Formation of Organogels by Intermolecular Hydrogen Bonding between Ureylene Segment

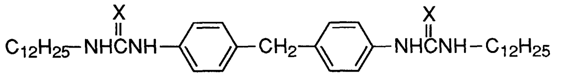
Kenji Hanabusa,* Kouji Shimura, Kazunori Hirose, Mutsumi Kimura, and Hirofusa Shirai
Department of Functional Polymer Science, Faculty of Textile Science & Technology, Shinshu University, Ueda, Nagano 386

(Received July 24, 1996)

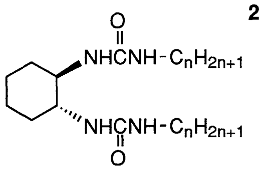
Low-molecular weight compounds having ureylene segment was able to cause physical gelation in organic solvents. The main driving force for gelation was intermolecular hydrogen bonding between ureylene units.

When isotropic solution of low-molecular weight molecule is cooled, it usually results in precipitating crystal or calming down to solution. However, a gel is rarely formed on the cooling process. Such a gel is called "thermoreversible physical gel", because it is easily transformed to the original isotropic solution by heating. Actually, about twenty families of small molecules[1-12] are known as gelling agent capable of causing thermoreversible gelation. The main driving forces for the physical gelation are reported to be intermolecular hydrogen bonding[1-8] and/or hydrophobic interactions.[9-12] The gelation mechanism is thought as follows: the macromolecule-like aggregates are formed from numerous molecules by above intermolecular interactions, then they are juxtaposed and interlocked, and finally immobilize the solvents. To design a new gelling agent we focused on intermolecular hydrogen bonding between ureylene segments, which has recently received special attention as a powerful organizing force for supramolecules.[13] Here, we report low-molecular weight ureylene compounds as new organogel-forming molecules. The main driving force for physical gelation is intermolecular hydrogen bonding between ureylene units.

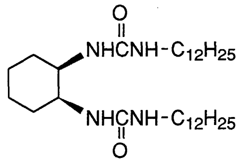
The bis-ureylene compounds were prepared from amine and ester of isocyanic acid, and the gel-forming ability was studied in popular solvents like ethanol, DMF, Me_2SO, THF, chloroform, tetrachloromethane, benzene, toluene, and nitrobenzene. A typical procedure for gelation test is described below: a weighed compound was mixed with organic liquid (1 cm^3) in a septum-capped test tube and the mixture was heated until the solid was dissolved. The resulting solution was cooled at 25 ℃ for 1 h and then the gelation was checked out visually. When it was formed, the gel was stable and the tube was able to be inverted without change of shape of the gel. The results of gelation test are summarized in Table 1. The 4,4'-didodecylureidodiphenylmethane (**1**) and 4,4'-didodecylthioureidodiphenylmethane (**2**) can make gel only in toluene and tetrachloromethane, respectively. On the contrary, trans-(*1R,2R*)-1,2-bis(dodecylureido)-cyclohexane (**4**) and trans-(*1R,2R*)-1,2-bis(octadecylureido)-cyclohexane (**5**) can cause physical gelation in a wide variety of organic solvents. Considering the restricted gel-forming ability of trans-(*1R,2R*)-1,2-bis(butylureido)cyclohexane (**3**), the long-chain alkyl segment seems to play an important role in physical gelation. The corresponding enantiomer, trans-(*1S,2S*)-1,2-bis(dodecylureido)cyclohexane, exhibited the essential same behavior as compared with **4**. It is important to note that the *cis*-1,2-bis(dodecylureido)cyclohexane (**6**) has no gel-forming ability toward any liquid. The minimum concentration of **4** necessary for gelation are summarized in Table 2. The value in this table means the mass (g) of **4** necessary to solidify 1 dm^3 of solvent. Surprisingly, this compound can solidify most organic solvents at very low concentration. For example, the amounts of **4** necessary to solidify 1 dm^3 of cyclohexane, methanol, 2-butanone, and DMF are 2 g, 3 g, 2 g, and 2 g, respectively. These mean that 1 molecule of **4** immobilizes *ca.* 2500 molecules of cyclohexane, *ca.* 4400 molecules of methanol, *ca.* 3000 molecules of 2-butanone, and *ca.* 3500 molecules of DMF.



1; X = O
2; X = S



trans(1R,2R)
3; n = 4
4; n = 12
5; n = 18



6

Table 1. Gelation test of ureylene molecules (**1**-**5**) toward organic solvents at 25 ℃[a]

solvent	1	2	3	4	5
ethanol	insol.	cryst.	soln.	gel	gel
DMF	cryst.	soln.	gel	gel	gel
Me_2SO	cryst.	soln.	gel	gel	gel
THF	insol.	soln.	insol.	gel	gel
chloroform	insol.	soln.	soln.	soln.	cryst.
tetrachloromethane	insol.	gel	insol.	gel	gel
benzene	insol.	cryst.	insol.	gel	gel
toluene	gel	cryst.	insol.	gel	gel
nitrobenzene	cryst.	cryst.	insol.	soln.	gel

[a] insol.= insoluble; soln.= solution; cryst.= crystallization.

Table 2. Minimum gel concentration of **4** necessary for gelation at 25 ℃

solvent	g dm^{-3} (**4**/solvent)	solvent	g dm^{-3} (**4**/solvent)
cyclohexane	2	acetonitrile	12
methanol	3	benzene	9
ethanol	4	toluene	7
2-propanol	5	chlorobenzene	13
2-butanone	2	Me_2SO	5
cyclohexanone	2	DMF	2
THF	2	*N,N*-dimethylacetamide	2
1,4-dioxane	3	salad oil	30
tetrachloromethane	15	kerosene	11
pyridine	2	light oil	15

The FTIR spectrum of a tetrachloromethane gel formed by **4** is characterized by broad bands at 3330 and 1630 cm^{-1} assigned to N-H and C=O stretching vibrations of intermolecular hydrogen bonding, whereas the chloroform homogeneous solution containing **4** shows 3442 and 1652 cm^{-1} indicative of non-hydrogen bonding stretching vibration. These spectral data correspond to what is expected if association occurs through intermolecular hydrogen bonding between N-H and C=O of ureylene segments.

Although the gels of **1**-**5** in sealed tubes were so stable that they did not crystallize even after a half year, xerogels were obtained as translucent films by slow evaporation at room temperature and atmospheric pressure. The wide angle X-ray diffraction pattern of xerogel obtained from tetrachloromethane gel of **4** is characterized by a series of three reflections of 15.1, 10.0, and 7.5 Å, which are almost exactly in the ratio 1/2 : 1/3 : 1/4. This means the xerogel has a layered structure as the interlayer distance corresponding to the (100) plane is 30 Å.

The image of molecular aggregate, formed by association through intermolecular hydrogen bonding, was caught by electron microscopy. The transmission electron micrograph (TEM) of a gel formed by **4** in methanol (Figure 1), negatively stained by osmic acid, shows the gathering of numerous slender fibers whose diameter is *ca.* 20-80 nm. The scanning electron micrograph (SEM) of a gel formed by **4** in methanol, shaded by gold, exhibits a huge aggregate which is three-dimensional and interlocking. Considering that the size of the smallest diameter of the huge aggregate is *ca.* 300 nm, it is assumed that the additional gathering of fibers observed in the TEM results in the intertwined huge aggregate in the SEM, and solvent molecules are encircled in a network of the intertwined huge aggregate.

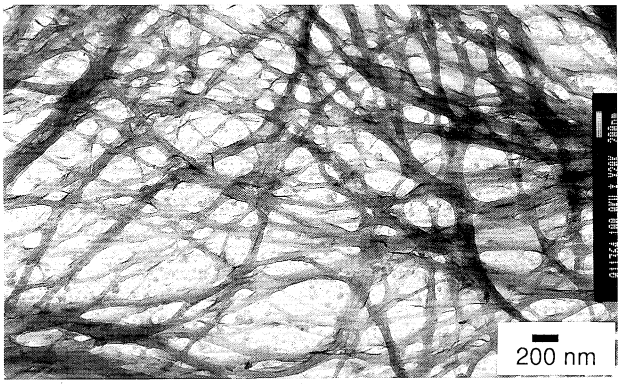


Figure 1. TEM of loose gel from **4** in methanol, negatively stained by osmic acid.

To study the chiral structure of the aggregate in a loose gel, circular dichroism (CD) spectra were measured for **4** in cyclohexane. The CD spectrum of loose gel of **4** at 0.745 mM (0.051 wt-%) revealed a strong negative peak due to ureylene unit; $[\theta]_{190} = -7 \times 10^4$. In contrast, the CD spectrum of the corresponding enantiomer, trans-(*1S*,*2S*)-1,2-bis(dodecylureido)cyclohexane, was characterized by the strong positive peak at 190 nm. The observed strong CD peak disappears at 0.0745 mM (0.0051 wt-%); **4** dissolves homogeneously in cyclohexane and gives the isotropic solution at this concentration. From the strong CD of the loose gel and the disappearance at low concentration, we conclude that the CD bands originate from the chiral aggregate of **4**, but not the chiral conformation itself. The compound **4** may be cooperatively organized for a helical stacking.

Thermal behavior of gel was studied by DSC measurement. The DSC on heating process of hard Me_2SO gel (16.7 wt-%) of **4** was characterized by a sharp endothermic transition (59 kJ mol^{-1}) at 74 ℃ and a broad one (57 kJ mol^{-1}) at 144 ℃. The hard Me_2SO gel (16.7 wt-%) of **5** also showed two endothermic transitions; 99 kJ mol^{-1} at 93 ℃ and 57 kJ mol^{-1} at 152 ℃. From the visual observation of the gel on heating process using a melting point apparatus, it is found that the transition at elevated temperature corresponds to the gel-to-sol phase transition. The other endothermic transition at elevated temperature may be caused by the cleavage of intermolecular hydrogen bonding between ureylene segments. It is assumed that the first endothermic transition at low temperature is attributed to the melting of long hydrocarbon chain of **4** and **5**. Actually, the hard Me_2SO gel (16.7 wt-%) of **3**, which has butyl groups, did not show the corresponding endothermic transition peak, though revealing the endothermic peak at 146 ℃ due to the gel-to-sol phase transition. The DSC results led us to conclude that the long hydrocarbon chain of **4** and **5** melts and moves with heating gel, however, the phase transition from gel to isotropic sol is caused by the cleavage of intermolecular hydrogen bonding at high temperature.

This work was supported by Grant-in-Aid for Scientific Research in Priority Areas of "New Polymers and Their Nano-Organized Systems" (No. 277/08246101) from the Ministry of Education, Science, Sports, and Culture of Japan.

References

1 K. Hanabusa, Y. Matsumoto, T. Miki, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1994**, 1401, and references therein.

2 K. Hanabusa, Y. Naka, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1994**, 2683.

3 M. Jokic, J. Makarevic, and M. Zinic, *J. Chem. Soc., Chem. Commun.*, **1995**, 1723.

4 H. T. Stock, N. J. Turner, and R. McCague, *J. Chem. Soc., Chem. Commun.*, **1995**, 2063.

5 F. M. Menger, Y. Yamasaki, K. K. Catlin, and T. Nishimi, *Angew. Chem., Int. Ed. Engl.*, **34**, 585 (1995).

6 T. Tachibana, T. Mori, and K. Hori, *Nature*, **278**, 578 (1979).

7 T. Tamura, T. Suetake, T. Ohkubo, and K. Ohbu, *J. Am. Oil Chem. Soc.*, **71**,857 (1994).

8 S. Yamasaki and H. Tsutsumi, *Bull. Chem. Soc. Jpn.*, **67**, 2053 (1994).

9 P. Terech, I. Furman, and R. G. Weiss, *J. Phys. Chem.*, **99**, 9558 (1995).

10 Y. Lin, B. Kachar, and R. G. Weiss, *J. Am. Chem. Soc.*, **111**, 5542 (1989).

11 K. Murata, M. Aoki, T. Suzuki, T. Harada, H. Kawabata, T. Komori, F. Ohseto, K. Ueda, and S. Shinkai, *J. Am. Chem. Soc.*, **116**, 6664 (1994).

12 T. Brotin, R. Utermöhlen, F. Fages, H. Bouas-Laurent, and J. Desvergne, *J. Chem. Soc., Chem. Commun.*, **1991**, 416.

13 X. Zhao, Y.-L. Chang, F. W. Fowler, and J. W. Lauher, *J. Am. Chem. Soc.*, **112**, 6627 (1990).