

Direct observation of molecular motions in soft materials: study of basic and applicational liquid crystal systems

The unique properties and functions of soft materials originate from the coexistence of microscopic structural ordering and molecular motions. Accordingly, understanding the relationships between microscopic structure and dynamics in soft matter provides crucial information on how macroscopic properties can be engineered from their microscopic origins. Liquid crystals are typical soft matter systems, and the nematic (*N*), cholesteric (*Ch*), and smectic (*Sm*) phases are the fundamental thermotropic liquid-crystal phases. In Fig. 1, we show the schematic figures of the molecular arrangements of these phases. In the *N* phase, the molecular symmetry axis is usually oriented along one direction. The *Ch* phase shows a similar orientational order locally. However, the average molecular direction in the *Ch* phase rotates continuously around a direction perpendicular to the director. These liquid crystals are widely used in liquid-crystal displays, e.g., twisted *N*-type displays. In the *Sm* phase, the molecular symmetry axis is usually oriented along one direction and the positions of the molecular center of gravity form a layered order. In the *Sm* “A” phase, the molecular direction is parallel to the layer normal. The translational molecular dynamics in these liquid-crystal phases has rarely been observed directly microscopically because of experimental limitations. Therefore, these microscopic dynamical images are virtually unknown despite their fundamental importance.

The synchrotron-radiation-based quasi-elastic gamma-ray scattering technique using multiline

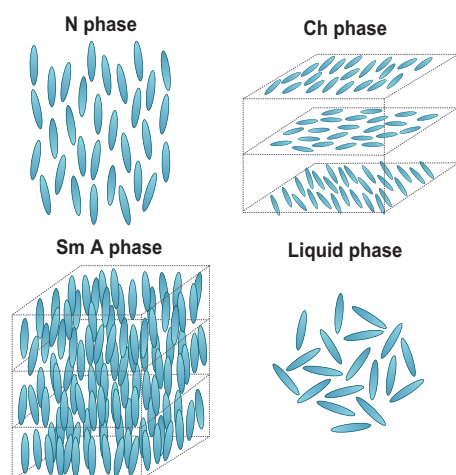


Fig. 1. Schematic figures of liquid crystal nematic (*N*), cholesteric (*Ch*), and smectic (*Sm*) phases and the liquid phase.

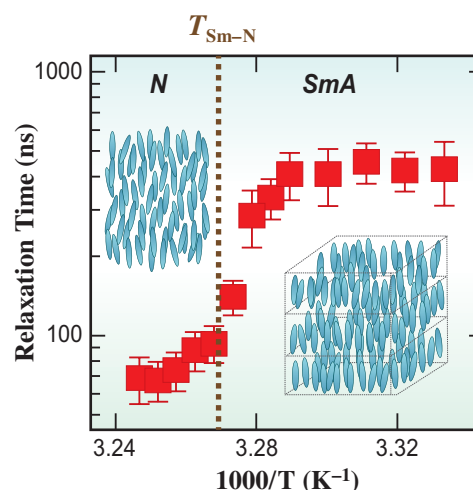


Fig. 2. Temperature dependence of relaxation times of 8CB in *N* and *Sm* phases. Schematic figures of *N* and *SmA* phases are also shown.

time-domain interferometry (TDI) allows us to study atomic/molecular-scale motions in soft matter [1-3]. The high energy resolution (4.7 neV) of the 14.4 keV Mössbauer gamma ray from the ⁵⁷Fe nucleus enables us to observe the density fluctuation on the atomic/molecular scale on the time scale of 100 ns. Regarding applications to soft-matter systems, we have thus far studied the diffusion motion of the polymer main chain and more local activation motions in pure polymer and model systems of tire by TDI [2,3].

We studied microscopic molecular dynamics in various liquid-crystal phases. The experiments were conducted at the nuclear-resonance scattering beamline, SPing-8 BL09XU. First, we introduce a study of microscopic molecular motions in *N* and *SmA* phases of a typical liquid-crystal molecule, 4'-n-octyl-4-cyanobiphenyl (8CB), by TDI [4]. In Fig. 2, we show the temperature dependence of the microscopic relaxation times of intermolecular correlations in the direction of the molecular long axis. The relaxation time reflects the time scale of the translational motion across the layer. Such molecular translational motions in the *Sm* phase have been observed microscopically for the first time. We could observe a marked increase in relaxation time in the *SmA* phase after the *N*-*SmA* transition temperature T_{Sm-N} . This increase in relaxation time is caused by the ordering of the layer structure on cooling. By applying a theory predicting the relationship between the microscopic relaxation

time and the layer order, we could microscopically evaluate the *Sm*-layer order parameter, which had not been determined microscopically thus far. The methodology used to obtain the layer order parameter from the microscopic dynamics can be used for many layered systems.

Next, we introduce results on the *Ch* phase and the cholesteric blue phase (*ChBP*) for a mixture system of the nematic liquid crystal 4'-heptyloxy-4-biphenylcarbonitrile (7OCB) and the chiral dopant (S)-4'-(2-methylbutyl)-4-biphenylcarbonitrile (CB15) [5]. *ChBP* exhibits a double-twist orientational order that differs from the single-twist order of the *Ch* phase and also shows a self-assembled three-dimensional lattice structure of defect lines of the orientational order on the mesoscopic spatial scale. We show the schematic figure of the structure in Fig. 3. The helical structure of the molecular orientation in *ChBP* brings the structural color and photonic band gap into the wavelength range of visible light. Therefore, *ChBP* has been studied for application to photonic elements and fast-response displays. We measured the molecular translational dynamics along the long molecular axis in the *Ch* phase, *ChBP*, and liquid phase. We show the relaxation time for each phase in Fig. 3. It was found

that the relaxation time of molecular translational motions in *ChBP* is of a similar time scale to that in *Ch* and liquid phases. Therefore, it was microscopically revealed that the molecular mobility in *ChBP* is as high as those in *Ch* and liquid phases even in the existence of mesoscopic lattice order. The mobility is interpreted to be one of the origins of its shorter response time for electro-optical switching, which is important for its application to fast display systems.

Our result demonstrates that the time scale of molecular motions in important liquid-crystal phases such as *N*, *Ch*, and *Sm* phases can be measured by quasi-elastic gamma-ray-scattering spectroscopy using TDI. We found that molecular translational motions in these liquid crystal phases occur on the time scale of nano- to microseconds. In addition, the microscopic molecular motion could be observed in the liquid-crystal phase *ChBP* with a complex structure. Our studies led to the expansion of the practicality of this spectroscopic technique to molecular-mobility studies of industrial materials, such as the study of the anchoring effect of molecular dynamics in liquid-crystal cells of display systems. Further studies on soft matter systems, e.g., lyotropic liquid crystal systems such as lipid bilayers, are in progress.

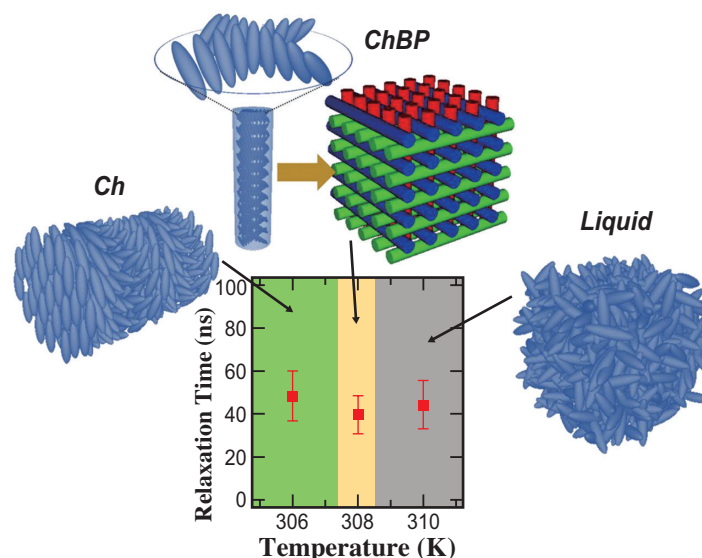


Fig. 3. Temperature dependence of relaxation times of the mixture system of 7OCB and CB15 in *Ch* phase, *ChBP*, and liquid phase. Schematic figures of *Ch* phase, *ChBP*, and liquid phase are also shown.

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