



## Gel-solution phase transition of organogels with photoreversibility: L-amino acid organogelators with azobenzene



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### ABSTRACT

Simple organogelators with organic salt structures by mixing of L-amino acid dodecyl esters and azobenzene-4-carboxylic acid, were synthesized and their organogelation properties were examined. These gelators formed organogels in many organic fluids. The acetonitrile gels showed a reversibly photochemical phase transition; they changed into the solution under ultraviolet light (365 nm), and then it was re-formed by visible light irradiation (450 nm). The gel-to-solution phase transition depended on the chemical structure of the L-amino acids. Such the dependency was caused by difference in the aggregation mode of the azobenzene moiety.

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### Introduction

Low-molecular-weight gelators and their supramolecular gels have attracted much attention because of their potential applications to the wide fields (academic interests and industrial materials). Many low-molecular-weight gelators have been reported, and their molecular designs, synthetic methods, gelation mechanisms, nanostructures, and physicochemical properties of the supramolecular gels have been elucidated by many scientists.<sup>1–3</sup> Common supramolecular gels are a physical gel and show the thermally reversible gel-solution phase transition (heating-cooling system). Furthermore, in the last decade, many efforts have been made to exploit supramolecular gel systems responsive to external stimuli, such as mechanical, ultrasound, pH, ions, redox, and enzyme.<sup>4</sup> For wide-ranging applications to, especially, biomaterials such as drug delivery and tissue engineering, and smart materials, it is necessary to have reversible control on the gelation.<sup>5</sup>

Light-induced control is one of the useful methods because it can be modified according to its wavelength, intensity, and polarization.<sup>6</sup> In most of the systems, low-molecular-weight gelators bearing a photosensitive moiety are designed.<sup>7</sup> Azobenzene is one of the well-known photosensitive molecules and is often used in the supramolecular systems.<sup>8</sup> Though it is difficult to construct photochemically reversible phase transition systems, light-induced gel-to-solution or solution-to-gel transition are achieved. There are a number of reversible light-induced gel-solution phase

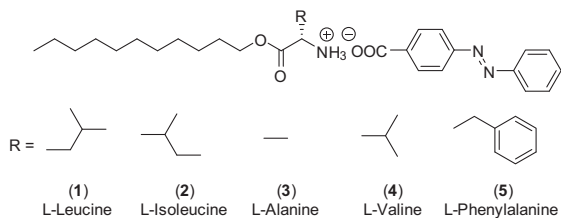
transition systems.<sup>6–8</sup> The aim of most of the systems is a fast phase transition. In contrast, a slow phase transition system may be used depending on the purpose: for example, controlled releases of chemicals. In this communication, we describe the photochemically reversible gel-solution phase transition of supramolecular organogels based on organic salt gelators consisting of L-amino acid dodecyl ester and azobenzene-4-carboxylate acid.

### Results and discussion

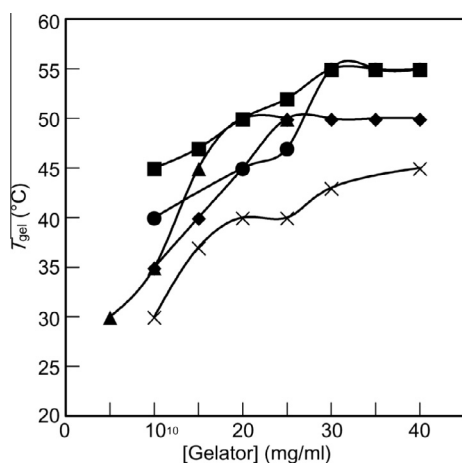
Gelators **1–5** were simply prepared with a high yield (Fig. 1). An L-amino acid was esterified with dodecanol and *p*-toluenesulfonic acid (as a catalyst), and then the organic salt exchanged from *p*-toluenesulfonate into azobenzene-4-carboxylate.<sup>9</sup>

When **1–5** were dissolved in an organic solvent under the heating (80–90 °C) and then the resulting solution was allowed to stand at 25 °C, the organogel was formed. The minimum gel concentration (MGC) was 5–40 mg/ml and most of organogels were opaque.<sup>9</sup> For sulfolane, propylene carbonate, and acetonitrile, these organogelators had a good organogelation ability that they formed the gels at low concentrations. The chemical structure of L-amino acids hardly affected the organogelation ability (MGC). Because the L-amino acid esters and azobenzene-4-carboxylic acid never functioned as an organogelator, the organic salt compounds formed by mixing of the two compounds acted as an organogelator. When the solutions of L-amino acid ester and azobenzene-4-carboxylic acid were mixed, the organogels were formed. The

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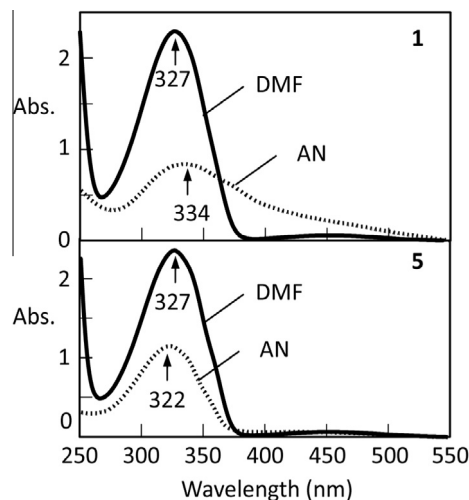
**Figure 1.** Chemical structures of organic salt organogelators.



**Figure 2.** Gel-to-solution transition temperatures ( $T_{\text{gel}}$ ) of acetonitrile gels versus gelator concentration: **1** (■), **2** (●), **3** (▲), **4** (◆), and **5** (×).

morphology of the gels was observed by using an electron microscope. All gelators formed the three-dimensional networks in the gels that the self-assembled nanofibers were complicatedly entangled. These nanostructures were similar to those that common low-molecular-weight gelators form in the supramolecular gels. The self-assembled nanofibers had a diameter of several hundreds of nanometers, and the relatively bold nanofibers may bring about the opaque gel.

**1–5** do not have a functional group which undergoes hydrogen bonding interaction. It is well-known that the hydrogen bonding interaction is one of the main driving forces, and many low-molecular-weight gelators form an organogel through the hydrogen bonding interaction. On the other hand, a number of low-molecular-weight gelators, which do not have a hydrogen bonding site, have also been reported.<sup>10</sup> These gelators form organogels through van der Waals interactions including between the alkyl chains and between aromatic groups ( $\pi$ -stacking). We have also reported the L-leucine ester *p*-toluenesulfonate functions as an organogelator that forms organogels through van der Waals interaction between



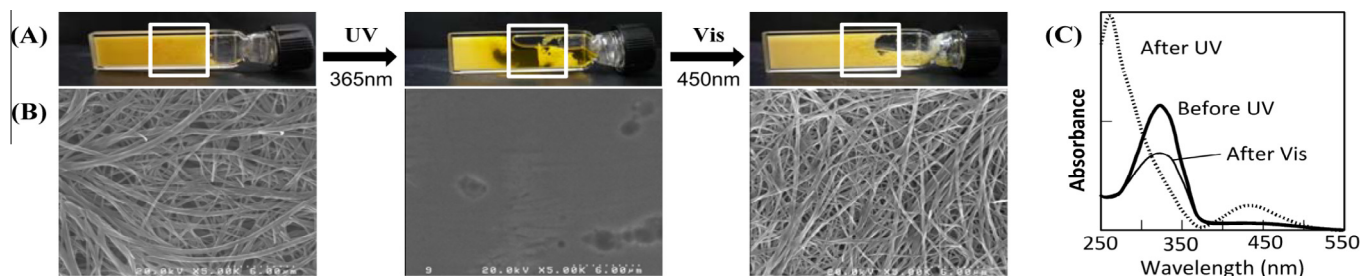
**Figure 4.** UV-Vis absorption spectra of acetonitrile gels and DMF solutions of **1** and **5**.

the alkyl chains and  $\pi$ -stacking of phenyl rings.<sup>11</sup> In the present case, van der Waals interaction, which is between the alkyl chains and between the azobenzenes ( $\pi$ -stacking), is the main driving force for the organogelation (Fig. 1).

The thermal properties of acetonitrile gels were evaluated by the gel-to-solution transition temperature ( $T_{\text{gel}}$ ). Figure 2 shows the  $T_{\text{gel}}$ 's of acetonitrile gels versus the gelator concentrations. For all gelators, the  $T_{\text{gel}}$  values increased with the increasing concentration of gelators. The acetonitrile gels of **1** and **2** were a high thermal stability, and their  $T_{\text{gel}}$  values were 55 °C. **5** could not form the acetonitrile gel over 45 °C; namely, the acetonitrile gel of **5** had the lowest  $T_{\text{gel}}$  value. These acetonitrile gels are relatively soft because the driving force is only van der Waals interaction. Furthermore, the thermodynamic analysis for the gel-to-solution transition was carried out using a van't Hoff relationship.<sup>12</sup> From the relationship between  $T_{\text{gel}}$  and MGC, the gel-to-solution transition enthalpy ( $\Delta H_{\text{gel}}$ ) was determined from the slope of  $\ln[\text{gelator}]$  versus  $(T_{\text{gel}})^{-1}$ . For these organogels, the plots gave a linear relationship. **1** and **2** had the high  $\Delta H_{\text{gel}}$  value (ca. 90 kJ/mol), and  $\Delta H_{\text{gel}}$  values of **3–5** were around 50 kJ/mol. The gel-to-solution transition depends on the enthalpy.

The  $T_{\text{gel}}$  and  $\Delta H_{\text{gel}}$  values depend on the strength of the interaction between the gelator molecules and/or between the nanofibers (entanglements). In the acetonitrile gels, **3–5** have the weaker interactions than **1** and **2**. As the result, the gel-to-solution phase transition of the acetonitrile gels based on **3–5** readily occur.

Interestingly, the acetonitrile gels based on these gelators underwent the isothermal phase transition (gel-to-solution and solution-to-gel) with photoreversibility. The photochemical phase



**Figure 3.** Reversibly photochemical phase transition of acetonitrile gel of **5**. Left: before light irradiation; center: after UV light irradiation (365 nm) for 4 h; right: after visible light irradiation (450 nm) for 30 min. (A) Photographs of phase transition (square is light irradiation spots). (B) FE-SEM images. (C) UV-Vis absorption spectra.

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