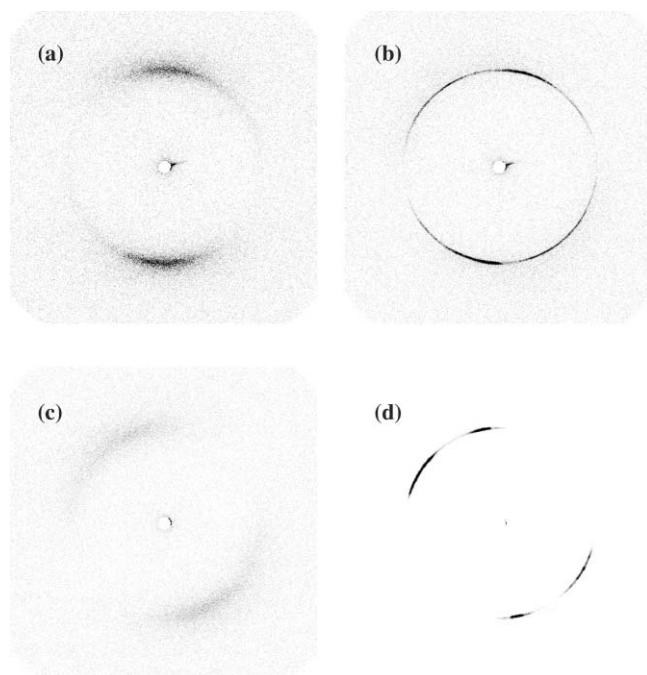
FIG. 5. Small angle x-ray diffraction photographs of the binary mixture ($n^* = 7.5$) and neat 8CB. (a) mixture in the N phase ($T = 14\,^\circ$C); (b) mixture in the SmA phase ($T = 0\,^\circ$C); (c) neat 8CB in the N phase ($T = 37\,^\circ$C); d) neat 8CB in the SmA phase ($T = 0\,^\circ$C).

focal conic texture is identified in the texture at 11.1 $^\circ$C shown in Fig. 4(b). Since the texture is characteristic to SmA phase, the phase induced by the addition of *n*-heptane is identified as the SmA phase. The identification is further confirmed later by comparing the x-ray diffraction patterns for both of N and SmA phases with those from neat 8CB as shown in Fig. 5. It is noted that the region of two-phase coexistence was experimentally not detected for fluid phases (SmA and N LC, and isotropic liquid mixture). This implies that the non-ideality of each phase be similar and nearly canceled out to each other because a wide coexistence region of two phases is expected unless so.

Now, it is ready to compare the phase diagrams between the binary and neat systems. It is emphasized that the presence (and absence) of the N phase in the present phase diagram is determined not by the relative thermodynamic stability of LC phases (N and SmA phases) and crystal but by those among fluid phases, where the 7CB and *n*-heptane are homogeneously (in macroscopic sense) mixed. The comparison with the neat system is therefore meaningful.

In the neat system of *n*CB, the N phase persists up to $n = 9$, while the SmA phase appears only at $n = 8$. In the phase diagram determined in this study (Fig. 3), the SmA phase is induced around $n^* = 7.5$ whereas the N phase disappears around $n^* = 9$. Experimentally, the presence of the N phase was confirmed at $n^* = 8.75$ whereas it was not at $n^* = 9.06$. Although the detailed shape of the phase diagram is different from each other, the characteristic magnitude of n^* is in good agreement. This implies that the QB picture holds for, at least, the overall geometry of the phase diagram.

It is noteworthy that the core in the QB picture is different from that in the chemical structure. In the case of *n*CB, for example, biphenyl that is just the chemical core of *n*CB, destabilizes N phase whereas *p*-terphenyl (a longer analogue of biphenyl with three benzene rings) stabilizes it.[35,37] In the case of ANBC(n), the addition of alkane to ANBC(14) reproduced the phase diagram of neat series of ANBC(n)(Ref. 22) whereas it was not the case when starting from ANBC(8).[21] These indicate that the alkyl chain certainly contributes, though only in part, to the elongation of the core as assumed by McMillan.[3]

It is noted that the induction of SmA phase has been reported for some mixtures of 7CB with other non-smectogenic mesogens,[41,42] or with alkanes.[36] Although the SmA phase induced in the mixture with other mesogens may suggest the tendency possessed by *n*CB of formation of SmA phase, the comparison with the present work is inadequate. On the other hand, it is necessary to compare the present results with that of the mixture with *n*-octane.[36] If the previous data were replotted against n^*, two phase diagrams essentially coincide as seen in Fig. 3. The coincidence of two phase diagrams strongly implies that the induced phase in 7CB–*n*-octane system in the previous study is certainly SmA phase though the identification of the induced SmA phase was insufficient. If this identification is assumed, the coincidence of phase diagrams in two systems supports the validity of the QB picture.

The tricritical behavior concerning the disappearance of N phase has been discussed for mixtures of 8CB and alkanes or *n*CB ($n > 8$).[43–46] The behavior seems consistent with the QB picture at least qualitatively. Detailed discussion on critical behavior is, however, beyond the scope of the present paper.

B. N–isotropic phase transition

The temperature of phase transition between N phase and isotropic liquid steeply decreases against n^* as seen in Fig. 3. Since the appearance of N phase can be explained within Maier-Saupe model[2] that takes only orientation-dependent intermolecular interaction into account, the N–isotropic phase transition reflects the thermotropic nature of the system, where the relevant director can be defined for 7CB molecules. The entropy involved in the transition was estimated for $n^* < 8$ as $\sim$0.3 J K^{-1} (mol of 7CB)$^{-1}$, which is comparable to the Maier-Saupe value of the entropy of transition.[2] The significant depression in the transition temperature implies that the orientation-dependent part of interaction is weakened by the introduction of *n*-heptane. The relative depression rate ($d \ln T_{N-IL}/dx|_{x=0} = 0.43$) is comparable to those for other *n*CB–alkane systems.[35,37]

C. SmA–N phase transition

The induction of the phase sequence N–SmA–crystal was further confirmed by small angle x-ray diffraction experiments. Typical diffraction photographs are shown in Fig. 5 together with those of neat 8CB. The similarity in photographs of each phase is evident between them, though small
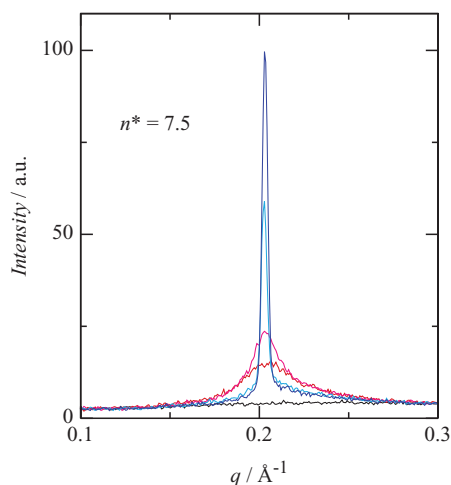
FIG. 6. Circular-averaged small angle x-ray diffraction patterns obtained for the binary mixture ($n^* = 7.5$) on cooling from the isotropic liquid state at $T = 33\,°C$ showing a flat background. A peak successively grows in the order of $T = 19\,°C$ and $14\,°C$ (N phase), and then $T = 9\,°C$ and $0\,°C$ (SmA phase).

difference is discernible in the in-plane anisotropy arising from uncontrollable alignment effects. The sample with a different composition ($n^* = 7.8$) essentially showed the same results. These observations definitely demonstrate the validity of the QB picture for nCB.

The diffraction intensity was circularly averaged, yielding the diffraction patterns shown in Fig. 6 for selected temperatures. As the sample has fluidity, it is hard to compare quantitatively the diffraction intensities. However, the diffraction peak from the N phase has a lower height with a definitely larger width in comparison with that from the SmA phase. Besides the main diffraction peak around $q = 0.2\,Å^{-1}$, slight asymmetry is certainly observed in the background. The diffraction pattern at each temperature was therefore fit to two components: a Gaussian peak for the main peak and a log-normal distribution function for the background. It is noted that the adoption of the log-normal distribution does not mean any physical model. It is only for convenience in data analysis. Indeed, the fit parameters for the background show no meaningful temperature dependence and are not considered anymore.

The temperature dependences of height and width (full width at half maximum, FWHM) of the main peak are shown for the sample of $n^* = 7.5$ in Fig. 7. Upon cooling, the width of the peak characteristic to the N phase gradually decreases reflecting the growth of the coherence length of the SmA order and becomes constant at a narrow level below the transition temperature, where the height of the peak assigned to the SmA phase increases sharply. The widths of the main peak both in N and SmA phases are comparable to those of neat 8CB. The increase in the height is seemingly continuous. From the temperature dependence, the SmA-N transition temperature is determined as 11.5 °C for the sample of $n^* = 7.5$. The temperature dependence of the intensity of the SmA diffraction is roughly proportional to $(T_{N-SmA} - T)^{2\beta}$ with $\beta \approx 0.2$, and that of the width of the N diffraction to $(T - T_{N-SmA})^{\nu}$ with $\nu \approx 0.3$. The trend of the temperature dependence of intensity is the same for the other sample
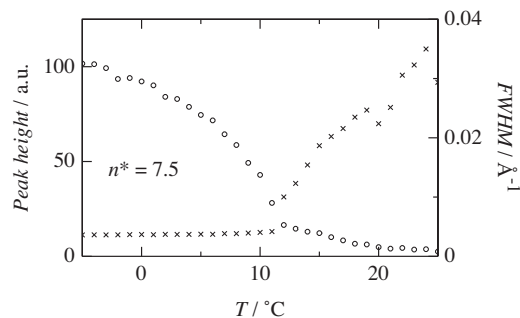

FIG. 7. Temperature dependence of the intensity (circle) and full width at half maximum (FWHM, cross) of the main diffraction peak from the sample of $n^* = 7.5$ in 7CB–n-heptane system.

($n^* = 7.8$) while the trend of width is hard to identify because of a smaller temperature range of the N phase. Although experimental temperatures are too far from the transition temperature, the exponents seem to differ significantly from the critical indices of 3D-XY universality class, which is basically expected for usual N–SmA phase transitions.[47]

The followings are generally observed for LC phase diagrams against the chain length:[14] the phase boundary to isotropic liquid from N and SmA phase decline whereas between SmA and N phase it inclines upward upon the elongation of chain. While the phase diagram obtained in this study (Fig. 3) certainly exhibits the former trends expected as discussed in Sec. III B, the latter not. This may be a manifestation of the limitation of the QB picture.

D. Layer spacing and structure of induced SmA phase

It is interesting to see the n^* dependence of layer spacing of the induced SmA phase in the binary system in comparison with the n dependence of the neat systems. The comparison is shown in Fig. 8. The present results are derived from the peak position of the main peak in SmA phase deduced from the peak fits. The ranges of its variation depending on temperature are indicated by bars. Although the present result for neat 8CB does not overlap with the data by Urban et al.,[48] it is in good agreement with the values reported by
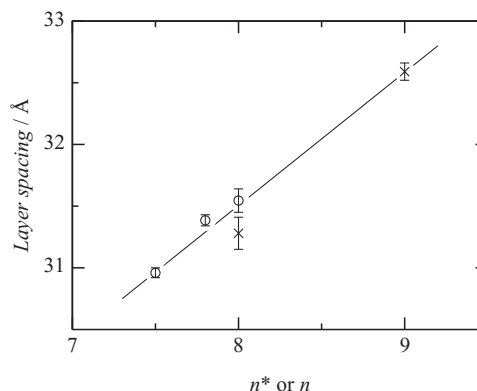

FIG. 8. Layer spacing as a function of the (effective) alkyl chain length. Present results for neat 8CB and binary mixtures (open circle) and data for neat 8CB and 9CB by Urban et al. (Ref. 48) (cross). Bars show the range of temperature dependence.
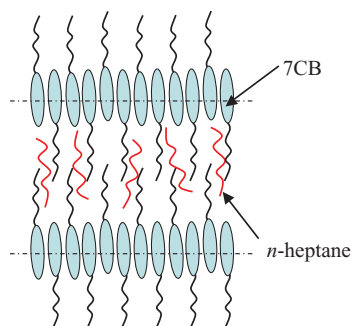
FIG. 9. Structural model of induced SmA phase in 7CB–*n*-heptane system (schematic).

other groups.[33,49] Figure 8 shows a smooth variation of the layer spacing, which indicates that the SmA phase is continuously swollen by *n*-heptane. This means that the QB picture also holds for structural aspects.

It is noteworthy that the radius of diffraction circle from the SmA phase is essentially the same as that from N phase of the same sample in the neat 8CB and binary mixtures. This fact implies that the local structures are similar in N and SmA phases in spite of large difference in the long range (nematic or smectic) order.

Having the n^* dependence of the layer spacing been consistent with the n dependence of the neat system, the structure of the induced SmA phase is discussed at molecular level. Leadbetter *et al.*[32,33] had clarified through detailed diffraction study that the SmA phase of 8CB is not a stack of simple monolayers, expected for ensemble of rigid rods, but composed of interdigitated bilayers, where the cores (including cyano groups) are interdigitated due to the strong interaction between electric dipoles of cyano groups. The strong interaction can be detected also in crystals of *n*CBs.[50–58] The smooth dependence of the layer spacing on n^* implies the continuous change in the aggregation structures. Taking the structural model established for 8CB into accounts,[32,33] the structural model shown in Fig. 9 can be constructed. In this model, *n*-heptane molecules are solved into chain layers and increase the layer spacing. The effect of relative length of the chains between 7CB and *n*-alkane is an issue to be considered in future. To date, it is certain that *n*-octane[36] and *n*-heptane successfully induce SmA phase in mixtures of 7CB. Too long alkane will behave differently from the present case (and/or shorter cases).

One may incline whether the model is in contradiction with the caution given long ago by Leadbetter *et al.*:[32] the effective sectional areas of benzene core and alkyl chain are roughly the same. The vertical drawing of the chains does not mean the real molecular packing in the SmA phase. Incompressibility of the alkyl chains results in the linear relation between the layer spacing and the effective chain length n^* if *n*-heptane is selectively solved into the chain layer. It is noted that a similar structure was suggested for a swollen SmA phase of MHPOBC (4-(1-methylheptyloxycarbonyl)phenyl-4′-octyloxybiphenyl-4-carboxylate) saturated by *n*-octane on the basis of the layer spacing and ^{2}H-NMR.[59]

E. Melting of *n*CB as lyotropic-thermotropic crossover

The molecule of *n*CB consists of a rigid biphenyl core (with a polar cyano group) and a flexible alkyl chain. It is well known that the molecules have a large electric dipole moment (∼4 D) mainly located on the cyano group. Rather strong interaction between the cyano groups is also widely assumed in crystals on the basis of short distances[50–58] though the crystal packing in detail may be different depending on compounds. The existence of a rather strong interaction between π-electrons on benzene rings is also well established. All of these implies that the *n*CB molecules has strong tendency to form clustered aggregates of mesogenic cores. In other words, *n*CB molecules are intrinsically amphiphilic (even though weak).

Starting from a completely ordered crystal at absolute zero temperature, thermal agitation gradually destroys its order on heating. At the melting temperature of the ordered crystal, the positional order of molecular centers of gravity is partially lost, resulting in the formation of SmA phase in the case of *n*CB with sufficient amphiphilic property. The dynamical amphiphilicity, arising from the tendency toward segregation because of the difference in molecular dynamics as suggested by Dowell,[8–12] also contributes to the formation of the SmA phase. These apply to *n*CB with a long alkyl ($n \geq 8$). In this sense, the melting to SmA phase is a manifestation of the amphiphilic nature of compounds. As demonstrated in this paper, indeed, the SmA phase can be induced lyotropically by adding the "solvent" to non-smectogenic 7CB.

On further heating of SmA phase, thermal agitation overwhelms the amphiphilic property (necessary for long range order), and the transition to N phase occurs. In the N phase, the positional order of the molecular center of gravity is completely (in long range) destroyed while the orientational order is maintained by the anisotropy of intermolecular interaction arising from the shape anisotropy of molecules. The mechanism that stabilizes the N phase is thermotropic in nature, accordingly.

Finally, the orientational (i.e., nematic) order is lost at the clearing temperature, resulting in the appearance of the isotropic liquid state. This is in accordance with a scenario written for thermotropic LC.

In summary, the melting process of *n*CB through the phase sequence, ordered crystal–SmA phase–N phase–isotropic liquid, is regarded as a shift of major interaction from lyotropic (amphiphilic) to thermotropic one. In this sense, it can be regarded as a lyotropic–thermotropic crossover.

IV. CONCLUSION

The QB picture of thermotropics, proposed previously by one of the present authors, was experimentally assessed for *n*CB. Addition of *n*-heptane to 7CB, which exhibits only the N phase as a mesophase on the course of melting from the ordered crystal in the neat, induced the SmA phase around $n^* \approx 7.5$ while the N phase disappeared around $n^* \approx 9$. Considering the presence of the SmA phase in neat 8CB below N phase and the absence of N phase in neat 10CB, the phase

behavior can be regarded as a support for the validity of the QB picture. The small angle x-ray diffraction showed that the layer spacing is a smooth function of n^* among the binary system of 7CB–*n*-heptane, neat 8CB and neat 9CB. This indicates that QB picture holds not only in the phase behavior but also in the structure. The melting of 8CB and 9CB to isotropic liquid via SmA and N LCs can be understood as a process involving the thermotropic–lyotropic crossover.

ACKNOWLEDGMENTS

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