Preparation of New Robust Organic Gels by *in situ* Cross-link of a Bis(diacetylene) Gelator

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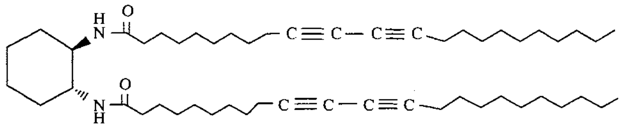
Polymerizable gelator **1** which has two diacetylene groups as well as two amide groups showed an excellent gelation ability for many organic solvents. Photoirradiation readily induced polymerization in the gel phase but the polymerization results were dependent upon the gelation solvent. It was shown that the three-dimensional cross-link of these organic gels resulted in new robust gels, retaining their gel fiber super-structure.

Exploitation of new organic gelators has been of much concern in the last decade.[1-8] In gelated solvents, these gelators form three-dimensional super-structures which basically show the crystal-like properties.[7] In the first stage of this chemistry, the primary concern has been the beauty of the super-structures which sufficiently stimulated the chemists' curiosity.[1-8] We consider that the coming second stage would be related to the functionalization of these fibrous gelator aggregates.

Organic gels are constructed by the assembly of low-molecular-weight compounds. This is inherently associated with their merit as well as their demerit: they show the excellent thermo-reversibility but are not stable mechanically. The drawback would be improved by *in situ* polymerization of fibrous gelator aggregates. Shimizu *et al.*[3] prepared organic gels from sugar-containing diacetylene derivatives and obtained the polymerized fibers. However, the one-dimensional polymer did not show any gelation ability. Feringa *et al.*[4] introduced two vinyl groups into a gelator and obtained a robust organic gel after *in situ* polymerization. We also prepared a robust gel by *in situ* cross-link of a sugar-containing gelator by toluene-2,4-diisocyanate.[5] These results consistently suggest that the three-dimensional cross-link is essential to reform the organic gels into the robust ones. We thus designed gelator **1** containing a bis(diacetylene) group and conducted the photochemical *in situ* cross-link. We found that polymerization can be readily induced by photoirradiation and the resultant polymerized gels show the high gelation stability.



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Compound **1** which has two diacetylene groups as a cross-link polymerization site and a diaminocyclohexane moiety as a gelation site was synthesized.[9] Compound **1** showed the excellent gelation ability for various organic solvents (Table 1). It is seen from Table 1 that **1** can gelate not only non-polar solvents but also several polar solvents. These slightly turbid, white gels (except for the cyclohexane gel) changed to blue by irradiation of UV light (a 500 W high-pressure Hg-lamp) at 25 °C for 1.0 min through the septum tube made of the Pyrex glass. The finding shows that **1** forms a gel fiber structure in which the diacetylene groups can inter-molecularly polymerize. The sol-gel phase-transition temperature (T_{gel}) of the hexane gel ([**1**] = 4.3 mmol dm^{-3}) was 46 °C before polymerization. The blue gel with λ_{max} 540 and 500 (shoulder) nm after polymerization was changed to the orange gel with λ_{max} 520 and 485 (shoulder) nm after heating at 50 °C for 15 min. (Figure 1A). The irradiated gel was stable up to 58 °C and then gradually shrank at higher temperature, releasing the solvent.

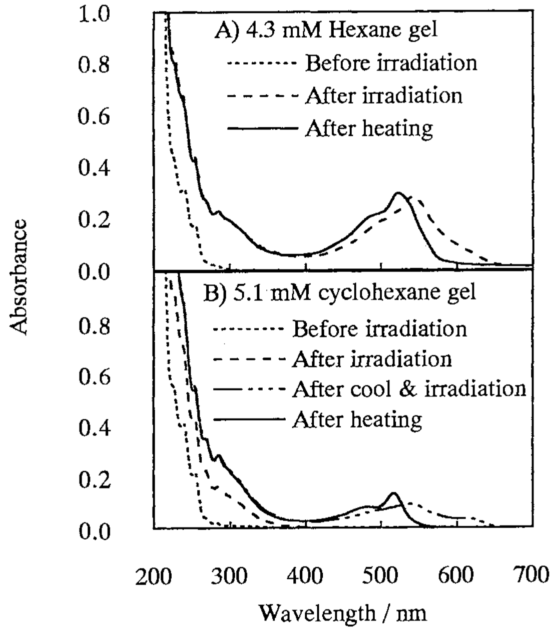

Figure 1. Absorption spectra of the **1** gels before and after polymerization at 25 °C: (A) hexane gel, [**1**] = 4.3 mmol dm^{-3}; (B) cyclohexane gel, [**1**] = 5.1 mmol dm^{-3}, cell width 1.0 mm.

Table 1. Gelation ability of **1**[a]

Solvent	Before irradiation	After irradiation
Benzene	S	S
Chloroform	S	S
Tetrachloromethane	S	S
1,2-Dichloroethane	S	S
Tetrahydrofuran	S	S
Cyclohexane	G_b	G_b
Methylcyclohexane	G_c	G_f
Hexane	G_c	G_f
Ether	G_c	G_f
Methanol	G_c	G_f
1-Butanol	G_c	G_f
Acetonitrile	G_c	G_f

[a] The solution (5 wt%) was warmed and then cooled to r.t. to grow the gel: S = transparent solution, G_b = transparent gel, G_c = turbid or white gel, G_f = blue gel. The gel formation was judged by the test-tube-tilting method.

The product analysis was carried out about a hexane gel of **1** (10.1 mmol dm^{-3}) polymerized by UV irradiation for 3.0 min. When the hexane gel was rinsed with chloroform, 5.1 wt% of the insoluble cross-linked product were isolated. The residual chloroform-soluble products were analyzed by MALDI-TOF. The strongest peak was the Na$^+$-complexed monomer ([M + Na]$^+$ = 793) and the next was the monomer ([M + H]$^+$ = 771), the ratio being 100 : 76.7. In addition, we could observe [M_2 + Na - $CO(CH_2)_8\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C_{10}H_{21}$]$^+$ (1234), [M_2 + Na]$^+$ (1563), and [M_3 + Na - $2CO(CH_2)_8\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}C_{10}H_{21}$]$^+$ (1675) with the ratio of 59.2 : 2.9 : 6.3 (relative to the peak intensity of [M + Na]$^+$. These results suggest that the major components in the polymerized gel fibers are oligomers.

The blue gels by photoirradiation were also obtained from the organic gels of methanol, 1-butanol, and acetonitrile. These gels were also slightly turbid and white. In contrast to these turbid gels, the cyclohexane gel of **1** resulted in a very homogeneous, transparent gel. Interestingly, the color change was not induced by photoirradiation through a Pyrex glass. To find the aggregate structure difference before polymerization, we measured the FT-IR spectra. However, the significant difference was not found between the cyclohexane gel and other organic gels. As shown in Figure 1B, the absorption band at around 250 nm increases. Probably, the diacetylene groups in the cyclohexane gel react only in a localized domain (*e.g.*, intermolecular reaction, dimerization, *etc.*). The product was soluble in chloroform. When this cyclohexane gel was cooled at 10 °C for 1 h, it was turned to a turbid gel. Photoirradiation of this turbid gel at 25 °C induced the conventional color change. The T_{gel} for the cyclohexane gel ([**1**] = 10.2 mmol dm^{-3}) changed by only 1 °C before (41 °C) and after (42 °C) polymerization. The results indicate that the polymerization was initiated in the heterogeneous micro-particles formed in the gel. The micro-particle of the cyclohexane gel did not grow too wide to stabilize gel structure.

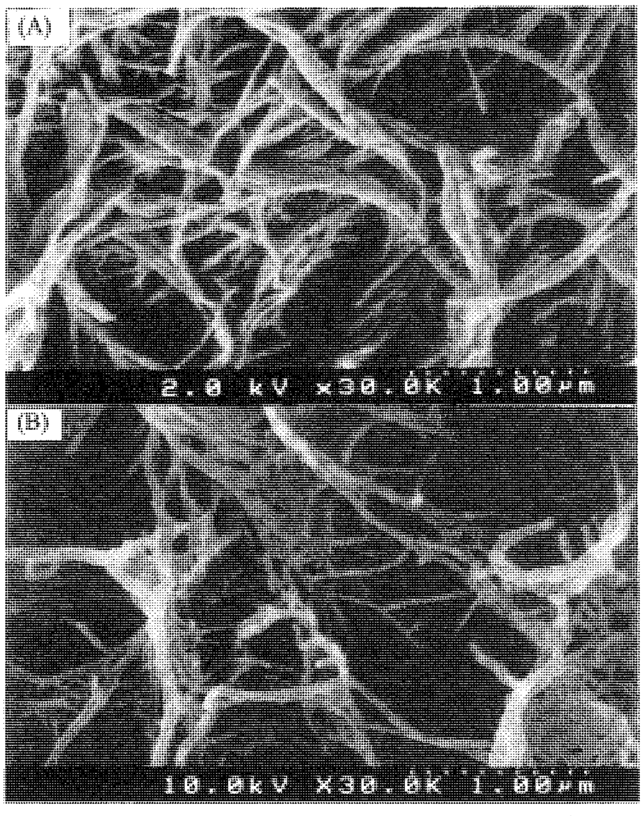

Figure 2. SEM pictures. (A): Xerogel prepared from acetonitrile gel (10.2 mmol dm^{-3}), (B): Insoluble material obtained from photo-polymerized **1** in the hexane gel (10.1 mmol dm^{-3}).

The SEM picture of the xerogel prepared from an acetonitrile gel ([**1**] = 10.2 mmol dm^{-3}) is shown in Figure 2A (it was difficult to prepare the solidified hexane gel suitable for the freeze dry even at –100 °C: instead, we used the acetonitrile gel). The presence of a dense net-work structure composed of fibrous aggregates (with 20-30 nm diameter) was confirmed. The polymerized hexane gel was rinsed by chloroform, the residual insoluble material being subjected to the SEM observation (Figure 2B). It is clearly seen from this picture that the fibrous structure with 20-30 nm diameter is fixed by the three-dimensional cross-link.

In conclusion, the polymerization of the gel state **1** can be readily initiated by photoirradiation. This distinguishing characteristic is useful not only for the expeditious preparation of robust gels but also for a novel lithographic method of organic gel systems.

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References and Notes

1 a) K. Hanabusa, K. Okui, T. Koyama, and H. Shirai, *J. Chem. Soc., Chem. Commun.*, **1992**, 1371 and references cited therein. b) K. Hanabusa, M. Yamada, M. Kimura, and H. Shirai, *Angew. Chem., Int. Ed. Engl.*, **35**, 1949 (1996).

2 a) K. Inoue, Y. Ono, Y. Kanekiyo, T. Ishi-I, K. Yoshihara, and S. Shinkai, *Tetrahedron Lett.*, **39**, 2981 (1998). b) K. Inoue, Y. Ono, Y. Kanekiyo, T. Ishi-I, K. Yoshihara, and S. Shinkai, *J. Org. Chem.*, in press.

3 M. Masuda, T. Hanada, K. Yase, and T Shimizu, *Macromolecules*, **31**, 9403 (1998).

4 M. de Loss, J. van Esch, I. Strkroos, R. M. Kellogg, and B. L. Feringa, *J. Am. Chem. Soc.*, **119**, 12675 (1997).

5 K. Inoue, Y. Ono, Y. Kanekiyo, S. Kiyonaka, I. Hamachi, and S. Shinkai, *Chem. Lett.*, in press.

6 a) E. Otsuni, P. Kamaras, and R. G. Weiss, *Angew. Chem., Int. Ed Engl.*, **35**, 1324 (1996) and references cited therein. b) P. Terech and R. G. Weiss, *Chem. Rev.*, **97**, 3133 (1997).

7 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) and references cited therein.

8 S. Shinkai and K. Murata, *J. Mater. Chem.*, **8**, 485 (1998).

9 Preparation of **1**. To a solution of 1R, 2R-(-)-diaminocyclohexane (13.7 mg, 0.120 mmol) and 10, 12-tricosadiynoic acid (87.4 mg, 0.252 mmol) in dry dichloromethane (30 ml) was added dropwise WSCI (N-ethyl-N'-dimethylanimopropylcarbodiimide, 77.2 mg, 0.403 mmol) in dry dichloromethane (20 ml) at 0 °C for 40 min under a nitrogen atmosphere. After the mixture was stirred at 0 °C for 1 h and at room temperature for 17.5 h, it was made alkaline by a treatment with 10% NaOH. The reaction mixture was extracted with CH_2Cl_2, washed with 10% HCl, dried over sodium sulfate, and evaporated *in vacuo*. The residue was purified by silica gel column eluting with $CHCl_3$/MeOH (9/1, v/v). Total yield was 49.7% (46.0 mg). White powder: mp (DSC) 72 °C; IR (KBr) νmax 3285, 2922, 2851, 1640, 1561, 1547, 1466, 1419, 723, 691 cm-1; ^{1}H NMR (300 MHz, CDCl3) δ 0.88 (t, J = 6.5 Hz, 6H, Me), 1.12-1.43 (m, 52H, paraffinic CH), 1.43-1.51 (m, 12H, paraffin CH), 1.68-1.83 (m, 2H, paraffinic CH), 1.84-2.06 (m, 2H, paraffinic CH), 2.06-2.16 (m, 4H, -CO-CH), 2.24 (t, J = 6.8 Hz, 8H, $C{\equiv}C\text{-}CH_2$), 3.56-3.74 (m, 2H, NCH), 5.85-6.05 (m, 2H, NH); SIMS (positive, NBA) m/z 771 [M+H]$^+$. Found: C, 80.75; H, 11.20; N, 3.65%. Anal. Calcd for $C_{52}H_{86}N_2O_2$: C, 80.98; H, 11.24; N, 3.63%.