A Hexagonally Organized Elemental Supramolecular Structure of a Sugar-Appended Organogelator Observed by Synchrotron X-ray Source (SPring-8)[1]

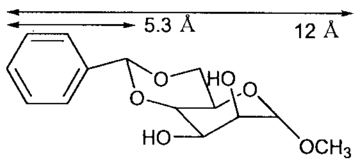
Kazuo Sakurai,* Taro Kimura,[†] Oliver Gronwald,[†] Katsuaki Inoue,[††] and Seiji Shinkai[†]
"Organization and Function" PRESTO, Japan Science and Technology, Kurume Research Center Bldg.,
2432 Aikawa, Kurume, Fukuoka 839-0861
[†]*Chemotransfiguration Project, Japan Science and Technology, Kurume Research Center Bldg.,*
2432 Aikawa, Kurume, Fukuoka 839-0861
[††]*SPring-8, Japan Synchrotron Radiation Research Institute (JASRI), 323-3 Mihara, Mikazuki, Sayo, Hyogo 679-5198*

(Received April 26, 2001; CL-010384)

Small angle X-ray scattering from methyl 4,6-*O*-benzylidene-α-D-mannopyranoside/*p*-xylene organogels was carried out with a synchrotron X-ray source at SPring-8, which revealed that the molecules assemble in a hexagonally packed motif in the gel state and this supramolecular structure completely disappears in the sol state.

Organogelators are a class of molecules that can undergo self-organization in a particular organic solvent to yield a fine fibrilar structure.[2–8] This elemental fiber can bundle each other to form a micrometer-scale fiber and this micro-fiber is connected to each other by a so-called "junction point".[2–7] Therefore, the entire morphology becomes sponge-like, thus it is considered suitable to absorb a large amount of solvent molecules by the capillary effect. This is the reason why this solution behaves as a gel and such compounds are called as organogelators. Organogels constitute an important class of material to their application in template materials,[9] drug delivery systems,[10] and biomimetics.[11] Recently, more and more researchers start to realize such importance of organogelators.

We have studied on a series of sugar-appended organogelators.[3,12,13] In this work,[13] we found that methyl 4,6-*O*-benzylidene-α-D-mannopyranoside (α-manno, see Figure 1 for the structure) can gelatinize *p*-xylene at considerably low concentrations (less that 1 %). One of the peculiar phenomena for the α-manno/*p*-xylene gel is that a clear thermal transition from the gel to sol states is observed upon heating. This paper explores how the supramolecular structure of the gel changes in accordance with the thermal transition.



α-manno

Figure 1. Chemical structure and molecular size of the mannose appended organogelator.

We synthesized α-manno according to a method described elsewhere[12] and prepared 0.5, 1.0, and 2.0 wt% *p*-xylene gels. The gel–sol transition temperatures (T_{gel}) for these samples were determined to be 39, 55, and 64 °C for 0.5, 1.0, and 2.0 wt%, respectively. The resultant values agree with those reported by Gronwald et al.[12] The samples were loaded into a quartz cell (Mark-Rohrchen) with 2 mm diameter, then the cell was sealed with an epoxy adhesive. Small angle X-ray scattering experiments were carried out at the BL40B2 station at SPring-8 in Japan. The SAXS intensity (I) was accumulated for 60 s in the range of q = 0.02–0.67 $Å^{-1}$ with a Rigaku R-AXIS IV++ (a 30 cm × 30 cm imaging plate), here q is the magnitude of the scattering vector.

The inset of Figure 2 exemplifies a two-dimensional scattering pattern that was observed at 35.6 °C for the 1.0 wt% gel. The pattern consists of concentric circles and the I vs q profile is independent of the azimuthal angle, indicating isotropy of the sample. Figure 2 compares the circularly averaged scattering profiles for different temperatures at 1.0 wt%. A typical lattice scattering is observed below T_{gel} (i.e., 55 °C) and the peak intensities decrease with increasing temperature. We can observe eight peaks, indicating that a highly ordered lattice is present in this organogel. As far as we know, no one has observed such higher order peaks in organogels. Above T_{gel} all peaks disappear, indicating that the observed lattice structure is corresponding to the gel nature. Another characteristic change upon heating is that the abrupt increment in I at low q is no longer observed above T_{gel}.

According to the scattering theory[14] for a hexagonally packing cylinder, the lattice peak position for the Miller index

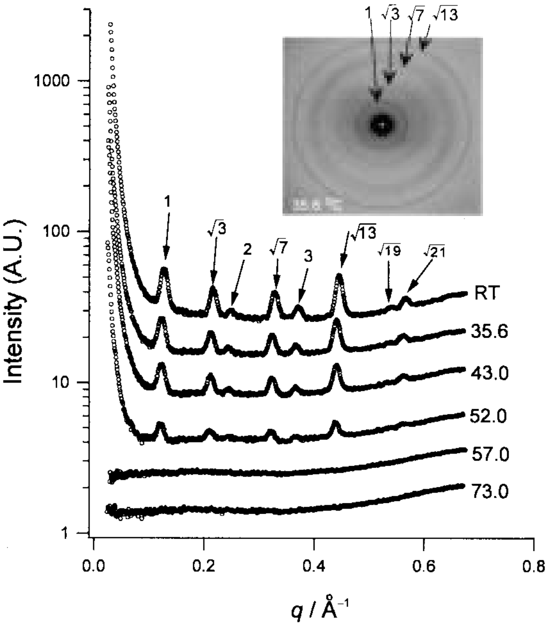


Figure 2. Two-dimensional scattering pattern and comparison of the I vs q profiles for different temperatures.

Table 1. Comparison of the peak positions between the experiment and a hexagonal packing model[a]

Miller Index		(1 0)	(1 1)	(2 0)	(2 1)	(3 0)	(2 2)	(3 1)	(3 2)	(4 0)	(4 1)
$(k^2 + kl + l^2)^{1/2}$		1	$\sqrt{3}$	2	$\sqrt{7}$	3	$\sqrt{12}$	$\sqrt{13}$	$\sqrt{19}$	4	$\sqrt{21}$
q_{kl}/q_{01} theory	(1)	1	1.73205	2.0000	2.64575	3.0000	3.4650	3.60555	4.35890	4.0000	4.58258
peak position / $Å^{-1}$		0.123	0.210	0.246	0.324	0.366	-	0.440	0.535	-	0.562
q_{kl}/q_{01} measurement	(2)	1	1.714	2.008	2.641	2.984	-	3.591	4.367	-	4.589
comparison between theory and experimant	(1)/(2)	1.000	1.010	0.996	1.002	1.005	-	1.004	0.998	-	0.999

[a] (4 0) and (2 2) diffractions cannot be observed because these are essentially higher order diffractions for (1 0) and (1 1), respectively.

of (k,l) is given by the following equation;

$$q_{kl} = a^{-1}\left(2/\sqrt{3}\right)\sqrt{k^2 + kl + l^2} \qquad (1)$$

Here, q_{kl} is the peak position and a is the unit cell length. Table 1 compares the lattice peak positions obtained from Figure 2 and those calculated from eq (1). Agreement between the theory and the experiment is attained within 1 %. Therefore, we can conclude that α-manno molecules form a cylinder-like fiber (i.e., elemental fiber) and these elemental fibers bundle themselves hexagonally. Using eq (1), a is evaluated to be 59 Å. This value is relatively larger than that of the α-manno molecule (see Figure 1). This difference suggests that a large amount of the solvent molecules exist between the elemental fibers. Since the sugar moiety is hydrophilic, the *p*-xylene solvent should make the sugar moieties assemble together. Furthermore, the electron density of the sugar moiety is lower than both *p*-xylene and the aromatic moiety of α-manno. We also can presume that the electron density between *p*-xylene and the aromatic moiety should be in the similar magnitude. Based on the above discussion, the scattering profiles can be explained by a model illustrated in Figure 3. Here, the sugar moiety undergoes self-organization to form a cylindrical domain and these domains assemble hexagonally. Although the data are not shown here, we have confirmed that the wide angle X-ray diffraction from the present gel sample shows only amorphous peaks and no trace of crystalline peak. This result indicates that the stacked sugar moieties are arranged in a disordered state. The solvent molecules are present between the cylindrical domains and probably the π–π interaction can stabilize the interface between the aromatic moiety and the *p*-xylene solvent.

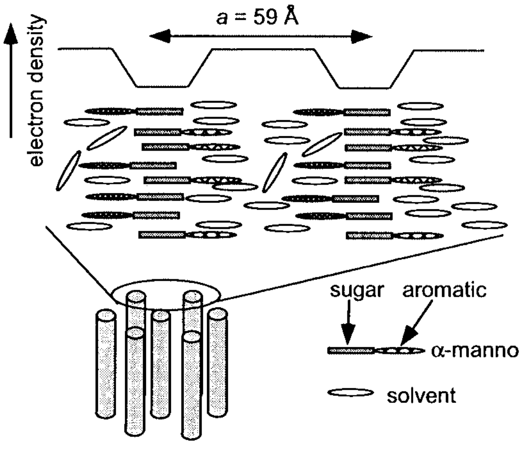


Figure 3. Schematic model showing how the *p*-xylene solvent molecules and α-manno molecules form the supramolecular structure. Based on this gel structure, we also proposed the electron density profile to explain the SAXS data.

As mentioned above, below T_{gel} an enormous increase is seen in I at $q < 0.06$ $Å^{-1}$. This feature suggests that there is a large scale structure; larger than at least a few hundred angstroms. This large structure should be related to the bundled fibers and the junction points formed by the bundles. However, it is difficult to estimate the present q range for such micrometer-scale structures. An important point is that this large-scale structure disappears in accordance with disappearance of the hexagonal packing. This coincidence allows us to derive a conclusion that the hexagonal packing structure is a fundamental and elemental constituent of the gel structure.

To the best of our knowledge, no one has observed such a highly ordered hexagonal structure. We are in the process of TEM, ultra-low angle SAXS, and extensive WAXS to reveal the hierarchic supramolecular structure of the present system.

This work is performed under the approval of SPring-8 Advisory Committee (2000B0227-NL –np).

References and Notes

1 This paper is Part 2 in the series of "Synchrotron X-ray Scattering from Organogels".
2 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Oseto, K. Ueda, and S. Shinkai, *J. Am. Chem. Soc.*, **116**, 6664 (1994).
3 N. Amanokura, K. Yoza, H. Shinmori, S. Shinkai, and D. N. Reinhoudt, *J. Chem. Soc., Perkin Trans. 2*, **1998**, 2585.
4 P. Terech and R. Weiss *Chem. Rev.*, **97**, 3133 (1997).
5 J. Esch, F. Schoonbeek, M. Loos, H. Kooijman, A. L. Spek, R. Kellogg, and B. Feringa, *Chem. Eur. J.*, **5**, 937 (1999).
6 R. Wang, C. Geiger, L. Chen, B. Swanson, and D. G. Whitten, *J. Am. Chem. Soc.*, **122**, 2399 (2000).
7 K. Hanabusa, K. Okui, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1992**, 1371; K. Hanabusa, M. Yamada, M. Kimura, and H. Shirai, *Angew. Chem., Int. Ed. Engl.*, **35**, 1949 (1996); T. Kato, G. Kondo, and K. Hanabusa, *Chem. Lett.*, **1998**, 193.
8 B. A. Simmons, C. E. Taylor, F. A. Landis, V. T. John, G. L. McPherson, D. K. Schwartz, and R. Moore, *J. Am. Chem. Soc.*, **123**, 2414 (2001).
9 J. H. Jung, Y. Ono, K. Sakurai, M. Sano, and Seiji Shinkai, *J. Am. Chem. Soc.*, **122**, 8648 (2000); J. H. Jung, Y. Ono, K. Hanabusa, and S. Shinkai, *J. Am. Chem. Soc.*, **122**, 5008 (2000); S. Kobayashi, K. Hanabusa, N. Hamasaki, M. Kimura, H. Shirai, and S. Shinkai, *Chem. Mater.*, **12**, 1523 (2000).
10 G. Haering and P. L. Luisi, *J. Phys. Chem.*, **90**, 5892 (1986).
11 R. J. H. Hafkamp, P. A. Kokke, I. M. Danke, H. P. M. Guerts, A. E. Rowan, M. C. Feiters, and R. J. M. Nolte, *Chem. Commun.*, **1997**, 545.
12 O. Gronwald, K. Sakurai, R. Luboradzki, T. Kimura, and S. Shinkai, *Carbohydr. Res.*, **331**, 307 (2001); O. Gronwald and S. Shinkai, *Chem. Eur. J.* in press.
13 O. Gronwald, R. Luboradzki, A. Ikeda, and S. Shinkai, *Chem. Lett.*, **2000**, 1148.
14 H. Tadokoro and R. E. Krieger, "Structure of Crystalline Polymers", Publishing Company, Florida (1990).