Nano-Structure and Dynamics of Isotropic Order[1]

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Summary

Liquid state has highest symmetry, so the X-ray diffraction pattern is completely uniform and symmetric in the space. Thus, space has complete spherical isotropic symmetry in liquid state. On the contrary, if temperature goes down to the solid phase or liquid crystalline phase, special regularity of the "order" breaks the symmetry of the space. So, both the "Ordering" and "Spherical isotropic symmetry" never coexist simultaneously. However, we have found the novel isotropic smectic blue phase ($SmBP_{Iso}$) [1], which show the appearance of the "Ordering" does not break the macroscopic "symmetry" of the space. We call this is "Isotropic order". Soft condensed matter system can form the huge length scale order. $SmBP_{Iso}$ is characterized by the simultaneous presence of the local order parameter of an helix and of a smectic layer, while being spontaneously isotropic without any characteristic discontinuity on a mesoscopic length scale. It is great advantage for the optical devices that the spectrum of the iridescent color of $SmBP_{Iso}$ is completely equivalent by the changing the viewing angle because of the special isotropic symmetry and its wavelength can be successively controlled by changing temperature. Recently, we found the color can be tuned by shining the strong pulsed laser light. Then we can artificially design the special pattern of the "structural color" by scanning and on/off the laser light beam.

Liquid state has highest symmetry, so the X-ray diffraction pattern is completely uniform and symmetric in the space. Thus, space has complete spherical isotropic symmetry in liquid state. On the contrary, if temperature goes down to the solid phase or liquid crystalline phase, special regularity of the "order" breaks the symmetry of the space. So, both the "Ordering" and "Spherical isotropic symmetry" never coexist simultaneously. However, we have found the novel isotropic smectic blue phase ($SmBP_{Iso}$) [1], which show the appearance of the "Ordering" does not break the macroscopic "symmetry" of the space. We call this is "Isotropic order". Soft condensed matter system can form the huge length scale order. If the characteristic length of the system reaches to the visible light wave length, the Bragg scattering takes places by illuminating the visible light. This is exactly equivalent to the "spontaneous photonic band-gap system. On the contrary to the finely fabricated "solid" hard materials, soft matter systems have large "tunability" due to the intrinsic softness of the spontaneous self-organized hierarchical structure.

It is surprising that six modulated phases appear in the mixture as indicated in Fig.1, while only the isotropic liquid and smectic-A phases appear in the pure monomer. We identified three different SmBP's, $SmBP_{X1}$, $SmBP_{X2}$ and $SmBP_{X3}$ which seem to be similar to the reported $SmBP_1$ $SmBP_2$ and $SmBP_3$, respectively as alredy found by French Group [2]. Thus, a fourth smectic blue phase, $SmBP_{Iso}$ is newly identified. The characteristic feature of $SmBP_{Iso}$ is that it displays a completely uniform color under polarizing microscope without any kind of macroscopic patterns or texture. Moreover, surprisingly, the color never changes when the sample is rotated in any direction, which proves that $SmBP_{Iso}$ has a completely isotropic optical nature. $SmBP_{X1}$ and $SmBP_{X2}$ can

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clearly be distinguished from $SmBP_{Iso}$ by their characteristic crystal like platelet texture.$SmBP_{Iso}$ is characterized by the simultaneous presence of the local order parameter of an helix and of a smectic layer, while being spontaneously isotropic without any characteristic discontinuity on a mesoscopic length scale. It is great advantage for the optical devices that the spectrum of the iridescent color of SmBPIso is completely equivalent by the changing the viewing angle because of the special isotropic symmetry and its wavelength can be successively controlled by changing temperature. Bandgap structure is quite different from conventional cholesteric phases. Shortwavelenth light completely inihibit to transimit the medium. Its characteristic wave-length is strongly dependent on the temperature and shifted towards the lower wavelength with dcrease in the temperature. We would like to call these novel systems "photonic liquid crystals".

During the X-ray experiment, only one broad scattering peak was observed in the small angle region. This is a direct confirmation that all six modulated phases–TGB, chiral line nematic (NL^*) [3, 4], $SmBP_{X1}$, $SmBP_{X2}$, $SmBP_{X3}$ and $SmBP_{Iso}$–have a finite smectic order with the exception of the order parameter difference. As shown in Fig. 2, the peak intensity begins to grow continuously from $SmBP_{X3}$ to the SA phase. The characteristic length derived from the peak position is smoothly connected to the layer repeat distance of SA in all the other phases. Thus,

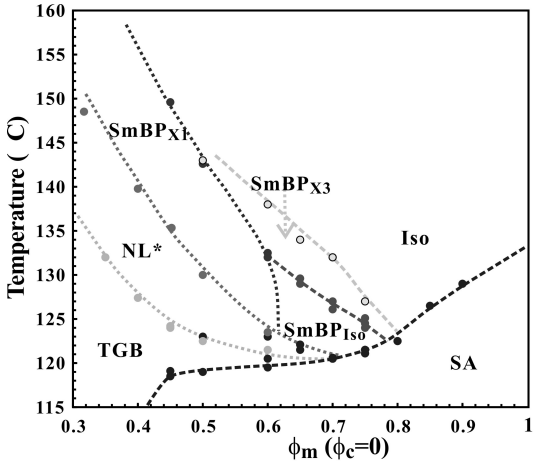

Fig.1 Phase diagram for the twin/monomer mixture as a function of the monomer concentration(ϕm) dependence, The TGB and NL^* phases can be identified easily under a polarizing microscope because of their large optical anisotropy and characteristic patterns.

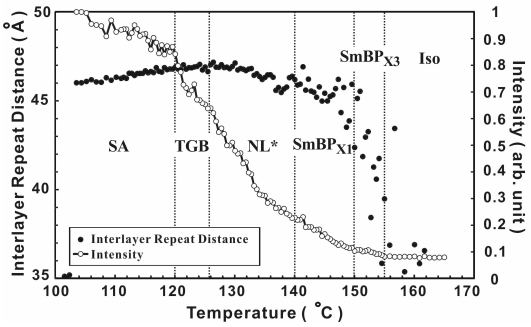

Fig.2 Temperature dependence of the smectic order measured by X-ray scattering obtained from a sample (ϕ m = 0.45). Only one scattering peak was detected in the small-angle region below 156°C, which confirms that with the exception of the Iso phase, all the phases have a finite local smectic order. The intensity of the scattering peak increases continuously from $SmBP_{X3}$ to SA, as indicated by the open circles. The characteristic length is smoothly connected to the layer repeat distance of SA, as indicated by the filled circles.

we can identify only the Iso-$SmBP_{X3}$ phase transition in the X-ray results.

On the other hand, $SmBP_{X3}$-$SmBP_{Iso}$ or $SmBP_{X3}$-$SmBP_{X1}$ phase transition can be clearly identified by viscoelastic behavior. Hence, the viscoelastic spectroscopy provides us 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 Fig. 3a. 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 Fig. 2b. Since both the real and imaginary parts become zero at a low frequency, it can be confirmed that $SmBP_{X3}$ still maintains fluidity. As temperature decreases toward the SmBPX3-$SmBP_{X1}$ phase transition, the relaxation frequency reduces drastically till it reaches a few 100 Hz (Figs. 3b and 3c). Finally, the frequency-independent finite real part appears in $SmBP_{X1}$ as shown in Fig. 3d. In the more monomer rich region, $SmBP_{Iso}$ appear instead of the $SmBP_{X1}$. Viscoelastic behavior of $SmBP_{Iso}$ is almost the same as $SmBP_{X1}$, nevertheless the characteristic of the visible light spectroscopy are completeley different from $SmBP_{X1}$. Thus, $SmBP_{X1}$ and $SmBP_{Iso}$ have an elas-

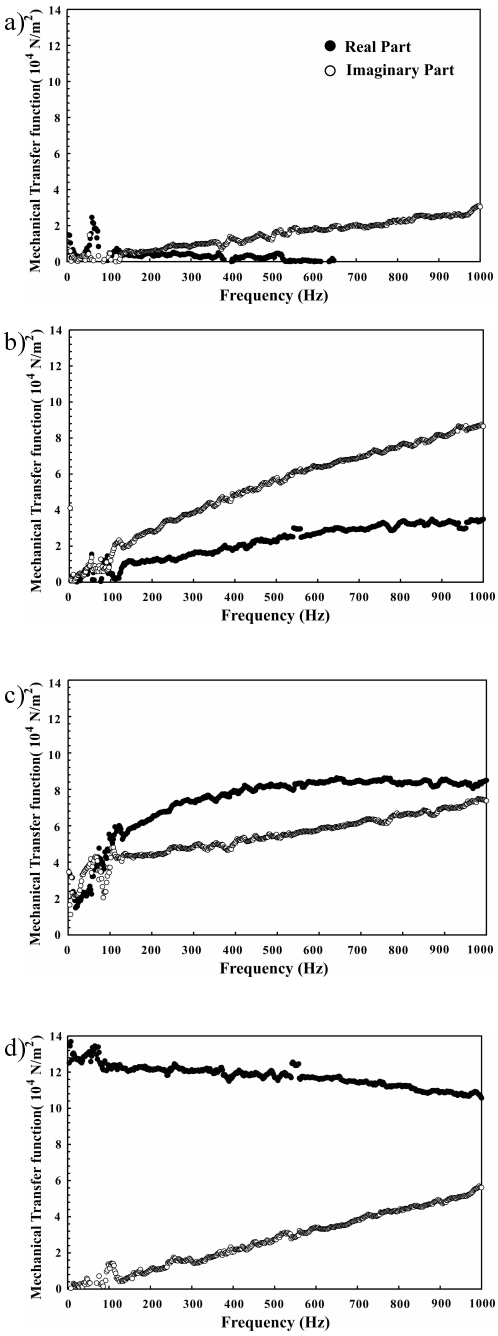

Fig.3 Frequency dependence of the mechanical transfer function measured by applying the longitudinal strain. Closed circles indicate the real part of the mechanical transfer function, whereas open circles indicate the imaginary part. a) Isotropic phase: The Isotropic phase behaves as a simple Newtonian 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.

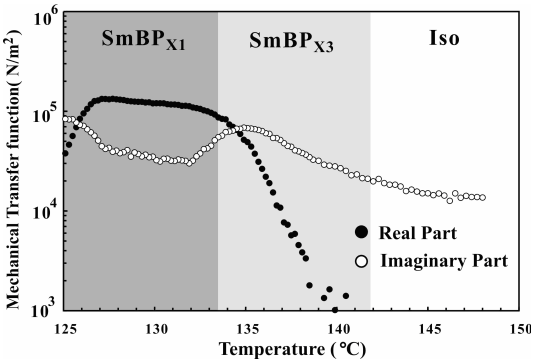

Fig.4 The temperature dependence of the mechanical transfer function at a fixed frequency (f∼100 Hz). Closed circles represent the real parts and open circles represent the imaginary part. It is evident that the macroscopic physical properties differ considerably across in the three phases, whereas the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

tic response to the static strain. Elasticity of the $SmBP_{X1}$ is almost independent of the temperature as shown in Fig.4, whereas both the real and imaginary parts strongly dependent on the temperature as ordinary seen in viscoelastic relaxation. We can clearly identify the $SmBP_{X3}$-$SmBP_{X1}$ phase transition on the contrary to the X-ray measurement.

Recently, we found the color can be tuned by shining the strong pulsed laser light. Then we can artificially design the special pattern of the "structural color" by scanning and on/off the laser light beam. Response time of the color shift is not so fast but not so slow (∼200msec) in spite of the existence of the complicated inter-connected multi-lamellar structure. We also confirms experimentally that the existence of the collective fluctuation mode just around the sub second by the dynamic light scattering measurement. Relaxation time can be assigned as reorientation motion of the helical pitch, which must be correlated to the dynamics of the shrinkage/elongation of the interconnected multi-lamellar structure through the coupling between two types of the liquid crystalline orders.

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