Novel Photoinduced Phase Transition Observed in Three-dimensional Liquid-crystalline Phase of Azobenzene Compound

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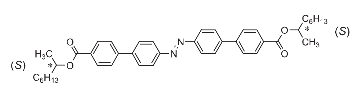
A novel dichiral azobenzene compound which shows two kinds of highly ordered liquid-crystalline phases was prepared. One of the mesophases was found, by miscibility studies, to be a chirality-induced three-dimensional (3D) liquid crystal phase. We, for the first time demonstrate the photoinduced phase transition of the liquid-crystalline 3D structure.

Liquid-crystal phases are so soft that varieties of structures can be generated by the induction of chirality; helical molecular assembly is one of the most typical effects. Macroscopic helical structures along a certain one direction are found in chiral nematic and twist grain boundary phases, whereas, for more strongly chiral liquid crystal systems, the helical nature sometimes generates an over-all three-dimensional (3D) structures.[1] Blue phases are the 3D structures seen in nematic liquid crystals, of which temperature range can be dramatically enhanced by polymer-stabilization of the defects,[2] which enable us to obtain room-temperature blue phase at ease that is important from the practical point of view. For smectics, various 3D structures are induced by chirality, i.e., "smectic" blue,[3] cubic,[4] and rather mysterious smectic Q (SmQ)[5,6] phases, of which stability is quite sensitive to the optical purity. The molecular orientations are not so sensitive, however, to the external electric field due to an intricate smectic ordering, thus it has been difficult to imagine practical applications of these structures.

We design a novel dichiral azobenzene compound possessing two chiral moieties at both peripheral ends of the molecular structure, of which structure is shown in Figure 1 (**(*S*,*S*)-AZO-PP**). This chiral architecture is known to be efficient to generate chirality-induced liquid-crystalline phases.[1] We report here that the azobenzene compound (**(*S*,*S*)-AZO-PP**) shows chirality-induced liquid-crystalline 3D structures and that the resulting 3D structure can be manipulated by "light" as an external stimulus instead of "electric field." Although photochromic reactions of azobenzene derivatives have so far been employed for optical control of physical properties and structures of common two-dimensional liquid-crystalline phases,[7] the first example of the photoinduced phase transition of liquid-crystalline 3D phase is reported in this paper.

(*S*,*S*)-AZO-PP was prepared from *p*-bromoaniline by four steps (see Supporting Information for the detailed preparation procedures and characterization of materials).[6] Liquid-crystalline properties were investigated using a polarizing optical microscope and a differential scanning calorimetry (DSC). **(*S*,*S*)-AZO-PP** shows two kinds of mesophases as follows: Cryst. 125 °C M_L 153 °C M_H 165 °C Iso., where the lower and higher temperature mesophases are described as M_L and M_H phases, respectively. Both mesophases exhibit a "mosaic" texture, as shown in Figure 2. At the transition from the M_L phase to the M_H phase transition, the birefringence drastically decreases.

Figure 3 shows a DSC thermogram of **(*S*,*S*)-AZO-PP** in a heating process (scan rate = 5 °C/min). The emergence of clear DSC peaks on the phase transitions indicates that the M_L and M_H phase are thermodynamically different phases in nature. It should be noted that both of the M_L-to-M_H and M_H-to-Iso phase transitions show only tiny peaks with enthalpies of 0.23 and 0.82 kJ/mol, respectively. Generally, the mosaic textures are obtained for the smectic B, E, F, and so on, in which molecules are highly ordered.[8] Therefore, the enthalpy changes on the phase transition are expected to be large. However, we observed



(*S*,*S*)-AZO-PP

Figure 1. Chemical structure of a novel dichiral azobenzene compound.

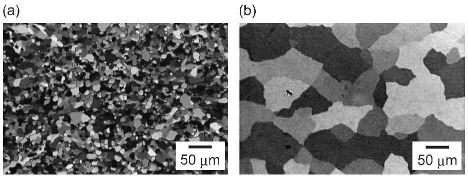


Figure 2. "Mosaic texture" observed for **(*S*,*S*)-AZO-PP**, (a) in the M_L phase at 145 °C, and (b) in the M_H phase at 152 °C.

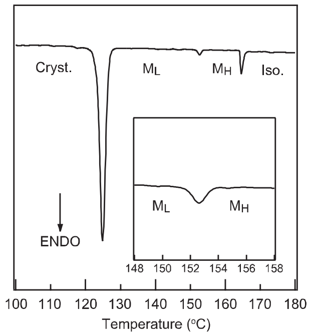


Figure 3. A DSC thermogram obtained for **(*S*,*S*)-AZO-PP** on heating (scan rate = 5 °C/min). An inset indicates an expanded view around M_L-to-M_H phase transition.

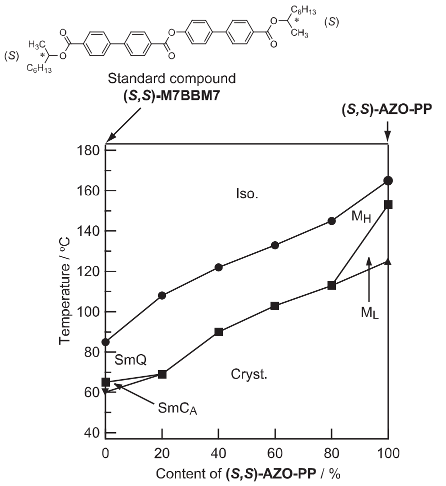


Figure 4. A miscibility phase diagram between **(*S*,*S*)-AZO-PP** and the standard compound (**(*S*,*S*)-M7BBM7**).[5b]

the quite small enthalpies indicating that the mesophases observed in this study have different structures from common higher-ordered smectic phases, such as smectic B phase.

One possibility is that the M_L and/or M_H phases is actually the SmQ phase which has been reported to show the mosaic texture as well.[1,5] The SmQ phase is one of the chirality-sensitive liquid-crystalline phase, and has been confirmed to possess the 3D structure by detailed X-ray diffraction analysis.[5c] In the previous reports,[1,5d] the small enthalpy changes on the phase transition around the SmQ phase are reported, which also agree to the result obtained for **(*S*,*S*)-AZO-PP**. In order to examine this possibility, we performed a miscibility study between **(*S*,*S*)-AZO-PP** and a standard compound (**(*S*,*S*)-M7BBM7**, see Figure 4) that has been reported to exhibit the SmQ and SmC_A phases.[5b] The SmQ phase of **(*S*,*S*)-M7BBM7** shows a "mosaic texture" similar to that of the M_H phase, and is found to be miscible with the M_H phase of **(*S*,*S*)-AZO-PP** (Figure 4). Thus, the M_H phase is assigned as the SmQ phase. The nature of the M_L phase is still unknown at this stage of work, however, it could be one of the SmQ families, as four different SmQ phases possessing distinct space groups have been reported.[5c]

It has so far been reported that the SmQ phase does not show any textural changes by the application of the external electric fields.[5e] In this study, we, for the first time, find clear textural changes of the SmQ phase, corresponding to the photoinduced phase transition, by means of the cis–trans photoisomerization of the built-in azobenzene moiety. Figure 5 shows the textural change of the M_L and M_H phases of **(*S*,*S*)-AZO-PP** by the irradiation with a focused ultra-violet ($\lambda = 365$ nm, 1 mW) beam. The phase assignments were performed by the textural observation. On the light irradiation, the M_L phase (Figure 5a) is changed into the M_H phase (Figure 5b) in the irradiated area. Similarly, the photoinduced phase transition form the M_H phase (Figure 5c) to the isotropic phase (Figure 5d) is clearly observed. After stopping the light irradiation, the photoinduced phases go back to the initial liquid-crystal phases. The mechanism of the photoinduced phase transitions can be basically explained by the destabilization of the phase structures by the cis isomers as reported previously.[7] In order to understand the details of the photoinduced phenomena, we are investigating the relationship between the phase structures and the yield of the photoisomerization. The further study will be reported elsewhere.

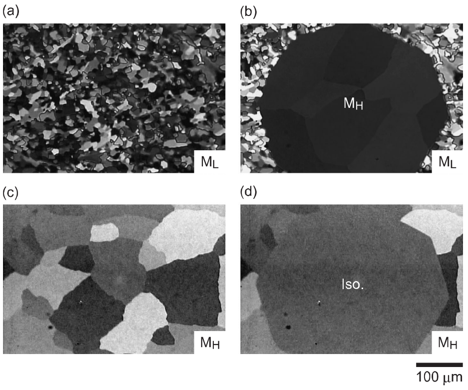


Figure 5. Photo-induced phase transitions of the M_L and M_H phases of **(*S*,*S*)-AZO-PP**: (a) and (b) are before and during irradiation at 143 °C (M_L), respectively; (c) and (d) are before and during irradiation at 159 °C (M_H), respectively. Textural changes occur in the irradiation area of ultra-violet light ($\lambda = 365$ nm, $I = 1$ mW).

In summary, we investigate the liquid-crystalline properties and photoresponse of the novel dichiral azobenzene compound. One of the mesophases is assigned, by the miscibility study, as the SmQ phase that is known to possess a liquid-crystalline 3D structure. By means of the photoisomerization of the azobenzene moiety, we, for the first time, demonstrate that the 3D structure of the SmQ phase can be controlled by light as an external stimulus, suggesting a possibility for new applications utilizing the liquid-crystalline 3D structure.

References and Notes

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