Self-Healing Materials

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Repeatable Photoinduced Self-Healing of Covalently Cross-Linked Polymers through Reshuffling of Trithiocarbonate Units**

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Self-healing materials are the subject of increasing interest,[1–5] because they can repair the internal and external damage thereby extending the lifetime of the material in numerous applications. The initial polymeric self-healing materials relied on microencapsulated healing agents within the bulk polymer. When the system was stressed, the microcapsules were ruptured releasing agents that reacted with the polymer matrix to repair the damage. This reaction was based on covalent bond formation.[6] The covalent bonds provided the desirable mechanical properties at the site of rupture of the microcapsules, but the repair could not be repeated owing to the consumption of the encapsulated agents.[7] On the other hand, systems based on noncovalent bond formation, such as hydrogen bonds and π–π stacking interactions, can provide a repeatable healing response as a consequence of their reversible reactivity.[8] For example, self-healing rubbers[9] and hydrogels[10] were reported as examples of self-healing materials, based on noncovalent bond systems. The challenge for such systems is to enhance the structural stability and mechanical strength of the materials.[9,10]

Recently, dynamic covalent chemistry[11,12] has attracted much attention. These systems employ the reversible covalent bonds that control the structure of the material[13] by modifying the thermodynamic equilibrium position. The concept has been applied to stimuli responsive polymer networks,[14–17] systems based on reversible cross-linking reactions,[18–22] and size-control of covalent networks.[20] Most recently, self-healing systems based on dynamic covalent chemistry have been developed [23,24] where the reversible covalent bonds enable the polymeric material to undergo repetitive self-repair, while providing mechanically stable structures. Typical approaches rely on multiple equilibrium states with functional groups that respond to external stimuli such as thermal stimulation[19,20,25] and chemical stimulation.[22,24] Photostimulation is an especially powerful technique because the stimulation can occur at room temperature, it is easy to handle, and exposure can be limited to targeted areas. Although some photostimulation of covalent self-healing systems have been reported,[26,27] no macroscopic self-healing polymeric systems that depend on photostimulation have been reported.

In a previous report,[24] our research group demonstrated self-healing reactions of polymer gels based on reshuffling reactions of trithiocarbonate (TTC) units through chemical stimulation procedures. The TTC units have the potential to undergo photostimulated reshuffling reactions because they can act as photoinitiators in RAFT polymerizations.[28,29] Herein, we show that systems based on TTC are photoresponsive and can indeed undergo repeatable self-healing resulting from dynamic covalent reshuffling of TTC units, as shown in Figure 1. To the best of our knowledge, this is the first example that achieves both a repeatable self-healing of covalently cross-linked polymers through photostimuli and macroscopic fusion of separate pieces, simultaneously.

Model reactions using low-molecular-weight TTC compounds **1** and **2** through UV irradiation were performed to investigate and confirm the photoresponsive reshuffling

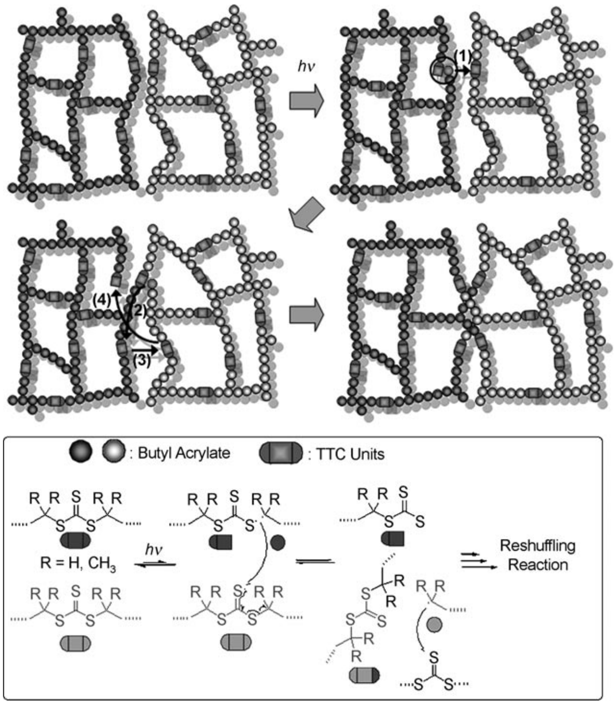

Figure 1. Model self-healing reactions by UV irradiation.

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capacity of TTC units, as indicated in Figure 2. The reactions were carried out by UV irradiation of an equimolar mixture of **1** and **2** in acetonitrile (0.04 M) in a nitrogen atmosphere. The molar ratios of **1**–**3** were estimated by high-performance liquid chromatography (HPLC). Figure 2 shows the variation of the molar fractions of each compound with increasing reaction time. The molar fraction of **1** and **2** gradually decreased and reached 0.25 after 1 hour, and the fraction of **3** concurrently increased to 0.50. The statistical ratio [**1**]/[**2**]/[**3**] = 1:1:2, reached at the equilibrium state indicates that the homolysis of C–S bonds triggered by UV irradiation resulted in efficient exchange reactions catalyzed by radicals. The carbon radicals react with other trithiocarbonate groups by degenerative exchange, as shown in Figure 1. Thus, the reshuffling reaction of TTC units via photostimulations confirmed dynamic covalent properties.

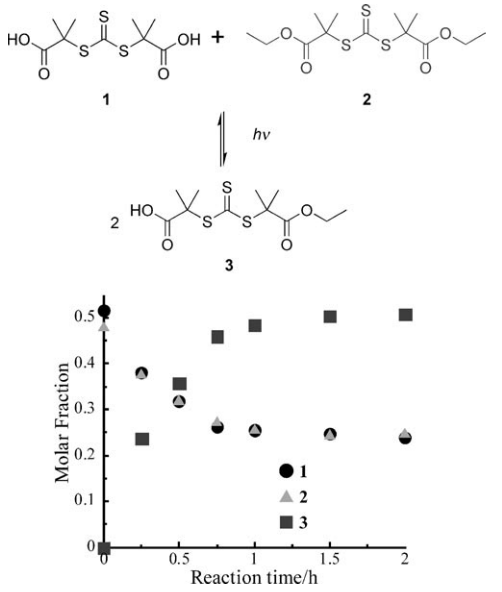
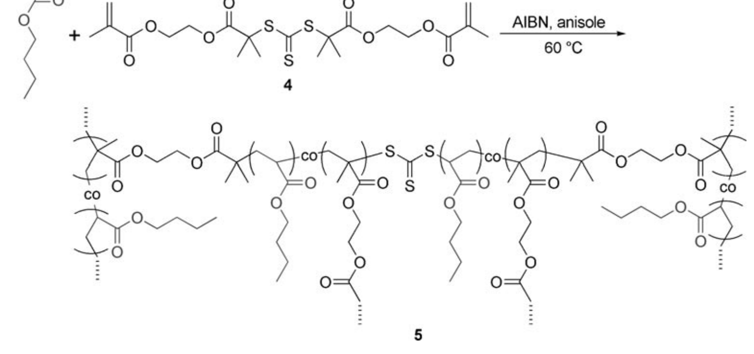


Figure 2. Variations of molar fractions over time in TTC reshuffling reactions between **1** and **2** in acetonitrile (0.04 M) by UV irradiation at room temperature.

A polymer cross-linked with TTC units (**5**) was synthesized by a RAFT copolymerization of *n*-butyl acrylate (BA) and a TTC cross-linker (**4**), as shown in Scheme 1. Poly(*n*-butyl acrylate) (PBA), a polymer with a low T_g value ($T_g \approx -50\,°C$), was selected as the matrix polymer owing to its high chain mobility at room temperature. The polymerization was carried out by heating a mixture of BA and **4** with 2,2′-azobis(isobutyronitrile) (AIBN) ([BA]/[**4**]/[AIBN] = 19/1/0.7) in anisole ([monomer]/[anisole] = 1/1 (v/v)) at 60 °C. The polymerizations of BA with TTC units was initiated by AIBN and accompanied by radical addition to the central sulfur in TTC units, thus triggering homolysis of C–S bonds to start the RAFT polymerization.[30] The solution gelled after heating for 40 minutes, and a high conversion was confirmed after 24 hours (99 + % determined by ^{1}H NMR spectroscopy). Thus, essentially no vinyl groups remained in the cross-linked polymer network. A significant feature of the design and structure of this cross-linked polymer is that almost all TTC units are located in the main chain or at branching points of PBA, as shown in Figure 1. After photostimulation, the TTC units generate radicals at formed reactive chain ends by bond homolysis, which provides additional mobility to the radicals. Three self-healing tests were attempted: 1) self-healing reaction in solution, 2) self-healing reaction in the bulk state, and 3) self-healing reaction of completely separated fragments of cross-linked polymers.



Scheme 1. Preparation of a cross-linked polymer by RAFT copolymerization of BA and **4**.

First, self-healing in the presence of a solvent was demonstrated by the macroscopic fusion of three pieces of cross-linked polymers into one piece. We chose acetonitrile as a reaction solvent because it does not absorb UV light and does not excessively swell the cross-linked polymers. The self-healing reactions were carried out by exposing to UV light a sample of polymer **5** that had been cut into three pieces and placed under mild pressure by a 4 gram weight, in acetonitrile and under nitrogen. When the cross-linked polymer was not exposed to UV irradiation, the three pieces retained their discrete states. However, as the photographs in Figure 3a show, after UV irradiation for 4 hours the three pieces were fused into a single sample. The weight of the cross-linked polymer after UV irradiation did not change (< 2 % yield), thus indicating no depolymerization under these conditions. The recovered tensile modulus value of sample after healing was (65 ± 11) kPa whereas that of an as-cured sample before being cut was (69 ± 6) kPa. These results indicated that the samples had undergone a photostimulated macroscopic self-healing fusion reaction.

The potential attractive point of dynamic covalent-bond chemistry is that the reversible covalent bonds enable repetitive changes in the network structure. To demonstrate this, a second self-healing reaction was carried out under the same conditions using the once healed cross-linked polymers. Figure 3b shows photographs of cross-linked polymers before and after 12 hours of photostimulation. As in the first reaction, the three pieces of the cross-linked polymers combined into one piece. To confirm the healing procedure, the resulting gel was dipped in anisole for 6 hours. In a good solvent, the material should swell the matrix and break, if the resulting gel was not chemically fused but rather physically entangled. Figure 3c shows a photograph of a swollen cross-

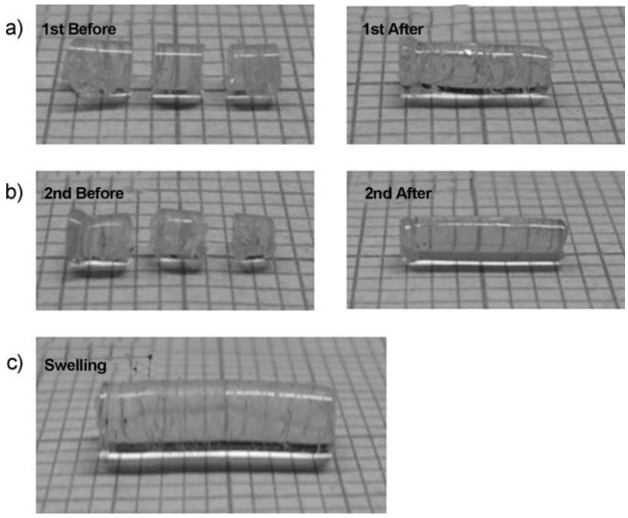


Figure 3. Photographs of cross-linked polymers in repetitive self-healing reactions under UV irradiation in acetonitrile a) before and after first reaction for 4 h, b) before and after second reaction for 12 h, and c) after swelling test in anisole for 6 h.

linked polymer dipped in anisole for 6 hours, after the second healing cycle. This outcome suggests that the final sample formed a clear and transparent single piece, thus indicating that repeatable self-healing was accomplished by UV irradiation of the TTC cross-linked material. These self-healing processes were successfully repeated at least five times.

Next, a self-healing reaction in the bulk state by UV irradiation was attempted. Considering the lower chain mobility in the bulk state than that in solution, or solvent swollen state, the reaction was performed for 48 hours, and the initial sample of the cross-linked polymer was only partly cut, as shown in Figure 4 a (left). The reaction was carried out by UV irradiation in a nitrogen atmosphere and under pressure of a 10 gram weight. The macroscopic crack almost completely disappeared after the UV irradiation, compared with original damage, as illustrated in Figure 4 a (right). This result indicates that the self-healing reaction proceeded also in the bulk state through TTC reshuffling at room temperature. However, because the cut surfaces were not in full contact with each other, a small crack remained on the surface. Additionally, as a result of the low diffusion of the molecular chains in bulk, a long reaction time was necessary. Generally, macroscopic fusion of a cross-linked polymer in the bulk state is challenging owing to the limited chain mobility. This model could be the first example of macroscopic self-healing of covalently cross-linked polymers in the bulk state under photostimulation, and is inspired by successful self-healing of the hydrogen-bonded system.[9]

Finally a self-healing reaction of pieces of completely separated cross-linked polymers was attempted. From the viewpoint of material recyclability, dynamic-covalently cross-linked polymers have the potential to be refabricated in easy and convenient steps. The reaction was carried out by UV irradiation of shredded cross-linked polymer samples **5** in a small quartz tube immersed in acetonitrile under a 10 gram weight pressure. Figure 4 b shows photographs of the samples before and after the 24 hours reaction. After the UV irradiation, the previously completely separated particles of the cross-linked polymers were combined into one piece and retained the cylindrical shape of the tube even after the anisole swelling test, thus confirming that the reshuffling reaction of TTC units in the cross-linked polymers had proceeded, and the polymer chains initially separated in discrete parts were chemically joined (Figure 1). These results indicate that the TTC units in the fragments of the network polymer could be broken and reformed again simply by placing the material in a mold and exposing it to UV irradiation. This approach could be applied to recycle covalently cross-linked polymers into complex-shaped parts.

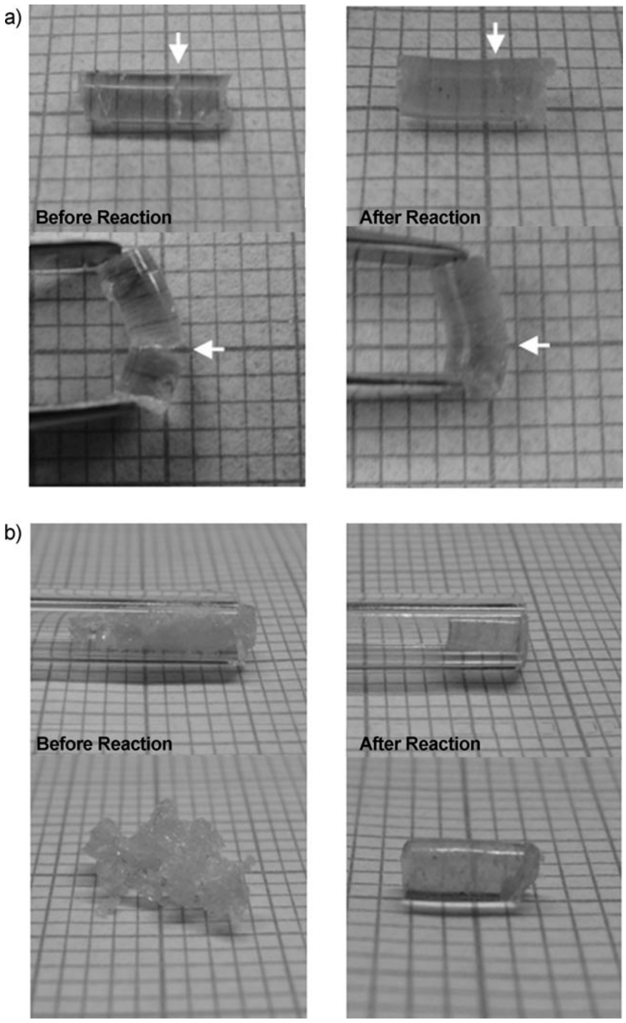


Figure 4. Photographs of cross-linked polymers before and after an UV irradiation under nitrogen: a) in bulk state for 48 h, and b) completely discrete polymers for 24 h.

In summary, we demonstrated the repeatable photo-induced self-healing nature of photoresponsive covalently cross-linked polymers. The model reshuffling of TTC units under photostimulation was monitored using the low-molecular-weight compounds. Then, a TTC cross-linked polymer was successfully prepared by RAFT copolymerization of BA and a TTC cross-linker. The repeatable photoresponsive nature of the self-healing system and macroscopic fusion of separate polymer pieces by UV irradiation of the TTC cross-linked polymers were first accomplished in the presence of a solvent. Next, the TTC cross-linked polymers were subjected to the self-healing reaction in bulk state, resulting in macroscopic fusion of completely separate polymer pieces. Polymers cross-linked with dynamic covalent moieties can be applied to prepare novel materials with repeatable healing and other desirable properties.

Experimental Section

Preparation of TTC diester **2**: Compound **1** (1.41 g, 5.00 mmol),[31] triphenylphosphine (3.93 g, 15.0 mmol), ethanol (1.2 mL, 15 mmol), and THF (25 mL) were charged to a 250 mL three-neck flask, then the solution was deoxygenated by nitrogen flow for 30 min. The flask was immersed into an ice bath, and then a solution of diethyl azodicarboxylate (2.6 g, 15 mmol) in toluene (5 mL) was added dropwise over 20 min. After stirring the reaction for 12 h at room temperature, the solution was heated at 40 °C for 4 h. Then, chloroform and a saturated aqueous sodium bicarbonate solution were added, and the aqueous layer was washed twice with chloroform. The combined organic layers were dried over magnesium sulfate, and concentrated under vacuum. The residue was purified by a flash column chromatography on silica gel ([ethyl acetate]/[hexane] = 1:10 (vol/vol)) to afford a dark orange solid (1.46 g, 86 % yield). ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 1.18$ (t, $J = 7$ Hz, 6H; CH_2CH_3), 1.59 (s, 12H; CH_3), 4.08 ppm (q, $J = 7$ Hz, 4H; CH_2CH_3); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 15.43, 26.62, 57.47, 174.08, 219.75$ ppm.

Reshuffling reaction of **1** and **2**: The TTC dicarboxylic acid **1** (28.2 mg, 0.1 mmol), TTC diester **2** (33.9 mg, 0.1 mmol), and acetonitrile (5 mL, including 0.2 % *o*-xylene as an internal standard) were charged to a two-neck glass tube, and then the solution was degassed by five freeze-pump-thaw cycles. The tube was filled with nitrogen and the solution was exposed by UV irradiation (200 W UV lamp with 330 nm bandpass filter in the range of 220–390 nm, 25 cm sample-to-light source distance, a 330 nm light intensity at the sample was 9×10^{-4} W cm^{-2}) at room temperature. The samples were extracted via syringe after specific reaction times to estimate time dependence of the reshuffling reaction. The molar ratios of **1**–**3** were evaluated by HPLC measurements (CH_3CN/water = 3:1 (v/v), flow rate: 1.0 mL min^{-1}), equipped with a Waters 2965 controller and a Waters 2487 detector.

Preparation of cross-linked polymer **5**: The TTC **4**[24] (1.01 g, 2.00 mmol), BA (5.6 mL, 38 mmol), anisole (5.8 mL), AIBN (230 mg, 1.40 mmol), and small glass tubes 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 and then immersed into an oil bath, and heated at 60 °C for 24 h. The obtained cross-linked polymer was purified by Soxhlet (dichloromethane) extraction for 15 h, and dried under vacuum to afford a yellow solid (99 + % conversion was determined by ^{1}H NMR spectroscopy).

Self-healing reactions: In a typical run, three pieces of cross-linked polymer **5** (43.4 mg) and acetonitrile (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 source distance, a 330 nm light intensity at the sample was 9×10^{-4} W cm^{-2}) for 8 h at room temperature, and the cross-linked polymer was dried under vacuum.

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