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Phase transition between fluid and elastic smectic blue phases

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Abstract

We have investigated the mixture of monomer and dimer chiral liquid crystal molecules. Optical and x-ray measurements confirm the simultaneous existence of two types of liquid crystalline orders—the smectic layer and the helix—in both the smectic blue phases, SmBP_{X1} and SmBP_{X3}. However, the order parameters of both the orders are small compared to those of the homogeneous smectic-A and cholesteric phases. Since the microscopic structure factor is similar in both phases, it is reasonable to assume that SmBP_{X1} and SmBP_{X3} have a common fundamental unit structure, which is formed by the spatial distribution of the smectic layer and the helix. On the other hand, macroscopic viscoelastic measurement clearly demonstrates the intrinsic difference between the fluid SmBP_{X3} and elastic SmBP_{X1} phases. It can be concluded that the spatial connectivity of the fundamental unit structure changes drastically at the SmBP_{X3}–SmBP_{X1} phase transition.

The planar multilayer stacked structure of the smectic phase always competes with the twisting structure of the helix produced by chirality because, with the exception of the conventional chiral smectic phases, SmC* [1] SmC_α, SmC_γ and SmC_A [2], both these liquid crystalline orders cannot coexist in the same space homogeneously at the same time. When both liquid crystalline orders coexist in the same space, the defect of the liquid crystalline order should be introduced in order to lower the strong chiral interaction energy and the spatial homogeneity of the liquid crystalline order breaks spontaneously. Subsequently, the liquid crystal system tends to rearrange and regularize the spatial distribution of defects in order to optimize the distortion elastic-free energy. The twist grain boundary (TGB) phase is an example of these modulated phases obtained due to the competition between the layer structure and the helix; this was initially predicted theoretically [3] and later confirmed experimentally [4]. On the other hand, in the case of a pure orientation order without the smectic layer, strong chirality produces the double helix and induces the cholesteric blue phases (ChBPs) [5], which consist of a three-dimensional regular arrangement of the helix with a regular defect array of the twist disclinations. ChBP_I and ChBP_{II} have cubic symmetry and exhibit a coloured platelet texture

under a polarizing microscope because the lattice constant of the regular lattice of the helix is equivalent to the length of the pitch, and this attains the value of the wavelength of visible light. In addition to cubic ChBPs, an isotropic but coloured ChBP_{III} phase has also been identified. Recently, smectic blue phases (SmBPs) have also been identified by a French group of researchers [6]. SmBPs exhibit a texture and physical properties that are similar to those of ChBPs, but the smectic layer and the helix exist simultaneously in SmBPs. While SmBP₁ and SmBP₂ have an optically cubic symmetry, SmBP₃ displays an optically isotropic nature similar to that of the ChBPs. However, due to the complicated coupling of the coexisting smectic layer order and helix, the internal structure and the stabilization mechanism of the SmBPs have not yet been fully investigated.

In this paper, our sample consists of the simple binary mixture of the chiral liquid crystal monomer (3BS) and twin (A6S) [7]. We fixed the concentration of the monomer ($\phi_m = 0.6$). Nevertheless the phase diagram, which is dependent on the monomer concentration, is fairly complicated [8]. We investigated the phase transition among the isotropic liquid phase (iso) and SmBPs using a polarizing microscope, linearly polarized visible light spectroscopy, x-ray diffraction and viscoelastic measurement [9]. The mixture reveals four modulated phases between iso and smectic-A (S_A) phases at a fixed monomer concentration ($\phi_m = 0.6$). All phase transitions are thermoreversible and follow the phase sequence given below:

S_A -118 °C–TGB-121.5 °C–NL*–124.5 °C–SmBP_{X1}-133.5 °C–SmBP_{X3}-142 °C–iso.

Details of the phase diagram will be reported in a separate work [8]. Lower-temperature TGB and NL* phases are optically anisotropic phases, which are easily identified under a polarizing microscope due to their characteristic texture. Higher-temperature SmBP_{X1} and SmBP_{X3} appear to be equivalent to SmBP₁ and SmBP₃, respectively, as has already been reported by the French group of researchers [6]. Due to its cubic symmetry and weak birefringence, SmBP_{X1} can be identified with the characteristic mosaic platelet texture only in a rather thick sample (>100 μm). It is considerably difficult to recognize SmBP_{X3} using a polarizing microscope because SmBP_{X3} appears fairly similar to the isotropic liquid. The optically isotropic nature and fluidity is still present in SmBP_{X3}, but the optical rotation becomes larger than that of the conventional isotropic liquid and viscoelastic relaxation is observed as described in the following section.

Figure 1(a) shows the temperature dependence of the spectrum of the optical rotatory power (ORP) on the visible light wavelength. The ORP was calculated from the analyser angle dependence of the transmitted light intensity when the sample was illuminated by linearly polarized light, which is generated by the Xe lamp source. The thickness of the sample was 1 mm, which is anomalously thick, in order to facilitate the accurate measurement of the small ORP in SmBP_{X3}. Subsequently, no transmitted light could be detected below the SmBP_{X1}–NL* phase transition due to the light scattering from the polydomain structure in strongly anisotropic NL*, TGB, and S_A phases. The ORP increases monotonically towards the shorter wavelength in the iso and SmBP_{X3}. We cannot identify the iso–SmBP_{X3} phase transition by ORP measurement. With a decrease in the temperature, the ORP attains a maximum value of approximately 10°mm^{-1} at 400 nm in the central region of SmBP_{X3}, and it subsequently decreases towards the SmBP_{X3}–SmBP_{X1} phase transition temperature as is the case with the ChBP_{III} to ChBP_{II} phase transition [10]. The ORP apparently becomes zero just above the SmBP_{X3}–SmBP_{X1} phase transition. It should be noted that the ORP has a large negative value in SmBP_{X1} as compared to that in SmBP_{X3}. The ORP decreases monotonically towards the shorter wavelength in SmBP_{X1}. The minimum value of the ORP also decreases with a decrease in the temperature, and falls below $-180^\circ \text{mm}^{-1}$ at 400 nm in the vicinity of the SmBP_{X1}–NL* phase transition. The inversion of the sign of the ORP in between SmBP_{X3} and SmBP_{X1} is

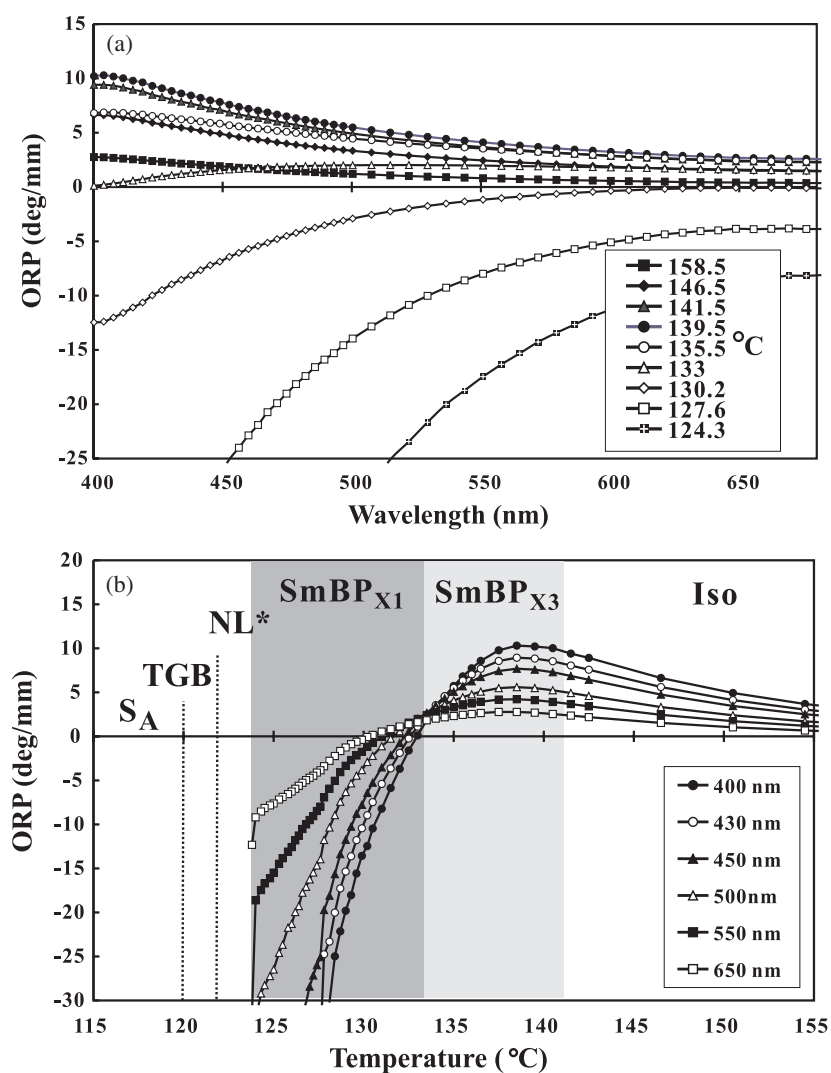


Figure 1. (a) Wavelength dependence of the ORP. Each line represents the temperature dependence as indicated in the figure. The ORP has a positive sign in iso and SmBP_{X3} , whereas the ORP has a negative sign in SmBP_{X1} . (b) Temperature dependence of the ORP re-plotted from figure 1(a). It is evident that the sign of the ORP changes at the SmBP_{X3} – SmBP_{X1} phase transition.

more evident in figure 1(b) wherein the ORP is plotted against the temperature. These results evidently prove the existence of the helix, but the ORP is rather small as compared to the uniformly oriented cholesteric phase. In SmBP_{X3} , the order parameter of the helix is expected to be very small because of the short correlation length of the order due to its coexistence with the smectic layer order.

By means of the x-ray diffraction measurements, a finite scattering peak was always detected in the small-angle region below the iso– SmBP_{X3} phase transition temperature. Figure 2 shows the temperature dependence of the characteristic length calculated from the scattering angle of the peak and its scattering intensity. Since the characteristic length of the scattering peak obtained repeatedly is identical to that of the layer repeat distance of the lowest-

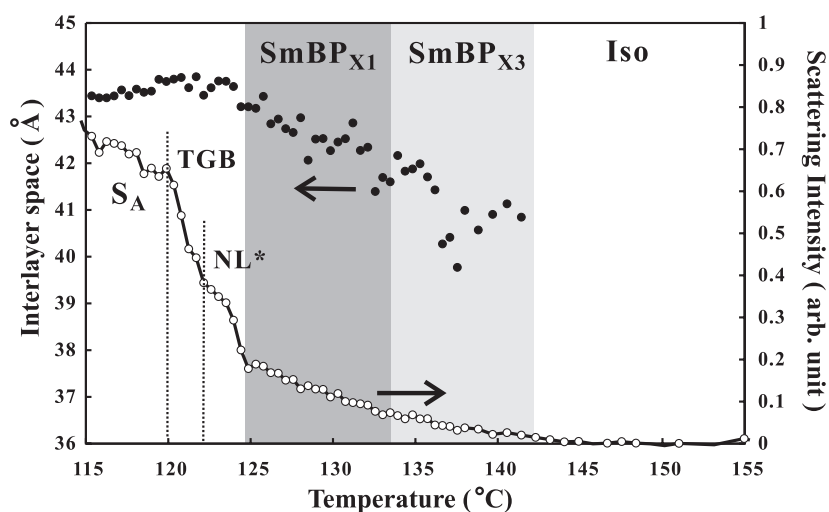


Figure 2. Temperature dependence of the interlayer spacing and the scattering intensity measured by x-ray diffraction. A microscopic smectic layer order appears just below the iso–SmBP_{X3} phase transition, and its order parameter gradually increases toward the lower-temperature smectic-A phase. The temperature dependence of the interlayer spacing appears weak and is always nearly equivalent to that in the smectic-A phase.

temperature S_A phase through the SmBP_{X1}, NL* and TGB phases, the broad scattering peak observed in SmBP_{X3} should originate from the layer structure of the smectic order. However, the peak intensity in SmBP_{X3} is almost one order smaller than that in the S_A phase. Since only one scattering peak was always detected in the small-angle region, it can be clearly confirmed that the macroscopic phase separation does not take place in any modulated phase. The fact that there is no clear indication of the SmBP_{X1}–SmBP_{X3} phase transition in the scattering peak and layer spacing, as is evident in figure 2, is far more important. Thus, we cannot identify the remarkable difference in the microscopic length structure between SmBP_{X3} and SmBP_{X1}.

On the other hand, the SmBP_{X3}–SmBP_{X1} phase transition can be clearly identified by viscoelastic behaviour. Hence, viscoelastic spectroscopy provides us with novel information on the internal structure of SmBP_{X3} and SmBP_{X1}. Figure 3 shows the frequency dependence of the real and imaginary part of the longitudinal mechanical transfer function in each phase. In the iso phase, the real part is almost zero, while the imaginary part is proportional to the frequency as is evident in figure 3(a). Thus, we can confirm that the iso phase is a Newtonian fluid and a true liquid state. On the other hand, the frequency-dependent real part is evident in SmBP_{X3} due to viscoelastic relaxation as shown in figure 3(b). Since both the real and imaginary parts become zero at a low frequency, it can be confirmed that SmBP_{X3} still maintains fluidity. As the temperature decreases towards the SmBP_{X3}–SmBP_{X1} phase transition, the relaxation frequency reduces drastically until it reaches a few hundred Hz (figures 3(b) and (c)). Finally, the frequency-independent finite real part appears in SmBP_{X1} as shown in figure 3(d). Thus, SmBP_{X1} has an elastic response to the static strain. The elasticity of SmBP_{X1} is almost independent of the temperature, as shown in figure 4, whereas both the real and imaginary parts are strongly dependent on the temperature as is ordinarily seen in viscoelastic relaxation. We can clearly identify the SmBP_{X3}–SmBP_{X1} phase transition in contrast to the x-ray measurement as shown in figure 2. We will report further details regarding the SmBP_{X1} phase, including the other SmBPs, in another paper [8].

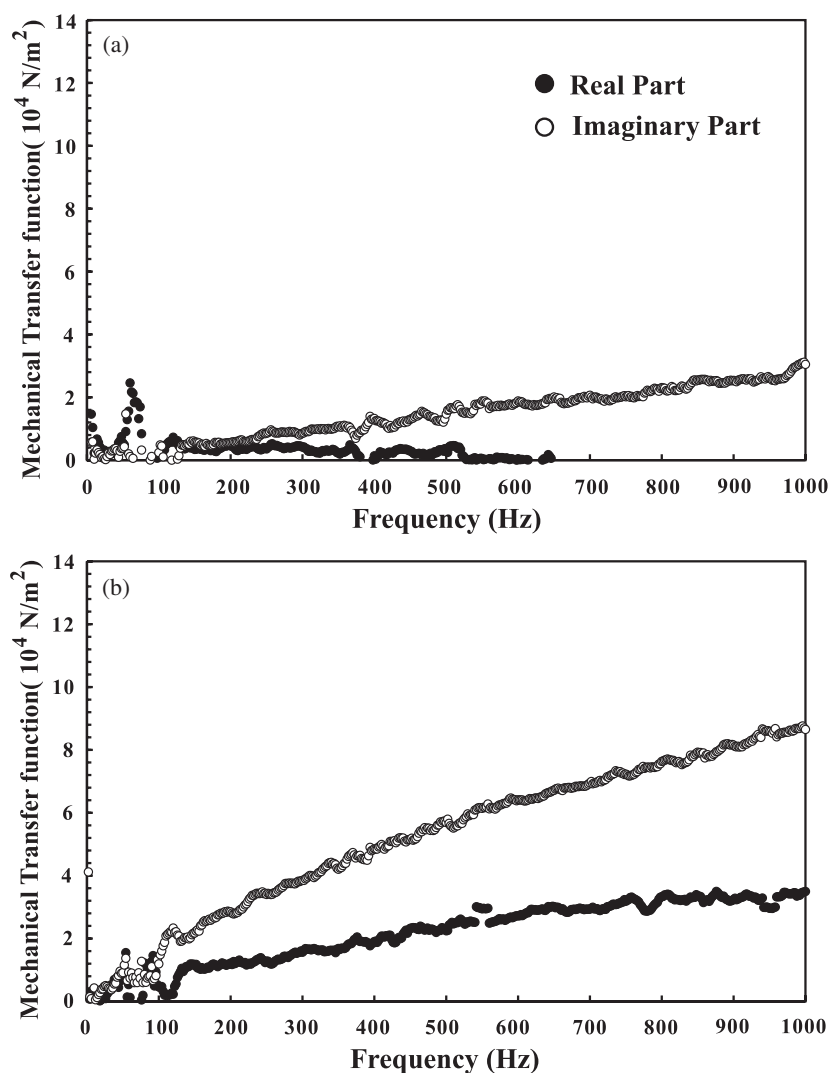


Figure 3. Frequency dependence of the mechanical transfer function measured by applying longitudinal strain. Closed circles indicate the real part of the mechanical transfer function, whereas open circles indicate the imaginary part. (a) Isotropic phase: the isotropic phase behaves as a simple Newtonian fluid. (b) High-temperature SmBP_{X3} phase: the finite frequency-dependent real part appears due to the viscoelastic relaxation. Since there is no transmitted viscoelastic stress at a very low frequency, SmBP_{X3} does not lose fluidity. (c) Lower-temperature SmBP_{X3} phase: the relaxation frequency decreases toward the SmBP_{X3} – SmBP_{X1} phase transition. (d) SmBP_{X1} : since this phase evidently differs from the aforementioned iso and SmBP_{X3} , the finite real part appears at the very low frequency region, which implies that SmBP_{X1} has an elastic response to the static strain.

Let us now discuss the SmBP_{X3} and SmBP_{X1} phases. On the basis of the spectrum of visible light and x-ray scattering, the smectic layer order and the helix order simultaneously coexist in both SmBP_{X1} and SmBP_{X3} . However, the order parameters of the above-mentioned liquid crystalline orders are rather small as compared to those in the homogenous S_A and Ch phases. As demonstrated by the viscoelastic measurement, it is evident that the macroscopic

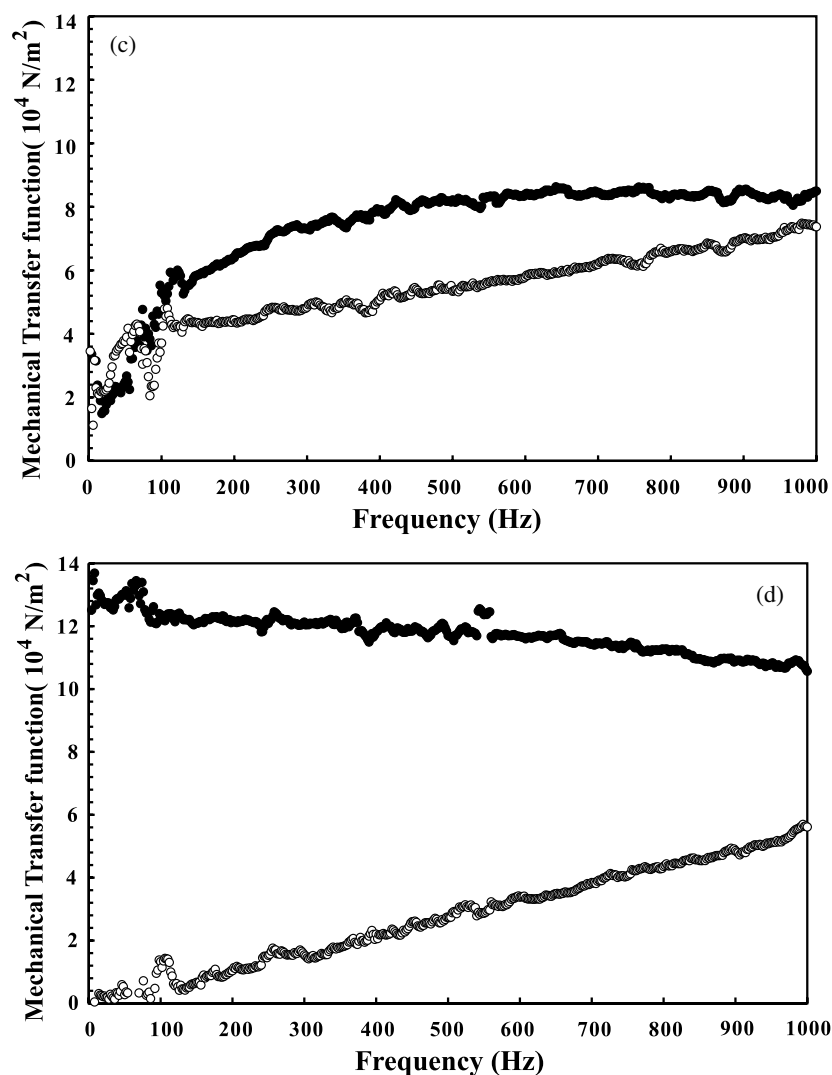


Figure 3. (Continued.)

physical properties are fairly different, whereas the microscopic order is very similar between SmBP_{X3} and SmBP_{X1} . It is reasonable to assume that the isolated static tiny clusters that are formed by the fragments of the smectic layer, which is superimposed with a twisting structure of the helix with shorter correlation length, are randomly dispersed in SmBP_{X3} . This is confirmed by the fact that SmBP_{X3} maintains fluidity and that the characteristic frequency of the viscoelastic relaxation is sufficiently low to deny the possibility of a dynamic structure, such as a pre-translational order parameter fluctuation. The correlation length of the fundamental unit structure gradually increases toward the SmBP_{X3} – SmBP_{X1} phase transition as is evidently indicated by the decrease in the relaxation frequency. It can be concluded that the spatial connectivity of the isolated clusters becomes infinite below the SmBP_{X3} – SmBP_{X1} phase transition, similar to the percolation transition in a sol–gel phase transition. That is why SmBP_{X1} is responsible for the static strain. While a schematic illustration of the configuration

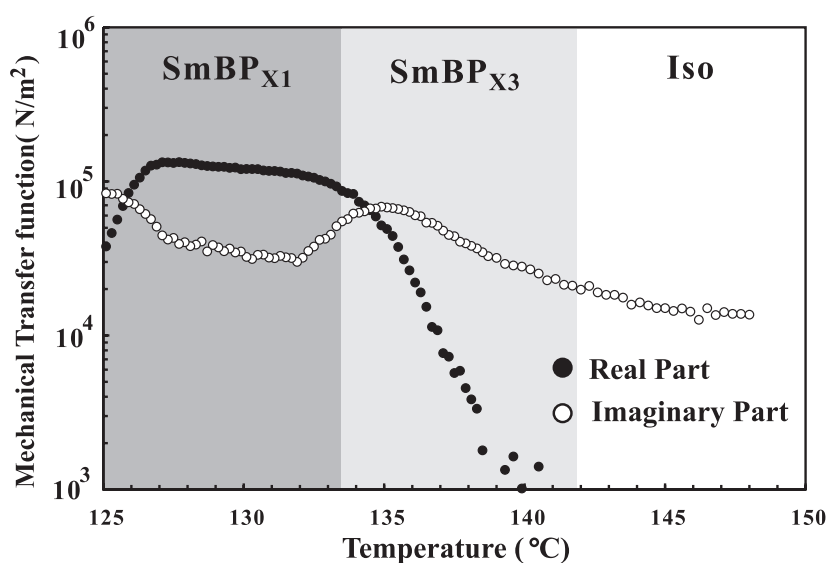


Figure 4. The temperature dependence of the mechanical transfer function at a fixed frequency ($f \sim 100$ Hz). Closed circles represent the real part and open circles represent the imaginary part. It is evident that the macroscopic physical properties differ considerably across the three phases, whereas the optical and x-ray measurements cannot identify the phase transition points.

of the smectic layer and the helix cannot be drawn in real space, the fact that the sign for the optical rotation is inverted through the SmBP_{X3} – SmBP_{X1} phase transition, provides us with an important hint for the internal structure of SmBPs. Further investigation is still necessary in order to explore the real structure of SmBPs. We will conduct a detailed study of the internal structure of SmBP_{X1} and SmBP_{X2} in the near future.

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