

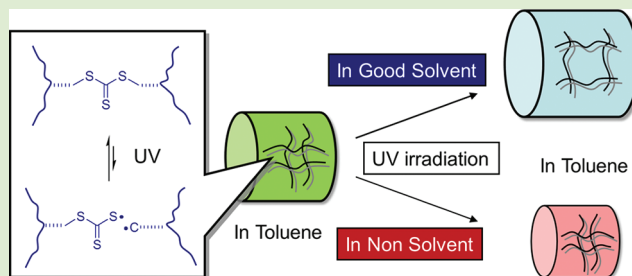
Changes in Network Structure of Chemical Gels Controlled by Solvent Quality through Photoinduced Radical Reshuffling Reactions of Trithiocarbonate Units

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ABSTRACT: Changes in the structure of networks of chemical gels cross-linked by covalent bonds have been investigated using reshuffling (i.e., degenerative exchange) reactions of the covalent bonds. These reactions can be applied to form functional materials including self-healing polymers, plasticity in cross-linked polymers, and shape-memory polymers. Herein, network structures of chemical gels were changed through radical reshuffling reactions of trithiocarbonate (TTC) units, and swelling degrees or network sizes were controlled by solvent quality. The chemical gels were prepared by RAFT copolymerizations of butyl acrylate and a TTC cross-linker, and the swelling degree was different for polymers prepared by solution or bulk polymerization. The cross-linked polymers were swollen in either good or nonsolvents and then exposed to UV light to trigger the radical reshuffling of the TTC units. The degree of swelling and network size in toluene increased in the presence of good solvents, whereas they decreased in nonsolvents. The repetitive changes in the degree of swelling were accomplished by changing the order of exposure to solvents.



The dependence of the degree of swelling of cross-linked polymers on different solvents is a unique typical feature of polymeric gels, and has been applied, for example, to recover solvents and to manufacturing soft materials. Gels can exhibit a discontinuous volume-phase transition.¹ Swelling is caused by the imbalance between the repulsive forces among the polymer chains and the contractile forces due to stretching of elastically active networked structures.^{2,3} Swelling degrees or swelling volumes are affected by the network structure. Gels with high solvent content have recently attracted much interest.^{4,5} The swelling degree for specific solvents increases with network size and decreases with cross-linking density. Nevertheless, while control over the size of the network is important, it is difficult to change network size of chemical gels after the polymerization, because the networks consist of robust covalent bonds.

Recently, there have been attempts to change the network structure of covalently cross-linked polymers by exploiting reshuffling of reversible (dynamic) covalent bonds^{6–9} and applied to produce smart materials including self-healing polymers,¹⁰ plasticity in cross-linked polymers,¹¹ and shape-memory polymers.¹² Controls over swelling degrees of chemical gels using reversible covalent bonds have also been investigated. It was reported that a network size of chemical gels cross-linked by alkoxyamine units could be controlled through nitroxide-mediated radical polymerizations of styrene derivatives.^{13,14} A similar method was applied for the preparation of amphiphilic polymer conetworks.¹⁵ These reactions, however, require additional monomers (styrene

derivatives) after the preparation of gels, and the polymerization irreversibly change the network structure. In addition, it was reported that the degree of swelling of polymer gels cross-linked by trithiocarbonate (TTC) units increased as a result of radical reshuffling reactions of the TTC units triggered by either a radical initiator or a CuBr/amine ligand catalyst.³ However, a reaction in a nonsolvent was not described and the effect of the solvent quality was not studied.

The reshuffling reaction of the TTC units can also be triggered by UV irradiation. Previously we applied this concept to prepare self-healing materials.¹⁶ In this report, we demonstrate changes in the network size of chemical gels via the reshuffling reactions of TTC units under UV irradiation. The use of UV light permits a simpler analysis of solvent effect on the network structures. We show how swelling degree, or network size, can be simply controlled by selecting solvents with different affinities for the polymers, as shown in Figure 1.

Polymers cross-linked with TTC units were prepared by RAFT copolymerization of butyl acrylate (BA) and a TTC cross-linker (1) using AIBN, as previously reported (Figure 1).¹⁶ The polymerizations were carried out under different conditions, a solution polymerization (2a) and a bulk polymerization (2b). Because the TTC units are located along the main chain, it is easy to induce changes in the

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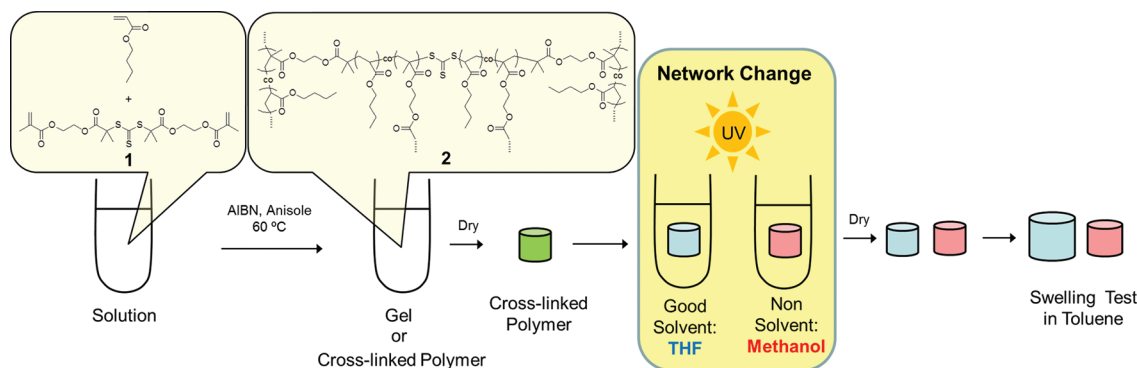


Figure 1. Procedure for changes in the network structure of chemical gels via the radical reshuffling reaction of TTC units. The cross-linked polymers were prepared by RAFT copolymerization of *n*-butyl acrylate and TTC cross-linker (1), and the network changes were carried out in good or nonsolvent, respectively.

Table 1. Preparation and Properties of Cross-Linked Polymers by RAFT Copolymerizations of Butyl Acrylate and a TTC Cross-Linker in a Solution and a Bulk Polymerization

	monomer ratio ([BA]/[1])	[monomer]/[anisole] (vol/vol)	conversion (%)	T_g (°C)	Young's modulus (kPa)	swelling degree in toluene (%)
2a	19:1	50:50 (solution)	99+	-31.4	106 ± 8	651 ± 22
2b	19:1	100:0 (bulk)	99+	-30.4	998 ± 56	254 ± 12

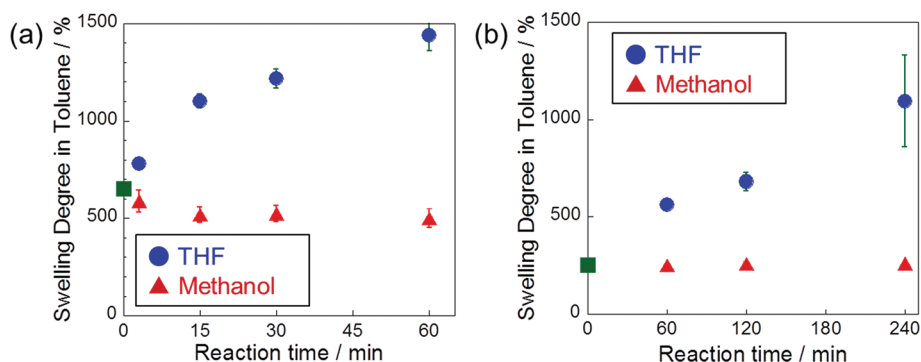


Figure 2. Degrees of swelling of cross-linked polymers 2a (a) and 2b (b) in toluene after exposing to UV light in THF or methanol for each reaction time. Each reaction was carried out three times, and the plots and the error bars show average values and standard deviations, respectively.

network structure. After the polymerizations were completed, the polymers were immersed in acetonitrile and dried under vacuum. Table 1 indicates glass transition temperatures (T_g), swelling degrees for toluene, and Young's moduli of the cross-linked polymers 2a,b after drying. All the polymerizations were driven to high conversions (over 99%), therefore, no unreacted vinyl groups remained. Thus, polymers should have almost the same original cross-linking densities. However, the mechanical properties are different, depending on polymerization conditions. The polymer prepared by solution polymerization has lower tensile modulus (solution (2a), 106 kPa; bulk (2b), 998 kPa). Also, the degree of swelling of 2a in toluene was much higher than that of the sample prepared in bulk polymerization (solution (2a), 651%; bulk (2b), 254%). These results indicate that the cross-linked polymer 2a had lower cross-linking density. Because the polymers should have almost the same overall covalent cross-linking densities, it can be envisioned that physical cross-linking (entanglements) and intramolecular (primary) cyclization made the differences. In the case of the bulk polymerization, because the concentration of polymer/monomer is higher, more entanglements were formed, resulting in high modulus and the low swelling degree. On the other hand, entanglements should have lower probability in the solution polymerization, which reduces tensile modulus.

Additionally, in solution, intramolecular cyclization could occur to larger degree than in bulk.¹⁷ It was reported that a formation of the primary cyclization occurred more frequently at lower monomer concentration, which increased swelling degrees and decreased moduli.¹⁸ In other words, the physical properties of the cross-linked polymers depended not only on the degree of chemical cross-linking, but also on the nature of physical cross-linking such as entanglements and the fraction of intramolecular cyclization.

The effect of changes in network structures was then examined. The cross-linked polymers were immersed in either THF (good solvent) or methanol (nonsolvent for poly(butyl acrylate), PBA) under a nitrogen atmosphere and exposed to UV light (330 nm) to induce reshuffling reactions of the TTC units. The solvents do not absorb UV light at the selected wavelength. As discussed in a previous report,¹⁶ the reshuffling reaction was triggered by homolysis of C–S bonds in the TTC units, followed by radical transfer and radical exchange reactions. The degree of swelling in toluene was investigated after drying (Figure 1). The swelling degree in toluene for sample 2a before the UV irradiation was 650%, after exposing to UV light in THF, the value increased with increasing reaction time, and reached 1440% after 60 min, as shown in Figure 2a. The network could expand via chain disentangle-

ment enabled by reshuffling the TTC units. On the other hand, the degree of swelling decreased from 650% (before UV) to 500% after UV irradiation in methanol for 60 min. In the nonsolvent, attractive interactions between the polymer chains dominated, the network collapsed and entanglements increased through the radical transfers of the TTC units. When the sample was not exposed to UV light and stored in a dark place for 4 h, the swelling degree showed almost no change (707% (THF) and 696% (methanol)).

The variations of the network structures in sample **2a** were investigated by small-angle X-ray scattering (SAXS) measurements, and the correlation lengths (ξ) of the polymer gels were evaluated. The correlation length represents a mesh size consisting of polymer chains in a semidilute solution,¹⁹ which was determined by fitting eq 1 to SAXS profiles. Equation 1 consists of two components, as structure of two phases (fractal dimension formalism)²⁰ and the correlation between the polymer chains (Ornstein–Zernike formalism),²¹ as follows:

$$I(q) = Aq^{-D} + \frac{I_1(0)}{1 + q^2\xi^2} \quad (1)$$

here A and $I_1(0)$ are constant values, D is a fractal dimension, and q is a scattering vector. Figure 3 shows SAXS profiles, fitting curves described by eq 1, and correlation lengths of the gels before and after exposure to UV light in each solvent (ξ).

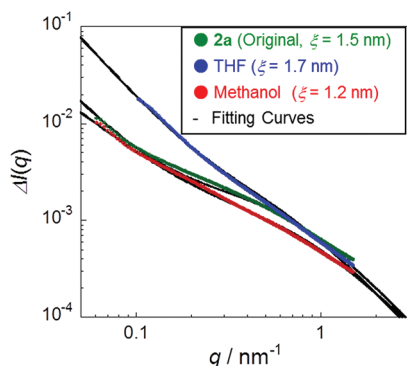


Figure 3. SAXS profiles of the original and reacted polymers **2a** swollen in toluene, their fitting curves described by eq 1, and the values of correlation lengths (ξ). The polymers were exposed to UV light for 30 min in THF or methanol.

Compared with the original polymer (**2a**), the correlation length of the polymer reacted in THF was increased from 1.5 nm (original **2a**) to 1.7 nm (THF). This result supports the concept that mesh size increased through the radical reshuffling reaction of the TTC units in the good solvent. In the case of methanol, the correlation length (1.2 nm) decreased as compared with the original polymer (1.5 nm), indicating that the mesh size of the chemical gels was reduced in the nonsolvent. This indicated that swelling degree and network size were both controlled by the quality of the solvent in the reshuffling reaction of the TTC units.

Network changes of the polymer **2b** were also evaluated. Figure 2b shows swelling degrees of the polymer **2b** after UV irradiation for each reaction time. In THF the degree of swelling increased with increasing the reaction time, same as the reaction of **2a**, and reached 1090% after 240 min. However, the reaction rate was slower than that of **2a**. The reorganization of the polymer chains in **2b** was limited because of the lower

chain mobility. In addition, a reduction of degree of swelling in methanol was not observed which was attributed to fact that the degree of physical cross-linking cannot be increased, because the cross-linking density was already high.

A characteristic feature of polymers with reversible bonds is repeatable reactions. Repetitive control over the degree of swelling was studied by sequentially changing the reaction solvents. Each reaction was carried out for 15 min in THF and for 30 min in methanol using the same procedures. Figure 4 represents the swelling degrees of the polymers **2a** in toluene after the UV irradiation. In the reaction of methanol–THF–

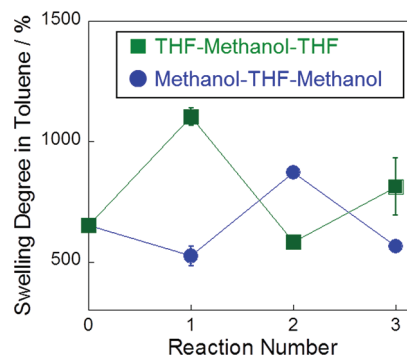


Figure 4. Repeatability changes in degree of swelling of the gels **2a** in toluene after exposing to UV light in THF for 15 min and methanol for 30 min.

methanol sequence, the swelling degree in the second reaction changed from 500% (methanol) to 870% (THF). The degree of swelling decreased to 564% (methanol) after the third reaction. Opposite changes were observed in the reaction sequence, THF–methanol–THF. These results support the concept that the repeatable changes in the network structures of the chemical gels are possible, and that the reaction proceeded without significant side reactions.

In summary, the network structure of the polymer gels cross-linked by the TTC units was controlled by UV irradiation in postpolymerization reactions in selected solvents. The cross-linked polymers were prepared by RAFT copolymerization of BA and TTC cross-linkers. After exposure to UV light, the degree of swelling of the polymers increased in the presence of good solvents and was reduced in the presence of nonsolvents, respectively. Changes in mesh sizes were confirmed by the SAXS measurements. Additionally, the repeatability of changes in degree of swelling was confirmed by changing the order of exposure to solvents. Although the phenomenon might be limited to this polymer structure, it provides a useful approach to obtain responsive gel properties and provide functionalized polymer gels. Since in the past few years, exchange reactions of reversible covalent bonds in polymer gels have been widely applied to the production of smart materials, the phenomenon of control over the mesh size by changes in solvent quality should be important.

EXPERIMENTAL SECTION

Preparation of Cross-Linked Polymer (2a). TTC **1** (504 mg, 1.00 mmol), BA (2.78 mL, 19.0 mmol), anisole (3.3 mL), and AIBN (32.8 mg, 0.2 mmol) were added to a two-neck glass tube and then the solution was degassed by three freeze–pump–thaw cycles. The flask was filled with nitrogen then the solution was immersed in an oil bath, and heated at 60 °C for 24 h. The obtained cross-linked polymer was

purified by swelling under CH₃CN overnight and dried under vacuum to afford a yellow solid (conv. (NMR) = 99+%).

UV Irradiation. In a typical run, cross-linked polymer **2a** and THF (5 mL) were charged to a quartz tube, and deoxygenation was carried out by purging with a nitrogen flow for 30 min. Then, the tube was exposed to UV light (200 W UV lamp with 330 nm bandpass filter in the range of 220–390 nm, 25 cm sample-to-light distance) for 4 h at room temperature, and the polymer was dried under vacuum.

Measurements of Degree of Swelling. Cross-linked polymers were immersed in toluene for 24 h, and their weights in the swollen state (W_{gel}) were evaluated. The swollen polymers were dried under vacuum for 12 h, and the weights in dry state (W_{dry}) were measured. The swelling degree was calculated using the following equation:

$$\text{swelling degree(\%)} = (W_{\text{gel}} - W_{\text{dry}}) / W_{\text{dry}} \times 100$$

SAXS Measurement. SAXS measurements were carried out at the BL40B2 beamline of SPring-8 using an incident X-ray with wavelength $\lambda = 0.150$ nm. Scattered X-rays were detected using a 300×300 mm imaging plate with a resolution of 0.1 mm/pixel and 2236 mm sample-to-detector distance calibrated by the average of three peaks of silver behenate. The measured gels were swollen in toluene and contained in 2 mm glass capillaries. The scattering intensity of the polymers ($\Delta I(q)$) was calculated by subtracting the scattering intensity of the solvent $I_{\text{solvent}}(q)$ from that of the solution $I_{\text{soln}}(q)$ adjusted through transmittance (T_{solvent} and T_{soln}), as in the following equation: $\Delta I(q) = I_{\text{soln}}(q)/T_{\text{soln}} - I_{\text{solvent}}(q)/T_{\text{solvent}}$. Then, the scattering vector was defined as $q = 4\pi \sin \theta / \lambda$.

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Notes

The authors declare no competing financial interest.

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