Photoinduced crystal-liquid phase transitions by photoisomerization of azobenzene

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Abstract

We report the photoinduced phase transitions between crystal and liquid phases of a photoresponsive organic compounds. It is a macrocyclic compound bearing two (**1**) and three azobenzenes (**2**). The compounds **1** and **2** undergo photoinduced phase transitions (crystal—isotropic phase) at room temperature on irradiation with ultraviolet (UV) light (365 nm). Heating enhances the thermal cis-to-trans isomerization and regenerated crystals of the initial state of trans/trans isomer.

1. Introduction

Melting (phase transition from solid to liquid) of substance is caused by heating under constant pressure. State of matter can be changed by light irradiation onto photoresponsive polymer (such as photoresists and photoresponsive adhesives). However, the change of photoresists is caused generally by irreversible reactions (polymerizing or decomposing reactions) and it is impossible to bring them back to the initial state in principle.

Azobenzene, one of well-known photochromic compounds, exhibits reversible photoisomerization between *trans* and *cis* isomers (Figure 1). Due to its reversible nature, azobenzene has been of interest and applied to various photoresponsive materials, so the properties of materials can be controlled repeatedly by light irradiation. For example, photoisomerization of azobenzene induces phase transitions between liquid-crystalline (LC) and isotropic phases [1-5]. However, its photoresponse strongly depends on the surrounding environment. Since photoisomerization of azobenzene requires a free volume for the reaction, azobenzene and its derivatives often suppressed by strong molecular packing in their crystal state, in polymer matrices, or self-assembled aggregates and monolayers.[6-8]

We would like to report here that newly synthesized organic materials consisting of macrocyclic azobenzenes (compounds **1** and **2**, Figure 2) exhibit photoinduced phase transitions from crystal to isotropic liquid [9,10]. The molecules **1** and **2** were designed by simply attaching flexible and long alkoxy chains to the macrocyclic cores. The phase transitions are achieved by the trans-cis isomerization of azobenzene. Change of molecular shape drastically changes the macroscopic properties such as melting points. In contrast to the traditional photoresists that exhibit irreversible response, these new materials show reversible property and the melted state easily solidifies with heat.

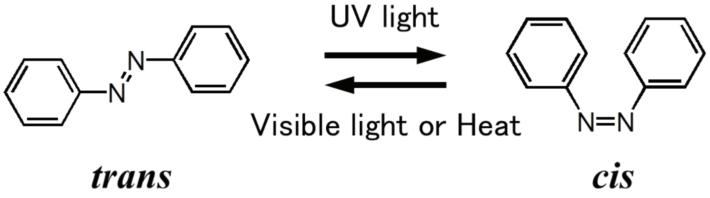

Figure 1 Photoisomerization of azobenzene. The *trans* isomer undergoes photoisomerization on irradiation with ultraviolet (UV) light, while the *cis* isomer exhibits photoisomerization on irradiation with visible light or thermal isomerization to give the initial *trans* isomer.

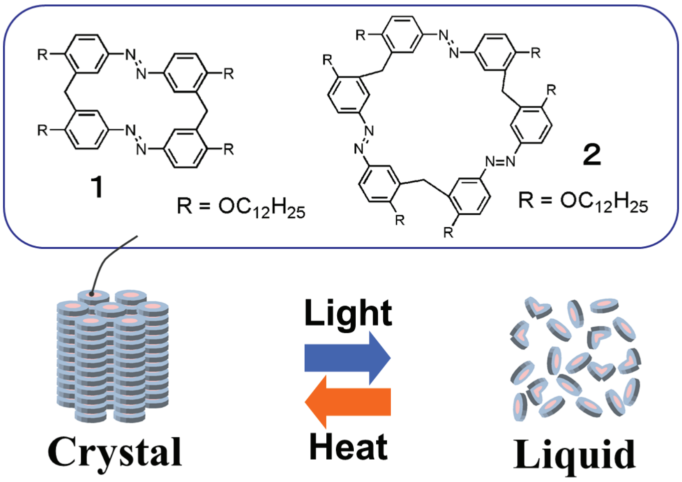

Figure 2 Molecular structures of macrocyclic azobenzenes (top) and schematic representation of phase transitions (bottom).

2. Experiment

2.1 Sample preparation

Compound **1** and **2** were synthesized according to the reported procedure [10]. Film samples for polarizing optical microscopy (POM) observations and UV/vis absorption spectroscopy were prepared by sandwiching the compound **1** or **2** with two cover glass plates (Matsunami micro cover glass (thickness: 0.12-0.17 mm)). Crystalline film samples of trans/trans-**1** were prepared by slow cooling from isotropic melt (150 °C) to room temperature. Thickness of the film sample was estimated by carefully peeling the glass plates and the surface of glass was analyzed by a microfigure measuring instrument (Kosaka Laboratory Ltd. SURFCORDER ET200) to be 0.7-0.8 μm. Temperature of film samples was controlled by a Linkam LK-600PM stage.

2.2 X-ray diffraction

X-ray diffraction (XRD) were measured using a Rigaku RU-300 using radiation (Cu Kα, 40 kV, 200 mA), or a Rigaku RINT-TTR (Cu Kα, 50 kV and 200 mA). The diffractions were measured in the 2θ-θ scan mode with 0.01 or 0.02° step.

2.3 Polarizing optical photomicrographs and irradiation experiments

Polarizing optical photomicrographs were taken by an OLYMPUS BX51 microscope equipped with a high pressure Hg lamp, optical filters and heat absorbing filters so that in-situ observation on photoirradiation was possible. Other photoirradiation experiments were performed by a high pressure Hg lamp (Asahi Spectra Inc. REX-250 for 365, 405, and 436 nm), LED's (Asahi Spectra Inc. POT-365 LED for 365 nm, Brainvision Inc. LEX2 for 465 nm, and home built LED for 525 nm). Light intensity was monitored by a Newport 1917-R optical power meter with 818-ST-UV photodetector.

3. Results and discussion

The photoisomerization of **1** and **2** were confirmed by the UV-vis absorption spectroscopy (Figure 3). In the chloroform solution, the absorption spectra clearly show that azobenzene moieties are in the *trans* configuration in the dark. The UV light (365 nm) irradiation brought both sample solutions to the *cis*-rich state. Similar change in the spectra was observed in the crystal film sample of **1** and **2**, clearly indicating the photoisomerization takes place in the crystal phase. Isomer ratio of the crystal film after the photoirradiation was estimated. For example, a film of **1**, when exposed to 365 nm light for 300 s (at the photostationary state (pss), consisted of 13, 10, and 77% of the trans/trans, trans/cis, and cis/cis isomer of **1**, respectively. The isomer ratio obtained in this experiment shows that the excitation light penetrates well through the film sample. Cis/cis isomer was obtained as a major product, and similar trend was observed in solution.

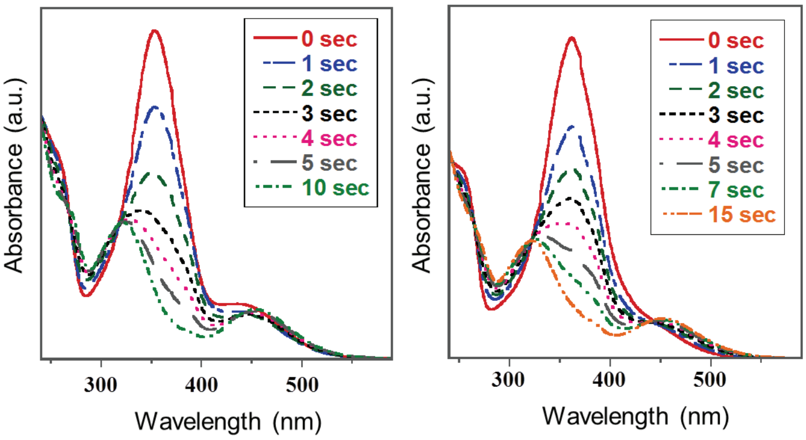

Figure 3 UV/vis absorption spectra of compound **1** (left) and **2** (right) in chloroform.

A crystal film sample of **1** or **2** was exposed to 365 nm light under polarizing optical microscope (POM) observation at room temperature. The irradiated area of the crystal rapidly lost its birefringence and became isotropic phase. A crystal film of **2** also exhibited the phase transition to the isotropic phase (Figure 4 and 5). After irradiation of 10 s, the shape of the crystal was lost completely. A crystalline film of 1 exhibited the loss of the birefringence after the irradiation of 2 s (Figure 5 a,b). These phase transition was also confirmed by X-ray diffraction (XRD) measurements. Thus, the photoinduced phase transition observed in POM and XRD experiments is attributed to the photoisomerization of azobenzene.

The reversible switching property has been achieved by simply heating. The back reaction to the crystal phase has been achieved by heating the sample around 100°C (Figure 5). Heating enhances the thermal cis-to-trans isomerization and crystallization of all-trans isomer. The resolidified crystals exhibited the photoinduced crystal-to-liquid phase transition, thus these materials can be used repeatedly.

Notably, these photoinduced crystal-to-liquid phase transitions occur at room temperature, although the melting points of these compounds are over 100°C. As far as we know, this is the first example of crystal to liquid phase transition by photoisomerization of azobenzene. In contrast to traditional photoresists and photoresponsive adhesives that exhibit irreversible response, these compounds show reversible property and have potential applications to reusable photoresponsive materials.

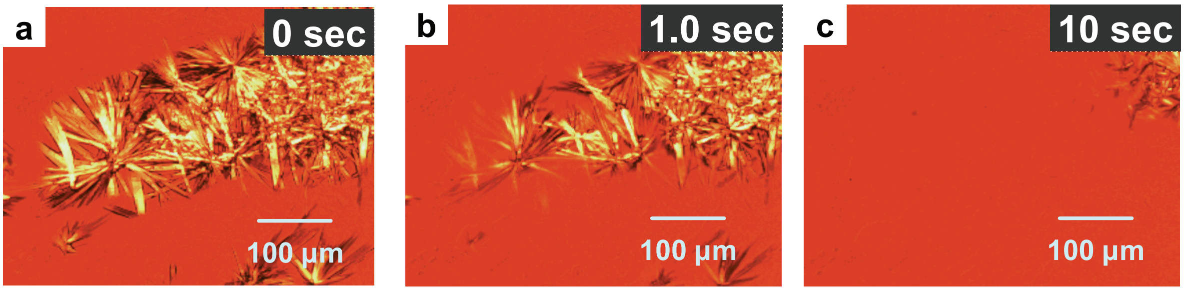

Figure 4 Polarizing optical photomicrographs of crystals of **2**, a) before light irradiation, b) after irradiation of 365 nm light for 1 second, and c) after irradiation of 365 nm light for 10 seconds. The angle between the analyzer and the polarizer of the POM was ca. 80° to enable clearer observation.

4. Conclusion

Photoinduced crystal-liquid phase transitions by photoisomerization of azobenzene have been demonstrated in macrocyclic azobenzene molecules. These results show that one can selectively control the phase of material (solid or liquid) by simply irradiating light to this kind of new materials.

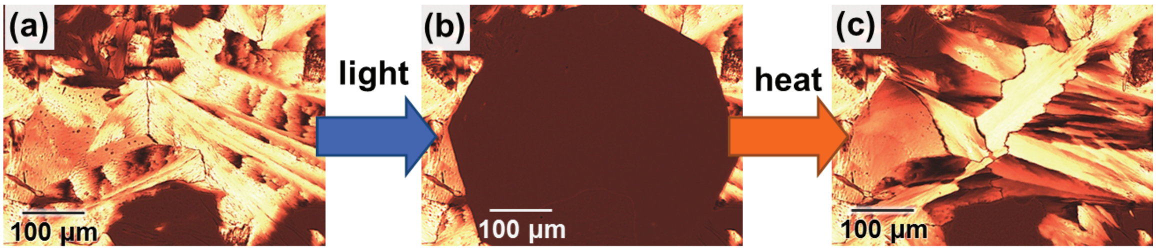

Figure 5 Polarizing optical photomicrographs of crystalline film of **1**, a) before light irradiation, b) after irradiation of 365 nm light for 2 seconds, and c) after heating the sample for 1 minute in the dark. All photographs were taken under crossed polarizers.

Acknowledgements

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