Organic Photofunctional Materials Composed of Azobenzene Derivatives: Liquid–solid Phase Transition in Multi Azobenzene Compounds with Partially Substituted Structures

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The light induced phase transition and reversible adhesive function were investigated for a range of D-mannitol derivatives partially substituted with multi-azobenzenes bearing free hydroxyl groups. Irradiation with UV and visible light induced liquefaction and solidification of the compounds, which adhered glass plates. Further, the adhesion force could be changed reversibly upon irradiation with light. Moreover, the adhesion forces were larger than those of the fully substituted compound.

Keyword: Adhesion, Sugar alcohol, Phase transition, Azobenzene

1. Introduction
Recycling and reuse are important in resource saving. However, they are not feasible if the recycling process consumes a large amount of energy and costs more than the use of disposable products. Low cost recycling systems are required, although materials with reversible function are expensive. Therefore, how valuable and/or limited materials are used must be considered. Materials such as covering agents and adhesives, which can work at interface and surface of products in small quantities but change the overall properties of the product, are available for recycling. The phenomenon, which occurs in such materials, is the change of state from liquid to solid. Therefore, the reuse and recycling of these materials requires a reversible phase change between liquid and solid. Although solid and liquid transitions are generally induced by changes in temperature, reversible photo reactions such as photoisomerization enable a similar phase transition. Azobenzene is well known as a photoisomerizable compound and possesses desirable characteristics such as ease of its synthesis and photochemical stability. Azobenzene derivatives that are without photoisomerization properties are used as pH indicators and dyes. Previous research into the isomerization of azobenzene has shown its use in changes in surface wettability,[1, 2] data recording,[3] drug delivery,[4] photoalignment films,[5, 6] etc.[7, 8, 9] Amongst them, we have recently reported light responsive, reworkable adhesives in multi azobenzene compounds with reversible liquid–solid phase change properties.[10] Related phase transitions have been reported for fluidization of azobenzene polymers using irradiation with light[11], changing the melting point in crystals of...
diarylethanes using photoisomerization\cite{12, 13} and “photomelting” of crystals of cyclic azobenzene dimers at room temperature \cite{14, 15}. Multi-azobenzene compounds that we demonstrated the first, reversible adhesion force change upon light stimulation are tetra-, hexa-, or octa-substituted sugar alcohols bearing mesogenic azobenzene chains. The number of substituents strongly affected the phase transition behavior. For example, mono- and di-substituted compounds did not show any phase change upon irradiation with light. All of the compounds tested consisted of sugar alcohols fully substituted with azobenzene moieties\cite{10}. In this study, we report our investigations on the effect of partial substitution on the phase transition behavior and performance of these adhesives.

2. Experimental

2.1. Materials

Thionyl chloride (1.9 g) was added to 11-[4-(4-hexylphenylazo)phenoxy]undecanoic acid (5.0 g). The solution was stirred at 80 °C for 1 h and concentrated in vacuo. Dichloromethane (12 mL) was added to the residue, and the resulting solution was added slowly to a solution of D-mannitol (0.22 g) in pyridine (2 mL). The reaction mixture was heated at reflux for 2 h, allowed to cool to room temperature, and then washed with deionized water. The reaction mixture was concentrated in vacuo, and the mixture of multi-azobenzene derivatives (0.6 g) was separated by column chromatography using dichloromethane including ethanol (ca. 5 %) as the eluent. Identification of the isolated compounds is described in the results and discussion section of this paper.

2.2. Measurement

\(^1\)H-NMR spectra of all samples were recorded using a Jeol JNM-ECX400 spectrometer using CDCl\(_3\) as the NMR solvent. DSC measurements were conducted using a Seiko DSC Exstar 6000 instrument operated at heating and cooling rates of 2 °C min\(^{-1}\). Sample irradiation was conducted using a high power light emitting diodes [Nichia NC4U033A for UV light (\(\lambda = 365\) nm), and Luxeon cyan 5W LXHL-LE5C for visible light (\(\lambda = 510\) nm)]. Matrix-assisted laser desorption ionization, time-of-flight mass spectrometry (MALDI-TOF MS) was conducted using an Applied Biosystems Voyager-DE Pro instrument operated in reflector mode. Samples were prepared by mixing a MeOH or CH\(_2\)Cl\(_2\) solution of the sample compounds with \(\alpha\)-cyano-4-hydroxycinnamic acid. The sample textures were observed using an optical polarizing microscope (Olympus BH2) equipped with a temperature controller (Mettler FP90) and a heat stage (Mettler FP82HT). Pictures of the samples were taken using a video recorder (Sony Handycam HDR-CX170) equipped with an ultra-macro lens (Raynox MSN-505). The shear tension strength of the materials for glass plates were estimated when two plates (1.5 cm \(\times\) 5 cm, t = 1 mm) were detached by pulling using a digital force gage (Shimpo FGJN-50). For this purpose, a sample (ca. 1.0 mg) was placed between two glass plates above the isotropic temperature, filled in an overlapped area of 1.5 cm \(\times\) 0.5 cm, and then allowed to cool to room temperature prior to testing.

![Figure 1. The chemical structure of compounds 1 and 2. Compound 1 contains fully substituted side chains bearing azobenzene units. Compound 2 is partially substituted and contains two free hydroxyl groups.](image-url)

3. Results and Discussion

3.1. Synthesis of multi-azobenzene compound

We have previously reported the synthesis of the hexamer derived from a D-mannitol in which the hydroxyl groups were esterified using [4-(4-hexylphenylazo)phenoxy]undecanoyl chloride.\cite{16} The yield of the hexamer was 40\%–70\%. The reaction also formed a by-product, which consisted of a mixture of partially substituted compounds bearing free hydroxyl groups. The \(^1\)H-NMR
spectra of the hexamer and the by-product are shown in Figure 2a and 2b.

![Figure 2](image-url)

Figure 2. $^1$H-NMR spectra of (a) Compound 1 and (b) Compound 2.

As shown in Figure 2a, the signals corresponding to the methine and methylene protons of the esterified D-mannitol backbone appeared at $\delta = 4.00, 4.25, 5.09,$ and $5.45$ ppm, respectively. The signals of the methylene protons $\alpha$ to the C=O group in the undecanoic moiety ($\delta = 2.3$ ppm) appeared as a multiplet in the product after the esterification reaction, which had initially appeared as a triplet in the starting material. The formation of a multiplet could be attributed to the effect of the stereochemical differences in the bonding position of the D-mannitol moiety. In Figure 2b, a similar change in the peaks at $\delta = 2.3$ ppm were also observed after the esterification reaction, which confirmed the introduction of the azobenzene functionality to the D-mannitol backbone. Many peaks appeared at $\delta = 4.0$–5.5 ppm and were attributed to the methine and methylene protons of the partially esterified D-mannitol backbone. The average number of substitution per D-mannitol was calculated to be 4 using integration. The MALDI-TOF MS spectra also exhibited a peak at $m/z = 1986$ Da corresponding to a tetra-substituted compound. A number of peaks at 4.0–5.5 ppm in $^1$H-NMR spectrum implicated that compound 2 was a mixture of regioisomers with differing at the position of the free hydroxyl groups.

3.2 Phase behavior

The hexamer was a monotropic liquid crystal. A smectic C and smectic I/F phases were observed at $109$ °C and $86$ °C respectively, only during the cooling process from the isotropic phase. On heating, it crystallized after a glass transition temperature at ca. $80$ °C. Figure 3 shows the DSC curves for compound 2, in which there are two broad peaks observed for both heating and cooling processes. Observation of using a polarizing optical microscope indicated that the liquid crystalline phases were enantiotropic smectic A, C, and I/F (Table 1). The glass transition temperature appeared around at ~40°C. There was no crystalline phase observed. Therefore, the solid state was a liquid crystalline glass.

![Figure 3](image-url)

Figure 3. The DSC curves observed for compound 2 upon a cooling and heating cycle for the second scan measured at 2 °C min$^{-1}$.  

<table>
<thead>
<tr>
<th>Rate/°C min$^{-1}$</th>
<th>Transition temperature/°C</th>
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<tbody>
<tr>
<td>1</td>
<td>Iso 109 SmC* 86 SmF(I)</td>
</tr>
<tr>
<td>2</td>
<td>Iso 95 SmA 80 SmC 70 SmF(I)</td>
</tr>
<tr>
<td>2</td>
<td>SmF(I) 72 SmC 81 SmA 100 Iso</td>
</tr>
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3.3. Photochemical phase transition

We have previously reported that compound 1 changes between a liquid and solid state upon irradiation with UV and visible light respectively. The small yellow pieces of compound 2 were irradiated with UV light (30 J cm$^{-2}$) as well as the solid of compound 1 (Figure 4a).
The initial solid states are different; the solid of compound 2 was rounded in shape with compared to the solid of compound 1. Compound 2 also changed to a droplet of orange liquid after irradiation with UV light. The change in color to orange implies the formation of the cis isomer of the azobenzene moieties in the compound. On irradiation with visible light, the droplet of orange liquid changed again to a yellow substance with the same shape. The yellow substance was no longer a liquid. As shown in Figure 4c, the yellow substance broke away after being pressed with microspatula. In this process, deformation of the droplet shape was observed before breaking, indicating it was a soft solid.

![Figure 4. Photographs of compound 2 (a) taken before and (b) after irradiation with UV light, (c) after a second irradiation with visible light, and (d) after pressing with a microspatula.](image)

3.4 Control of Adhesion

The hexamer can be used as an adhesive for glass plates. The adhesion forces have been estimated by the shear tensile strength. The preliminary pulling test for compound 1, in which the glass slides were manually separated, revealed that the adhesion force changed from 50 N cm\(^{-2}\) to <1 N cm\(^{-2}\) after irradiation with the UV light, and subsequent irradiation with visible light recovered the initial adhesion force. The adhesion forces on compound 2 were measured in a similar manner. Before irradiation, the adhesion force was 125 N cm\(^{-2}\). The irradiation with UV light reduced it by one sixth (ca. 20 N cm\(^{-2}\)). Subsequent irradiation with visible light enlarged the adhesion force up to 200 N cm\(^{-2}\). These values were higher than those for compound 1. There are two possible explanations for the improvement in the adhesion force observed for compound 2: (i) the difference in viscoelastic properties and (ii) the hydrophilic free hydroxyl groups enhance the adhesion force for the glass plates.

4. Conclusions

The photo induced liquid–solid phase transition was observed in the partially substituted derivative of D-mannitol bearing azobenzene moieties. The compound can be obtained as a by-product of the synthesis of the fully substituted compounds, which have practical value. While the liquid crystallinity is thermodynamically stable, the solid state generated after irradiation with visible light is ambiguous. The quantitative estimation of the viscoelastic properties of the compound will be required for further discussion. The adhesion force could be controlled by irradiation with light. In addition, a stronger adhesion force was achieved upon the irradiation process.

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