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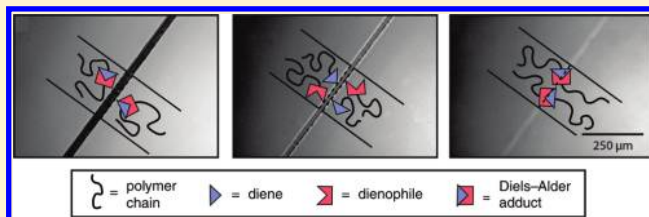
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S Supporting Information

ABSTRACT: This laboratory experiment exposes students to the chemistry of self-healing polymers based on a Diels–Alder reaction. Students accomplish a multistep synthesis of a monomer building block and then polymerize it to form a cross-linked polymer. The healing capability of the polymer is verified by differential scanning calorimetry (DSC) experiments. Furthermore, healing is demonstrated by damaging and heat-treating a thin polymer film.

KEYWORDS: Upper-Division Undergraduate, Laboratory Instruction, Organic Chemistry, Polymer Chemistry, Hands-On Learning/Manipulatives, Calorimetry/Thermochemistry, Materials Science, NMR Spectroscopy, Polymerization, Synthesis



One fundamental difference between biological systems and man-made synthetic materials is a self-repairing ability embedded in living systems. Imagining a world where broken objects are repaired in a similar way to the healing of broken bones is an appealing idea. First steps toward this vision are at the forefront of materials science research and polymers capable of self-healing by reestablishing broken cross-linking bonds were recently developed.^{1–4} The following laboratory experiment is aimed at bringing this novel material to the undergraduate laboratory. Students accomplish a multistep synthesis of a monomer building block and then polymerize it to form a cross-linked polymer. The healing capability of the polymer is verified by differential scanning calorimetry (DSC) experiments. Furthermore, healing is demonstrated by damaging and heat-treating a thin polymer film. This lab ties together organic synthesis and materials science while demonstrating how understanding a reaction mechanism at the molecular level can be translated to a useful macro-level phenomenon.

Polymers are common constituents of many modern products. Highly cross-linked, thermosetting polymers are frequently used in structural applications, but they are particularly susceptible to microcrack damage and fatigue failure. For inexpensive consumer products, this is not a serious issue as the cost of replacement is manageable. But repair or replacement is an acute problem for more complex or remote systems. For example, incorporating polymers into medical implants or satellites requires significant safety factors to mitigate long-term damage accumulation. Self-healing materials present an attractive solution for overcoming problems associated with the formation of microcracks and may substantially extend the life span of polymeric materials.

Microcracks in thermoplastic polymers can be healed by heating the material and enhancing the diffusion of polymer chains across the interface (Figure 1A). Upon cooling, the polymer regains structural integrity but its mechanical properties are often inferior to those of the virgin material. Thermosetting polymers, by contrast, are highly cross-linked and do not melt or flow with the application of heat. Two approaches have been developed to enable healing of such polymers. One approach relies on embedding catalysts and microcapsules of healing agent into the polymer.¹ A propagating crack will puncture the microcapsules, releasing the agent into the crack where it encounters the embedded catalyst and polymerizes. A second approach exploits the reversibility of chemical reactions such as the Diels–Alder (DA) reaction.² Monomers carrying diene or dienophile groups are reacted to yield a cross-linked polymer. Healing of cracks can be achieved by heating the polymer above the temperature required for a reversible DA reaction (Figure 1B). The heat causes a partial disconnection of the polymer chains and increases the mobility of individual chains. Upon cooling, new DA bonds are formed and the chains are cross-linked again.

In this experiment, the polymer relies on a DA reaction between furan as the diene and maleimide as the dienophile (Figure 2). To facilitate the experiment, we chose to synthesize the furan building block and to use a commercially available maleimide. A high degree of cross-linking is achieved by attaching four furan groups to a common anchor (Figure 2, 4FS). We found 1,1'-(methylenedi-4,1-phenylene)bismaleimide (DPBM) to be

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a reliable partner for copolymerization and formation of a healable polymer.

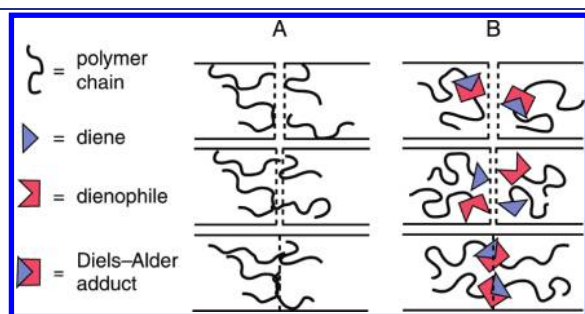


Figure 1. Thermo mending (A) and chemical healing (B) of a polymer.

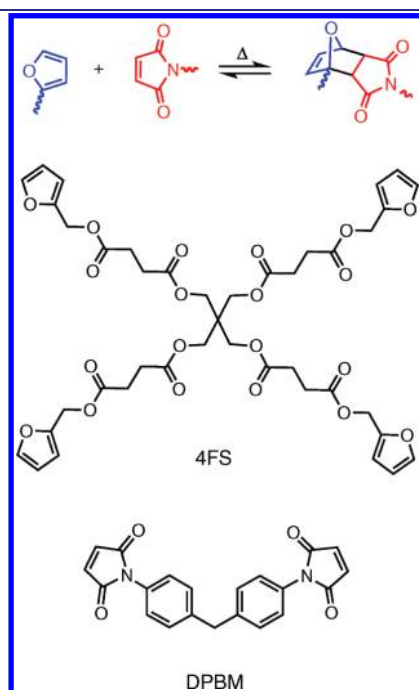
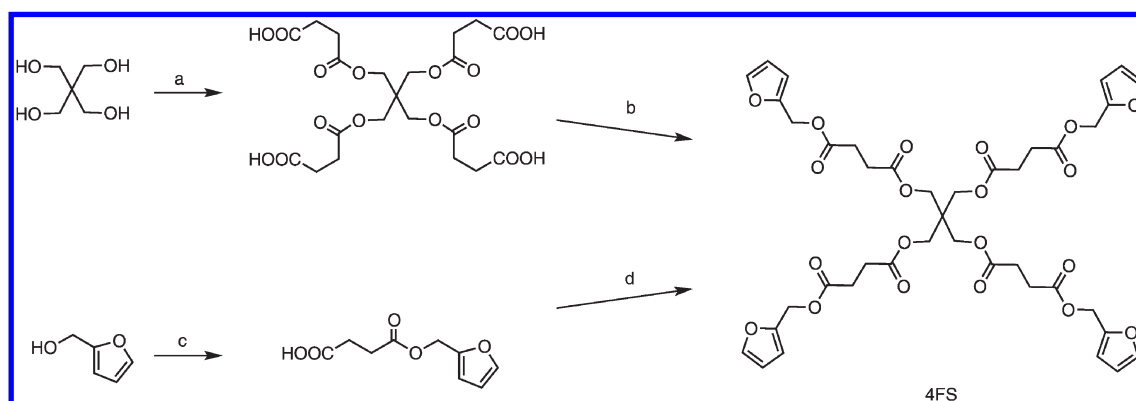


Figure 2. Tetrauran derived from pentaerythritol (4FS) and diphenyl bismaleimide (DPBM) serve as building blocks for a cross-linked polymer via Diels–Alder reaction.

Scheme 1. Linear (Top) and Convergent (Bottom) Approaches toward the Synthesis of the Tetrauran Monomer (a, Succinic Anhydride; b, Thionylchloride/ Et_3N , Then Furfuryl Alcohol; c, Succinic Anhydride; d, Pentaerythritol/DCC/DMAP



MULTISTEP SYNTHESIS OF THE MONOMER

The synthesis of 4FS offers students an opportunity to compare and contrast linear and convergent synthesis strategies (Scheme 1). The linear approach relies on extending pentaerythritol through a reaction with succinic anhydride and coupling the resulting tetra acid with furfuryl alcohol. Each step involves reacting four functional groups simultaneously, leading to a total of eight reactions to complete the synthesis. Theoretically, if each functional group reacts at 95% yield, the overall yield is only 66%. Therefore, maximizing the yields will require a relatively large excess of reagents that will complicate purification of the final product. Another drawback of this route is the high polarity of the tetra acid intermediate, which inhibits purification, leading to the telescoping of impurities and unreacted material to the next step. A convergent synthesis approach first extends the furan unit through a reaction with succinic anhydride and leaves the connection to pentaerythritol for a second step. The intermediate is hydrophobic and is easily purified. This approach reduces the total number of reactions from eight to five. Assuming a theoretical yield of 95% for each reaction, the overall yield will increase to 77%.

The synthesis of 4FS is indeed accomplished more efficiently via the convergent route. We found that the reaction between furfuryl alcohol and succinic acid can be carried out under solvent-less conditions if 4-dimethylaminopyridine (DMAP) is added as a nucleophilic catalyst in a typical yield >90%. Thus, the reaction can serve as an example of a green reaction. After purification, the acid is reacted with pentaerythritol in the presence of N,N' -dicyclohexylcarbodiimide (DCC). The product is purified over a silica column to give up to 80% of pure 4FS. When obtaining the ^1H NMR, accurate integrations require extending the delay time between pulses to 10 s due to different relaxation behavior of protons on the furan ring and the rest of the molecule.⁵

POLYMERIZATION AND HEALING PROCESS

Differential Scanning Calorimetry

The polymerization and healing process can be studied by performing experiments with differential scanning calorimetry (DSC) or providing the students with the data given in the Supporting Information. A sample of 4FS and DPBM monomers in an appropriate molar ratio is hand-mixed and placed in a DSC pan, which is subsequently sealed. The sample is heated from 30

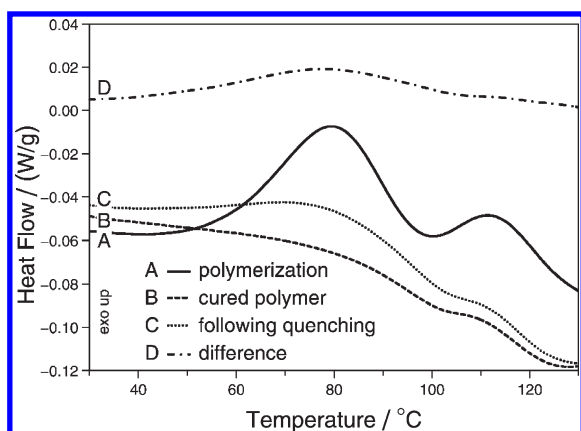


Figure 3. Total heat flow as measured by DSC: (A) a mixture of tetrauran and bismaleimide monomers is heated to allow polymerization, (B) heating of the resulting polymer sample, (C) heating of a sample that was quenched at the end of the previous cycle by liquid nitrogen, and (D) difference between scans C and B.

to 130 °C while measuring the heat flow. Two exothermic peaks are observed during this scan with maxima at 79 and 115 °C (Figure 3, scan A). Although DPBM is a solid with a high melting point, mixing it with 4FS results in its melting and dissolution at a significantly lower temperature. The exothermic peak observed at 79 °C is attributed to the DA polymerization reaction. The second exothermic peak is consistent with heat released owing to packing of the polymer chains. At the end of the first scan, the sample is cured at 100 °C for 1 h to ensure completion of the reaction and crystallization. A subsequent scan of the cured sample reveals that both exothermic peaks are missing, indicating the sample is fully polymerized (Figure 3, scan B). A glass transition is observed at 97 °C followed by an endothermic peak from 110 to 130 °C. This peak is attributed to the reverse DA reaction. Slow cooling of the sample allows for reestablishment of the broken DA bonds. Consecutive heating and cooling cycles result in nearly identical behavior of the sample (graphs omitted for clarity). At the end of the fifth heating cycle, the hot sample is quenched by dropping the sealed DSC pan into a bath of liquid nitrogen. The rapid cooling of the sample prevents re-establishment of broken DA bonds. A subsequent DSC scan of the sample yields an exothermic peak where the bonds reestablish. Subtracting curve B (prequenching) from curve C (postquenching) reveals exothermic peaks similar to those observed during the initial polymerization (Figure 3, scan D). The smaller area of the peaks indicates that only a fraction of the bonds are breaking and the majority of the polymer remains intact. A slight shift in the maximum of the first peak (from 79 to 75 °C) is attributed to the differences between polymerization conditions. During the initial polymerization, heat is consumed by the dissolution of the solid DPBM, a process that is not present in the quenched polymer. This experiment clearly demonstrates the healing potential of the polymer. Heating the backbone leads to a partially disconnected polymer via a reverse DA reaction, and slow cooling allows the broken bonds to reconnect via a forward DA reaction.

Microscope

The healing phenomenon can also be visualized by preparing a thin film of polymer, slitting it, and then heating the damaged film to promote a reverse DA reaction. A film is prepared by hand-

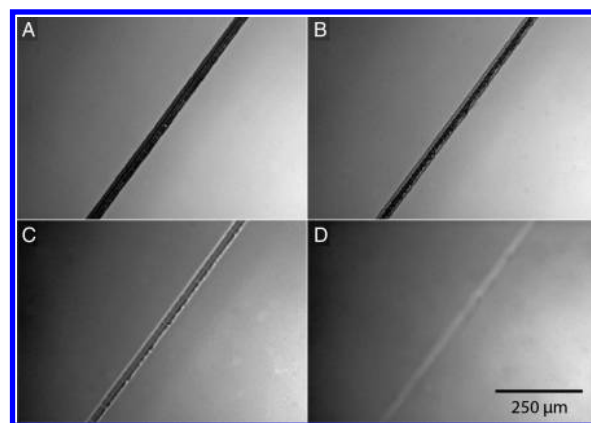


Figure 4. The healing of a damaged polymer film: (A) a polymer film on a glass slide is slit with scalpel, (B) after 15 min heating at 120 °C, (C) after 30 min heating, and (D) after 2 h heating.

mixing a stoichiometric ratio of the two monomers, dissolving the mixture in methylene chloride, and dripping the resulting solution onto a hot glass slide. After the solvent evaporates, the slide is placed in a 120 °C oven to complete the polymerization and cure the film. A typical healing process of a damaged polymer film as viewed through optical microscope at various time intervals is shown in Figure 4. Heating for 2 h at 120 °C causes the slit to virtually disappear. Quantitative fracture experiments have previously demonstrated that a similar polymer based on 4FS can regain its mechanical toughness via healing.⁴

HAZARDS

Hexane, ethyl acetate, and tetrahydrofuran are highly flammable. 1,1'-(Methylenedi-4,1-phenylene)bismaleimide, *N,N*-dimethylformamide and *N,N'*-dicyclohexylcarbodiimide are toxic. Tetrahydrofuran may form explosive peroxides. *N,N'*-dicyclohexylcarbodiimide may cause an allergic skin reaction. Furfuryl alcohol, succinic anhydride, and 4-dimethylaminopyridine cause significant irritation to skin, eyes, and respiratory tract and may be harmful if swallowed or inhaled. Pentaerythritol is only slightly irritating in case of skin contact, eye contact, ingestion, and inhalation.

SUMMARY

The importance of reaction reversibility is generally not well appreciated by undergraduate students. This experiment demonstrates the significance and applicability of back-reactions. The impressive healing process is both engaging and promotes understanding of fundamental principles at the molecular level.

ASSOCIATED CONTENT

Supporting Information

List of chemicals and equipment, student handout, notes for the instructor and DSC data. This material is available via the Internet at <http://pubs.acs.org>.

AUTHOR INFORMATION

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