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Supramolecular Crosslinked Linear Poly(Trimethylene Iminium Trifluorosulfonimide) Polymer Gels Sensitive to Light and Thermal Stimuli**

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A gel is a kind of soft material which is strong enough to swell and retain solvents due to its 3D network structure comprising polymers or supramolecular assemblies of fibers.^[1] Organogels,^[2] prepared from low-molecular-weight organic compounds, and physical gels,^[3] prepared from linear polymers, are thermosensitive materials that exhibit a reversible sol-gel phase transition upon heating and cooling in an appropriate solvent. The thermoreversible properties of these gels have been attributed to the non-covalent crosslinking of the polymers in the physical gels, and to the crosslinking of the fibrous supramolecular assemblies in the organogels. The introduction of functional groups that can reversibly change the structures of organogels or physical gels by stimuli other than heat has been of much interest as a method to design multiresponsive materials where reversible sol-gel phase transitions can be induced by two or more stimuli.^[4] In the case of organogels, the gel phase is successfully collapsed into the sol phase by light or other stimuli; however, the reverse transition from the sol phase to the gel phase often does not successfully occur.^[5] Regeneration of the gel phase often requires reconstruction of the gels by a heating and cooling cycle to promote the back reaction after exposure to the appropriate stimulus.^[6] To overcome the lack of reversibility in these gel systems, we have developed new multiresponsive reversible polymer gels that do not require any heat treatment. The reversible sol-gel phase transition in our gels is based on the supramolecular crosslinking of polymers by bifunctional crosslinkers. Our strategy is based on the formation of selective supramolecular attachments between multiple hydrogen bond donors on the polymer and two hydrogen bond acceptors in the crosslinkers (Fig. 1). The hydrogen bonds crosslink the polymer chains to form a 3D polymer network. One would expect that noncovalent crosslinking would be quite widely used for mediating thermally reversible sol-gel phase transitions. Surprisingly,



Figure 1. Schematic illustration of the formation of the supramolecular crosslinked network via hydrogen bonding.

there are very few examples of supramolecular crosslinking of polymers by low-molecular-weight crosslinkers.^[7]

In addition, we have introduced an azobenzene group as a photoresponsive functional group in the crosslinker; thus, the trans–cis isomerization of this group influences the crosslinking of the polymer networks. The molecular design of such a supramolecular crosslinked gel is based on the 1:1 complexation of the 2,6-bis(benzoxazol-2-yl) pyridine (bzpybox) ligand and secondary dialkyl ammonium salts, mediated by complementary hydrogen bonds.^[8] The former acts as a hydrogenbond acceptor and the latter as a hydrogen-bond donor. In this report, we demonstrate new thermally sensitive and photoresponsive supramolecular gels consisting of poly(trimethylene iminium trifluorosulfonimide) (PTMI) as the polymeric secondary dialkyl ammonium salt and the bifunctional bzpybox ligand with an azobenzene group (1) as the crosslinker (Fig. 2a).

The PTMI polymer (6.9 mg, 20 mmol per unit)^[9] and 1 (14 mg, 14 mmol) are mixed in acetonitrile (200 µL) in a small snap vial. The suspended solution is heated with vigorous stirring to obtain a clear homogeneous solution. Upon cooling to room temperature, the entire solution solidifies and an orange-red transparent gel is obtained. When the vial is inverted, no fluid can be seen in the vial and the gel sample does not move at all, as shown in Figure 2b. Under the same conditions, the individual components do not form any gels or gel-like matter, and the viscosity of the solutions remains low. Dilute solutions with less than 80 mM of PTMI provide viscous solutions upon mixing; the critical gelation concentration (cgc) in acetonitrile is ~ 55.5 g L^{-1} (55 mM) of **1**. Other organic solvents, such as dichloromethane, chloroform, tetrahydrofuran (THF), and ethyl acetate, do not yield gels at similar concentrations due to the low solubility of PTMI. Heating the re-



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Figure 2. a) Molecular structures and b) image of the PTMI/1 gel: [PTMI] = 80 mm, [1] = 55 mm in acetonitrile.

sulting PTMI/1 gel in acetonitrile turns the non-fluidic gel into a viscous orange-red solution. Upon cooling to room temperature, the resulting solution became a gel again. The sol-gel phase-transition temperature ($T_{\rm gel}$) was found to be 324 K by repeated heating treatments. This thermal behavior is characteristic of thermally reversible physical gels and organogels. Therefore, the PTMI/1 gel undergoes a thermoreversible solgel phase transition due to the collapse of the hydrogenbonded crosslinking between PTMI and 1.

In order to investigate the supramolecular crosslinking of PTMI, we have investigated the complexation of PTMI and **1** under dilute conditions. UV-vis titration (10 μ M) experiments have been performed in 2:1 (v/v) CHCl₃/CD₃CN. Figure 3 shows the changes in the UV-vis absorption of **1** upon the addition of PTMI. As PTMI is added to the solution of **1**, the absorption maximum at 315 nm decreases in intensity, and a new absorption band at 345 nm begins to emerge. This red-

shift is attributed to the stacking of the bzpybox groups of 1. The average binding constant K and the coordination number nhave been estimated by a Scatchard plot^[10] at 315 nm. using the absorbance The binding constant is found to be 2.3×10^6 M⁻¹, and *n* is found to be 1.4. The average binding constant is significantly higher than that of the 1:1 complex of bzpybox 2 and dibenzylammonium trifluoromethanesulfonimide, which forms a single-site model complex.^[8] The association of the crosslinker along the polymeric secondary ammonium cations is assisted by π - π stacking between the bzpybox ligands, leading to the formation of ladderlike supramolecular structures, which in turn form the fibrous aggregate. Moreover, the absorption of the azobenzene group does not change. This indicates that the azobenzene groups are not stacked on each other, since

they are linked by the relatively flexible spacers between the two bzpybox groups.

We have further carried out atomic force microscopy (AFM) studies of the dilute solution of PTMI/1 cast on mica. As shown in Figure 4, the PTMI/1 complexes form a 3D network, and twisted fibers that are longer and wider than the original PTMI fibers are seen. The PTMI/1 complexes form polymeric bundles, and these bundles are crosslinked to form the 3D network. The supramolecular structures of PTMI are only observed in the presence of the crosslinker 1. This suggests that these structures are formed due to hydrogen bonding between the secondary ammonium cations and the bzpybox ligands. The crosslinker 1 acts as a supramolecular crosslinking agent, leading to the formation of the physical gel. Actually, a decrease in the molar ratio of 1 to PTMI to less than 0.5 results in a large decrease in the viscosity. First,



Figure 3. Changes in the UV-vis absorption of 1 upon the addition of PTMI: $[1] = 10 \ \mu M$ in acetonitrile.



Figure 4. AFM image of a dilute solution of PTMI/1 cast on a mica substrate.



PTMI and **1** form ladderlike supramolecular assemblies, subsequently followed by the formation of extended fibers and fiber bundles;^[11] this causes a slight increase in the viscosity of the solution. The excess amount of the crosslinker **1** then links the bundles together to form the 3D network structures, thereby producing the physical gel. Therefore, the formation of the gel and the thermally reversible phase transition of the resulting gel both originate from the non-covalent crosslinking of PTMI by **1** through hydrogen bonds between the secondary dialkyl ammonium units and the bzpybox ligand.

Finally, we have investigated the photosensitive sol-gel phase transitions of PTMI/1. Upon irradiating the composite gels with UV light, their viscosity is significantly changed. Irradiation for about 30 min at room temperature leads to an increase in the fluidity of the gel, and the gel begins to flow along the wall of the vial due to gravity. This implies that the gel is transformed into the sol phase upon irradiation with UV light (220–410 nm). The resulting viscous solution is transformed into a non-fluidic gel under visible light. Thus, the light-induced gelation of PTMI/1 occurs without any heat treatment. The change in the viscosity of PTMI/1 in acetoni-trile upon photoirradiation is shown in Figure 5. Repeated cycles of UV and visible-light irradiation induces sol-gel phase



Figure 5. Cyclic changes in the solution viscosity (η_s) of PTMI/1 in acetonitrile upon photoirradiation.

transitions. The sol-gel phase transition induced by light is reversible, and is apparently related to the cis-trans photoisomerization of azobenzene.^[12] It has been confirmed that the absorption peak at 360 nm, attributed to the trans isomer, decreases upon irradiation with UV light and increases again under sunlight. The cis conformation destabilizes the ladder-like supramolecular assemblies and breaks up the crosslinked bundles. This induces the sol-gel phase transition by light.

In this study, we have demonstrated a new functional stimuli-sensitive gel that has a reversible sol–gel phase transition induced both by heat and light. The thermally reversible crosslinking is caused by the supramolecular assembly of the polymer chain, mediated by complementary hydrogen bonds between the main polymer chain and bifunctional crosslinkers. In addition, incorporation of an azobenzene group into the crosslinker imparts photosensitive properties to the gel due to controlled cis-trans isomerization upon irradiation with light. Therefore, supramolecular crosslinking of polymers by low-molecular-weight crosslinkers is shown to be a useful strategy for designing and constructing thermally reversible gels. By appropriate molecular design of the crosslinker, it should be possible to obtain many reversible gels that undergo sol-gel phase transitions under various stimuli. The viscoelastic properties of the PTMI/1 gel and other new functional reversible gels are currently under investigation.

Experimental

Materials: PTMI was prepared as described previously [9]. **1** was synthesized by the coupling of the bzpybox moiety with azobenzene. The spectral data for **1** are as follows: ¹H NMR (600 MHz, 2:1 (v/v) CDCl₃/CD₃CN): δ 2.42 (t, 4H, J = 5.9 Hz), 2.51 (s, 12H), 4.32 (t, 4H, J = 5.8 Hz), 4.53 (t, 4H, J = 5.9 Hz), 7.07 (d, 4H, J = 8.9 Hz), 7.29 (d, 4H, J = 8.2 Hz), 7.61 (d, 4H, J = 8.3 Hz), 7.62 (s, 4H), 7.84 (d, 4H, J = 8.8 Hz), 8.03 (s, 4H) ppm. Matrix-assisted laser desorption time-of-flight mass spectrometry (MALDI-TOF-MS): *m/e* Calcd. for C₆₀H₄₈N₈O₈ 1009.1; found, 1009.6 [M+H]⁺.

UV-Vis Measurements: The UV-vis spectra were measured using a Shimadzu UV-2500PC instrument. Compound **1** was dissolved in 2:1 (v/v) CHCl₃/CH₃CN to prepare a 10 μ M solution. The solution was poured into a UV cell with a 1.0 cm optical path. The 1.0 mM PTMI solution was titrated up to 50 μ M of [PTMI]_{unit}.

AFM Observations: A TopoMetrix TMX 1010 instrument was used for AFM measurements. The PTMI/**1** gel was diluted with a large amount of acetonitrile. The solution was cast on a fresh mica surface. The AFM imaging was carried out in non-contact mode after drying.

Viscosity Measurements: The viscosity of the PTMI/1 mixture was calculated according to the Hagen–Poiseuille law. The PTMI/1 gel was placed in a quartz-glass tube with a radius of 3.0 mm or 0.75 mm. The length by which the gel moved down the tube was measured over a period of 30 min. The gel was irradiated with UV light for a few minutes using an Ushio Optical Modulex Deep UV500 lamp and a filter that passed UV light with a wavelength of 220–410 nm. The time taken by the PTMI/1 sol to fall 70 mm was measured.

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