X-ray and SEM Observations of Smectic A Phase and Dried Gel Fibers Formed in a Fine Capillary

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(Received August 22, 2005; CL-051072)

Gel fibers of 2-oxochromen-6-yl 4-(*S*)-(2,6-dimethylheptyloxy) and 4-(*S*)-(3,7-dimethyloctyloxy)benzoates in cyclohexane were observed to grow along the surface of wall in a fine capillary. The structure of the oriented fibers was characterized by SEM and X-ray diffraction measurements, and the fiber structure was compared with the layer one in the smectic A phase.

The self-assembly of molecules produces some thermodynamically interesting states such as crystal, liquid crystal (LC), gel, colloid, and so on, and is one of the current interests in connection with development of functional nanomaterials.

For gelation, generally, intermolecular interactions such as hydrogen bonding, ionic and π–π ones, and van der Waals forces are considered to be important factors, as well as the solvophobic effect.[1] Similar interactions sometimes give rise to lyotropic and/or thermotropic LC states.

Recently, we reported that some lactone compounds incorporating chromen-2-one and benzofuran-2-one skeletons have broad gelation ability for various organic solvents,[2] and simultaneously, most of these derivatives reveal thermotropic LC phases.[3,4] In a previous paper, we proposed that polar interactions involving the dipole around the broad lactone moiety are responsible for both gelation and LC properties, because the lactone core has an abnormally large dipole moment (≈4 D) among conventional organic functional groups.[4] We are interested in factors influencing for the formation of both gel and LC states, their structures, and also any correlation between them.

In this paper, we describe the structural correlation between gel fibers and smectic A phase on the basis of small angle X-ray diffraction and SEM observations. For the purpose, two low mass gelators, 2-oxochromen-6-yl 4-(*S*)-(2,6-dimethylheptyloxy)- (**1**-*S*-7) and 4-(*S*)-(3,7-dimethyloctyloxy)benzoates (**1**-*S*-8) were designed and prepared. The chemical structures are shown in Figure 1.

The phase-transition behavior of **1**-*S*-7 and **1**-*S*-8 is shown in Table 1, and also **2**-*n* ($n = 8$) for comparison. For the series of **2**-*n*, the $n = 8$ homologue reveals a monotropic nematic (N) phase, and a monotropic SmA one is formed from the nonyloxy homologue.[3] On the other hand, introduction of an (*S*)-2,6-di methylheptyl group or an (*S*)-3,7-dimethyloctyl one facilitates the appearance of the SmA phase, though the SmA–I transition temperatures are lower by ca. 30 °C than the N–I one of **2**-8. Therefore, the chiral derivatives, **1**-*S*-7 and **1**-*S*-8 are considered to be suitable for present materials. We have already reported that the most homologues of **2**-*n* have broad gelation ability for various organic solvents.[2] Both **1**-*S*-7 and **1**-*S*-8 can also gelate *n*-octane, cyclohexane, some alcohols such as ethanol, 1-octanol, and so on. Preparations of gel and LC samples are shown in Scheme 1.

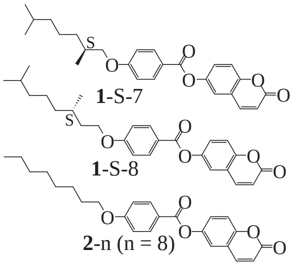


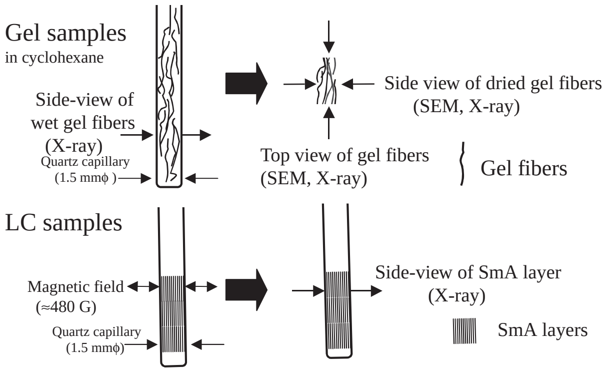
Figure 1. Chemical structures of **1**-*S*-7, **1**-*S*-8, and **2**-8.

Table 1. Phase-transition behavior of **1**-*S*-7, **1**-*S*-8, and **2**-8[a]

	Transition temperatures /°C							Latent heats /kJ mol^{-1}	
	C		SmA		N		I	$\Delta H_{\mathrm{SmA–I}}$	$\Delta H_{\mathrm{N–I}}$
1-*S*-7	•	63	(•	50)	—		•	1.8	
1-*S*-8	•	68	(•	54)	—		•	1.5	
2-8	•	105	—		(•	88)	•		0.8

[a] C, SmA, N, and I indicate crystal, smectic A, nematic, and isotropic phases, respectively. Parentheses indicate a monotropic transition.

A sample (ca. 20 mg) was dissolved in cyclohexane (1.0 mL) by heating, and the resulting solution was packed into a quartz capillary (1.5 mmϕ) then stored overnight. The capillary tube is originally a cell for X-ray measurement of LC materials. The solvent, cyclohexane, was removed by a freeze-dry method, and the residual white or colorless lumps (dried gel fibers) were taken by physical destruction of the capillary. The X-ray and SEM observations were carried with a piece of the lumps, as shown in Scheme 1. The LC samples for the X-ray observation were also prepared in the quartz capillary, where the isotropic solution of both derivatives was gradually cooled down to 46–52 °C under a magnetic field of ca. 480 G. Both **1**-*S*-7 and **1**-*S*-8 do not show the N phase, so that the molecular alignment with-



Scheme 1. Preparations of gel and LC samples.

in the capillary may be incomplete.

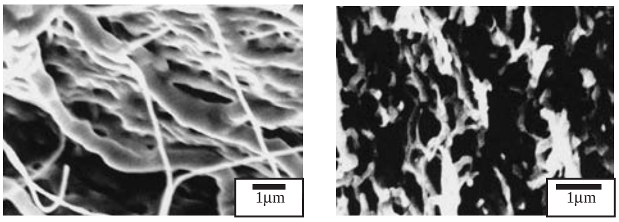
The observation of the polarizing microscope (100×) indicated that the interior (the gel state) of the capillary is optically uniform and has an apparent birefringence below the gel–sol transition temperature.

The SEM pictures viewed from the side and top directions of the dried gel fibers for **1**-*S*-8 are shown in Figure 2.

The gel fibers for **1**-*S*-8 in the side-view picture in Figure 2 have a right-handed helix, where the pitch appears to be on the order of μm. On the other hand, the top-view picture of the gel fibers shows circles rather than fibers, where the diameter is 100–200 nm, and the size seems to be fairly uniform. These results indicate that the gel fibers grow along the surface of the wall on average, namely longitudinal direction of the fine and long capillary. On the contrary, the dried gel of **1**-*S*-7 forms similar fibers with a left-handed helix. Interestingly, the helical twist sense is identical with that in a chiral smectic C phase for 4-pentylphenyl 4-alkoxybiphenyl-4′-carboxylates incorporating a chiral atom and some related LC materials.[5,6]

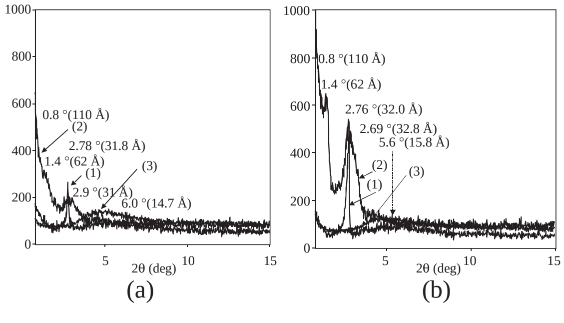
The gel samples were characterized by small angle X-ray diffraction measurement, and the results are shown in Figure 3. Both gels of cyclohexane (ca. 5.0 wt %) in the capillary are almost transparent. The wet gels did not show any reflection peak in a small angle region, probably owing to the very weak intensity. In fact, highly minute experiments suggest that Bragg's reflection phenomena are observed even in an wet gel state, and the reflection angle can be well correlated with the thickness of the elemental gel fibers.[7,8]

On the other hand, the dried gels taken from the capillary are white in appearance due to diffused reflection, and the X-ray profiles show a characteristic feature, as shown in Figure 3. The side-view profile for the dried gel of **1**-*S*-7 shows three reflection peaks at $2\theta = 0.8$ (shoulder (sh)), 1.4 (sh), and 2.9° with a half width of ca. 13 Å as well as a weak and broad one around $2\theta = 15$–$20°$. A broad and weak reflection may be present around $2\theta = 6°$. Interestingly, the top-view profile in Figure 3a does not show any reflection peak. Similarly, the side-view profile for the dried gel of **1**-*S*-8 shows three reflection peaks at $2\theta = 0.8$ (sh), 1.4, 2.76° with a half width of ca. 10 Å as well as a weak and broad one at 15–20°. The top-view profile of **1**-*S*-8 in Figure 3b also does not show any reflection peak. These results indicate that the reflection peaks can be observed only in the side-view profiles of the dried gel fibers, and the gel fibers arrange along the longitudinal direction of the fine capillary, on average.



(a) (b)

Figure 2. SEM pictures of dried gel fibers for **1**-*S*-8: (a) side-view and (b) top-view (refer to Scheme 1).



(a) (b)

Figure 3. X-ray profiles of: (a) **1**-*S*-7 and (b) **1**-*S*-8. The profiles, (1), (2), and (3) are in the SmA phase at 46 °C (**1**-*S*-7) and 52 °C (**1**-*S*-8), dried gel fibers viewed from the side and top, respectively.

On the other hand, the X-ray profiles for the SmA phase of **1**-*S*-7 and **1**-*S*-8 in the capillary show a sharp reflection maximum at $2\theta = 2.78°$ (31.8 Å) at 46 °C and 2.69° (32.8 Å) at 52 °C, respectively. The longitudinal lengths of **1**-*S*-7 and **1**-*S*-8 were calculated by MOPAC2000 to be 23.0 and 23.8 Å, respectively. Therefore, the wide layer spacings indicate that **1**-*S*-7 and **1**-*S*-8 form so-called "partially bilayer[9]" arrangement of the molecules in the SmA phase, where the ratios of layer spacing to the molecular length for both **1**-*S*-7 and **1**-*S*-8 are 1.38.

In our previous paper, we supposed that polar interactions around the terminal lactone moiety play some important roles for the formation and stabilization of the polar SmA phase.[4]

It is worthy of note that the reflection peaks arising from the layer structure of the SmA phase are also found in the profiles for dried gel fibers of **1**-*S*-7 and **1**-*S*-8, while the shape of the peaks, namely the half width is considerably different. These results suggest that the similar molecular arrangement or the layer structure to the SmA phase is present in the gel fibers as an elemental unit.

The assembly of these lactones would build the orientational and/or translational orders in the neat state, revealing nematic and/or SmA phases if requisites for LC formation are satisfied, and build the gel fiber network in solvents, if physical conditions such as solvent, concentration, temperature, and so on are suitable.

Present results should be very important information for explaining the correlation between LC and gel states, and further examination is now underway.

This work was supported by a Grant-in-Aid for Scientific Research No. 17750181 from the Ministry of Education, Culture, Sports, Science and Technology of Japan.

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