

Smectic liquid-crystalline physical gels. Anisotropic self-aggregation of hydrogen-bonded molecules in layered structures

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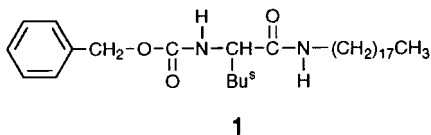
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Smectic liquid-crystalline states have been successfully gelled by low molecular weight hydrogen-bonded molecules and anisotropic fibrous aggregates of the gelling agents are obtained when the sol-gel transition occurs within the smectic temperature range.

In recent years, a number of low molecular weight compounds have been found to gel various organic solvents.¹ The self-aggregation of the gelling agents through intermolecular interactions, such as hydrogen bonding, leads to the formation of solid fibrous networks in organic solvents. Recently, we have shown that nematic liquid crystals can be gelled by these hydrogen-bonded compounds.² Faster electro-optic responses of nematic materials induced by this physical gelation have been achieved in twisted nematic cells.³ These mixtures of liquid crystals and gelling agents show three thermoreversible states: isotropic liquid, isotropic gel, and liquid-crystalline gel.^{2,3} In these cases, the aggregation of the gelling agent occurs in the isotropic state of mesogenic molecules on cooling the sample from the isotropic liquid, which results in the formation of random networks of dispersed fibres. The liquid-crystalline gel is obtained at the transition of the isotropic state to the liquid-crystalline state of mesogenic solvents.

Smectic liquid crystals have higher molecular order which leads to potential applications in functional devices.⁴ We expect that the molecular self-organization in smectic mesomorphic order leads to the fabrication of smectic gels, which are a new type of anisotropic material.

Here, we report the anisotropic aggregation of a hydrogen-bonded compound in a smectic molecular structure and the gelation of a smectic liquid crystal. A commercially available ferroelectric liquid crystal, SCE8 (Hoechst), which is a mixture of low molecular weight compounds, was used as a smectic material. On cooling, SCE8 exhibits isotropic-nematic, nematic-smectic A, smectic A-chiral smectic C phase transitions at 102, 78 and 58 °C, respectively. Amino acid derivative **1**, which is able to gel various organic solvents and nematic liquid crystals by the formation of intermolecular hydrogen bonds,⁵ was chosen as the gelling agent.



When the gelling agent was added to SCE8 and then cooled to room temperature, **1** effectively gelled the smectic liquid-crystalline state. Fig. 1 shows the phase transition behavior of a mixture of SCE8 and **1** as a function of the concentration (wt%) of **1** on cooling. In this system, the sol-gel transition occurs within the range of smectic A and chiral smectic C phases. In the gelation process of SCE8 with **1**, the growth of fibrous network aggregates of **1** and the microphase separation in the poly-

domain of the smectic liquid-crystalline state have been observed under a polarizing optical microscope.

In order to control the aggregation process of **1** in the smectic liquid-crystalline state, a mixture of SCE8 and **1** was placed between polyimide-coated glass substrates, which had been rubbed in the parallel direction. The mixture was then heated to an isotropic state, and slowly cooled to the required temperature. The formation of fibrous solids ordered in one direction was formed in the smectic liquid-crystalline medium. A polarized photomicrograph of the mixture of SCE8 and **1** containing 1.0 wt% of **1** in a parallel rubbed cell is shown in Fig. 2(a). Interestingly, the growing direction of the fibres is perpendicular to the rubbing direction, *i.e.* to the direction of the long axis of the liquid-crystalline molecular order. The scanning electron micrograph (SEM) in Fig. 2(b) represents the directional ordering of the bundles of the fibres.† FTIR measurements of the mixture of SCE8 and the anisotropic fibre of **1** in the parallel rubbed cell showed that the absorbance of the amide bond of **1** at 3294 cm⁻¹ (N-H stretch) and 1647 cm⁻¹ (C=O stretch) was at a maximum value when the polarized light was perpendicular to the molecular orientation of liquid-crystalline molecules, whereas the minimum absorbance was observed when the polarized light was parallel to the long axis of the liquid crystal.‡ These results suggest that compound **1** forms an anisotropic aggregation structure as shown schematically in Fig. 3.

In contrast to the results of the SCE8 mixture, for covalently bonded polymers that are formed in liquid crystals,⁶ the direction of the fibre is parallel to the molecular axis of the anisotropic solvents. For the formation of hydrogen-bonded aggregates of compound **1**, the compound is also aligned in the direction of the molecular axis of SCE8 and thereby the hydrogen bonding chains develop in the direction perpendicular to the molecular long axis between the smectic molecular layers.

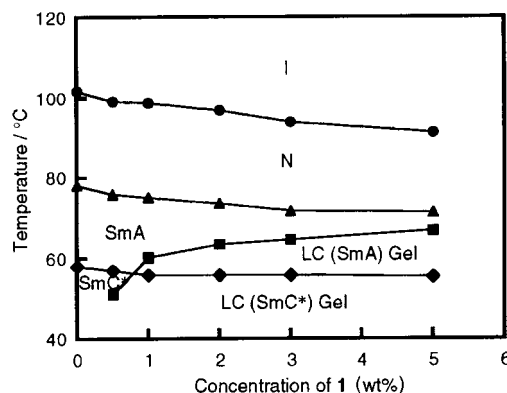


Fig. 1 Phase behavior of a mixture of SCE8 and **1** on cooling. I: isotropic; N: nematic; SmA: smectic A; SmC*: chiral smectic C; LC: liquid-crystalline.

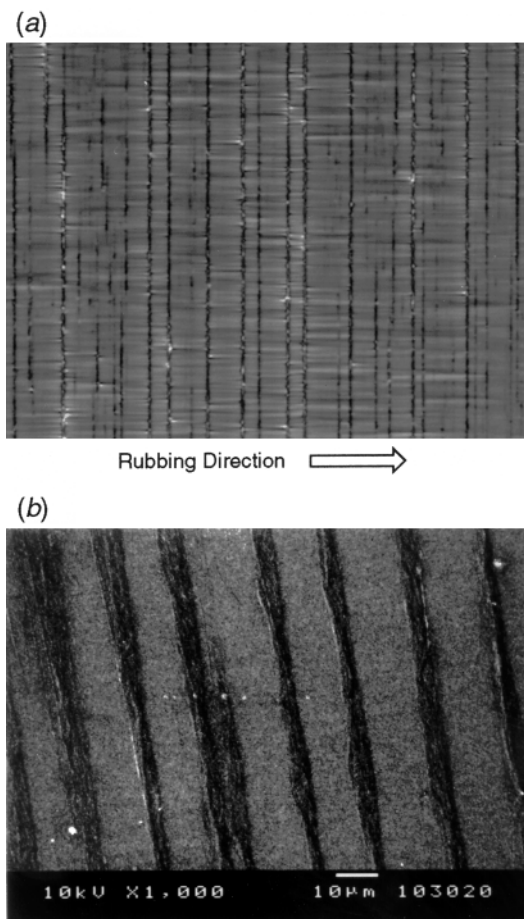


Fig. 2 (a) Optical polarized photomicrograph of a mixture of SCE8 and **1** (1.0 wt%) at 60 °C in a parallel rubbed cell; (b) SEM image of oriented fibres made of **1** after the extraction of SCE8.

Up until now, although molecular self-aggregation in isotropic solvents has been extensively studied, no attention had been paid to molecular assembly in anisotropic solvents. The present results show a controlled molecular aggregation in anisotropic solvents, which is a new class of self-assembly.

The composite materials of covalently bonded polymers and ferroelectric liquid crystals are studied for potential electro-optic systems.⁷ The smectic liquid-crystalline gel reported here is a new material, which is a molecular composite consisting of a molecular aggregate and a smectic solvent. It offers potential applications in dynamically functional molecular materials.

Notes and references

† For SEM observation, samples in the cells were prepared by immersing the liquid-crystalline materials in hexane for two days to remove the liquid-crystalline solvent and finally drying at room temperature.

‡ For polarized FTIR measurements, sample cells were prepared by using BaF₂ substrates instead of glass cells.

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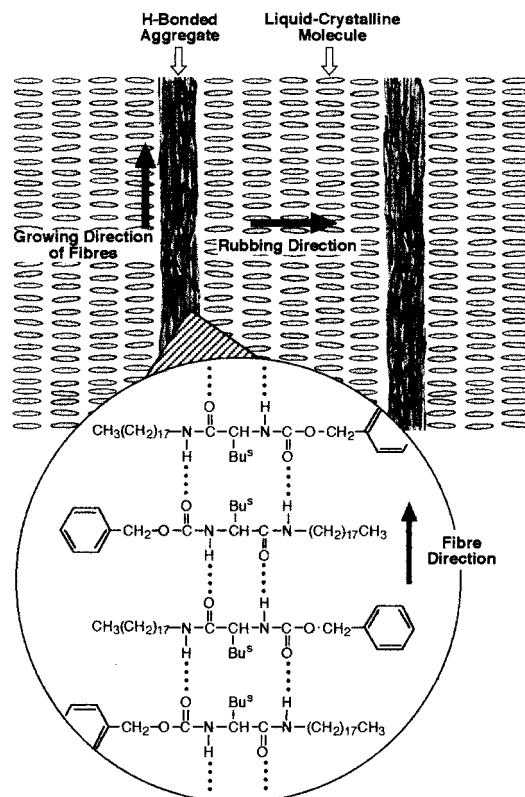


Fig. 3 Schematic representation of the anisotropic aggregation structure of **1** in a smectic liquid crystal.

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