SHORT COMMUNICATIONS

Photopatterning of Discotic Liquid-Crystalline Gels

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Liquid crystals are self-organized fluids exhibiting unique properties due to their dynamic molecular order.^{1,2} To apply liquid crystals to functional materials such as an information display, information storage, and electronic nano-devices, it is necessary to control micro- and nanostructures of liquid crystals. The fabrication of micropatterns is one of the useful techniques for this approach. The utilization of light is useful for easy production of the micropatterns. Photochromic reactions have an advantage for the photopatterning of liquid crystals.^{3–10} They can reversibly change liquid-crystalline molecular order and microscopic structures. We expected reversible and stable photopatterning is achieved for liquid-crystalline physical gels, which are anisotropic soft solids consisting of gelators forming fibrous aggregates and liquid crystals.^{11–18} In our previous study, we succeeded in rewritable micrometer-sized photopatternings due to the structural changes of liquid-crystalline physical gels.¹⁹ We prepared photoresponsive liquid-crystalline physical gels incorporating a gelator with photochromic azobenzene units. They exhibit photoinduced reversible structural changes between nematic and chiral nematic gels. In this case, photopatterned structures of the nematic and chiral nematic gels are fixed by the aggregates of gelators.

Photocontrol of discotic liquid-crystalline alignment has received much attention^{20,21} because some discotic liquid crystals have an ability in high mobilities for charge carrier in columnar mesophases.²² Discotic liquid-crystalline gels can also be applied to photoconductive materials.²³ Here we report photoinduced structural changes and photopatterning of liquid-crystalline gel materials consisting of discotic columnar liquid crystal, 2,3,6,7,10,11-hexahexyloxytriphenylene (**1**) and photoresponsive hydrogen-bonded gelator **2**.

EXPERIMENTAL

Materials

Discotic liquid crystal, 2,3,6,7,10,11-hexahexyloxytriphenylene (**1**) was synthesized by the etherification of 2,3,6,7,10,11-hexahydroxytriphenylene and 1-bromohexane. This synthesized compound exhibits a hexagonal columnar liquid-crystalline (Col_h) phase between 69 and 100 °C on heating. Photoresponsive gelator **2** was prepared by the amidation of *trans*-(1*R*,2*R*)-diaminocyclohexane and 11-[4-[(4-cyanophenyl)-azo]phenoxy]-undecanoic acid.¹⁹

Sample Preparations

The composites were prepared by mixing **1** and **2** in sample tubes. The mixtures were sandwiched between two glass substrates, heated to an isotropic state at 160 °C, and then cooled to desired temperatures. The irradiated samples were obtained by cooling down

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from 120 to 65 °C under the exposure to UV light ($\lambda = 365$ nm, 20 mW cm⁻²).

General Method

Differential scanning calorimetry (DSC) measurements were performed with a NETZSCH DSC204 Phoenix[®] at a scanning rate of 5 °C min⁻¹. Transition temperatures were determined from the value of transition peaks on cooling. UV irradiation was carried out by using a high pressure mercury lamp (Ushio, 500 W) with appropriate glass filters (Asahi Techno-glass UV-35 and UVD-36C) as an irradiation source. An Olympus BX51 polarizing optical microscope equipped with a Mettler FP82HT hot stage was used for the visual observation.

RESULTS AND DISCUSSION

In the liquid-crystalline gel materials, two kinds of transitions are observed independently: one is sol–gel transition due to aggregation of gelators, and the other is isotropic–anisotropic transition of liquid-crystalline media. Therefore, these materials can be classified into two types: $T_{\text{sol-gel}} > T_{\text{iso-lc}}$ (Type 1) and $T_{\text{iso-lc}} > T_{\text{sol-gel}}$ (Type 2).¹⁶

The composites based on **2** with *trans*-azobenzene units (*trans*-**2**) and **1** show structural transitions of Type 1. Figures 1 and 2 show phase behavior of the mixtures on cooling and its schematic illustration, respectively. The phase behavior was determined by DSC measurements. When *trans*-**2**/**1** is cooled from the isotropic liquid state, *trans*-**2** first aggregates in the isotropic liquid of **1**, leading to the formation of a normal isotropic gel (Figure 2, (a)→(b)). The aggregation is driven by the formation of hydrogen bonds

Figure 1. Phase behavior of *trans*-**2**/**1** mixtures on cooling. ●: The sol–gel transition temperature ($T_{\text{sol-gel}}$). ▲: The isotropic–anisotropic transition temperature ($T_{\text{iso-lc}}$). ■: The anisotropic–crystalline transition temperature.

of the amide moieties of **2**. The $T_{\text{sol-gel}}$ of the mixture rises with increase in the concentration of *trans*-**2**. For example, $T_{\text{sol-gel}}$ of the mixture containing 3 wt % of *trans*-**2** is 102 °C. On further cooling, **1** forms the Col_h phase in the network of *trans*-**2** aggregates at 93 °C (3 wt % of **2**), inducing the transition to the liquid-crystalline gels (Figure 2, (b)→(c)). The Col_h gels have fine domains due to randomly dispersed aggregates of *trans*-**2**. The Col_h gels are kept until they crystallize at 51 °C.

On the other hand, when **2**/**1** is cooled from the isotropic states under the UV irradiation, the isotropic–Col_h transition first occurs before the sol–gel transitions (Figure 2, (a)→(d)). The UV irradiation induces *trans*–*cis* photoisomerization of the azobenzene units

Figure 2. Schematic illustration of the phase transition behavior of **2**/**1** on cooling.

in the gelator. Compound **2** with *cis*-azobenzene moieties (*cis*-**2**) becomes more soluble in **1** than *trans*-**2**. In other words, *cis*-**2** does not have gelation ability. Upon UV irradiation, the $T_{\text{sol-gel}}$ is lowered by the increase in the concentration of *cis*-**2** and by the decrease of the gelator *trans*-**2**. Therefore, sol-gel transitions occur in the Col_h phases. After the UV irradiation is off, thermal *cis-trans* isomerization of azobenzene moieties causes the complete gelation with the aggregates of the *trans*-**2** that is isomerized from *cis*-**2** (Figure 2, (d)→(e)). These photoinduced behavior is apparent from the structural changes of the Col_h gels as described later. These results indicate that photoisomerization of the azobenzene units of **2** induces the change in the phase transition sequence of the liquid-crystalline gel materials from Type 1 to Type 2 as shown in Figure 2.

The patterning by the photoinduced structural changes has been observed with a polarizing microscope. Figure 3 shows the polarized photomicrograph of the sample obtained after cooling to 65 °C under UV irradiation of **1/2** (3 wt %) through a line-&-space photomask. We have succeeded in the photopatterning of the discotic columnar liquid-crystalline gel. In the irradiated area, larger domains of the Col_h phase and partially homeotropic alignment are observed, compared with the fine domains in the non-irradiated area. The difference of the observed textures between irradiated and non-irradiated area is caused by the photoinduced type change of the liquid-crystalline gels. In the irradiated region which is Type 2, the Col_h domains can grow until the gelator aggregates. Then, the liquid-crystalline domains are fixed by the aggregates of **2**, therefore, this photopattern is maintained. However, when the maintained patterns are heated

to isotropic states and subsequently cooled, the patterns are erased.

We have reported the hole mobility of a discotic liquid-crystalline triphenylene compound is enhanced by the appropriate composition with aggregates of a hydrogen-bonded gelator.²³ Shimizu and co-workers have shown that IR induced alignment changes of a discotic liquid crystals have been achieved.²¹ The combination of these techniques and the photopatterning in this report may provide a new technology to fabricate molecular materials for information storage and electronic devices.

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Figure 3. Optical polarized photomicrograph of the patterned sample at 65 °C prepared by cooling under UV irradiation through a photomask of 180-μm lines and spaces.

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