PHYSICAL REVIEW E, VOLUME 63, 062701

Observation of a pretransitional effect near a virtual smectic-A–smectic-C^* transition

Seiji Shibahara,[1] Yoichi Takanishi,[1] Jun Yamamoto,[2] Toyokazu Ogasawara,[1] Ken Ishikawa,[1] Hiroshi Yokoyama,[2] and Hideo Takezoe[1]

[1]*Department of Organic and Polymeric Materials, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-8552, Japan*

[2]*Japan Science and Technology Corporation, Tokodai, Tsukuba, Ibaraki 300-2635, Japan*

(Received 16 August 2000; published 15 May 2001)

Unusual softening of the layer compression modulus B has been observed near the phase boundary where the smectic-C^* phase vanishes in a naphtalene-based liquid crystal mixture. From the systematic study of x-ray and layer compression measurements, this unusual effect is attributed to the pretransitional softening near a virtual smectic-A–smectic-C^* phase transition in the smectic-A phase, which no longer appears on the thermoequilibrium phase diagram. This phenomenon is similar but not equivalent to supercritical behavior.

DOI: 10.1103/PhysRevE.63.062701 PACS number(s): 61.30.−v, 62.20.Dc, 64.70.Md

Liquid crystal phases are characterized by long-range orientational order. In addition, smectic liquid crystal phases have quasi-long-range positional order; a one-dimensional solid and a two-dimensional liquid [1]. There exist so many types of smectic phases. Thus, we can clarify the intrinsic nature for various types of phase transition phenomena and spontaneous symmetry breaking by investigating smectic-to-smectic phase transitions. Mechanical properties are directly related to the stability of the low symmetry phases because elastic constants are the second order derivative of the free energy itself. As a result, the measurement of the viscoelastic constants, which directly couple to the internal order or its fluctuations, is a powerful probe of the critical phenomena [2]. In this paper, we demonstarate the critical slowing down of the layer compression modulus near a virtual phase transition to a hindered phase that no longer appears in the real thermodynamic phase diagram. In general, our findings provide a basic understanding for the pseudocritical phenomena beyond the critical points where no finite order-parameter change takes places.

In the smectic liquid crystal phases, the smectic-A (Sm-A) phase is characterized by a one-dimensional density wave, in which the average long molecular axis is along the layer normal. If the constituent molecule is optically active, the chiral smectic-C (Sm-C^*) phase is often observed below the Sm-A phase. In the Sm-C^* phase, the molecular axis is tilted with respect to the layer normal and precesses around the direction perpendicular to the smectic layer to form a helical structure. Since de Gennes's proposal that the Sm-A–Sm-C (Sm-C^*) phase transition should be in the three-dimensional XY universality class ($d=3$, $n=2$) [3], considerable attention has been paid to study the nature of the Sm-A–Sm-C^* phase transition [4–6].

Generally, at the Sm-A–Sm-C^* phase transition, the smectic layer spacing shrinks due to the tilt of molecules. To maintain the volume of each layer, a chevron layer structure is often induced, resulting in the introduction of zigzag defects [7,8]. Zigzag defects reduce the contrast ratio of ferroelectric liquid crystal displays, which is an obstacle to realizing an excellent electro-optic device. To avoid this problem, Mochizuki *et al.* synthesized naphtalene-based liquid crystal mixtures that exhibit very small shrinkage at the Sm-A–Sm-C^* transition [9]. These materials exhibit an ideal quasibookshelf layer structure. From a scientific point of view, however, the mechanism of the smectic layer thickness variations near the Sm-A–Sm-C^* phase transition is not clear [9–13].

Here, we report the results of layer compression modulus measurements near the Sm-A–Sm-C^* transition of several chiral smectic liquid crystal mixtures showing quasibookshelf layer structures. We found an anomalous pretransitionallike softening of the layer compression modulus in an appropriate concentration range as if the Sm-A–Sm-C^* phase transition had occurred. However, the Sm-A phase was confirmed to be entirely stabilized in the whole temperature region by static probes such as x-ray diffraction and polarizing microscope. This phenomenon is similar to the supercritical behavior [1,14], but is not quite equivalent in view of the continuity of the behavior across the phase boundary, as will be discussed below. We also discuss the mechanism of the quasibookshelf layer structure.

The samples used were the mixtures of the naphtalene derivative pure compound MTLC-8010 (Mitsui Chemicals) and ZLI-4139 (Merck) containing phenyl pyrimidine derivatives mixture [9]. In this paper, we label each sample ''MTw'' (where w is the weight percent of MTLC-8010), e.g., ''MT20'' means that the mixing ratio of MTLC-8010 to ZLI-4139 is 20 to 80. Figure 1 shows the chemical structure of MTLC-8010 and the phase diagram of the binary system of MTLC-8010 and ZLI-4139. Phase transition temperatures of isotropic-chiral nematic (N^*) and N^*–Sm-A are almost independent of the mixing ratio. On the other hand, the Sm-A–Sm-C^* phase transition temperature T_{AC^*} decreases with increasing concentration of MTLC-8010.

In the smectic layer spacing measurements, we prepared homeotropically aligned (director perpendicular to the glass plates) free surface films on glass plates. The temperature dependence of the layer thickness was measured by the conventional scattering technique [1]. For measuring the layer compression modulus B, we prepared homeotropically aligned cells. Using piezoelectric ceramics with longitudinal vibrations, the longitudinal mechanical transfer function $Z(\omega)$ was measured over a frequency range 2 Hz–500 Hz. $Z(\omega)$ is defined as the ratio of the complex stress experienced by a receiving glass plate to the complex longitudinal strain of a driving glass plate. Based on continuum theory,

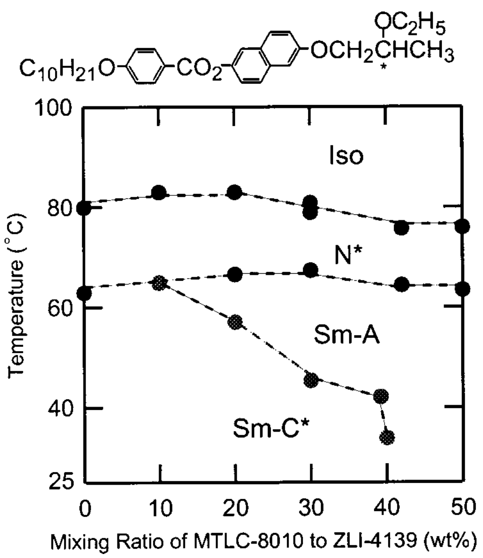

FIG. 1. Temperature-mixing ratio phase diagram of the compounds MTLC-8010 and ZLI-4139. Shown above is the MTLC-8010 molecular structure.

$Z(\omega)$ can be expressed as $Z(\omega)=B+i\omega(\eta_1-\eta_2+\eta_4+2\eta_5)$ [15], where η_1, η_2, η_4, and η_5 are the Martin-Parodi-Pershan viscosity coefficients [16]. The details of our layer compression modulus measurement technique have been reported elsewhere [17].

The smectic layer spacing as a function of T-T_{AC*} in the various mixing ratios of the compounds MTLC-8010 and ZLI-4139 is shown in Fig. 2. The figure shows that with increasing concentration of MTLC-8010, the amount of layer shrinkages at the Sm-*A*–Sm-*C** phase transition decreases. Accordingly, a larger percentage of MTLC-8010 causes a reduction of the tilt angle and also changes the smectic layer structure from chevron to quasibookshelf type. These results are confirmed by texture observations of homogeneously aligned samples in the Sm-*C** phase. Zigzag defects, which are typical of the chevron layer structure, are observed in MT30 but not in MT39. In the case of MT39, the layer spacing barely shrinks at the transition. Behavior similar to that observed in MT39 has been found in several other materials [9–13]. Before the discovery of this behavior, de Vries [10] proposed a model in which the molecules are tilted both in the Sm-*A* and Sm-*C* phases. In this model, the molecular tilt direction is randomly distributed in the Sm-*A* phase, whereas the molecules are tilted in a particular direction in the Sm-*C* phase. From the apparent optical tilt angle measurements, however, Takanishi *et al.* claim that de Vries's model is not appropriate, at least in the case of naphtalene-based liquid crystal mixture [9]. As we show below, the results of layer compression modulus measurements clearly prove Takanishi's claim. In MT39, it was found that the apparent optical tilt angle and the tilt angle estimated from x-ray results are about 10° and 5°, respectively, at a temperature 10 °C below the Sm-*A*–Sm-*C** transition. These results indicate that the tilt angles of the molecular core and flexible tails are different, as observed in other naphtalene-based liquid crystal mixture [9].

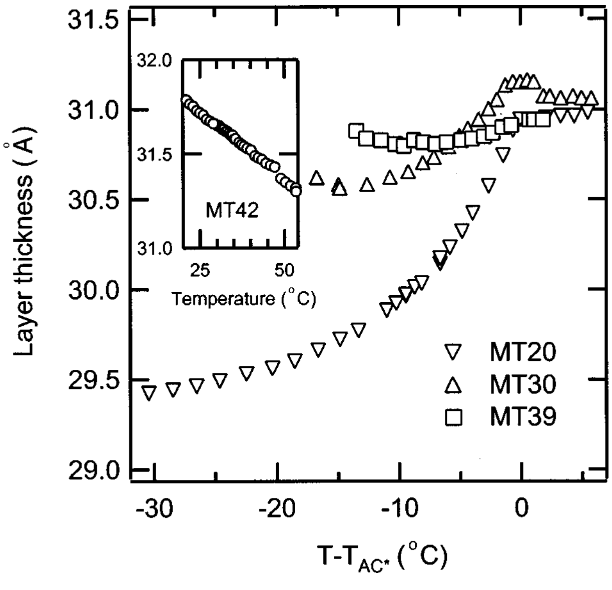

FIG. 2. Smectic layer spacing as a function of T-T_{AC*} in the various mixing ratios of the compounds MTLC-8010 and ZLI-4139. The inset shows the temperature dependence of smectic layer spacing in MT42.

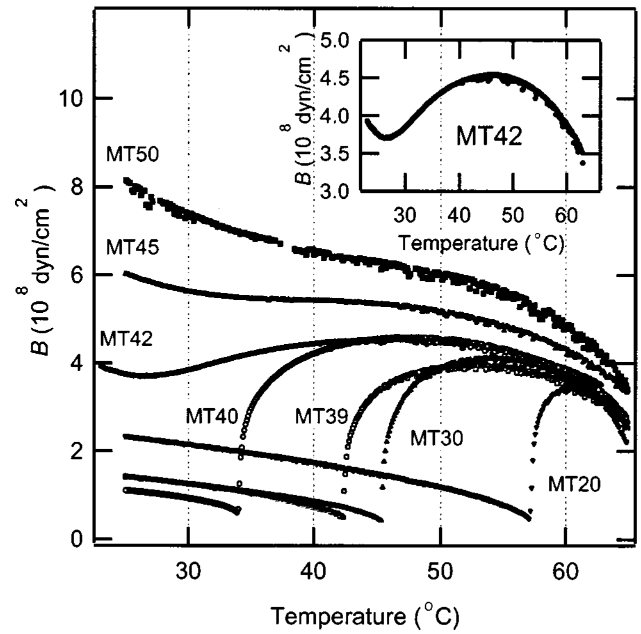

FIG. 3. Temperature dependence of *B* in the various mixing ratios of the compounds MTLC-8010 and ZLI-4139. The inset shows the temperature dependence of *B* in MT42.

The temperature dependence of the layer compression modulus *B* in the various mixing ratios of the compounds MTLC-8010 and ZLI-4139 is shown in Fig. 3. In the cases of MT20, MT30, MT39, and MT40, *B* increases with decreasing temperature and reaches a maximum, then decreases toward a minimum at the Sm-*A*–Sm-*C** transition, and then increases with decreasing temperature in the Sm-*C** phase. This substantial pretransitional softening above the Sm-*A*–Sm-*C** transition reflects the order-parameter fluctuations [6,18]. The cusplike behavior of *B* is generally observed near the phase transition from the untilted Sm-*A* to a tilted smectic phase [18]. In the case of MT20, MT30, MT39, and MT40, *B* always shows this characteristic behavior irrespective of the smectic layer spacing behavior at the Sm-*A*–Sm-C^* phase transition. Therefore, in this system we conclude that the molecules begin to tilt at the Sm-*A*–Sm-C^* transition, which is in contradiction to the model proposed by de Vries [10]. These results confirm that the Sm-*A*–Sm-C^* transition with little or no shrinkage of the smectic layer spacing is caused by the interdigitation of molecules and/or the conformation change of the hydrocarbon chain [9]. In spite of the very small tilt angle in the Sm-C^* phase of MT39 and MT40, *B* clearly shows pretransitional softening and exhibits a cusp at the transition point. These results indicate that the layer compression modulus measurements are very sensitive to the pretransitional effects of the untilted-tilted phase transition. The behavior of *B* in the vicinity of the Sm-*A*–smectic-C_α^* (Sm-C_α^*) phase transition is another illustration of the same point [18]. The Sm-C_α^* phase is a tilted smectic phase just below the Sm-*A* phase with a small tilt angle [19].

On the other hand, the temperature dependence of *B* in MT42 exhibits peculiar behavior as shown in the inset of Fig. 3. In this case *B* increases and then decreases with decreasing temperature, and shows a local minimum near 26 °C, but does not show cusplike behavior. Also, the minimum value of *B* is clearly higher than in the mixtures mentioned above. These results indicate that MT42 has no phase transition from Sm-*A* to Sm-C^* near 26 °C, but remains in the Sm-*A* phase in this temperature range. Actually, the smectic layer spacing of MT42 shown in the inset of Fig. 2 is linearly dependent on the temperature, suggesting the absence of a phase transition. We also studied the electro-optic behavior by using an ellipsometer [20] of freely suspended films of MT42 in this temperature range, which shows no indication of a Sm-*A*–Sm-C^* phase transition. Therefore, we conclude that there is no phase transition near 26 °C in MT42.

What is the nature of the softening of *B* at this local minimum? Fig. 4 shows the frequency dependence of *B* in MT42 (a) at 40 °C and (b) at 26 °C. *B*'s at 40 °C as well as at 26 °C are independent of frequency with no distinguishing characteristics between them. Therefore, it is difficult to consider that the origin of the softening of *B* around 26 °C is the occurrence of a new relaxation mode, e.g., defect-induced mode. One plausible model of this local minimum is as follows. It has been proposed that at the Sm-*A*–Sm-C^* transition, the average molecular tilt is caused by the induction interaction between the off-center transverse dipoles and the polarizable core of neighboring molecules [21]. These interactions probably depend on the molecular orientation and the intermolecular vector. As shown in Fig. 1, the temperature range of the Sm-*A* phase becomes wider for mixtures with a high percentage of MTLC-8010. Accordingly in the present system, with an increasing amount of MTLC-8010, the Sm-*A* phase stabilizes and then drives the Sm-C^* phase away in MT42. Molecules of MT42 are nearly in a frustrated state between the Sm-*A* and Sm-C^* phase. The system is in the Sm-*A* phase in reality, but it is very close to the boundary of diminishing the Sm-C^* phase. Therefore, it is reasonable to suppose that the softening of *B* towards the depression point is caused by the pretransitional effect near a *virtual* Sm-*A*–Sm-C^* phase transition, though Sm-C^* never appears as a thermodynamically stable phase. This assumption is supported by the results of MT45 and MT50. Moving away from this *virtual* phase transition, i.e., MT42 to MT50 through MT45, this depression fades away. Moreover as already mentioned, in the x-ray results, the layer thickness shows a linear temperature dependence, which suggests no structural change. In addition, no texture change was observed in this temperature range. Consequently, we can say with fair certainty that this depression in MT42 is due to the order-parameter fluctuations near the *virtual* Sm-*A*–Sm-C^* phase transition. We may say that these results indicate a supercritical-like behavior. In this study, however, this phenomenon was observed in the vicinity of a curved critical line; on the other hand, supercritical behavior was observed beyond the isolated critical point that terminates the first-order line [1,14]. The relatively large amplitude of *B* around this depression suggests that the untilted smectic layer structures are sufficiently maintained despite the existence of microscopic molecular frustration between untilted and tilted states. It is worth noting that the observation of the *virtual* Sm-*A*–Sm-C^* phase transition is possible only by methods that can sensitively detect a pretransitional fluctuation such as the present layer compression modulus measurements.

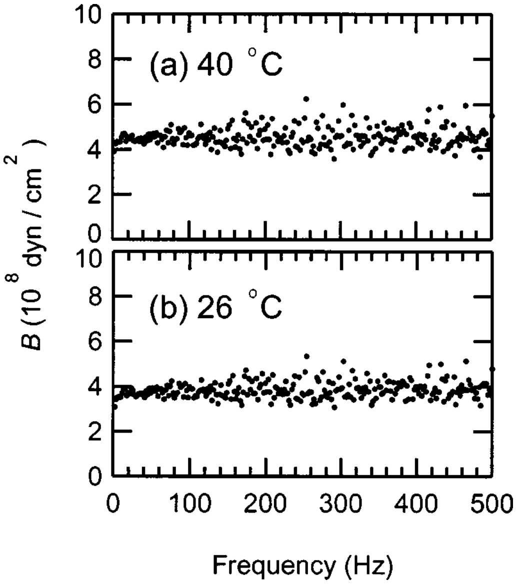

FIG. 4. Frequency dependence of *B* in MT42, (a) at 40 °C and (b) at 26 °C.

Kortan *et al.* [22] studied the correlation length by high-resolution x-ray scattering near the boundary where the Sm-*A* phase vanishes. In this case, the phase sequence is *N*–Sm-*A*–reentrant-*N*. They observed a decrease in the correlation length away from the boundary. Moreover, Lushington *et al.* [23] carried out calorimetric investigation of this same compound. With decreasing temperature range of the Sm-*A* phase, the excess heat at the *N*–Sm-*A* phase transition decreases. The excess heat cannot be observed in the region showing no Sm-*A* phase, nor near the boundary where the Sm-*A* phase vanishes. In this study, the softenings of *B* near the phase transition boundary is clearly observed in MT42, and fades away in the mixtures MT42 to MT50 through MT45. This decrease of softening reflects the detachment from the *virtual* phase transition, which no longer appears on the thermoequilibrium phase diagram. Although the phenomenon is apparently similar to the correlation length results by x-ray diffraction [22], the following differences should be borne in mind. First, the phase sequence in the present study is distinct from that by Kortan *et al.* [22]. Moreover, the correlation length by x-ray studies gives a rather continuous change across the phase boundary. In the layer compression modulus measurements, however, the behavior distinctly changes across the boundary, i.e., depending on whether the phase transition exists or not, cusplike behavior or a broad local minimum appears, respectively. Since elastic constant measurements are more sensitive to the fluctuation effects near the phase transition than the other measurements [2,18], we succeeded in observing the pretransitional softening of *B* even though the phase transition does not exist in reality.

In conclusion, we report measurements of the temperature dependence of *B* near the Sm-*A*–Sm-C^* phase transition in the naphthalene-based liquid crystal mixture. By increasing the percentage of naphtalene-based liquid crystal, the layer structure changes from a chevron type to the bookshelf type in the Sm-C^* phase. At the same time, the temperature range of the Sm-*A* phase becomes wider and finally the Sm-C^* phase vanishes. Near the phase boundary where the Sm-C^* phase vanishes, *B* shows a remarkable pretransitional effect near a virtual Sm-*A*–Sm-C^* phase transition in the Sm-*A* phase.

We are indebted to Professor K. Ema for stimulating discussions. We are also grateful to Dr. D. R. Link and D. Bundy for a critical reading of this manuscript.

[1] P. G. de Gennes and J. Prost, *The Physics of Liquid Crystals* (Clarendon, Oxford, 1993).

[2] L. Benguigui and P. Martinoty, Phys. Rev. Lett. **63**, 774 (1989); J. Phys. II **7**, 225 (1997).

[3] P.G. de Gennes, Mol. Cryst. Liq. Cryst. **21**, 49 (1973).

[4] P. E. Cladis, in *Handbook of Liquid Crystals*, edited by D. Demus, J. Goodby, G. W. Gray, H. W. Spiess, and V. Vill (Willey-VCH, Weinheim, 1998), Chap. 7.

[5] C.C. Huang and J.M. Viner, Phys. Rev. A **25**, 3385 (1982).

[6] D. Collin, J.L. Gallani, and P. Martinoty, Phys. Rev. Lett. **61**, 102 (1988).

[7] Y. Ouchi, H. Takano, H. Takezoe, and A. Fukuda, Jpn. J. Appl. Phys., Part 2 **26**, L21 (1987).

[8] T.P. Rieker, N.A. Clark, G.S. Smith, D.S. Parmar, E.B. Sirota, and C.R. Safinya, Phys. Rev. Lett. **59**, 2658 (1987).

[9] A. Mochizuki, Y. Yoshihara, M. Iwasaki, M. Nakatsuka, Y. Takanishi, Y. Ouchi, H. Takezoe, and A. Fukuda, in Japan Display 89, Proceedings of 9th International Display Research Conference, Kyoto [Proc. SID **31**, 123 (1990); Y. Takanishi, Y. Ouchi, H. Takezoe, A. Fukuda, A. Mochizuki, and M. Nakatsuka, Jpn. J. Appl. Phys., Part 2 **29**, L984 (1990); Mol. Cryst. Liq. Cryst. **199**, 111 (1991).

[10] A. de Vries, Mol. Cryst. Liq. Cryst. **41**, 27 (1977).

[11] F. Giesselmann, P. Zugenmaier, I. Dierking, S.T. Lagerwall, B. Stebler, M. Kaspar, V. Hamplova, and M. Glogarova, Phys. Rev. E **60**, 598 (1999).

[12] M.D. Radcliffe, M.L. Brostrom, K.A. Epstein, A.G. Rappaport, B.N. Thomas, R. Shao, and N.A. Clark, Liq. Cryst. **26**, 789 (1999).

[13] P. Mach, P.M. Johnson, E.D. Wedell, F. Lintgen, and C.C. Huang, Europhys. Lett. **40**, 399 (1997).

[14] H. N. V. Temperley, J. S. Rowlinson, and G. S. Rushbrooke, *Physics of Simple Liquids* (North-Holland, Amsterdam, 1968).

[15] K. Okano and J. Yamamoto, Jpn. J. Appl. Phys., Part 1 **29**, 1149 (1990).

[16] P.C. Martin, O. Parodi, and P.S. Pershan, Phys. Rev. A **6**, 2401 (1972).

[17] J. Yamamoto and K. Okano, Jpn. J. Appl. Phys., Part 1 **30**, 754 (1991).

[18] S. Shibahara, J. Yamamoto, Y. Takanishi, K. Ishikawa, H. Takezoe, and H. Tanaka, Phys. Rev. Lett. **85**, 1670 (2000); S. Shibahara, J. Yamamoto, Y. Takanishi, K. Ishikawa, and H. Takezoe, Phys. Rev. E **62**, R7599 (2000).

[19] Y. Takanishi, K. Hiraoka, V.K. Agrawall, H. Takezoe, A. Fukuda, and M. Matsushita, Jpn. J. Appl. Phys., Part 1 **30**, 2023 (1991).

[20] Ch. Bahr and D. Fliegner, Phys. Rev. A **46**, 7657 (1992).

[21] B.W. Van der Meer and G. Vertogen, J. Phys. (Paris) **40**, C3-222 (1979).

[22] A.R. Kortan, H.V. Kanel, R.J. Birgeneau, and J.D. Litster, Phys. Rev. Lett. **47**, 1206 (1981); J. Phys. (Paris) **45**, 529 (1984).

[23] K.J. Lushington, G.B. Kasting, and C.W. Garland, Phys. Rev. B **22**, 2569 (1980).