



Photoinduced reinforcement of supramolecular gels based on a coumarin-containing gelator

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Abstract

The mechanical strength of supramolecular gels is usually low compared to that of cross-linked polymer gels, which sometimes limits practical applications of supramolecular gels. We report here photoinduced reinforcement of supramolecular gel structures using photodimerization of coumarin moieties introduced on a *trans*-(1*R*,2*R*)-1,2-cyclohexanediamine-based gelator. UV irradiation ($\lambda > 300$ nm) of toluene gels containing mixtures of *trans*-(1*R*,2*R*)-1,2-cyclohexanediamine-based gelators with and without coumarin moieties induced an enhancement in both the thermal and mechanical stabilities of the gels.

Introduction

Supramolecular gels obtained by the self-assembly of low-molecular-weight gelators (LMWGs) have received significant attention because of their potential for wide-ranging applications [1–6]. Self-assembled fibers consisting of bundles of one-dimensional (1D) assemblies of gelator molecules are entangled to form a three-dimensional (3D) network in a solvent, resulting in gelation. Since supramolecular gels are based on weak noncovalent interactions, such as hydrogen bonding, π – π stacking, and van der Waals interactions, they exhibit thermoreversible gel–sol transition behavior, which is advantageous for the introduction of dynamic functions to materials [5]. On the other hand, the mechanical strength of supramolecular gels is usually low compared to that of covalently cross-linked polymer gels, which sometimes limits practical applications of supramolecular gels. A number of approaches have been reported to overcome this problem. The addition of covalent polymers improves the mechanical strength of gels [7]. The

introduction of polymerizable groups such as acrylate and diacetylene to gelator molecules enables polymerization in the self-assembled fibers of the gelator, and the thermal stability of the gels can be improved [8–10]. However, such a polymerization process partially reduces the reversibility of molecular assembly because the formation of covalent bonds is usually irreversible. A dynamic covalent cross-linking approach [11] is a promising way to achieve reversible reinforcement of supramolecular gels.

Coumarins are known to exhibit UV light-triggered reversible photodimerization at different wavelengths. The photodimerization proceeds by the [2 + 2] cycloaddition of the ethylenic groups of coumarin molecules upon UV irradiation at $\lambda > 300$ nm, resulting in the formation of cyclobutane rings. The dimers revert to the monomers by the photocleavage of the cyclobutane ring upon UV irradiation at $\lambda < 300$ nm. Such a reversible photodimerization process of coumarins has been utilized in reversible photo-cross-linking of polymers [12–14]. Macroscopic changes such as swelling behavior and sol–gel conversion of polymer gels have been reported [13, 14]. On the other hand, only a few examples of LMWGs have been reported using a coumarin moiety as a photo-cross-linking unit [15, 16]. Photodimerization of coumarins can also be employed for the reversible chain extension of polymers [12, 17]. When two or more coumarin moieties are introduced to a “monomer”, intermolecular photodimerization leads to polymerization or chain extension, while photocleavage allows polymers to revert to monomers. Therefore, if such

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monomers act as an LMWG, polymerization in self-assembled fibers can be a reversible process.

We report here the gelation and photoresponsive properties of an LMWG containing two coumarin moieties to achieve a reinforced fibrous network of gelators with covalent bonds using a photodimerization reaction.

Experimental procedure

General

Unless otherwise noted, the chemical reagents and solvents were used without further purification. 7-Hydroxy-4-methylcoumarin was purified with activated charcoal followed by recrystallization from methanol. *N,N*-Dimethylformamide (DMF) was dried over 4 Å molecular sieves prior to use. All reactions were carried out under a nitrogen atmosphere. ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-ECS 400 spectrometer. Infrared spectra were recorded on a Jasco FT-IR 4200 spectrometer. UV-Vis spectra were recorded on a Shimadzu UV-1800 spectrometer. SEM observations were performed with a JEOL JSM-6510LA microscope at an accelerating voltage of 15 kV. All the samples for the SEM observations were coated with gold. UV irradiation was carried out by an Asahi Spectra LAX-C100 xenon light source (100 W) with mirror modules (UVA and UVB) and a bandpass filter (HQBP254-UV). Rheology measurements were performed with a TA Instruments DHR 2. Gel permeation chromatography (GPC) measurements were performed on a Jasco PU-2080 plus HPLC pump equipped with a Jasco CO-1560 column oven, a Jasco UV-2075 plus detector, and Shodex KF-803L and KF-806L columns using chloroform as the eluent. Polystyrene standards were used for the calibration.

Synthesis of **1**

Potassium carbonate (0.468 g, 3.39 mmol) and *trans*-(1*R*,2*R*)-1,2-bis(11-bromoundecanoylamino)cyclohexane [18] (0.501 g, 0.823 mmol) were added to a solution of 7-hydroxy-4-methylcoumarin (0.309 g, 1.75 mmol) in DMF (70 mL). The reaction mixture was stirred for 8 h at 80 °C and then poured onto saturated aqueous NH₄Cl. The precipitate was filtered off and washed with ethyl acetate and then water. The solid was purified by recrystallization from methanol to afford compound **1** (0.568 g, 0.711 mmol) as a white solid in 86% yield. Mp. 160 °C.

¹H NMR (CDCl₃, 400 MHz): δ 7.46 (d, *J* = 9.0 Hz, 2H), 6.83 (dd, *J* = 8.7, 2.4 Hz, 2H), 6.77 (d, *J* = 2.7 Hz, 2H), 6.10 (d, *J* = 1.2 Hz, 2H), 5.89 (d, *J* = 7.2 Hz, 2H), 3.98 (t, *J* = 6.6 Hz, 4H), 3.58–3.68 (m, 2H), 2.38 (d, *J* = 1.2 Hz, 6H), 2.06–2.16 (m, 4H), 2.05–1.95 (m, 2H), 1.72–1.82 (m,

6H), 1.54–1.61 (m, 4H), 1.40–1.47 (m, 4H), 1.12–1.34 (m, 24H); ¹³C NMR (CDCl₃, 67.5 MHz): δ 173.88, 162.31, 161.44, 155.37, 152.68, 125.53, 113.47, 112.74, 111.87, 68.67, 53.76, 37.02, 32.48, 29.56, 29.47, 29.41, 29.38, 29.05, 26.02, 25.88, 24.79, 18.74. Elemental analysis (%) calcd. for C₄₈H₆₆N₂O₈: C, 72.15; H, 8.33; N, 3.51; found: C, 72.17; H, 8.17; N, 3.40.

Gelation test

A mixture of a weighed sample and solvent was heated in a test tube until a clear solution was obtained. The resultant solution was allowed to cool to room temperature. Then, gelation was checked visually. When the tube could be inverted without any flow, it was considered a gel.

Determination of the gel–sol transition temperatures

For the determination of the gel–sol transition temperatures (*T*_{gel–sol}) of the gels, the “dropping-ball” method [19] was used. A steel ball was placed on top of the gel in a sample tube made of quartz. Then, the tube was sealed and heated in a stirred oil bath with a thermometer. As the temperature gradually increased, the position of the ball was monitored as well as the temperature of the bath. The temperature at which the steel ball reached the bottom of the tube was used as *T*_{gel–sol}.

Results and discussion

Gelation properties

The coumarin-containing diamide compound **1** shown in Figure 1 was prepared by the reaction of a bromo-terminated diamide and 7-hydroxy-4-methylcoumarin. Two coumarin moieties are attached to the alkyl terminals of the *trans*-(1*R*,2*R*)-1,2-cyclohexanediamine-based scaffold which is known as an excellent gelator (**2**) reported by Hanabusa et al. [20]. The results of the gelation test of compound **1** and mixtures of **1** and **2** are summarized in Table 1. Compound **1** gels a wide range of solvents. For example, the minimum gel concentration of **1** for acetone is 17 g L⁻¹. The gels based on **1** are turbid with ethanol and translucent with other solvents, which disturbs the efficient absorption of incident light by coumarin moieties due to light scattering. The addition of **2** to **1** has a positive effect on the transparency of the gels. The transparency of gels improved as the content of **2** increased. Transparent gels were obtained for benzene and toluene using **1/2** mixtures. Figure 2 shows the appearance of the toluene gels and the SEM images of xerogels of **1** and **1/2** mixtures. 3D network

structures of self-assembled fibers are observed. The addition of **2** seems to have only a slight effect on the morphology of the fibers. The FT-IR measurements of the tetrachloromethane gels of **1** indicate that these fibers are formed by intermolecular hydrogen bonding between amide groups as well as **2** since the N–H and the C=O stretching bands appear at 3277 and 1636 cm^{-1} , respectively. The introduction of coumarin moieties does not affect the formation of hydrogen bonding because coumarin moieties are separated from the amide groups by a long alkyl chain. Molecules of **1** and **2** are thought to co-assemble into 1D assemblies through hydrogen bonding.

Photoresponsive behavior

We examined the photoresponsive behavior of the coumarin moieties introduced to **1**. Changes in the absorption spectra of a tetrahydrofuran (THF) solution of **1** on UV irradiation

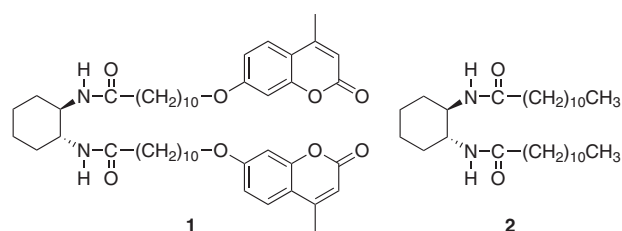


Fig. 1 Molecular structures of gelators **1** and **2**

(Figure S1a) indicate photodimerization and photocleavage of coumarin moieties. Before UV irradiation, compound **1** has an absorption band at approximately 320 nm, which can be ascribed to the coumarin moieties. This band decreases upon UV irradiation at $\lambda > 300$ nm, indicating that the photodimerization of coumarin moieties occurs. Subsequent UV irradiation at $\lambda = 254$ nm restores the 320 nm band, indicating the recovery of monomeric coumarin. These spectral changes indicate that 92% of the coumarin moieties in **1** dimerize upon UV irradiation at $\lambda > 300$ nm, and 67% of dimers revert to monomeric coumarin upon UV irradiation at $\lambda = 254$ nm. In the case of the toluene gel of a **1/2** mixture (**1:2** = 1:10), dimerization of coumarin moieties upon UV irradiation at $\lambda > 300$ nm was also observed (Figure S1b). However, the proportion of dimerized coumarin was 69%, which was lower than that observed in the THF solution. The irradiated light may be partially scattered by self-assembled fibers, which disturbs the efficient dimerization. Upon the irradiation of UV light at $\lambda = 254$ nm, only 13% of the dimers return to monomeric coumarin due to absorption by the solvent. Long exposure to UV light does not promote further conversion and may cause decomposition of the coumarin moieties. Unfortunately, transparent gels with less light scattering are obtained only with aromatic solvents such as benzene and toluene, which have absorption bands that overlap with the irradiated light. Efficient reversibility of dimerization of coumarin moieties

Table 1 Gelation properties and minimum gel concentrations of **1** and **1/2** mixtures

Solvent	1	1/2			
		1:1	1:3	1:5	1:10
Acetone	TLG (17/0.021)	TLG (17/0.027)	TLG (20/0.036)	TLG (17/0.032)	TLG (14/0.028)
Ethyl acetate	TLG (25/0.031)	TLG (14/0.022)	TLG (14/0.025)	TLG (14/0.026)	TLG (13/0.026)
Dichloromethane	P	TBG (50/0.078)	TBG (33/0.059)	TBG (25/0.047)	TBG (33/0.065)
Chloroform	S	S	S	S	S
Tetrachloromethane	TLG (20/0.025)	TLG (33/0.052)	TLG (25/0.045)	TLG (20/0.038)	TLG (14/0.028)
Methanol	P	TBG (33/0.052)	TBG (25/0.045)	P	WG
Ethanol	TBG (33/0.041)	TBG (50/0.078)	TLG (33/0.059)	WG	TLG (50/0.098)
Benzene	TLG (17/0.021)	TLG (17/0.027)	TPG (20/0.036)	TPG (17/0.032)	TPG (17/0.033)
Toluene	TLG (20/0.025)	TLG (17/0.027)	TPG (14/0.025)	TPG (14/0.026)	TPG (13/0.026)
Tetrahydrofuran	TLG (50/0.063)	TLG (33/0.052)	TLG (50/0.089)	WG	WG

Minimum gel concentrations in parentheses are given in g L^{-1} (left) and mol L^{-1} (right). Concentrations are calculated as the total concentration of the cyclohexane unit of **1** and **2**

TPG transparent gel, TLG translucent gel, TBG turbid gel, WG weak or unstable gel at room temperature, P precipitation, S solution

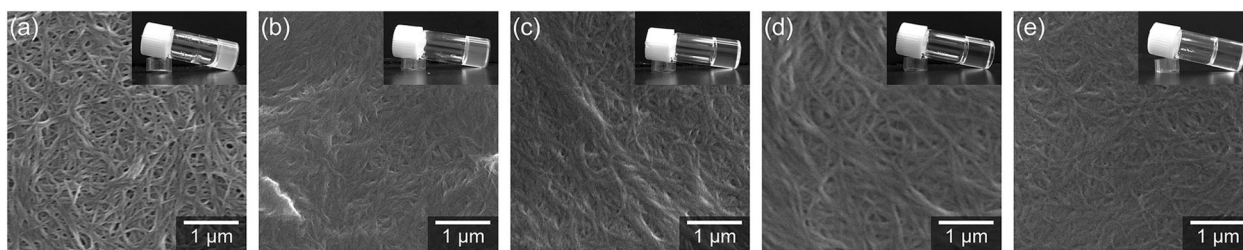


Fig. 2 SEM images of the self-assembled fibers of **1** and **1/2** mixtures formed in toluene. **a 1**, **b 1:2 = 1:1**, **c 1:2 = 1:3**, **d 1:2 = 1:5**, **e 1:2 = 1:10**

in **1** has not been observed thus far. Regarding the morphology of the self-assembled fibers, no significant changes were observed after UV irradiation (Figure S2).

Effects of UV irradiation on the gel properties

Photodimerization of the coumarin moieties in the self-assembled fibers of gelators is expected to improve the robustness of the 3D network structures of supramolecular gels. The gel–sol transition temperature ($T_{\text{gel-sol}}$) reflects the thermal stability of network structures. Figure 3 shows the $T_{\text{gel-sol}}$ values of toluene gels with **1/2** mixtures at various molar ratios before and after UV irradiation at $\lambda > 300$ nm. The $T_{\text{gel-sol}}$ values increase with UV irradiation. As the proportion of **1** increases, the increase in $T_{\text{gel-sol}}$ becomes larger, except for the 1:1 mixtures. In the case of the 1:3 mixture, $T_{\text{gel-sol}}$ increases from 75 °C before irradiation to 97 °C after irradiation. For the 1:1 mixture, the increase in $T_{\text{gel-sol}}$ is smaller than that of the 1:3 mixture because the gel is translucent, which partially disturbs photodimerization. The effects of UV irradiation on $T_{\text{gel-sol}}$ are almost lost once the stabilized gels are melted by heating. This result is because the stabilized gel structures are not completely recovered due to the rearrangement of gelator molecules in the fibers after thermal dissociation.

Rheological studies on the toluene gels of a **1/2** mixture (**1:2 = 1:10**) were carried out to investigate the changes in the mechanical properties of the gels before and after irradiation. Strain sweeps of the gels show viscoelastic responses typical for supramolecular gels (Figure S3). The storage modulus (G') is higher than the loss modulus (G'') up to approximately 0.1% strain. When the strain is beyond this level, both G' and G'' start to decrease, and G'' is higher than G' , which indicates collapse of the gels. Frequency sweeps at a strain of 0.05%, as shown in Fig. 4, indicate the enhancement of mechanical stability by irradiation. The G' values for the gels before and after irradiation are 2.1×10^5 and 4.3×10^5 Pa, respectively, at 1 Hz.

GPC measurements were carried out for the **1/2** mixtures taken from the xerogels after UV irradiation to obtain information on the molecular weight of the gelators. The results indicate that photodimerization leads to the

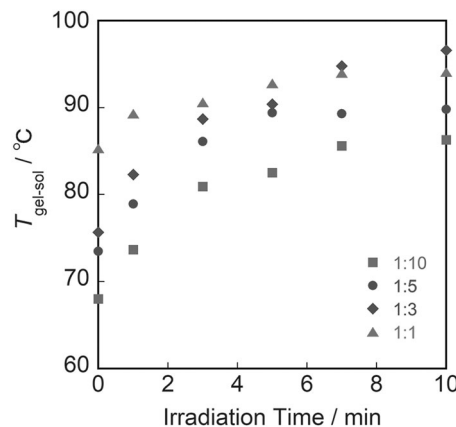


Fig. 3 Comparison of the $T_{\text{gel-sol}}$ values of toluene gels of **1/2** (7.8×10^{-2} mol L $^{-1}$) after UV irradiation at $\lambda > 300$ nm

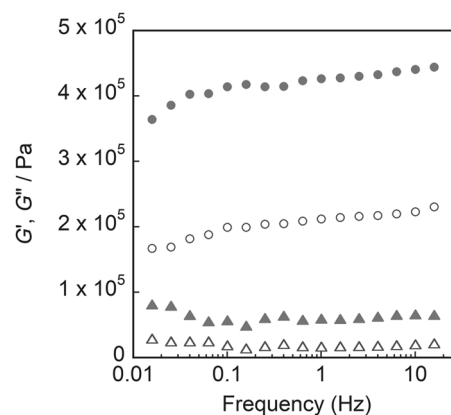


Fig. 4 Frequency sweeps of toluene gels containing 7.8×10^{-2} mol L $^{-1}$ of **1/2** (1:10 by molar ratio) at a strain of 0.05% before (G' : \circ , G'' : \triangle) and after (G' : \bullet , G'' : \blacktriangle) UV irradiation at $\lambda > 300$ nm

generation of dimers, trimers, and tetramers at most of **1** by UV irradiation of the gels (Figure S4). This is due to the existence of nondimerizable **2**. Therefore, photodimerization seems to occur mainly between 1D assemblies of gelator molecules which make up fibers, or intramolecularly based on the content of coumarin moieties. This explains why the increase in $T_{\text{gel-sol}}$ after UV irradiation shown

above is relatively small compared to that observed in previous studies using polymerizable gelators with acrylate and diacetylene moieties [8–10]. The results of the $T_{\text{gel-sol}}$ measurements and rheological studies show that reinforcement of supramolecular gel structures is achieved though the products of the photoreaction are oligomers rather than polymers, and that the degree of reinforcement is tunable based on the content of coumarin moieties.

Conclusion

Photoinduced reinforcement of supramolecular gel structures has been achieved using photodimerization of coumarin moieties introduced to gelator molecules. The photodimerization reaction in the self-assembled fibers of gelators enabled the enhancement of both the thermal and mechanical stabilities of the gels. At present, there is still room for improvement to achieve efficient and reversible reinforcement due to the limitation of the gelation solvents and the low content of coumarin moieties. However, our results described here serve as a promising approach to widen the applications of supramolecular gels.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

1. Weiss RG, Terech P, editors. *Molecular gels: materials with self-assembled fibrillar networks*. Dordrecht, the Netherlands: Springer; 2006.
2. Hirst AR, Escuder B, Miravet JF, Smith DK. High-tech applications of self-assembling supramolecular nanostructured gel-phase materials: from regenerative medicine to electronic devices. *Angew Chem Int Ed Engl*. 2008;47:8002–18.
3. Hanabusa K, Takata S, Fujisaki M, Nomura Y, Suzuki M. Fluorescent gelators for detection of explosives. *Bull Chem Soc Jpn*. 2016;89:1391–401.
4. Ihara H, Takafuji M, Kuwahara Y. Polymer functionalization by luminescent supramolecular gels. *Polym J*. 2016;48:843–53.
5. Kato T, Uchida J, Ichikawa T, Soberats B. Functional liquid-crystalline polymers and supramolecular liquid crystals. *Polym J*. 2017;50:149–66.
6. Yamanaka, M. Supramolecular gel electrophoresis. *Polym J*. <https://doi.org/10.1038/s41428-018-0033-y> (in press). 2018
7. Hanabusa K, Itoh A, Kimura M, Shirai H. Terephthaloyl derivatives as new gelators; excellent gelation ability and remarkable increase of gel strength by adding polymers. *Chem Lett*. 1999;28:767–8.
8. Tamaoki N, Shimada S, Okada Y, Belaïssaoui A, Kruk G, Yase K, Matsuda H. Polymerization of a diacetylene dicholesteryl ester having two urethanes in organic gel states. *Langmuir*. 2000;16:7545–7.
9. de Loos M, van Esch J, Stokroos I, Kellogg RM, Feringa BL. Remarkable stabilization of self-assembled organogels by polymerization. *J Am Chem Soc*. 1997;119:12675–6.
10. Eimura H, Yoshio M, Shoji Y, Hanabusa K, Kato T. Liquid-crystalline gels exhibiting electrooptical light scattering properties: fibrous polymerized network of a lysine-based gelator having acrylate moieties. *Polym J*. 2012;44:594–9.
11. Khalily MA, Goktas M, Guler MO. Tuning viscoelastic properties of supramolecular peptide gels via dynamic covalent cross-linking. *Org Biomol Chem*. 2015;13:1983–7.
12. Trenor SR, Shultz AR, Love BJ, Long TE. Coumarins in polymers: from light harvesting to photo-cross-linkable tissue scaffolds. *Chem Rev*. 2004;104:3059–77.
13. Chujo Y, Sada K, Saegusa T. Polyoxazoline having a coumarin moiety as a pendant group. Synthesis and photogelation. *Macromolecules*. 1990;23:2693–7.
14. Moriyama M, Okano T, Ono S, Nagano S, Shirieda N, Yabuuchi K. Macroscopic photoinduced and reversible sol–gel conversions of polymer materials containing photoreactive coumarin moieties. *Trans Mater Res Soc Jpn*. 2015;40:211–4.
15. Yu H, Mizufune H, Uenaka K, Moritoki T, Koshima H. Synthesis and properties of coumarin-derived organogelators. *Tetrahedron*. 2005;61:8932–8.
16. Draper ER, McDonald TO, Adams DJ. Photodimerisation of a coumarin-dipeptide gelator. *Chem Commun*. 2015;51:12827–30.
17. Chen Y, Chen K-H. Synthesis and reversible photocleavage of novel polyurethanes containing coumarin dimer components. *J Polym Sci A Polym Chem*. 1997;35:613–24.
18. Jung JH, Ono Y, Shinkai S. Sol–gel polycondensation in a cyclohexane-based organogel system in helical silica: creation of both right- and left-handed silica structures by helical organogel fibers. *Chem Eur J*. 2000;6:4552–7.
19. Takahashi A, Sakai M, Kato T. Melting temperature of thermally reversible gel. VI. Effect of branching on the sol–gel transition of polyethylene gels. *Polym J*. 1980;12:335–41.
20. Hanabusa K, Yamada M, Kimura M, Shirai H. Prominent gelation and chiral aggregation of alkylamides derived from trans-1,2-diaminocyclohexane. *Angew Chem Int Ed Engl*. 1996;35:1949–51.