Thermoreversible Self-Organized Gels of a Liquid Crystal Formed by Aggregation of *trans*-1,2-Bis(acylamino)cyclohexane Containing a Mesogenic Moiety

Takashi Kato,* Gohta Kondo, and Kenji Hanabusa†
Department of Chemistry and Biotechnology, Graduate School of Engineering,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113
†*Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, Nagano 386*

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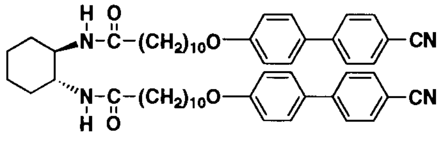
A novel class of anisotropic gels has been obtained by the formation of a self-associated molecular network in a liquid crystal. The gels exhibit thermoreversible two gel states derived from liquid-crystalline and isotropic states of the mesogenic molecule.

Anisotropic gels have great potential as functional materials such as active and passive optical devices and stimuli-responsive materials.[1-5] Generally, thermotropic anisotropic gels have been prepared from cross-linked polymer networks and low molecular weight liquid-crystalline molecules. In these cases, small amounts of covalently cross-linked networks are formed by polymerization of reactive monomers in thin film states of liquid crystals.[1] However, we have considered it important to explore gelation of anisotropic fluids in bulk, which will attract both scientific and technological interests.

We demonstrate here that a novel class of self-organized gels, which is based on self-associated molecular networks and mesogenic molecules, clearly exhibits thermoreversible two gel states derived from liquid-crystalline and isotropic states. Recently, a number of low-molecular-weight gelling agents for common organic solvents have been developed.[6-14] Hanabusa and coworkers reported that the aggregation of compounds derived from *trans*-1,2-aminocyclohexane results in efficient gelation of various common organic solvents.[8,9] We focused on this type of compounds for the gelling agent of thermotropic liquid crystals. *trans*-1,2-Bis(acylamino)-cyclohexane containing a mesogenic moiety (**1**) was designed and prepared as a gelling agent for thermotropic liquid crystals. Diamide compound **1** was prepared from (*1R,2R*)-(–)-1,2-bis(amino)cyclohexane and 11-(4-cyanobiphenyl)undecanoic acid. Compound **1** melts at 157 °C and shows no mesomorphic behavior on heating and cooling runs. A thermotropic mesogenic molecule, 4-heptyloxy-4'-cyano-biphenyl (**2**) was used as an anisotropic solvent. Compound **2** exhibits a nematic state from 54 to 74 °C on heating. The testing of gelation was checked for mixtures of **1** and **2** (ca. 0.2 g) in sealed test tubes. The mixtures were heated to isotropic liquid states and then cooled to the desired temperatures in thermo-controllable oil baths.

Compound **2** has been successfully gelled by compound **1** both in nematic and isotropic states. On heating, the mixtures finally form fluid isotropic liquid states because all of components are low molecular weight compounds. Once the gel state is formed on cooling, the test tube filled with the gelled sample can be turned upside down without flow. The gels exhibit thermoreversible phase transitions including sol-gel, gel-gel, and gel-solid transitions. The DSC thermogram of a mixture of **1** and **2** containing 4.0 mol% of **1** on cooling is shown in Figure 1. When the isotropic liquid of the mixture is cooled, the sol-gel transition from the isotropic liquid to the gel state is seen at 84 °C. The enthalpy change at the sol-gel transition is 4.7 J/g, which corresponds to 47.2 kJ per mole of **1**. It is the association energy of **1** through the formation of the intermolecular hydrogen-bonded network. On further cooling, two exothermic peaks are seen at 73 and 31 °C. The enthalpy changes are 3.1 and 59.2 J/g, respectively. The appearance of the gel formed between 84 and 73 °C is essentially the same as those of normal gels obtained from common organic solvents, while the gel from 73 to 31 °C looks milk-white charasteristic of liquid crystals in bulk. For the single component of **2**, the isotropic-nematic transition is observed at 74 °C and no transition is seen at 84 °C. These results suggest that the isotropic liquid state of **2** is gelled from 84 to 73 °C and the gel-gel transition from the normal gel to the anisotropic gel occurs at 73 °C.



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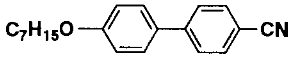

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Figure 2 presents the phase transition behavior as a function of the concentration of **2** for the mixture on cooling. The sol-gel transition temperatures from the isotropic state to the normal gel state show great decrease as the concentration of **2**

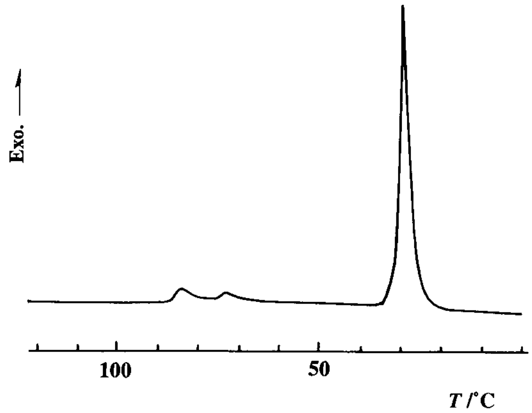

Figure 1. DSC thermogram of a mixture of **1** and **2** containing 4.0 mol% of **1** on cooling.

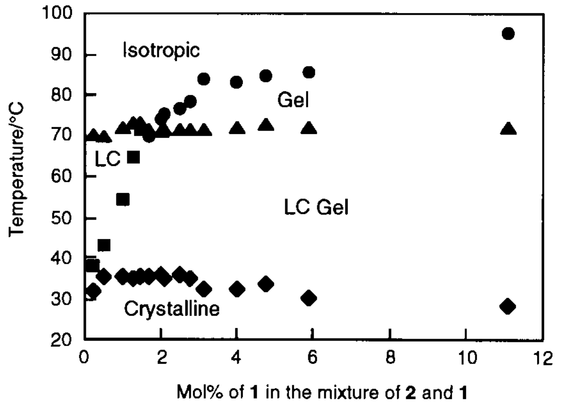

Figure 2. Phase behavior of the mixture of **1** and **2** on cooling. LC: Liquid crystalline.

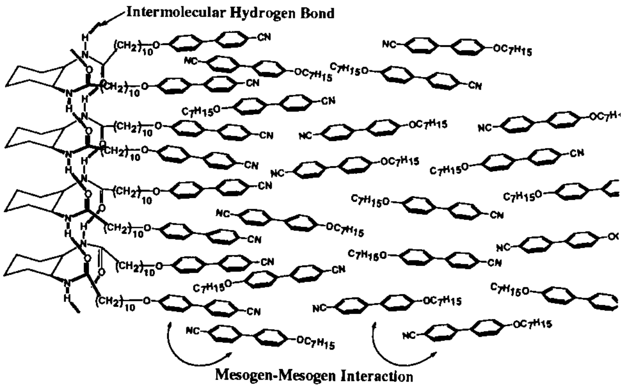

Figure 3. Schematic illustration of the hydrogen-bonded associate of **1** which gels **2** in the nematic state.

decreases. The gelation of the isotropic state of **2** is observed when the concentration of **1** is more than 1.8 mol%. For a mixture containing 1.4 mol% of **1**, the transition from isotropic to a chiral nematic state is observed at 73 °C on cooling. A fingerprint texture of the chiral phase is clearly seen on cooling from the isotropic state. The subsequent transition observed at 69 °C corresponds to the transition from a chiral nematic phase to a liquid-crystalline gel phase. This cholesteric phase is induced by the chiral gelling agent. On further cooling, the transition from the chiral nematic to the anisotropic gel is seen at 67 °C.

FT-IR spectra of the gels show two bands at 3285 and 1637 cm^{-1}, which correspond to the N-H and C=O stretching bands involving hydrogen bonds respectively. This observation shows that compound **1** forms a molecular tape through the formation of hydrogen bonding chains.[8] Schematic illustration of the structure of the liquid-crystalline gel is shown in Figure 3. In contrast, in isotropic states, these bands shift to 3400 and 1671 cm^{-1}, indicating the dissociation of the hydrogen bonds.

A diamide compound, *trans*-1,2-bis(acylamino)cyclohexane **1** containing a mesogenic moiety functions as a gelling agent for isotropic and liquid-crystalline states of a cyanobiphenyl, which is one of representative molecules for liquid crystals. The self-organized gels are easily prepared by simple mixing of a liquid-crystalline molecule and a gelling agent. Significantly, the thermoreversible four states, solid, liquid-crystalline gel, normal gel, and isotropic liquid are achieved for this self-organized gel. Such clear phase transitions are first observed for anisotropic molecular systems. This material can be used for new dynamic gels which respond to various stimuli in bulk. Studies on various properties of the gels are in progress.

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