Liquid-Crystalline Physical Gels: Self-Aggregation of a Gluconamide Derivative in Mesogenic Molecules for the Formation of Anisotropic Functional Composites

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Liquid-crystalline physical gels have been obtained by the self-aggregation of a gluconamide derivative through intermolecular hydrogen bonding in liquid crystals. These liquid-crystalline gels are microphase-separated composites consisting of the solid fibrous aggregates of the gelling agent and the liquid-crystalline phase of mesogenic molecules. Thermoreversible three states, isotropic liquid, normal (isotropic) gel, and liquid-crystalline gel, have been achieved for the mixtures of liquid crystals and the gelling agent. As the concentration of the gelling agent increases, the sol−gel transition temperature and the enthalpy change of the transition from isotropic to anisotropic increase. The increase of the enthalpy change suggests that some mesogenic molecules are anchoring strongly to the surface of the fibrous gelling agents. Variable-temperature infrared spectra show that the association and the dissociation of intermolecular hydrogen bonding of the gelling agent occur in the process of the sol−gel transition. Liquid-crystalline gels are responsive to electric fields in a twisted nematic (TN) cell. These anisotropic gels would be applicable to new dynamically functional materials.

Liquid crystals are unique molecular materials because of their anisotropic nature and molecular dynamics.[1,2] Although these materials have been developed as advanced materials for electrooptical devices and high-strength polymeric materials, they are expected to have great potential as dynamically functional materials for an even greater variety of applications. On the other hand, physical gels of common organic solvents obtained by the aggregation of low-molecular-weight compounds have attracted attention from the viewpoint of supramolecular chemistry and material science.[3−5] In such normal physical gels, solvents possess isotropic structures and no anisotropic dynamic behavior is introduced. We expected that liquid crystals would be gelled by low-molecular-weight gelling agents for common solvents, which results in the formation of a new type of functional material. Liquid-crystalline physical gels were successfully obtained by the molecular association of amide compounds in thermotropic liquid crystals.[6−9] Such anisotropic physical gels are microphase-separated composites consisting of the solid phase of fibrous aggregates and the liquid-crystalline phase of mesogenic molecules. Significant dynamic response and interesting structural features were observed for these gels.[6−9] For example, they were able to respond to electric fields in macroscopically soft-solid states because these materials have both properties of liquid crystals and physical gels.[6,7] Faster response to electric fields was attained for nematic anisotropic gels.[7] Fibrous aggregates oriented to one direction, which lead to ordered molecular composites, were developed in smectic physical gels.[8] In contrast to chemical anisotropic gels,[2,10,11] these physical gels were fabricated by simple self-assembly processes of hydrogen-bonded molecules and they exhibited thermoreversible structural changes between anisotropic gels and isotropic liquid states.[6−9] Amino acid derivatives and diamide compounds were used for the gelation of liquid crystals.[6−9] Sugar compounds are also capable of forming molecular associates with unique structures

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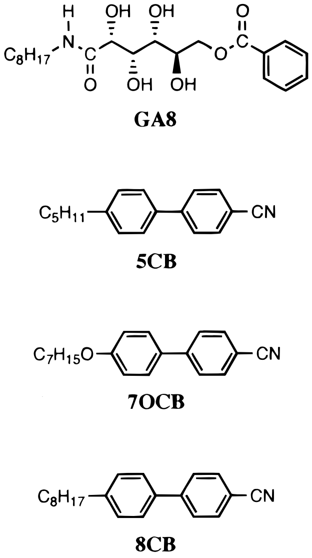
Chart 1



and properties,[5,12−15] which would be useful for the fabrication of functional anisotropic gels. Compound **GA8**, which has four hydroxyl groups and one amide group, was shown to gel common organic solvents efficiently.[5] Such gluconamide derivatives were reported to exhibit a variety of associated structures.[12−14] In the present paper, we report the formation of liquid-crystalline physical gels by the self-aggregation of **GA8** through intermolecular hydrogen bonding in the mesogenic molecules, **5CB**, **7OCB**, and **8CB** (Chart 1).

Experimental Section

Preparation of Anisotropic Gels. The synthetic procedure of gluconamide derivative **GA8** was described previously.[5b] **GA8** and a liquid crystal were mixed in a sealed test tube. The mixture was heated to an isotropic liquid state and then cooled to appropriate temperature.

Characterization of Anisotropic Gels. Phase behavior of the samples was determined by DSC measurements and microscopic observation. DSC measurements were performed with a Mettler DSC 30. Heating and cooling rates were 5 °C/min in all cases. Transition temperatures were taken at the maximum of transition peaks. A polarizing microscope, Olympus BH2 equipped with a Mettler FP82HT hot stage was used for visual observation. Variable-temperature FT-IR measurements were performed on a Jasco MFT-2000 spectrometer equipped with a Mettler FP82 hot stage. A mixture of **5CB** and **GA8** containing 2.0 mol % of **GA8** was used for SEM (scanning electron micrograph) observation. The sample was heated to an isotropic liquid state between slide glasses. This glass cell was cooled to room temperature. A SEM sample was prepared by immersing the glass cell in hexane to extract the liquid-crystalline solvent followed by drying at room temperature. The cover glass was removed and the sample was shaded with gold. SEM observation was performed with JEOL JSM-5400/LV.

Measurement of Electrooptic Effects. Measurements of electrooptic effects in the anisotropic gels were performed with ITO (indium tin oxide) glass sandwich cells (1 cm × 1 cm × 16 μm) coated with polyimide (JSR AL1254) layers, in which the rubbing direction of the two surfaces was perpendicular. Response time was measured at 10 V. Alternating current (ac) fields (300 Hz) were applied to the cells. He−Ne laser (633 nm) was used as a light source.

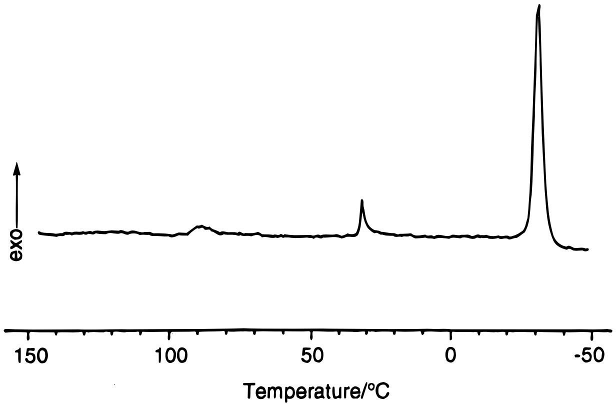


Figure 1. DSC thermogram of the mixture of **5CB** and **GA8** containing 2 mol % of **GA8** on cooling.

Table 1. Thermal Properties of the Mixtures of 5CB and GA8

mixture mol % of **GA8**	isotropic−anisotropic transition temperatures[a] (°C)	sol−gel transition temperatures[b] (°C)
0[c]	33 (0.65)[d]	
1.0	33 (0.80)	80 (20.3)
2.0	32 (0.80)	89 (20.6)
4.8	30 (0.84)	109 (21.1)
9.1	29 (1.13)	113 (21.5)
100[e]		131 (46.2)[f]

[a] Enthalpy change in parentheses (kilojoules per mole of **5CB**). [b] Enthalpy change in parentheses (kilojoules per mole of **GA8**). [c] The single component of **5CB**. [d] The transition from isotropic to nematic. [e] The single component of **GA8**. [f] The transition from isotropic melt to crystal.

Results and Discussion

Liquid crystals **5CB**, **7OCB**, and **8CB** have been successfully gelled by gluconamide derivative **GA8**. Once the gel is formed on cooling from an isotropic liquid state, the mixture does not flow. On heating, the mixture finally forms a fluid isotropic liquid. Figure 1 shows the DSC thermogram of a mixture of **5CB** and **GA8** containing 2.0 mol % of **GA8** on cooling. It exhibits three exothermic peaks, which are attributable to sol−gel transition, gel−gel transition, and crystallization, respectively. The normal (isotropic) gel state appears between 89 and 34 °C. On further cooling, the isotropic−anisotropic transition to liquid-crystalline gel state is seen at 34 °C.

Parts a and b of Figure 2 show the phase transition behavior of the mixtures of **GA8** and liquid crystals **5CB** and **7OCB** as a function of the mol % of **GA8** on cooling. Table 1 gives thermal properties of the gel consisting of **5CB** and **GA8**. The sol−gel transition temperatures from isotropic liquid states to normal gels increase as the concentration of **GA8** increases. The enthalpy changes on the sol−gel transitions also slightly increase. These results suggest that with the increase of the mole % of **GA8** the aggregated structures of **GA8** become similar to that of a neat crystal, which is more stable. The temperatures from isotropic gels to anisotropic gels slightly decrease with the increase of mole % of **GA8**. This decrease may be caused by a small amount of **GA8** dissolved in the liquid crystals. It is noteworthy that

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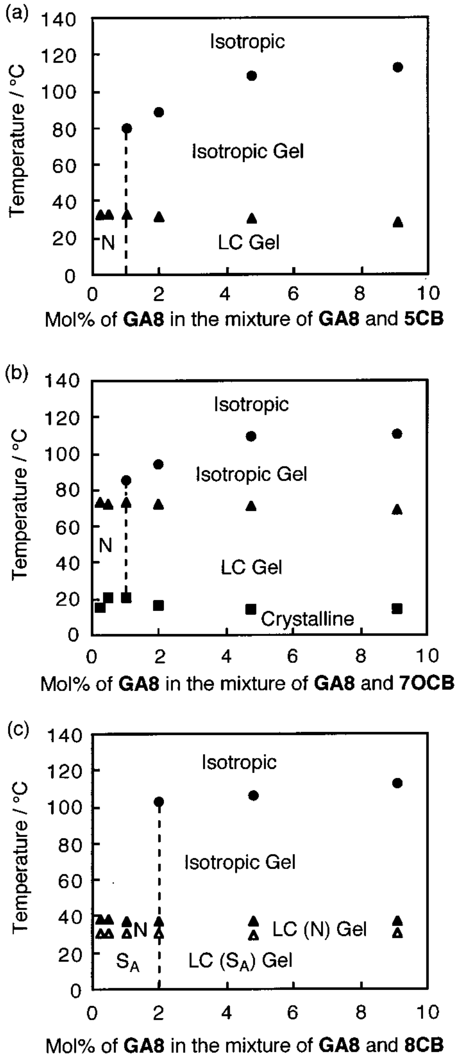


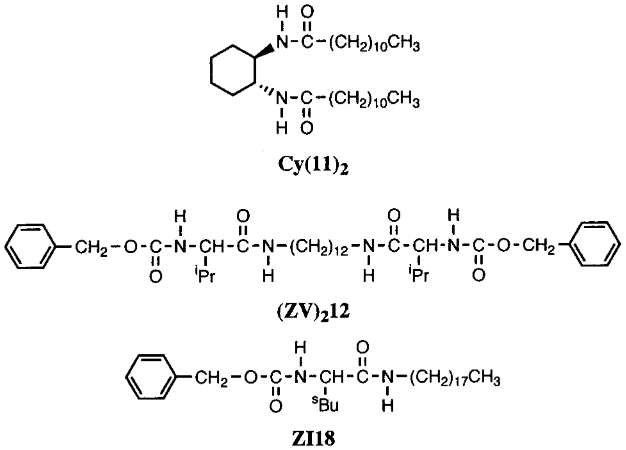
Figure 2. Phase diagrams of the mixture of **GA8** with liquid crystals (a) **5CB**, (b) **7OCB**, and (c) **8CB**, on cooling. Abbreviations: LC, liquid-crystalline; N, nematic.

Table 2. Comparison of Sol–Gel Transition Temperatures of Anisotropic Gels Consisting of 5CB and Gelling Agents

	transition temperatures (°C)	
gelling agent	2.0 mol %[a]	4.8 mol %[a]
GA8	89	109
Cy(11)$_2$[b]	84	95
(ZV)$_2$12[c]	92	100
ZI18[c]	49	55

[a] Concentration of gelling agent. [b] Reference 6. [c] Reference 7.

Chart 2



Cy(11)$_2$

(ZV)$_2$12

ZI18

as the concentration of the gelling agents increases, the enthalpy change of the transition from isotropic to anisotropic increases. This observation suggests that some of mesogenic molecules are anchoring strongly to the surface of fibrous gelling agents in the anisotropic gel state. For compound **8CB**, both smectic A and nematic states have been gelled by **GA8** as is shown in Figure 2c. The sol–gel transition temperatures of the mixture of **8CB** and **GA8** show a similar increasing trend to those based on **5CB** and **7OCB**. The nematic–smectic transitions occur in the gel state and these temperatures are almost free of the concentration of gelling agent. The sol–gel transition temperatures of the gel consisting of **GA8** do not depend on the liquid crystal components. In previous papers,[6,7] we reported that **Cy(11)$_2$**, **(ZV)$_2$12**, and **ZI18**, were able to gel **5CB**. Table 2 compares the sol–gel transition temperatures of the anisotropic gels based on **5CB**. It is considered that the temperatures reflect the stability of the H-bonded molecular aggregates of the gelling agents. The gels obtained by **GA8** exhibit high thermal stability. The sol–gel transition of the gel obtained by **(ZV)$_2$12**, which is a bolaform amino acid compound, shows the highest temperature at the concentration of 2.0 mol %. For the concentration of 4.8 mol %, the transition temperature of the gel obtained by **GA8** becomes the highest. As for the minimum concentration for the gelation of **5CB**, the concentration of 1.0 mol % is needed for **GA8**, while less than 0.5 mol % should be added for **Cy(11)$_2$**, **(ZV)$_2$12**, and **ZI18** (Chart 2). **GA8** has four hydroxyl groups together with an amide group. It is known that stable hydrogen-bonded networks are formed for amphiphilic polyhydroxyl compounds.[12–15] The gels based on **GA8** exhibit more thermal stability at higher concentrations due to the formation of more stable H-bonded network by four hydroxyl groups.

To examine aggregated states of **GA8** in the mesogenic molecules, variable-temperature infrared measurements have been performed on the gels and on the isotropic states of the mixture of **GA8** and **5CB**. Figure 3 shows the infrared spectra in the range of 1500–1800 and 3100–3800 cm^{-1} from 140 to 50 °C. In isotropic liquid states, broad hydroxyl bands are seen at 3459 cm^{-1}, which suggests hydroxyl moieties are free of H bonding. Once the mixture becomes the gel state, these peaks shift to 3277 cm^{-1}, indicating that H bonding is formed at the sol–gel transition. The C=O bands of the amide group are observed between 1680 and 1660 cm^{-1} in isotropic liquid states, which shows the amide group is free of hydrogen bonding. In gel states, two bands are observed at 1665 and 1616 cm^{-1}. The 1616 cm^{-1} band is ascribed to the C=O band involved in hydrogen bonding. This band overlaps with the stretching band of the aromatic group. These changes suggest that in the gel states most of the amide groups are involved in hydrogen bonding, while some amide groups remain free of hydrogen bonding. In contrast, no free carbonyl peak was seen for the gel of cyclohexanediamide **Cy(11)$_2$**.[6] For the C=O band of the ester group, the shift from 1722 to 1703 cm^{-1} in the process of the sol–gel transition shows that hydrogen bonding is formed for the ester groups in the gel states. For **GA8**, the assembly of the

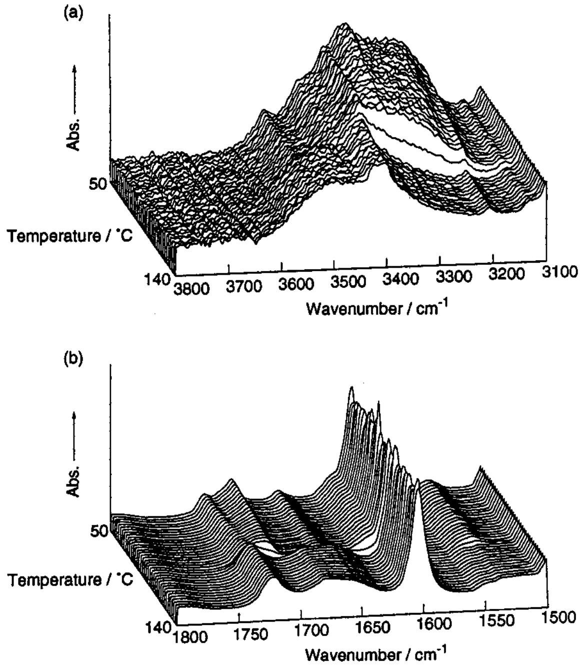


Figure 3. Infrared spectra of the mixture of **5CB** and **GA8** containing 2 mol % of **GA8** in the range (a) 3100−3800 cm^{-1} and (b) 1500−1800 cm^{-1}, from 140 to 50 °C.

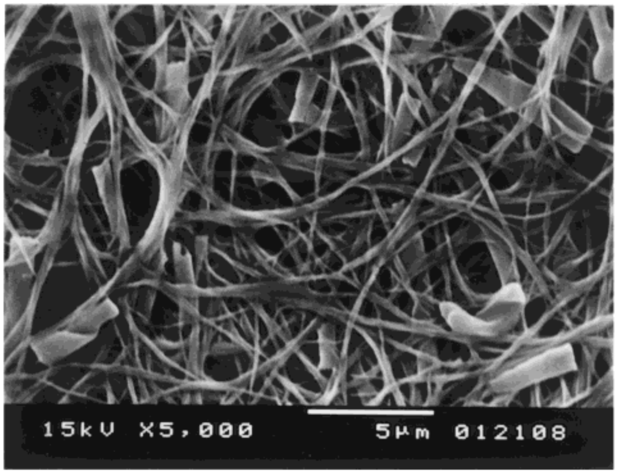


Figure 4. SEM image of fibrous aggregates of **GA8** assembled in **5CB** after the extraction of **5CB**.

hydroxyl groups, the ester group, and the amide group through hydrogen bonding leads to the formation of fibrous aggregates in liquid crystals. This observation agrees with the result that the enthalpy changes at sol−gel transitions are smaller than that of the melting of the crystal of **GA8**, which is shown in Table 1.

Figure 4 shows a SEM picture of **GA8** fibers obtained by its self-assembly process in an isotropic state of mesogenic molecules. Recently, we found that oriented fibrous aggregates of the gelling agents were obtained when the sol−gel transition occurs in the temperature range of the smectic state.[8] For the mixture of **5CB** and **GA8**, the aggregation due to H bonding occurring in the isotropic state results in the formation of randomly oriented fibrous aggregates as shown in Figure 4. The diameter of the fibers ranges from 0.2 to 1.0 μm.

Response to electric fields has been measured on the anisotropic gels consisting of **GA8** and **5CB**. The gels were placed in a conductive glass TN cell coated with a polyimide where the rubbing direction of two surfaces was perpendicular. Figure 5 shows the change of light transmittance of the gels as a function of voltage. The gels are responsive to electric fields. For the gel of **5CB** containing 1.0 mol % of **GA8**, the threshold voltage is 1.6 V, while that of the single component of **5CB** is 1.2 V. The contrast becomes low for the gel with 4.8 mol % of **GA8**. The response time of the gel with 1 mol % of **GA8** is 16 ms, while that of **5CB** alone is 12 ms. For the gels based on **GA8**, faster response, which was attained for the gels based on **ZI18**,[7] is not observed. However, it should be noted that the anisotropic gels obtained by **GA8**, which forms structurally stable physical gels, are responsive to electric fields, while no response is observed for the gels by **(ZV)$_2$12**,[7] which also forms stable gels.

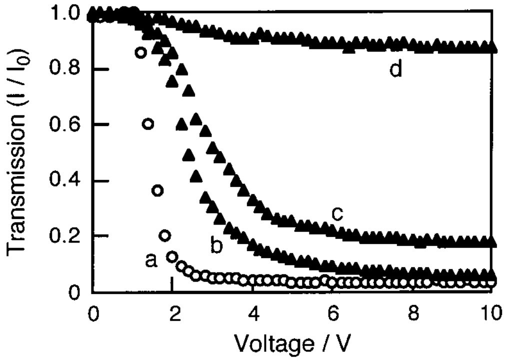


Figure 5. Relationship between transmittance and applied voltage for liquid-crystalline gels consisting **5CB** and **GA8** in a TN (twisted nematic) cell. Mole % of **GA8** in the mixture: (a) 0 mol %; (b) 1.0 mol %; (c) 2.0 mol %; and (d) 4.8 mol %.

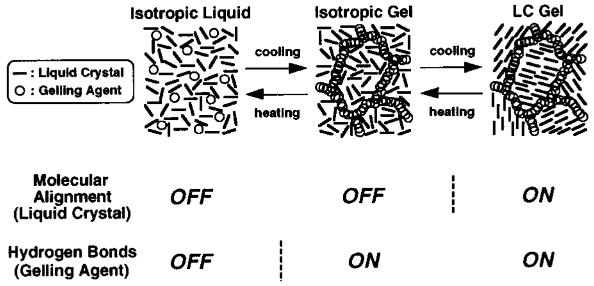


Figure 6. Schematic illustration of thermoreversible transitions of an anisotropic physical gel system.

The anisotropic liquid-crystalline physical gels are a new type of materials, which would be applicable to new dynamically functional materials. The phase transition behavior of the anisotropic physical gels reported here is schematically shown in Figure 6. For the mixtures of liquid crystals and the gluconamide, thermoreversible three states, isotropic liquid, normal (isotropic) gel, and liquid-crystalline gel, have been achieved by the on−off control of the hydrogen bonding and the anisotropic−isotropic phase change of the mesogenic molecule. It should be noted that each of sol−gel and isotropic−anisotropic transitions can be tuned independently by the choice of gelling agents and liquid crystals, respectively.

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