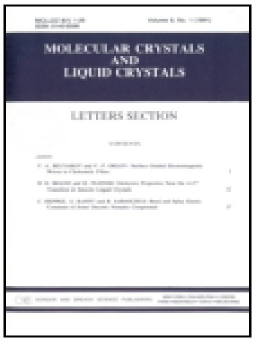

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Photochemical Liquid–Solid Transitions in Multi-dye Compounds

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We report the synthesis of liquid crystalline materials, which repeatedly liquefied and solidified when irradiated with ultraviolet (UV) and visible light at room temperature. The materials are the derivatives of the sugar alcohols, D-mannitol, D-sorbitol, and allitol, in which all hydroxyl groups were substituted with multi-mesogenic azobenzenes. The thermal phase transition behavior and stability of the liquid crystal phase were changed according to the sugar alcohols, but photochemical phase transition behaviors were not different. In addition, when applied as an adhesive layer to glass substrates, the materials exhibited changes in the adhesion force when irradiated with light.

Keywords Sugars; azobenzene; liquid crystals; photochemistry; adhesives

Introduction

The reversible liquid–solid transitions of materials are usually induced by a temperature change. Isothermal and reversible phase transitions need the application of an external factors such as pressure, an electric field, or a magnetic field. For example, light-induced phase transitions have been reported in photoisomerizable azobenzene derivatives between the nematic–isotropic or gel–sol transition [1–4]. The principle involved dictates that the transition temperature is changed with reversible *trans–cis* photoisomerization. Conversely, solid–liquid phase transitions promoted by light have rarely been observed because the energy barrier that should be overcome for this transition is larger than that for the transition to intermediate phases of the liquid crystal or gel. One example of a drastic liquid–crystal (solid) transition was observed on the surface of diarylethene crystals at 30°C or above [5, 6]. Another example is that of photo-fluidization, confirmed in a polymer film containing azobenzene during light irradiation [7, 8]. In contrast to these aforementioned examples,

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we have previously reported photochemically reversible solid–liquid phase transitions of two different kinds of molecules at room temperature where relatively stable liquid and solid states were obtained after light irradiation ceased [9–11]. One is a cyclic multi-azobenzene derivative, which exhibits a crystal-liquid transition at room temperature, whereas the other is a multi-azobenzene compound containing sugar alcohol scaffolds that exhibit transitions between liquid and crystal or liquid crystalline glass. In the latter case, photo-controllable adhesion properties were demonstrated using glass plates. The number of azobenzene units in sugar alcohol derivatives is critical for the photo-functional properties; four or more azobenzene moieties are necessary. This approach indicates that the tethering of multiple azobenzenes to one sugar alcohol is effective at modifying the behavior of such materials. Among these, the corresponding hexamer has previously been synthesized from D-mannitol, which is easily obtained from natural products; the azobenzene units were attached via long alkyl spacers (C10) to the central sugar alcohol core. However, the structural effects of the central core on the properties of such a material are not known, and there are no reports of such an investigation. In this study, we prepared three different sugar alcohol based compounds, each of which contained a $C_6H\text{-}_8O_6$ core (D-mannitol, D-sorbitol, and allitol), and investigated the structural effects of modifying the core by comparing the stereoisomers.

Experimental

Materials: The compounds investigated in this work are listed in Fig. 1. The synthesis of hexakis-*O*-{11-[4-(4-hexylphenylazo)phenoxy]undecanoyl}-D-mannitol, **M**, has been described previously [12]; hexakis-*O*-{11-[4-(4-hexylphenylazo)phenoxy]undecanoyl}-D-sorbitol, **S**, and hexakis-*O*-{11-[4-(4-hexylphenylazo)phenoxy]undecanoyl}-allitol, **A**, were synthesized in a similar manner from 11-[4-(4-hexylphenylazo)phenoxy]undecanoic acid and the corresponding sugar alcohol.

S; yield; 70.5%. ^{1}H NMR (400 MHz, 25°C, $CDCl_3$): δ (ppm) 0.88 (t, $J = 7.0$ Hz, 18H, CH_3), 1.29 (s, 96H, CH_2), 1.45 (br s, 12H, $CH_2C_2H_4COO$), 1.62 (m, 24H, CH_2CH_2Ar, CH_2CH_2COO), 1.79 (br s, 12H, CH_2CH_2OAr), 2.25-2.34 (m, 8H, CH_2COO), 2.37 (t, $J = 7.4$ Hz, 4H, CH_2COO), 2.65 (t, $J = 7.7$ Hz, 12H, CH_2Ar), 3.99 (t, J = 6.5 Hz, 12H, CH_2OAr), 4.01–4.08 (m, 2H, *H*-1a, *H*-6a), 4.26 (dd, $J = 3.6$, 12.4 Hz 1H, *H*-1b), 4.37 (dd, $J = 3.6$, 12.2 Hz, 1H, *H*-6b), 4.38 (dd, $J = 3.5$, 12.2 Hz 1H, *H*-1b, *H*-6b), 5.06 (m, 1H, *H*-2), 5.22 (m, 1H, *H*-5), 5.41–5.47 (m, 2H, *H*-3, *H*-4), 6.96 (d, $J = 9.1$ Hz, 12H, Ar-*H*),

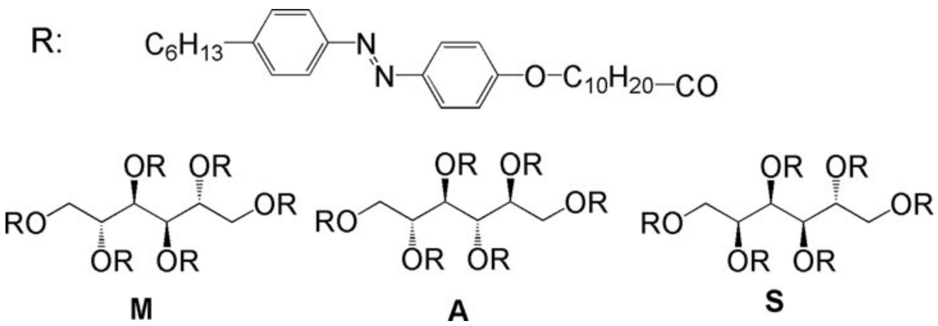

Figure 1. Chemical structure of multi-azobenzene compounds.

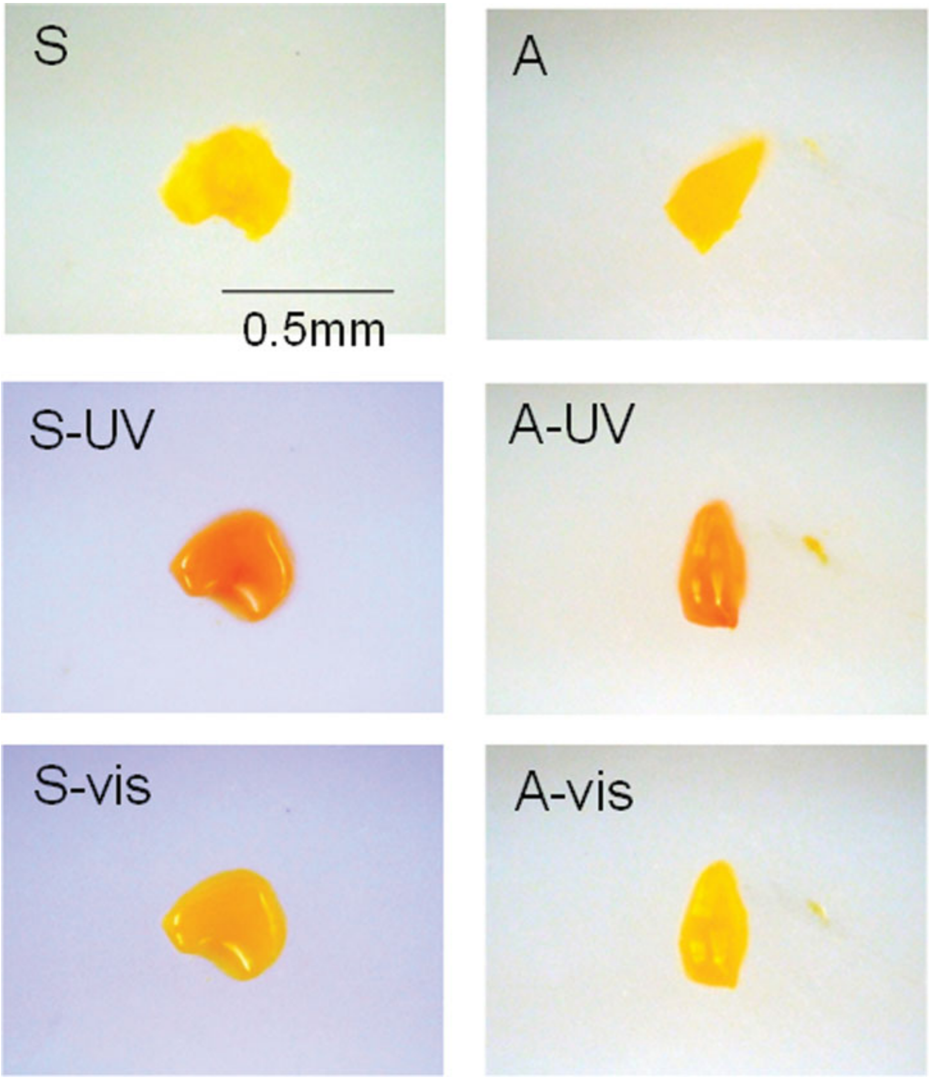

Figure 2. Photographs of **S** (S) and **A** (A) before and after irradiation with 365-nm light at 80 mW cm^{-2} for 10 min (S-UV, and A-UV) and after irradiation with 525-nm light at 20 mW cm^{-2} for 5 min (S-vis and A-vis).

7.27 (d, J = 8.3 Hz, 12H, Ar-H), 7.77 (d, J = 8.3 Hz, 12H, Ar-H), 7.86 (d, J = 8.8 Hz, 12H, Ar-H). MS (MALDI-TOF): 2912.4 [M + K]$^+$.

A; yield; 48.2%. ^{1}H NMR (400 MHz, 25°C, CDCl$_3$): δ (ppm) 0.88 (t, J = 6.7 Hz, 18H, CH_3), 1.31 (s, 96H, CH_2), 1.45 (br s, 12H, CH$_2$C$_2$H$_4$COO), 1.62 (m, 24H, CH$_2$CH$_2$Ar, CH$_2$CH$_2$COO), 1.79 (br s, 12H, CH$_2$CH$_2$OAr), 2.25 (t, J = 7.9 Hz, 6H, CH_2COO), 2.30-2.38 (m, 6H, CH_2COO), 2.66 (t, J = 7.7 Hz, 12H, CH_2Ar), 3.99 (t, J = 6.3 Hz, 12H, CH_2OAr), 4.10 (dd, J = 7.0, 12.5 Hz, 2H, H-1a, H-6a), 4.45 (dd, J = 3, 12.5 Hz, 2H, H-1b, H-6b), 5.27 (br s, 2H, H-2, H-5), 5.37 (d, J = 4.2 Hz, 2H, H-3, H-4), 6.96 (d, J = 9.0 Hz, 12H, Ar-*H*), 7.27 (d, $J = 8.2$ Hz, 12H, Ar-*H*), 7.78 (d, $J = 8.2$ Hz, 12H, Ar-*H*), 7.86 (d, $J = 8.9$ Hz, 12H, Ar-*H*). MS (MALDI-TOF): 2875.4 $[M + H]^+$.

Physical measurements: Differential scanning calorimetry (DSC) studies were conducted on a SII EXTAR6000 instrument. The irradiations were conducted using high-power light-emitting diodes [Nichia NC4U133A for ultraviolet (UV, 365 nm) light and Luxeon green LXHL-LM5C for visible (525 nm) light]. The textures of the samples were observed using an Olympus BH2 microscope equipped with a Mettler FP90 temperature controller and a Mettler FP82HT heat stage. The pictures and videos of the samples were acquired by a video recorder (Sony Handycam HDR-CX170) with an ultra-macro lens (Raynox MSN-505). The absorption spectra were measured on a UV–Vis spectrophotometer (Agilent 8453). Tensile shear strengths were estimated using a Shimadzu Autograph with a 1-kN load cell (SLBL-1kN) and holding apparatus (SCG-1kNA). Two glass plates (1.5 cm × 5 cm, 1 mm thickness) connected to stainless steel plates (0.2 mm thickness) were attached by adhesives (2–3 mg) covering an area of 1.5 cm × 1.5 cm (see Figure S2). The glass plates were pulled in the opposite direction at 0.2 mm min^{-1} while monitoring the stress until they separated.

Results and Discussion

Phase transition: The three compounds were obtained as powdered solids at room temperature. For the observation of photochemical phase transitions, each sample of solid material (**S** and **A**) was irradiated with UV light at room temperature. Both materials changed to an orange color from yellow, and then transformed into droplets of liquid. The color change corresponds to the typical *trans* to *cis* isomerization of azobenzene moieties by UV irradiation. The *cis* isomer of azobenzene has a stronger n-π^* absorption band in the visible region (400–550 nm), resulting in a darker orange color. The fluid state was stable for at least half a day in the dark at room temperature. The liquefied samples were irradiated with green light (525 nm, 20 mW cm^{-2}) for 5 min. The color changed again from orange to yellow corresponding to a *cis* to *trans* photoisomerization. The resultant yellow mass could be picked up or cracked using a micro spatula, which indicated the liquid had been converted to a solid by irradiation with visible light. The phase transition could be repeated several times. Such photochemically induced phase transition behaviors were similar to those observed in **M**. Thus, the effect of structurally varying the central core on the liquid–solid phase transition behaviors was not observed.

Adhesion

The photochemical liquid–solid transition materials described above have potential application in reusable, light sensitive adhesives; adhesives work on the principle of the solidification of liquid materials during assembly. For the measurement of adhesion force, thermally fused samples were spread between two glass plates, and then cooled to room temperature resulting in bonded glass plates. The two glass plates were pulled in opposite directions by a tensile strength-testing machine until each glass plate separated. From the values of the maximum tension, the adhesive forces were calculated. Table 1 summarizes the adhesive forces under each condition; data were measured three times under the same condition and averaged. As shown in Table 1, there are no critical differences between the compounds. Before irradiation, adhesion forces were 40–50 mN cm^{-2}. The thermally attached glass plates were irradiated with UV light for 3 min. The entire adhesive layer

Table 1. Adhesion forces of azobenzene compounds for glass plates

	Adhesion forces / N cm^{-2}		
	Without irradiation	With UV light	With visible light
M	42.4 ± 1.1	>0.3	100.3 ± 5.6
S	47.4 ± 12.7	>0.3	122.8 ± 10.7
A	51.4 ± 3.2	>0.3	104.3 ± 6.2

changed to a transparent orange color. In this state, the adhesive forces were nearly zero ($<$0.3 mN cm^{-2}), which meant each plate slided without stress, thus indicating the compounds between the glass plates liquefied. The short irradiation time was due to the thin adhesive layer ($<$10 μm); the speed of the photoresponse was limited by the penetration length of the light. After liquefaction by irradiation with UV light, the adhesive layer was irradiated with visible light for 3 min. As a result, the adhesion layer changed to a yellow color, and the adhesive forces increased to almost double (100–120 mN cm^{-2}). The adhesive layers were solidified by irradiation with visible light, but the photochemically generated sold state was probably different from the thermally generated solid state. The photocontrolled adhesion behaviors were observed to be quite similar among these compounds.

Thermal Properties

The thermal phase behaviors were investigated by DSC and X-ray diffraction (XRD) analysis. Figures 3 and 4 show the thermal phase transition behavior of **S** and **A**. Compound **S** exhibited liquid crystalline phases upon cooling which were determined to be smectic C and smectic I/F, but on heating it converted to crystalline or highly-ordered phases after the glass transition temperature. Such monotropic liquid crystallinity was also observed in **M**; their thermal behaviors were quite similar because both were observed to possess two solid states. When cooled quickly, the compound **S** was a liquid crystalline glass, but after gradual cooling from the thermally fused state, it was a crystalline solid. The difference appeared in the glass transition; the glass transition temperature of **S** (ca. 70°C) was a little lower than that of **M** (ca. 80°C). In contrast to these two compounds, **A** exhibited

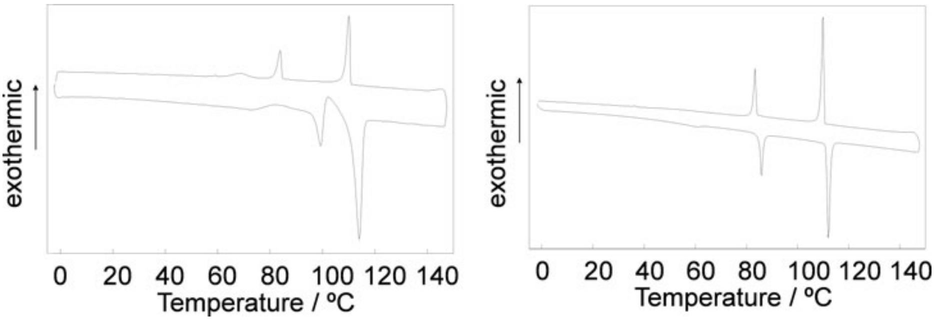

Figure 3. Differential scanning calorimetry (DSC) curves of **S** (left) and **A** (right) on heating and cooling scan at 2°C min^{-1}.

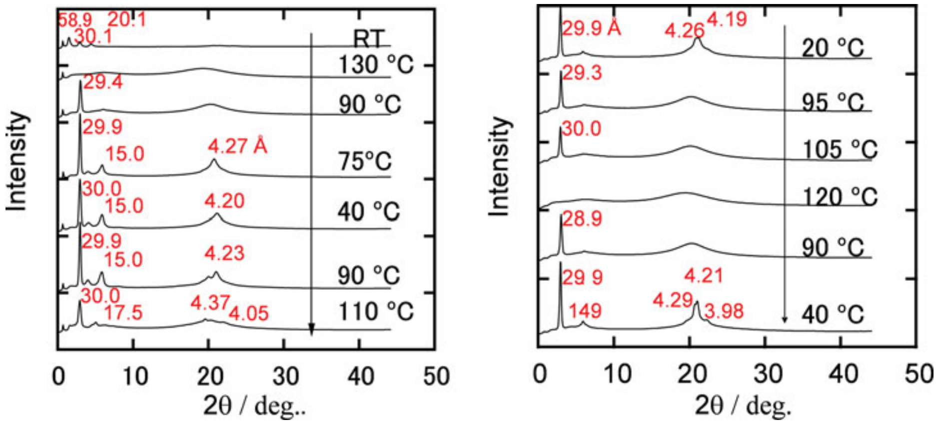

Figure 4. Temperature dependence of X-ray diffraction spectra of **S** (left) and **A** (right).

two liquid crystalline phases, which were determined to be smectic C and smectic I/F, both on heating and cooling, such that they were enantiotropic liquid crystals. The glass transition temperature (ca. 60°C) was lower than those of the other compounds, **M** and **S**. A single solid phase, a liquid crystalline glass, appeared in **A** independent of the cooling rate, thus demonstrating that the stereochemistry of the sugar alcohol drastically influences the material's properties.

Conclusions

We have demonstrated the photoinduced liquefaction of solid materials with multi-azo-arms, and its reverse transition, the photoinduced solidification, at room temperature. There were no obvious differences in the photoresponsive behavior of the three compounds with different sugar alcohol scaffolds, but there were marked differences in their thermal phase behavior. Liquid crystalline properties at high temperatures were observed for all compounds, of which **M** and **S** were monotropic liquid crystals and **A** was an enantiotropic liquid crystal, thus indicating that the stereoisomers can affect solid structure at room temperature. In addition, glass transition temperatures slightly increased in the order **A** < **S** < **M**. By utilizing the isothermal phase transition, the photo attachment and detachment of glass plates at room temperature were demonstrated as promising applications for reusable adhesives. From a practical point of view, the thermal stability is important. Therefore, the choice of sugar alcohol, which affects the glass transition temperature, is central to the behavior reported in this work, and further investigations into other core structures may reveal materials with even more promising properties.

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