

# Controlling a Polymer Adhesive Using Light and a Molecular Switch

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**S** Supporting Information

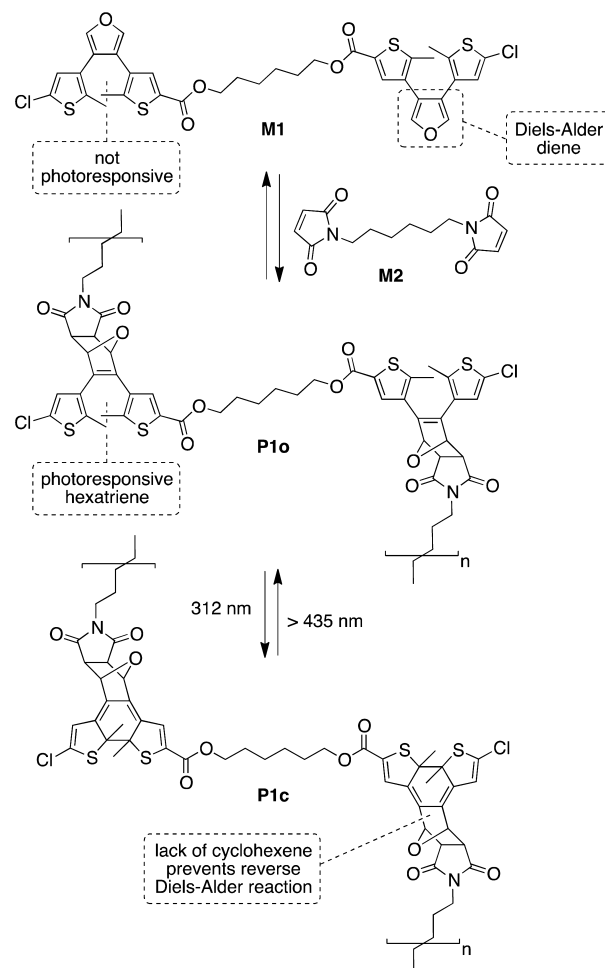
**ABSTRACT:** A thermally remendable polymer was synthesized by the Diels–Alder reaction between dithienylfuran and maleimide monomers to generate a photoresponsive diarylethene. UV light (312 nm) and visible light (>435 nm) “gate” the reversibility of the Diels–Alder reaction and turn the self-healing properties of the polymer “off” and “on”, respectively. After exposure to UV light, the strength of the polymer as an adhesive is enhanced. Visible light weakens the adhesive.

The reversible, temperature-dependent nature of the Diels–Alder reaction explains why it has been widely used in many technology areas<sup>1</sup> such as building dynamic combinatorial libraries,<sup>2</sup> developing new delivery systems,<sup>3</sup> and assembling/disassembling nanosystems,<sup>4</sup> dendrimers,<sup>5</sup> surfactants,<sup>6</sup> and polymers.<sup>7</sup> We believe that while the temperature sensitivity of the Diels–Alder reaction offers a versatile means to control bond-forming and bond-breaking reactions, it will always be limited in use unless a second external stimulus is included in the design. By adding a mechanism to “lock” and “unlock” the Diels–Alder reaction “on-command”, the user can decide when to convert a system that is stable at elevated temperatures into one that spontaneously undergoes the reversible Diels–Alder reaction. This heightened level of control increases the possible environments where these dynamic systems can be used by preventing unwanted thermolysis reactions.

Light is one of the most appealing stimuli to control molecular and polymolecular systems. It can be focused to trigger local reactions on a very small scale and tuned to target specific chromophores to minimize background and side reactions as long as the polymer is designed with appropriate light-absorbing properties. We have recently demonstrated that we can “gate” reverse Diels–Alder reactions in small molecules by integrating the diene component into a photoresponsive hexatriene.<sup>8</sup> In this new development, we show that this approach works equally well to control the properties of linear polymers made up of furan rings as the dienes and maleimides as the dienophiles.

The operation of our system is illustrated in Scheme 1 and is based on the same diene–dienophile partners as used by Wudl when he described one of the most impactful examples of remendable Diels–Alder polymers.<sup>7e</sup> When their highly cross-linked polymer was heated, the Diels–Alder equilibrium was established, allowing rapid bond breaking and bond making.<sup>7e</sup> Cooling the material “froze” the equilibrium, and any fractures were mended. Reheating the material re-established the equilibrium and caused a reduction in the polymer’s mechanical

**Scheme 1.** Absorption of Visible Light by Polymer P1c Triggers a Photochemical Bond-Breaking Reaction That Produces Polymer P1o, Which Can Undergo the Reverse Diels–Alder Reaction and Produce M1 and M2



integrity. Our system helps mitigate this limitation. Monomer M1 contains two dithienylfuran groups. When these two dienes undergo spontaneous cycloaddition with the maleimides in monomer M2, a linear polymer (P1o) is formed. These reactions should be reversible, as observed for similar systems.

The rearrangement of the double bonds during the formation of P1o creates for each [4 + 2] addition a photoresponsive hexatriene component that mimics the well-

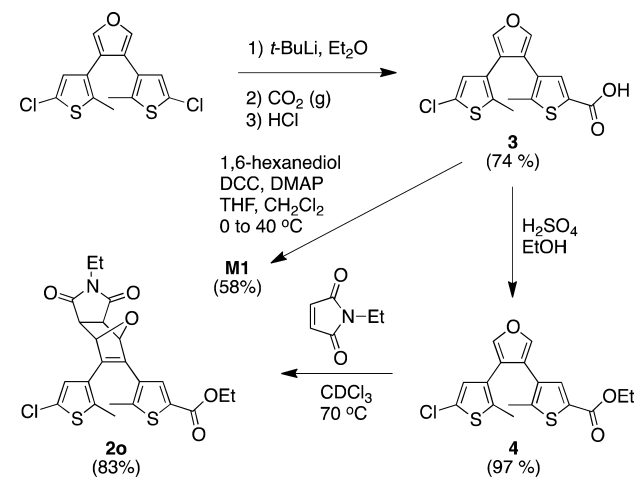
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known dithienylethene, a molecular backbone found in numerous photochromic systems.<sup>9</sup> Ultraviolet light triggers ring closing and produces polymer **P1c**. Because this photoinduced ring-closing reaction removes the cyclohexene created during the [4 + 2] reaction, the system is “locked” into this form and the reverse Diels–Alder reaction is prevented. Exposing the system to visible light reverses the photoreaction, regenerates the ring-open isomer (**P1o**), and “unlocks” the system.

The key thiophene-containing components were prepared as illustrated in Scheme 2<sup>10</sup> starting from the dichloride derivative

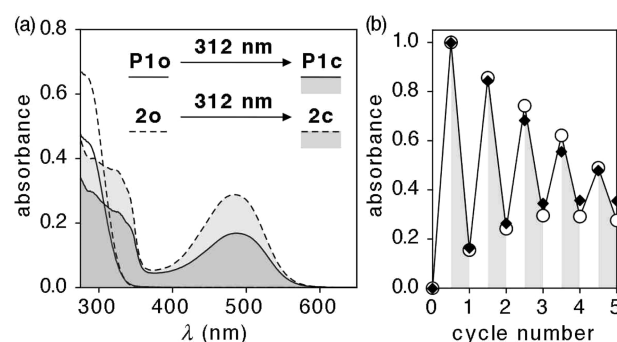
### Scheme 2. Syntheses of Dithienylfuran Monomer **M1**, Control Diene **4**, and the Photoresponsive Product **2o** Formed by Treating **4** with *N*-Ethylmaleimide



we previously published.<sup>8</sup> Conversion of this compound to carboxylic acid **3** followed by esterification produced monomer **M1** as a solid. The bis(maleimide) **M2** was prepared by aminolysis of maleic anhydride according to the published procedures.<sup>7f,d</sup> Scheme 2 also shows the synthesis and [4 + 2] cycloaddition reaction of compound **4**, which we used to assess the optical properties and photochromic behavior of our eventual linear, remendable polymer **P1o**.

The formation of polymer **P1o** is best carried out in the solid state and without the use of solvent. When an equimolar mixture of bis(diene) **M1** and bis(dienophile) **M2** was heated to 85 °C in the dark, polymerization to **P1o** was complete after 24 h, as shown by the disappearance of the signals in the <sup>1</sup>H NMR spectrum corresponding to the starting materials.<sup>10</sup> On the other hand, the Diels–Alder reaction between monoester **4** and *N*-ethylmaleimide to produce **2o** can be carried out at 70 °C in CDCl<sub>3</sub>, as also described in the Supporting Information. Monitoring this reaction using <sup>1</sup>H NMR spectroscopy showed it to be complete after 44 h. Polymer **P1o** is hard, fully transparent, colorless, and soluble in THF. Gel-permeation chromatography (GPC) estimated the weight- and number-average molecular weights of the polymer as  $M_w = 39\,442$  and  $M_n = 19\,256$ , respectively, giving a polydispersity index (PDI =  $M_w/M_n$ ) of 2.03.

The photoinduced ring-closing reactions of the Diels–Alder products (those in polymer **P1o** and in the control **2o**) are best monitored by measuring the changes in the UV–vis absorption spectra (Figure 1a and Figures S9, S11, and S12 in the Supporting Information). For example, when a THF solution of polymer **P1o** was exposed to UV light (312 nm), the high-

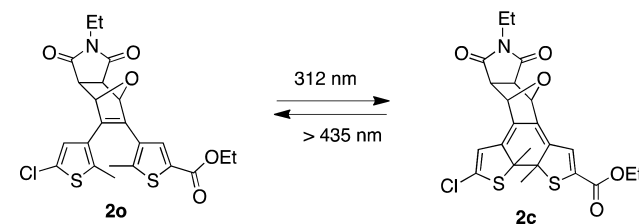


**Figure 1.** (a) UV–vis absorption spectra of a THF solution (0.05 mg/mL) of **P1o** (solid lines) and a CH<sub>3</sub>CN solution (0.05 mg/mL) of **2o** (dashed lines) before (unshaded) and after irradiation with 312 nm light (gray-shaded) for 50 s. (b) Changes in the normalized absorbance at 483 nm corresponding to the ring-closed isomers in **P1c** (O) (0.004 mg/mL) upon alternate irradiation with 312 nm light for 50 s (nonshaded regions) and >435 nm light for 6 min (gray-shaded regions). The normalized absorbances corresponding to the solution of **2c** (0.05 mg/mL) are shown as black diamonds (◆) for comparison. All measurements were performed at 23 °C.

energy bands in the spectrum (~245–250 nm) immediately decreased in intensity and new broad bands appeared in the visible region of the spectrum (centered around 483 nm), which explains why the solution turned from colorless to orange-red.<sup>10</sup> These spectral changes are typical for the ring-closing reactions of dithienylethene derivatives and parallel the behavior we observed in our original Diels–Alder systems.<sup>8</sup> In the case of the photoreaction of our polymer (**P1o** → **P1c**), the optical changes stopped after 50 s of irradiation when the photostationary state (PSS) was reached; the PSS contained ~63% ring-closed isomer **P1c**, as estimated by comparing the respective signals in the <sup>1</sup>H NMR spectrum. Exposing this orange-red solution to visible light ( $\lambda > 435$  nm) triggered the reverse, ring-opening reaction, regenerating the original spectrum corresponding to polymer **P1o**.

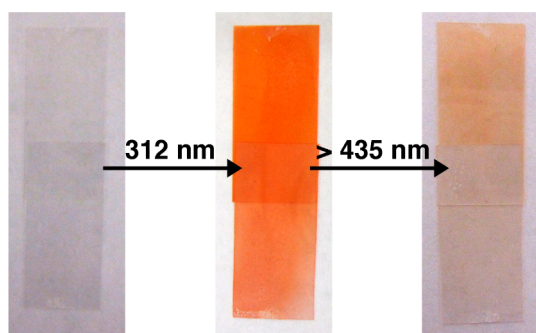
Similar changes were observed when a CH<sub>3</sub>CN solution of compound **2o** was exposed to UV and visible light (Scheme 3 and Figures 1 and S9). The changes stopped after 50 s when a PSS containing 70% ring-closed isomer **2c** was reached.<sup>11</sup>

### Scheme 3. Reversible Photoinduced Interconversion of Ring-Opened (**2o**) and Ring-Closed (**2c**) Isomers of the Control Compound



The ring-closing/ring-opening reactions were prone to fatigue as solutions of the polymer were subjected to alternating UV and visible light (Figure 1b). This photofatigue is likely not due to any reversible Diels–Alder reaction of the ring-opened isomers in **P1o**, as the control compound (**2o**) showed similar fatigue and did not undergo the reverse cycloaddition reaction. Instead, we attribute this behavior to photodegradation, as we discussed in our previous publication.<sup>8</sup>

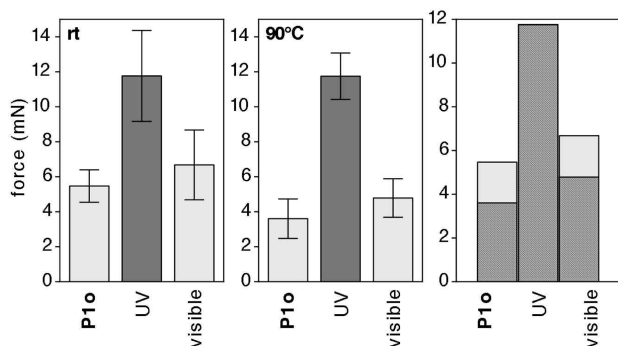
The use of visible light to “unlock” polymer **P1c** and control its ability to act as an adhesive was demonstrated by measuring the tensile shear strengths of two pieces of plastic glued together by the polymer at two different temperatures. Three sets of four transparent noncoated poly(ethylene terephthalate) (PET) strips were spray-coated with a solution of **P1o** (32 mg/mL). The strips were cut in half, and the two halves were glued together by pressing them under load at 90 °C (Figure 2).<sup>10</sup>



**Figure 2.** Photographs of PET strips glued together by polymer **P1o** and heated under pressure at 90 °C before irradiation (left), after irradiation with UV light (middle), and after irradiation with UV light followed by visible light (right).

This temperature was critical to ensure that the Diels–Alder reaction equilibrium would occur and to soften the polymer during the sample preparation process. The polymer underwent the color change from colorless to orange-red in a similar fashion as observed when solutions of them are exposed to UV light (Figure 2).

Figure 3 shows a summary of all of the shear force measurements on these plastic strips. The shear force at 90 °C



**Figure 3.** Average shear forces of PET strips glued together using polymer **P1o** before irradiation, after irradiation with 312 nm light for 5 min (“UV”), and after irradiation with 312 nm light for 5 min followed by >435 nm light for 120 min (“visible”) at 23 and 90 °C and at 500  $\mu\text{m/s}$  displacement. The graph at the far right highlights the differences at the two temperatures (23 °C, light gray; 90 °C, dark gray) for all three samples. The data are the results from four samples for each set of strips.

for the strips glued together using polymer **P1o** was 66% of that at room temperature [from  $5.469 \pm 0.927$  to  $3.603 \pm 1.127$  mN (95% confidence intervals) at 500  $\mu\text{m/s}$  displacement].<sup>10</sup> This behavior was expected for **P1o** because the Diels–Alder equilibrium is established at elevated temperatures, which results in a mixture of polymer and monomers and lowers the adhesive properties. When the strips were exposed to UV light

(312 nm) to convert the ring-opened isomers **P1o** to the PSS containing a mixture of **P1o** and **P1c**, the adhesive properties of the polymer increased, as shown by the observation that the average shear force was 2.15 times higher than that for **P1o** at room temperature.<sup>12</sup> This difference increased to almost 3.26 times at 90 °C, highlighting the fact that while the ring-opened isomers of the photoresponsive building blocks in polymer **P1o** are able to undergo the reverse Diels–Alder reaction, those in **P1c** cannot.<sup>13</sup> The fact that the polymer containing the ring-closed isomers had the same adhesion strength at room temperature and 90 °C shows that the system is effectively “locked” in this form. This phenomenon can be reversed by exposing the orange-red films to visible light ( $\lambda > 435$  nm), which triggers the ring-opening reaction, regenerates the ring-opened isomers and polymer **P1o**, and lowers the adhesive properties of the photoresponsive “glue”.

In this work, we have demonstrated how two wavelengths of light can be used to regulate the adhesive properties of a photoresponsive polymer by inducing ring-closing and ring-opening reactions of the polymers’ building blocks. We anticipate that this proof-of-concept example can be potentially helpful in the development of future generations of self-healing polymers.

## ■ ASSOCIATED CONTENT

### Supporting Information

Detailed descriptions of experimental methods, synthetic procedures, characterization of new compounds, and additional absorption spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

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(10) Statistical analyses were performed using Student's *t* test, and the data are expressed as mean  $\pm$  standard deviation. See the Supporting Information for details.

(11) The content of the PSS was measured using  $^1\text{H}$  NMR spectroscopy ( $\text{CD}_3\text{CN}$ ). See the Supporting Information for more details.

(12) The shear forces were measured to be  $11.76 \pm 2.60$  and  $5.47 \pm 0.93$  mN (95% confidence intervals) for **P1c** and **P1o**, respectively.

(13) The shear forces were measured to be  $11.75 \pm 1.33$  and  $3.60 \pm 1.13$  mN (95% confidence intervals) for **P1c** and **P1o**, respectively.