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Self-Healing Materials

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Self-Healing of Chemical Gels Cross-Linked by Diarylbibenzofuranone-Based Trigger-Free Dynamic Covalent Bonds at Room Temperature**

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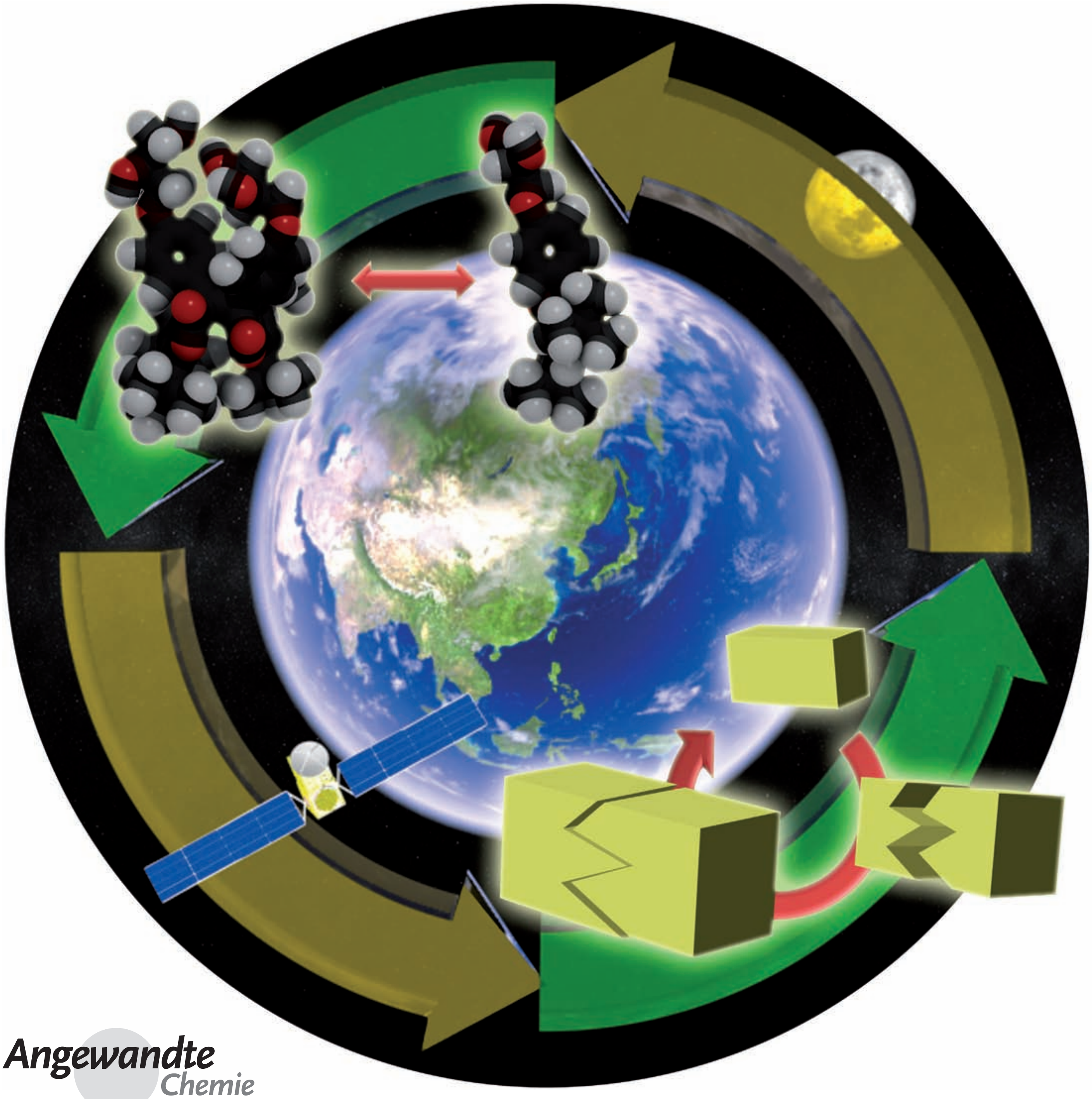
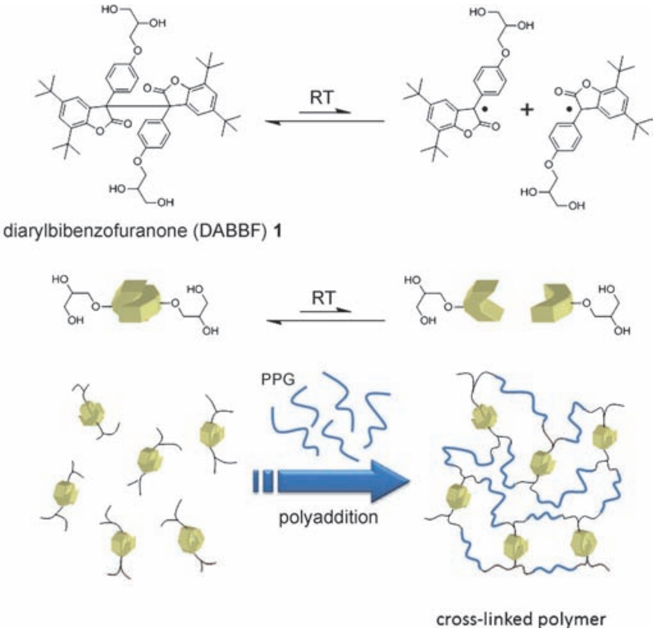


Dynamic materials[1,2] that can exhibit reversible properties have attracted much attention because of their wide range of responses from self-healing to mechanical work. These materials have the potential to revolutionize technologies such as sensors and actuators, and they also have numerous biomedical applications. Thus far, two approaches have been developed to obtain these dynamic materials. The first method makes use of noncovalent (supramolecular) chemistry,[3] such as hydrogen bonding and π–π stacking. Noncovalent bonds have been used for the development of stimuli-responsive healable materials,[4–7] self-healing materials,[8,9] and aqua materials.[10] Moreover, host–guest molecular recognition has been also applied for macroscopic self-assembly.[11] These supramolecular dynamic materials have the potential to be employed in many applications. The second route uses dynamic covalent chemistry[12,13] based on the thermodynamic equilibrium of bond breaking and reformation. Most of the previous research about dynamic covalent bonds reported that external stimuli such as heating, light, chemical species, and mechanical stress were necessary for the transformation of the structures.[14,15] For example, Deng et al. synthesized healable cross-linked polymer gels that have reversible covalent acylhydrazone bonds under acidic conditions.[16] Matyjaszewski and co-workers described the synthesis of self-healing cross-linked polymers and gels having trithiocarbonate units in their structures. Their self-healing behaviour was triggered by radical-generating reagents or UV light.[17,18] Reversible Diels–Alder units have been investigated for thermally healable materials.[14,19,20] Lehn and co-workers reported new Diels–Alder units that display reversible structural transformation at room temperature in the absence of external stimuli, although no mechanical data on these materials was reported.[21,22]

Herein, we present dynamic materials that have the ability to autonomously self-heal under mild conditions such as under air at room temperature, using a novel dynamic covalent bond unit. Diarylbibenzofuranone (DABBF) was employed as a dynamic covalent bond (Scheme 1). DABBF is a dimer of arylbenzofuranone (ABF), a known antioxidant. Scaiano and co-workers reported that DABBF does not need special stimuli to reach a state of thermodynamic equilibrium.[23–27] Moreover, radical species formed from cleaved DABBF tolerate oxygen.[28] In this study, we prepared cross-linked polymeric gels that included the DABBF unit as a cleavable and reversible cross-linker under air at room temperature. The chemical and mechanical properties of these macroscopic self-healing materials were evaluated.



Scheme 1. Chemical structures of diarylbibenzofuranone (DABBF) **1** and of polymers cross-linked by DABBF **1** units.

To form three-dimensional dynamic materials, we designed cross-linked polymer **2**. DABBF **1** was prepared as a cross-linker from 4-hydroxymandelic acid and 2,4-di-*tert*-butylphenol in three steps. Cross-linked polymer **2** was synthesized by polyaddition of DABBF **1** and a toluene-2,4-diisocyanate-terminated poly(propylene glycol) (PPG, $M_n = 2400$), in the presence of di-*n*-butyltin dilaurate (catalyst) in 1,4-dioxane. The PPG was chosen as the main chain because of its high solubility and the flexibility of its molecular chains and the resulting simplicity in using it in the reaction. The fluidity of the reaction mixture slowly decreased during the course of the reaction. The reaction mixture finally lost fluidity after 48 h, indicating that polymerization was successful. A typical cross-linked polymer **3** was prepared and used as a control sample. It was prepared from tetrahydric bisphenol A and diisocyanate-terminated PPG in a manner outlined for polymer **2**.

To confirm whether or not DABBF units in cross-linked polymer **2** were a state of equilibrium and could exchange their bonds, de-cross-linking reaction of cross-linked polymer **2** was performed in DMF under air at room temperature by adding excess DABBF **1**. Figure 1 shows results of the de-cross-linking reaction, the chemical structures of cross-linked polymers **2** and **3**, and expected de-cross-linked **2**. After de-cross-linking for 24 h, a THF-soluble high-molecular-weight

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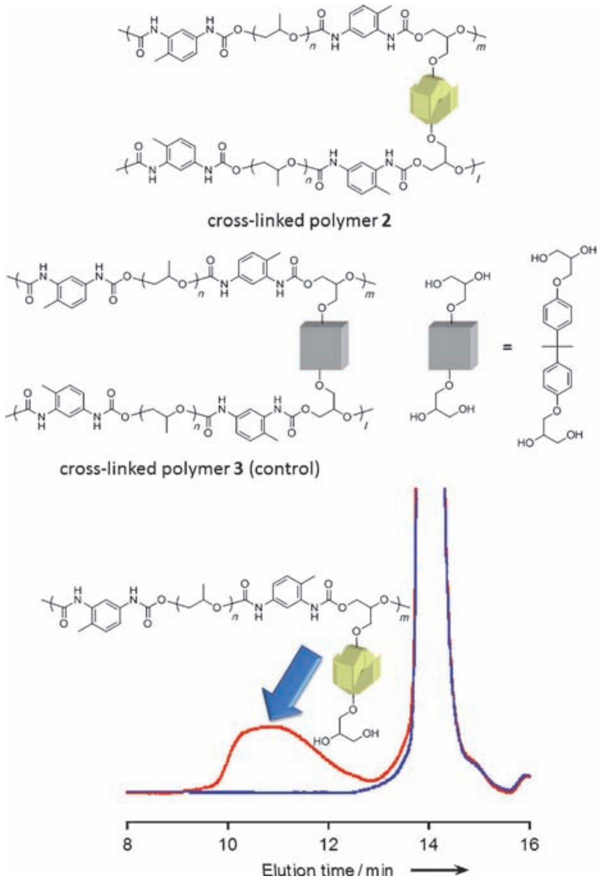

Figure 1. Chemical structures of cross-linked polymer **2** and **3**, and GPC curves of the solution of de-cross-linked **2** (red) and control (blue).

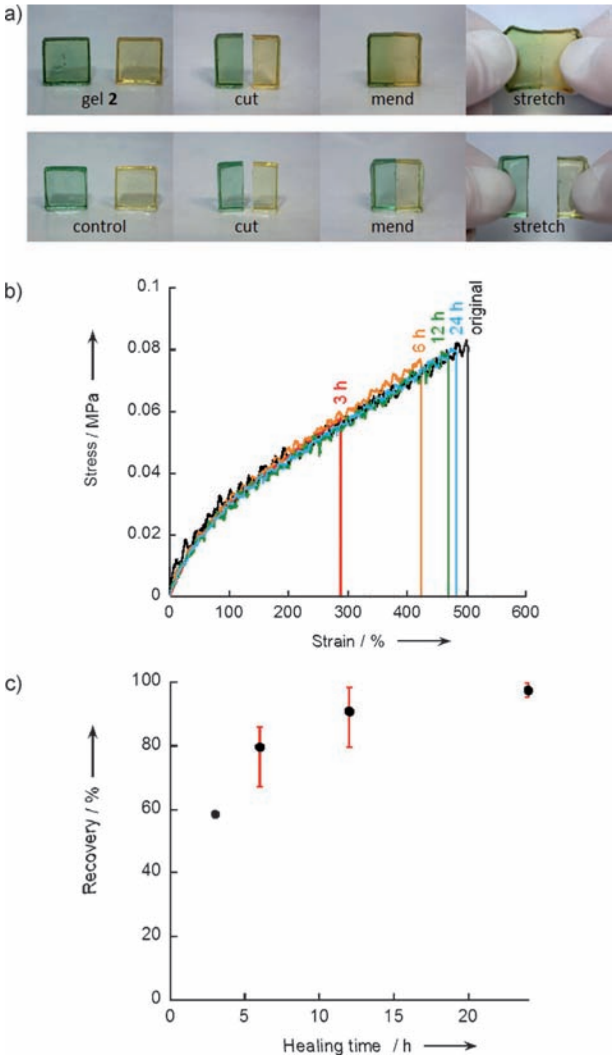

Figure 2. a) Photographs of self-healing behavior of cross-linked polymer gels **2** compared with conventional cross-linked polymer gels **3** under air at room temperature; original, cut, mended, and stretched state, respectively, after 24 h. b) Typical stress–strain (stress–strech ratio) curves of cross-linked polymer gels **2** before and after self-healing measured under air at room temperature. Cut pieces were contacted immediately after cutting and were healed for different times. Colored vertical lines correspond to elongation at breaking for given healing times. c) Degree of recovery of healed cross-linked polymer gels **2** in elongation at breaking depends on healing times. Error bars show maximum and minimum values of three samples.

component ($M_n = 28300$) was detected by GPC measurement. It was expected to be linear polymers and/or cross-linked oligomers. Although we tried to perform a detailed analysis by fractionating this component, the cross-linking reaction occurred again after fractionation. However, the ^{1}H NMR spectrum of the solution without fractionation after de-cross-linking clearly indicated the presence of soluble PPG, which had constituted a three-dimensional network. In contrast, these results were not observed in the case of the control experiment. Consequently, we confirmed that the above-mentioned reorganization of the cross-linked polymer **2** was due to the autonomously exchangeable DABBF units.

The self-healing property of the cross-linked polymer gel **2** was also investigated under air at room temperature. DMF was selected as a solvent for the gels, because it prevents the urethane units from hydrogen bonding and it has low volatility. The gel samples of **2** with and without indigo (0.1 mg mL^{-1}) for better visibility were prepared and cut with a razor blade to expose fresh surfaces (Figure 2 a). The fresh surfaces were wetted with a small amount of DMF to contact tightly and then were brought together immediately without pressing them in an overly strong-handed manner. The in-contact samples were kept at room temperature under air. After 24 h, self-healing of the contacted samples could be observed and the scars had almost disappeared. Even after manually stretching the sample, no destruction occurred. A similar self-healing test was performed on the gel of **3**. This control chemical gel does not possess dynamic covalent bonds. The cut pieces of the control gel could not be coalesced and easily separated into two pieces by manual stretching of the sample (Figure 2 a). Furthermore, the self-healing behavior of cross-linked polymer gels **2** under air at 0 °C was not observed, indicating that the self-healing behavior depends on the temperature. In the present system, at room temperature, an autonomously self-healing system was successfully achieved.

Tensile tests were performed to quantitatively evaluate self-healing properties. The healing process of the samples was performed in the dark under saturated vapor pressure of DMF to avoid the evaporation of DMF and to eliminate the effect of light, which may generate radicals. Figure 2 b shows typical stress–strain (stress–strech ratio) curves of mended cross-linked polymer gels **2** after different healing times. As shown in Figure 2 c, longer healing times led to better healing. A recovery of 98 % of the original elongation at breaking was possible over periods of 24 h. An important result is that most of the healed samples did not break at the contacted surface under the tensile testing. This observation indicates that the mechanical strength of the cut samples recovered after being healed for 24 h and a state of equilibrium had been reached. In contrast, the control samples cross-linked by bisphenol A units showed a recovery of less than 5 % of the original elongation at breaking even after healing for 120 h, although their original specimens showed two times larger strain and several times larger stress at breaking than those of cross-linked polymer gels **2**. This finding can be attributed to the differences in the structures of the cross-linkers and can also be explained by the bonding energies of the C–C bonds in DABBF (23 kcal mol^{-1})[25] and bisphenol A (typical C–C bond: 90 kcal mol^{-1}).

In most of the earlier research regarding self-healing systems using reversible bonds, the freshness of the surfaces was shown to strongly influence their self-healing properties. The reason for this is deactivation of the fresh surfaces by humidity, air, etc.[8,10] Our self-healing system is based on the radical exchange reaction of DABBF units and it is expected to be tolerant of humidity and air. Thus, we investigated the effect of the freshness of the surfaces on self-healing properties. The tolerance of the cross-linked polymer gels **2** was evaluated by tensile tests. The specimens of the gels were cut into two pieces and the pieces were kept in the dark under vapor pressure of DMF at room temperature for different times (waiting times) without contacting the pieces. After a certain time, the cut surfaces were wetted with a small amount of DMF, were contacted, and again kept in the dark at room temperature for 24 h. Figure S3a shows typical stress–strain curves of mended cross-linked polymer gels **2** after different waiting times and after healing for 24 h. As shown in Figure S3b, the cut samples could efficiently heal even though 120 h elapsed before they were first brought into contact. Surprisingly, most of the mended gels did not break at the contacted surfaces and the mechanical property of the mended gels showed recovery of 70–90 %. Also, adhering of two pristine pieces was observed. These findings clearly indicate that DABBF units are sufficiently dynamic and can exchange their central C–C bonds under ambient conditions at the contacted interfaces of the gels. Moreover, the exchangeability of DABBF molecules is still active even after exposure to air for long periods. This behavior is different to what has been previously reported for non-covalent bonds such as hydrogen bonding.

In conclusion, we have demonstrated the autonomously self-healing nature of covalently cross-linked chemical gels under mild conditions. This system does not require any stimuli. Cross-linked polymers that contain a DABBF unit, which is a novel dynamic covalent bond unit, were successfully prepared by polyaddition of diisocyanate compounds and a DABBF cross-linker. The autonomous structural transformation and the macroscopic mending of separated gel pieces under air at room temperature without any stimuli were accomplished by a dynamic covalent approach. Furthermore, the cross-linked gels could self-heal on other surfaces and the self-healing property was shown even after 5 days of being separated. Polymers cross-linked with dynamic covalent bonds have the potential to be applied to novel materials with semi-permanent healing and other desirable properties.

Experimental Section

Preparation of cross-linked polymer **2**: In a typical run, DABBF **1** (60 mg, 73 μmol), tolylene 2,4-diisocyanate-terminated poly(propylene glycol) ($M_n = 2400$, 350 mg, 150 μmol), and 1,4-dioxane (0.41 mL) were combined on a Teflon-coated petri dish. A THF solution of 10 vol % di-*n*-butyltin dilaurate (10 μL, 1.8 μmol) was dropped into the mixture through a syringe under a nitrogen atmosphere at room temperature. After 48 h, the gel was purified by immersing in water for 48 h and freeze-drying. The samples for the self-healing tests were prepared by a similar method in DMF.

De-cross-linking reaction of cross-linked polymer **2**: Cross-linked polymer **2** (20 mg) and a DMF solution (2.69 mL) of DABBF **1** (20 equiv./DABBF in cross-linked polymer **2**) were charged into a sample tube. The mixture was then stirred under air at room temperature. After 24 h, the reaction mixture was evaluated by GPC analysis at 40 °C; experimental set-up: guard column (Tosoh TSK guard column Super H-L), three subsequent columns (Tosoh TSK gel SuperH 6000, 4000, and 2500), differential refractive index detector, and a UV/Vis detector.

Self-healing: Gel samples of cross-linked polymers **2** and **3** were cut and contacted immediately or after being kept apart in the dark under saturated vapor pressure of DMF at room temperature for different periods of time; the cut area was wetted with a small amount of DMF to contact these surfaces tightly. The healing process was performed in the dark under saturated vapor pressure of DMF at room temperature for different times.

Tensile tests: Gels of cross-linked polymers **2** and **3** were fabricated into ISO 37-4 specimens (dumbbell shape, 12 mm × 2 mm × 0.6–1 mm) and were fixed at both ends on thin Al plates with glue and adhesion tape. The specimens were stretched in tensile tests under air at room temperature by using a Shimadzu EZ graph equipped with a 50 N load cell at a crosshead speed of 5 mm min^{-1}. The measurements were performed using more than six test pieces for each healing time and each waiting time; three of them were chosen. Average values were determined from these three samples.

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