Facile Preparation of Robust Organic Gels by Cross-link of a Sugar-integrated Gelator by Toluene-2,4-diisocyanate

Kazuhiko Inoue, Yoshiyuki Ono, Yasumasa Kanekiyo, Shigeki Kiyonaka,† Itaru Hamachi,† and Seiji Shinkai*
Chemotransfiguration Project (JST), 2432 Aikawa, Kurume, Fukuoka 839-0861
†Department of Chemistry and Biochemistry, Graduate School of Engineering,
Kyushu University, Hakozaki, Higashi-ku, Fukuoka 812-8581

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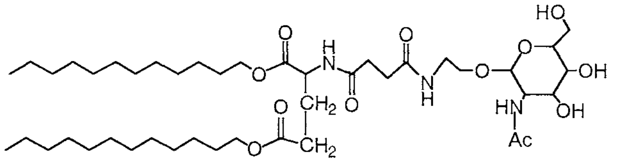
Gelator **1** which has two aliphatic chains, three amide groups, and one glucosamine unit showed an excellent gelation ability for many organic solvents. The *in situ* cross-link of these organic gels by toluene-2,4-diisocyanate resulted in new robust gels with high T_{gel} values, retaining their gel fiber super-structure.

The development of new gelators of organic solvents has recently received much attention. They not only gelate various organic solvents but also create novel supramolecular networks with fibrous aggregates which can be characterized by SEM pictures of the xerogels.[1-10] The gelators can be classified into two major categories according to the difference in the driving force for the molecular aggregation, *viz.* hydrogen-bond-based gelators and nonhydrogen-bond-based gelators. Typical examples of the former group are the aliphatic amide or the sugar derivatives,[1-4] whereas those of the latter group are cholesterol derivatives.[6-9] More recently, two essential progresses have been reported which may be eventually led to the practical application of organic gel systems.[11,12] Ono *et al.*[11] reported that a novel mesoporous silica with a tubular structure is prepared using organic gel fibers as a template. Feringa *et al.*[12] reported that *in situ* radical polymerization of organic gel fibers is useful to prepare robust gel systems. A concept common between these two reports is to immobilize or to transcribe the gel super-structures as they are. Very recently, we found that compound **1** which has two long aliphatic chains, three amide groups, and one glucosamine unit serves as an excellent gelator of many organic solvents.[13] The gels should be stabilized by the intermolecular hydrogen-bonding interaction among the amide groups and OH groups.[1-4] It occurred to us that if the OH groups are appropriately cross-linked in the gel state, one can not only "fix" their gel fiber super-structures but also "reinforce" their gelation ability. In this communication, this idea was tested using toluene-2,4-diisocyanate (TDI) as a cross-link reagent.



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In benzene and *p*-xylene compound **1** (1.0×10^{-2} mol dm^{-3}) gave the sol-gel phase-transition temperature (T_{gel})[3,7,8] at 40 °C and 58 °C, respectively.[3] SEM (Scanning electron micrograph) observations of the xerogels showed that **1** assembles to straight fibrous aggregates with 20-200 nm diameter (Figure 1A). This is a typical gel super-structure observed for the gel which futures a relatively strong intermolecular interaction.[3b, 8]

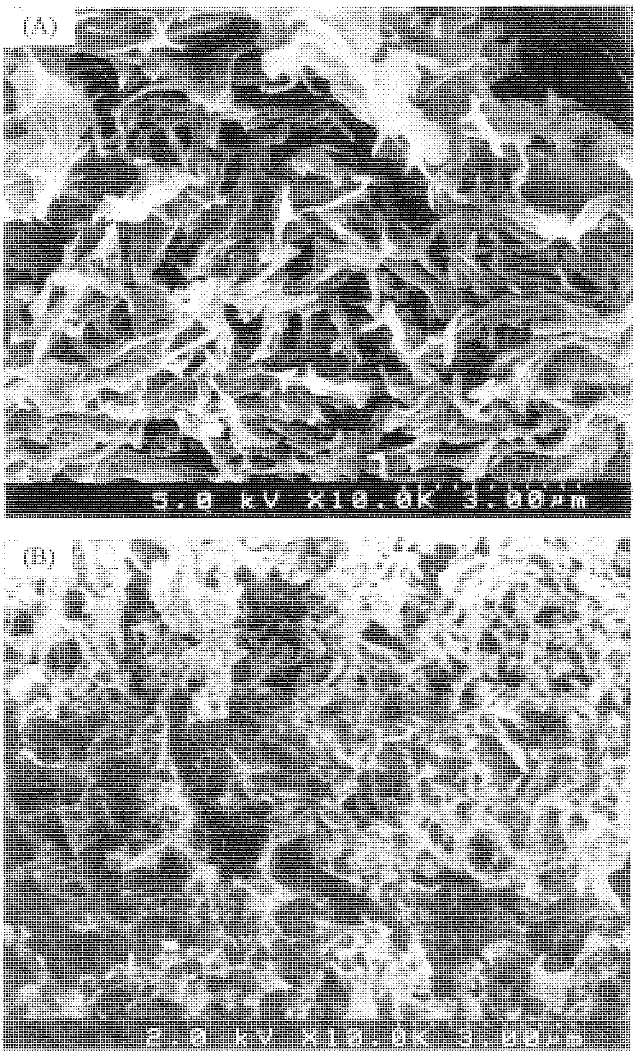

Figure 1. SEM pictures of xerogels prepared from **1** (1.0×10^{-2} mol dm^{-3}) in *p*-xylene (A) in the absence and (B) in the presence of TDI.

When **1** and TDI were treated in the benzene gel in a 1:10 molar ratio at room temperature for 14 days, the T_{gel} was enhanced up to 70 °C (it could keep the gel phase even at the temperature very close to the bp). The xerogel was not soluble even by high-dilution in chloroform, indicating that **1** has been cross-linked into the three-dimensional network by TDI. The IR spectra showed, however, that the xerogel contains a considerable amount of unreacted TDI (as shown by a peak at ν_{NCO} 2276 cm^{-1}).

To estimate the ultimate gelation ability without unreacted TDI, we repeated the gelation experiment in a 1:1 molar ratio in *p*-xylene (14 days, room temperature). Very excitingly, the T_{gel} was enhanced up to 118 °C! The IR spectra of the xerogel showed that TDI has totally reacted with **1** (no ν_{NCO}) and the SEM observations showed that the straight fibrous superstructure is still retained (Figure 1B). The IR-spectral and elemental analysis data[14] showed that the conventional addition reaction to give the urethane group takes place between the OH group and the isocyanate group. However, the xerogel was soluble in chloroform under the high-dilution conditions. Average molecular weight of this xerogel was estimated to be (Mn =) 2-6 x 10^3 by the GPC measurement (with polystyrene std.).[15] This implies that although the cross-link of **1** by TDI really occurs, the molecular-weight is not necessarily high under the 1:1 molar ratio reaction condition. On the other hand, the reaction with TDI in the sol state resulted in cross-linked powder polymer which was insoluble in chloroform and did not show any fibrous network structure.

In conclusion, the present system has demonstrated that the *in situ* cross-link of the gel fibers comprised from a sugar-integrated gelator can result in a robust gel system. The essential difference between polymeric gels and low-molecular-weight organo-gels is that the former system features the cross-link of one-dimensional polymer chains whereas the latter system features the assembly of the crystal-like particles. In this context, one may consider that the present system is a sort of hybrid gel in which the cross-linked polymer is created on the molecular assembly.

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References and Notes

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14 Found: C, 61.16; H, 8.74; N, 6.66%. Anal. Calcd for $C_{43}H_{79}N_3O_{12}$+$C_9H_6N_2O_2$+H_2O: C, 61.10; H, 8.58; N, 6.85%. The result indicates that the simple addition reaction took place.

15 This is the Mn of the polymeric fraction. The amount of unreacted and non-cross-linked **1** was estimated to be less than 30 mol% by GPC.