

SELF-HEALING AND MECHANOCROMISM OF DIARYLBIBENZOFURANONE-BASED DYNAMIC COVALENT POLYMERS

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ABSTRACT

Covalent bonds with the ability to reach an equilibrium state between combination and dissociation under certain conditions have been studied, and systematic method for controlling the structures of compounds and polymers based on these reversible covalent bonds has been spotlighted as dynamic covalent chemistry. In the present study, diarylbibenzofuranone (DABBF)-based dynamic covalent polymers were designed with two notable functionalities, self-healing of polymer gels cross-linked by DABBF and mechanochromism of DABBF-containing linear polyurethanes.

Cross-linked polymers with exchangeable dynamic covalent bond at room temperature were synthesized by polyaddition of DABBF-tetraol and tolylene diisocyanate terminated polypropylene glycol. The self-healing property of the DABBF-containing cross-linked polymer gel was investigated under air at room temperature. The gel samples were prepared and cut with a razor blade to expose fresh surfaces. The fresh surfaces were brought together immediately in the absence of external force. 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. Tensile tests were also performed to quantitatively evaluate self-healing properties. A recovery of 98 % of the original elongation at breaking was possible over periods of 24 h.

Stimuli-responsive polymers which show color change by mechanical stress were also synthesized and their mechanochromic behavior was investigated. Since the central C-C bonds in DABBF have lower bond dissociation energy, DABBF can reversibly cleave to the corresponding radicals with blue color. We employed DABBF as a mechanochromic unit. DABBF-containing polyurethane films were prepared and their elongation-induced color change was observed.

1. INTRODUCTION

Self-healing polymers attract much attention because they can repair their internal and/or external damage by themselves, thereby extending the lifetime and potential to be applied to many applications. Covalent bonds with the ability to reach an equilibrium state between combination and dissociation under certain conditions have been studied, and systematic method for controlling the structures of

compounds and polymers based on these reversible covalent bonds has been spotlighted as dynamic covalent chemistry [1,2]. Diarylbibenzofuranone (DABBF) derivatives show equilibrium between DABBF and arylbibenzofuranone (ABF) radicals even at room temperature (Figure 1), because the central C-C bonds in DABBF derivatives have lower bond dissociation energy. In the present study, DABBF-based dynamic covalent polymers were designed with two notable functionalities, self-healing of polymer gels cross-linked by DABBF [3] and mechanochromism of DABBF-containing linear polyurethanes.

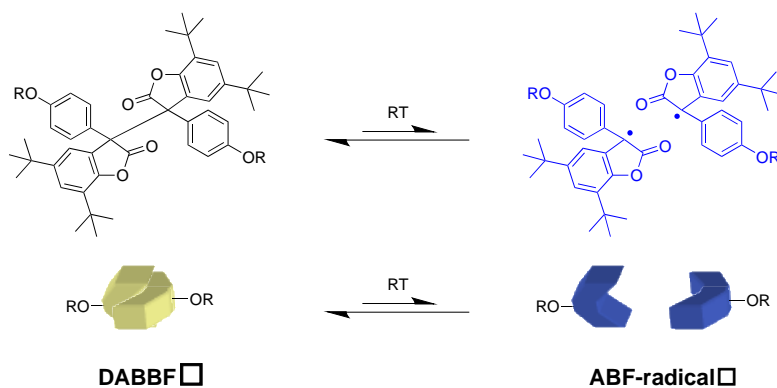


Figure 1: Equilibrium between DABBF and arylbibenzofuranone (ABF) radicals.

2. MATERIALS

As monomers for the synthesis of linear and cross-linked DABBF-based dynamic covalent polymers, we prepared **DABBF-diol** and **DABBF-tetraol** derivatives from 4-hydroxymandelic acid and 2,4-di-*tert*-butylphenol in three steps. As shown in Figure 2, DABBF-containing linear polyurethane (**DABBF-PU**) and cross-linked polymers (**DABBF-XL**) were prepared by polyaddition of **DABBF-tetraol** and a toluene-2,4-diisocyanate terminated poly(propylene glycol) (PPG, $M_n = 2400$), in the presence of di-*n*-butyltin dilaurate (catalyst) in *N,N*-dimethylformamide (DMF) or 1,4-dioxane. PPG was chosen as the main skeleton because of its high solubility and flexibility of its molecular chains and the resulting simplicity in using it in the reaction. In the case of linear polymer, the viscosity of the reaction mixture gradually increased during the course of the reaction. For the preparation of the cross-linking polymer, the fluidity of the reaction mixture decreased and finally gel was formed after 48 h, indicating that polymerization was successful. As a control sample, covalently cross-linked polymer (**BisA-XL**) was prepared from tetrahydric bisphenol A (**BisA-tetraol**) and diisocyanate-terminated PPG in a manner outlined for **DABBF-XL**.

3. METHODS

Self-healing experiment: Gel samples of cross-linked polymers (**DABBF-XL** and **BisA-XL**) were cut and contacted immediately. Healing process was performed in the dark under saturated vapor pressure of DMF at room temperature for different times.

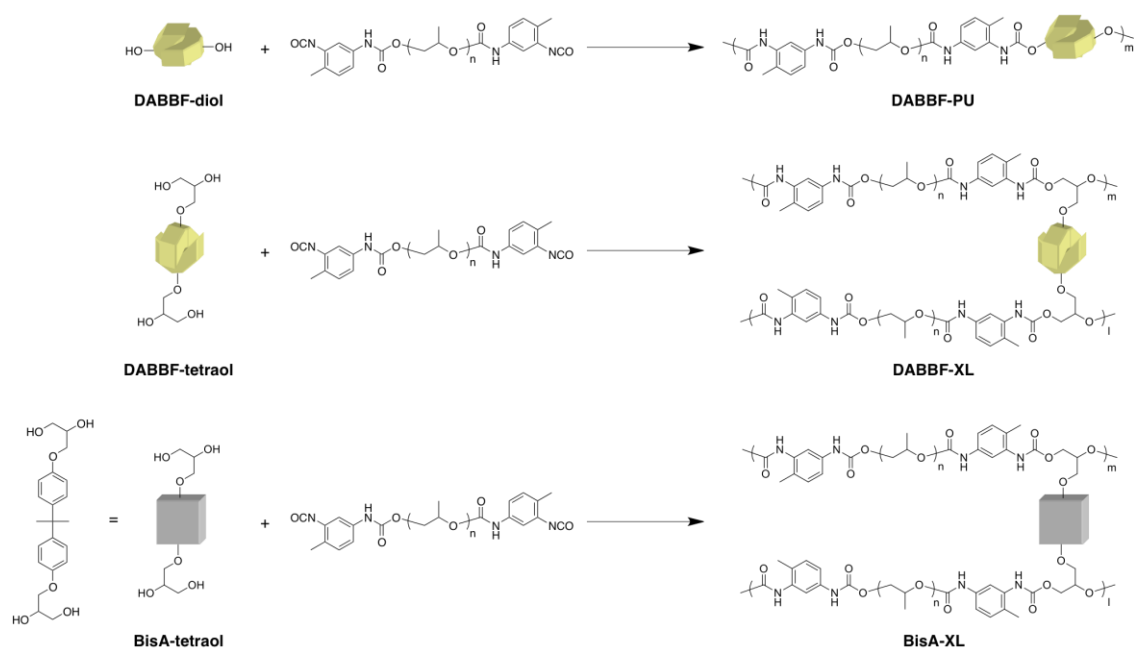


Figure 2: Preparation of DABBF-containing linear polyurethane (**DABBF-PU**) and cross-linked polymer (**DABBF-XL**), and bisphenol A-containing cross-linked polymer (**BisA-XL**).

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

4. RESULTS AND DISCUSSION

Cross-linked polymers with exchangeable dynamic covalent bonds at room temperature were synthesized by polyaddition of **DABBF-tetraol** and tolylene diisocyanate-terminated PPG. The self-healing property of the **DABBF-XL** gel was investigated under air at room temperature. The gel samples were prepared and cut with a razor blade to expose fresh surfaces. The fresh surfaces were brought together immediately in the absence of external force. 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 (Figure 3). Tensile tests were also performed to quantitatively evaluate self-healing properties. A recovery of 98 % of the original elongation at breaking was possible over periods of 24 h.

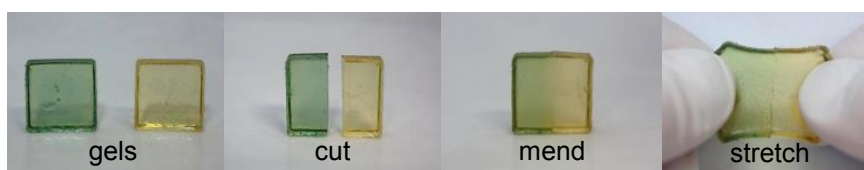


Figure 3: Self-healing behavior of **DABBF-XL** gel.

Stimuli-responsive polymers which show color change by mechanical stress were also synthesized and their mechanochromic behavior was investigated. Since the central C-C bonds in DABBF derivatives have lower bond dissociation energy, DABBF can reversibly cleave to the corresponding radicals with blue color. We employed DABBF as a mechanochromic unit. DABBF-PU films were prepared and their elongation-induced color change was clearly observed (Figure 4).

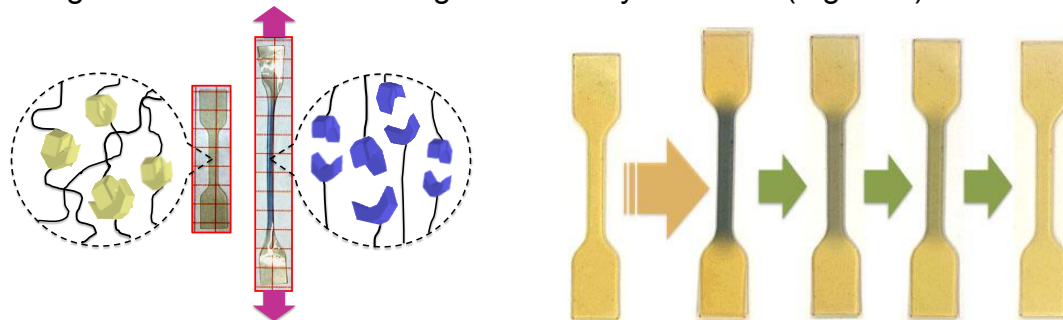


Figure 4: Mechanochromism of a DABBF-PU film.

5. CONCLUSIONS

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 containing 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. Also, we have demonstrated mechanochromism of DABBF-PU.

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