



# Self-healing bio-based furan polymers cross-linked with various bis-maleimides



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## ABSTRACT

A series of bio-based self-healing polymers was prepared by cross-linking a furan polymer, poly(2,5-furandimethylene succinate), with bis-maleimide compounds by means of Diels–Alder reactions. In addition to the amount of the bis-maleimide linker, the molecular structure of the bis-maleimide played a key role in determining the extent of the Diels–Alder reaction and the mechanical and healing properties of the polymers. Bis-maleimides with phenylene rings markedly enhanced the tensile strength of the network polymers but hindered healing. In contrast, bis-maleimides with a flexible molecular structure tended to improve the polymer elongation, affording polymers with excellent healing ability. The efficiencies of self-healing (=healing without any external stimulus) and healing with an assistance of solvent (CHCl<sub>3</sub>) were over 70% and 80%, respectively, for the network polymer cross-linked by bis-maleimide with flexible long-alkyl segment. Thus, our results indicate that the choice of bis-maleimide linker is an important factor for designing furan-maleimide-based self-healing polymers.

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## 1. Introduction

Research on self-healing polymers has become an exciting field, and much effort has been devoted to designing polymers with excellent healing performance. Many approaches for preparing self-healing polymers have been proposed [1–3]. Among them, the formation of reversible dynamic bonds by means of the Diels–Alder (DA) reaction is one of the most extensively investigated. Since the groundbreaking work by Wudl and co-workers [4], a number of healing materials have been created on the basis of the DA reaction [5–12]. The controllable thermoreversibility of the reaction allows for repeated reconfiguration and healing in response to damage [3]. However, most of the polymers prepared by this method require a stimulus such as heating [4–9] or immersion in a solution of bis-maleimide [10] for healing.

One of the most widely applied DA reactions in polymer chemistry is the reaction between furan and maleimide. The forward cycloaddition reaction between them is usually conducted at moderate temperature (below 80 °C), whereas the retro-DA reaction of the adduct occurs at temperatures above 100 °C. This

thermoreversibility temperature allows the synthesis of polymers with unique dynamic properties, such as reversible cross-linking [13–17], shape memory [9,18,19], soft–hard converting ability [20–22], and healing ability [4–10]. The molecular design of main chains and cross-linkers is an important factor to determine the performances of these polymers. The effects of structural variations in the furan [17,23] and maleimide [4,13,24,25] constituents on the reversibility, thermal and mechanical properties, and healing ability of the polymers have also been reported, but few systematic studies of these effects have been published.

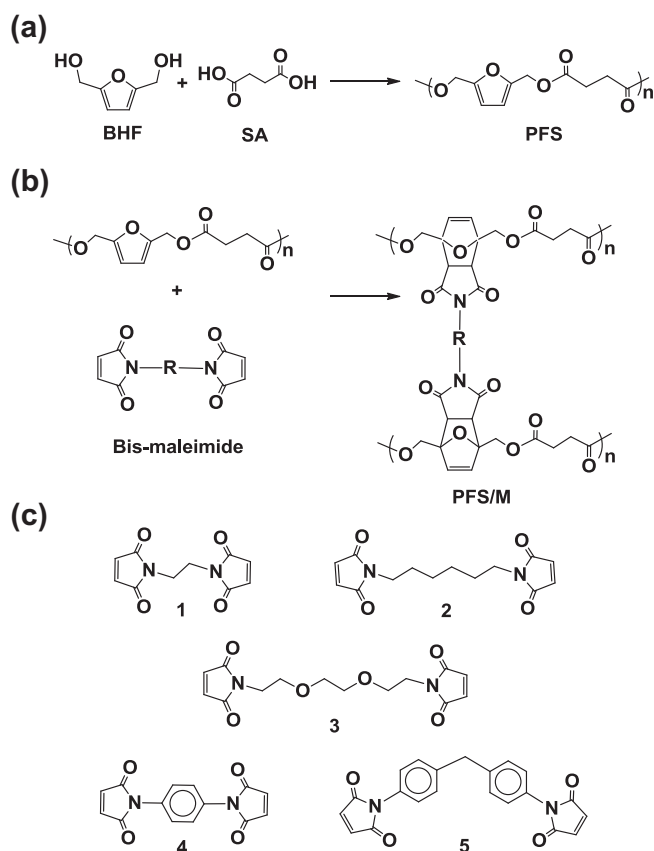
A growing number of platform chemicals and polymer materials are derived from biomass [26–28]. Among them, 5-(hydroxymethyl)furfural is a promising renewable resource [29] owing to its availability from carbohydrates [30–32] and its rich chemistry, which enables its conversion into various compounds including potentially valuable monomers [33–35]. For example, furandicarboxylic acid, an oxidation product of 5-(hydroxymethyl)furfural, can be polymerized into bio-based materials with attractive properties [36–38].

We previously reported a method for preparing bio-based healing polymers from bis(hydroxymethyl)furan (BHF), a product of 5-(hydroxymethyl)furfural reduction [39]. The polyester, poly(2,5-furandimethylene succinate) (PFS), was synthesized from BHF and succinic acid (SA) (Scheme 1a) and then cross-linked by a DA reaction with 1,8-bis(maleimido)triethylene glycol (**3**), a bis-

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**Scheme 1.** Cross-linking of PFS with bis-maleimides 1–5.

maleimide linker with a flexible ethylenedioxy structure. The cross-link density and mechanical properties of the resulting network polymers can be controlled by adjusting the molar ratio of furan to maleimide groups (F/M ratio). The polymers heal well when their broken surfaces are activated by bis-maleimide solutions or solvent. The polymers also display excellent self-healing ability (=healing without an assistance of any external stimulus at room temperature).

In this work, PFS was cross-linked with structurally varied four bis-maleimides (Scheme 1b and 1c, **1**, **2**, **4**, and **5**). We analyzed the DA reaction rate, as well as the thermal properties, mechanical properties, and healing ability (including self-healing and healing with solvent activation) of the resulting polymers; and we compared them with the network polymers cross-linked with **3** reported in our previous paper [39]. The structural effects of the cross-linkers were discussed to obtain valuable information for designing bio-based materials with high healing efficiency. The effects of the linker structures on the DA reactivity and mechanical properties were investigated to get a better understanding of the relation between them and the healing efficiency. Comparison of the solvent assisted healing efficiencies among linkers could bring more information of the healing mechanism of materials based on the DA reaction.

## 2. Experimental section

### 2.1. Materials

5-(Hydroxymethyl)furfural, SA, *N,N'*-(1,4-phenylene)bismaleimide (**4**), 1,1'-(methylenedi-4,1-phenylene)bismaleimide (**5**), *N,N*-dimethyl-4-aminopyridine, *N,N'*-diisopropylcarbodiimide, and dehydrated

dichloromethane were purchased from Tokyo Chemical Industry. Sodium borohydride was purchased from Aldrich. BHF,<sup>39</sup> PFS,<sup>39</sup> bismaleimidoethane (**1**) [40], bismaleimidohexane (**2**) [40], and 1,8-bis(maleimido)triethylene glycol (**3**) [40] were synthesized as previously reported. Other reagents and solvents were purchased from Wako Pure Chemical Industries. All chemicals were used as received.

### 2.2. Measurements

<sup>1</sup>H NMR spectra were recorded in CDCl<sub>3</sub> solution on a JEOL JNM-AL400 spectrometer at 400 MHz. Gel permeation chromatography was carried out with a Tosoh HLC-8220GPC instrument equipped with two Shodex GPC LF-804 columns. Polystyrene standards with low polydispersity were used to construct a calibration curve. Attenuated total reflection Fourier transform IR (ATR-FTIR) spectra were obtained with a Thermo Scientific Nicolet iS10 FT-IR spectrometer equipped with a ZnSe crystal on a Smart iTR sampling accessory. IR spectra were recorded over a wavenumber range of 600–3800 cm<sup>-1</sup> with 2-cm<sup>-1</sup> resolution. The intensities of absorption peaks were calculated with the Fit Multiple Peak tool of OriginPro 8 software (OriginLab Corporation). Differential scanning calorimetry (DSC) was carried out on a Seiko EXSTAR6000 equipped with a DSC6220N. Samples (2–5 mg) in an aluminum pan were analyzed from –60 to 150 °C or 200 °C at a heating rate of 10 °C min<sup>-1</sup> under a N<sub>2</sub> atmosphere. The mechanical properties of the polymer samples were evaluated with a Shimadzu EZ Test tensile testing machine at a cross-head speed of 5 mm min<sup>-1</sup> at room temperature. No. 2 (1/5) dumbbell-shaped specimens described in JIS K 7113 (active region: 7.0 mm × 1.4 mm × 0.3–0.4 mm) were used. Each measurement was repeated at least four times, and the average values were determined to ensure the reproducibility of data.

### 2.3. Cross-linking of PFS with bis-maleimides 1–5

Mixtures of PFS and bis-maleimides **1–5** (F/M ratio = 2/1, 3/1, 4/1, or 6/1) were prepared as films cast from chloroform solution. Films were compression-molded between two Teflon sheets with an aluminum spacer (0.2-mm thickness) by means of a hot press (Imoto, Japan) at 130 °C for 5 min under a pressure of 5 MPa. The samples were quenched to 40 °C, held at this temperature for 3 h, and then held at room temperature at least 24 h to generate PFS/M network polymers.

### 2.4. Healing experiments

In self-healing experiments, dumbbell-shaped specimens were first broken by the tensile test. The two broken surfaces were then immediately reunited with gentle pressure and stored horizontally at room temperature for 1–5 days without pressure. To test healing promoted by CHCl<sub>3</sub>, we immersed the broken surfaces in CHCl<sub>3</sub> for about 1 s and then immediately reunited them and kept them at room temperature for 5 days without pressure.

## 3. Results and discussion

### 3.1. Preparation of PFS/M

Polycondensation of BHF and SA gave PFS with degree of polymerization, *n*, of 31 (*M<sub>n</sub>* = 6.6 × 10<sup>3</sup>, *M<sub>w</sub>* = 1.45 × 10<sup>4</sup>). PFS was cross-linked with linkers **1–5** by the DA reaction between the furan and maleimide moieties (Scheme 1). The F/M ratio was set to 2/1, 3/1, 4/1, or 6/1. Hereafter, the network polymers are designated as PFS/M<sub>x</sub>-y/1, where *x* is the cross-linker (*x* = **1–5**) and *y*/1 is the F/M ratio.

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