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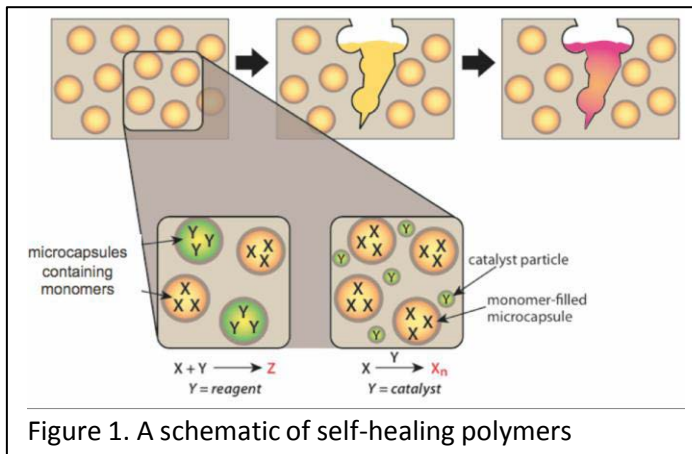
Microencapsulation of Diels-Alder Monomers in Self-Healing Materials

Student: Bryan Ingolia

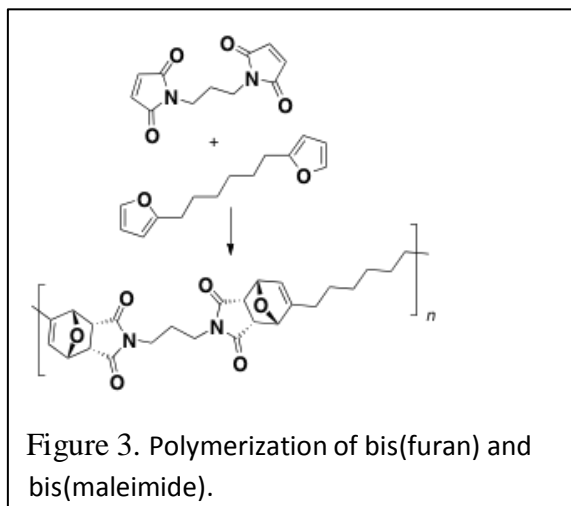
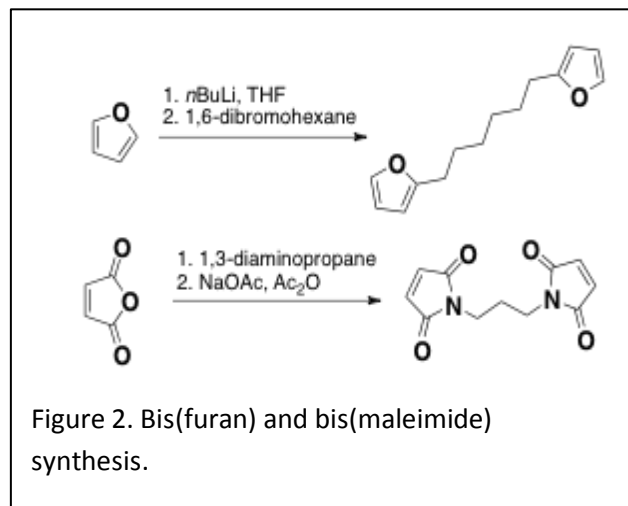
Faculty Mentor: Susan Odom

Project Background and Goals

Developing a polymer in which mechanical damage is autonomically restored has widespread application in structural materials, coatings, and electronics.[1] In particular, I have committed to designing a system utilizing core-shell microcapsules and a particular organic reaction – the Diels-Alder reaction, specifically one that occurs at room temperature. These microcapsules were incorporated into polymer films, which were then scratched to release the core components of the microcapsules in order to repair the mechanical damage. The benefits to my approach include inexpensive and non-toxic components, no need to apply heat or use expensive catalysts, and can be considered a “green” reaction (i.e. organic solvents are not used and reaction yields are high).



In the Diels-Alder reaction, an electron-rich diene reacts with an electron-poor dienophile to form new carbon-carbon bonds. In my system, each reactant was bis-functionalized: the reactive portions of the molecules are the same on each side. I thus selected a bis(furan) as the diene and a bis(maleimide) as the dienophile (Figure 2). The monomers, when combined upon rupturing the microcapsules, form a repeating polymer unit under ambient conditions (Figure 3).



Methods

In order to create the Diels-Alder system, each monomer had to be custom synthesized. The bis(furan) monomer was created by reacting furan with *n*-butyl lithium followed by 1,6-dibromohexane (Figure 2). The bis(maleimide) was synthesized by reacting maleic anhydride with 1,3-diaminopropane, followed by a ring-closing reaction with sodium acetate and acetic anhydride (Figure 2). The poly(urea-formaldehyde) core-shell microcapsules were made by emulsification polymerization around a chlorobenzene core. Capsules were isolated by size range using a RoTap® (Figures 4 and 5).

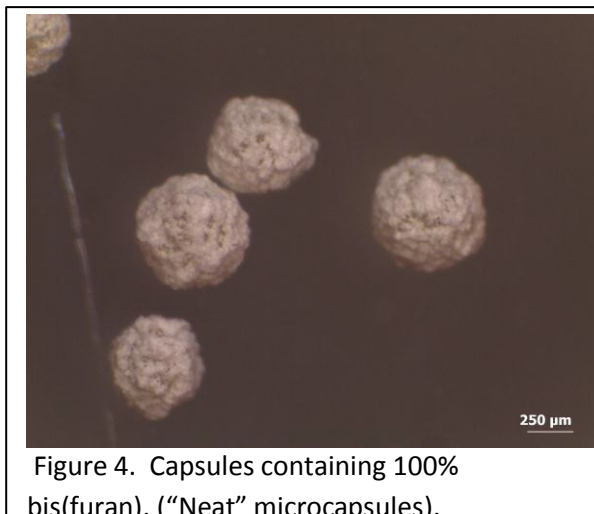


Figure 4. Capsules containing 100% bis(furan). (“Neat” microcapsules).

Several diagnostic techniques were used to characterize the organic compounds synthesized throughout this project. Gas chromatography/mass spectrometry (GCMS) combined with ¹H Nuclear Magnetic Resonance (NMR) spectroscopy were used in order to confirm that the synthesis and encapsulation of each monomer. In addition, polymerization reactions were analyzed by Matrix-Assisted Laser Desorption/Ionization (MALDI), a type of mass spectrometry.

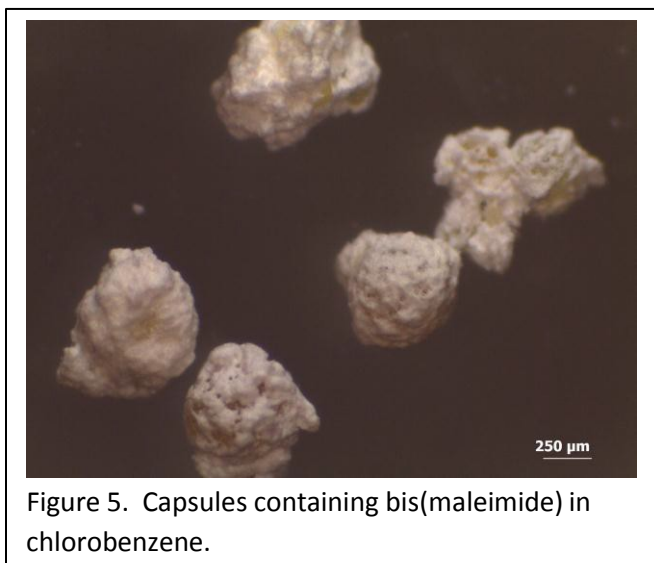


Figure 5. Capsules containing bis(maleimide) in chlorobenzene.

Once microcapsules were prepared on a multi-gram scale and were separated by size, they were incorporated into several kinds of polymer films: epoxy-amine, poly-acrylic acid, and a polyurethane elastomer—which were doctored on to epoxy-coated steel plates. Each film was scratched and immersed in a salt water bath in order to see if rusting occurred. If healing occurs efficiently, rusting will be prevented.

Results

The synthesis of each Diels-Alder monomer was successful and supported by NMR data. The bis(furan) reaction had a 96% yield which was distilled to improve purity. The bis(maleimide) reaction, while successful, only gave a 18% yield. Since the bis(maleimide) synthesis was not successful on a multi-gram scale, I searched for alternative dienophiles and identified a similar maleimide, 1-1-(methylenedi-4,1-phenylene)bismaleimide, shown in Figure 6. Both dienophiles do indeed undergo a room-temperature Diels-Alder reaction, as evidenced by the NMR

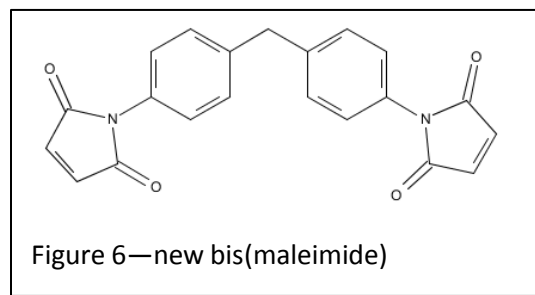


Figure 6—new bis(maleimide)

spectrum of the products and qualitatively by the brown solid formed when the two monomers are mixed, shown in Figure 7.

Since beginning my research I have made progress and also met challenges to overcome. I first incorporated chlorobenzene, an organic solvent, into poly(urea-formaldehyde) microcapsules. However, within a few days, the core had diffused out of the microcapsule wall, depleting their function. In order to resolve this issue, I added Desmodur L75, a polyisocyanate, to my microcapsule recipe. The role of Desmodur L75 is to form a second polyurethane shell in addition to the urea-formaldehyde wall; a diagram is shown in Figure 8 to indicate the difference in microcapsule integrity. Microcapsules made using the Desmodur L75 recipe keep their cores for at least 8 weeks without drying out. I isolated each microcapsule core individually and analyzed them by ^1H NMR spectroscopy. To date, I have successfully made four distinct capsule types: chlorobenzene, bis(maleimide) in chlorobenzene, bis(furan) in chlorobenzene and more recently, bis(furan) with no solvent (called a “neat” capsule as the bis(furan) is a liquid and does not require a solvent to be put into a microcapsule).



Figure 7—bis(furan) and bis(maleimide) polymerization.

The next step was to incorporate monomer microcapsules into a polymer film for scratch testing. However, the bis(maleimide) does not dissolve well in chlorobenzene, thus those microcapsules contained a low weight percent of bis(maleimide). To overcome this obstacle, solid bis(maleimide) was incorporated into the polymer film itself, along with bis(furan)-containing microcapsules in a system similar to the right-most diagram in Figure 1. Opting for this particular system film excluded the epoxy-amine film because the amine reacted with the bis(maleimide), effectively destroying the monomer. Alternate film choices included poly-acrylic acid and the polyurethane elastomer; however, I discovered that poly-acrylic acid dissolves in water, rendering it a non-ideal film. Thus I identified the polyurethane elastomer as the best option for creating films containing bis(maleimide) and microcapsules with a bis(furan) core.

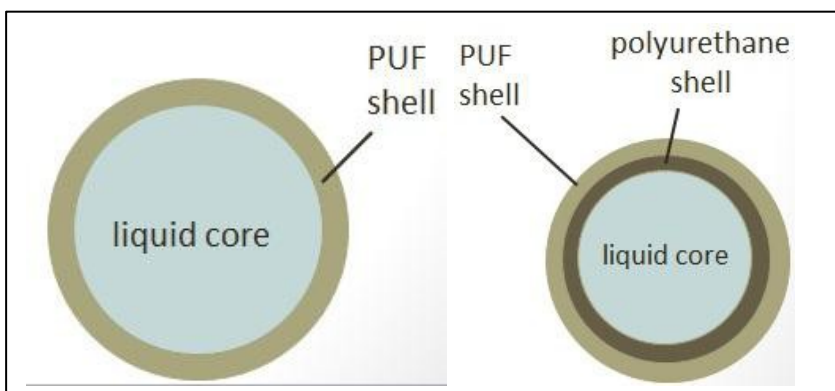


Figure 8—Diagram of core-shell microcapsules with (right) and without (left) Desmodur L75 polyurethane shell wall.

After incorporating bis(maleimide) and bis(furan) microcapsules into a viable polyurethane film, the films were scratched and left alone for two days before immersion in the salt water bath. After a day in the salt water, evidence of rusting was observed in plates with and without microcapsules (Figure 10). Possible future goals for the Fall semester include alternate forms of scratch testing and the investigation of internal phase separation in order to get a higher weight

percentage of bis(maleimide) into microcapsules in order to see a significant amount of self-healing.

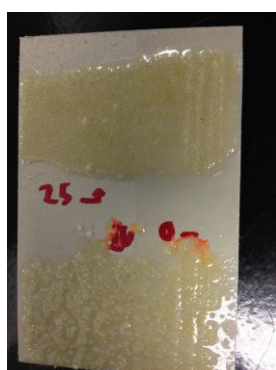
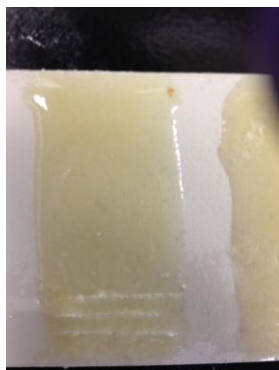


Figure 9—Polyurethane films; without microcapsules (left) and with microcapsules (right).

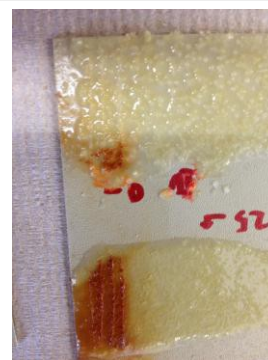


Figure 10—Polyurethane films after salt water bath; without microcapsules (left) and with microcapsules (right).

Discussion

Analysis of each ^1H NMR spectrum shows that the monomers have been synthesized. Furthermore, each monomer was successfully encapsulated into a microcapsule. The difficulty of encapsulating a high weight percent of the bis(maleimide), or alternatively incorporating it into the polymer film, appear to indicate that this Diels-Alder reaction may not be ideal for microencapsulation. Investigating internal phase separation could prove a solution to this problem,[2] or perhaps identifying another dienophile that is more soluble in organic solvents.

Since scratched films rusted regardless of the presence of microcapsules, the polymerization reaction that presumably occurs likely did not form a long enough chain to protect the underlying steel substrate from corrosion. Possible issues could arise from any non-homogeneity regarding the location of the solid bis(maleimide), especially if a minute amount is present in the scratch gap.

References

- [1] Caruso, M.M.; Davis, D.A.; Shen, Q.; Odom, S.A.; Sottos, N.R.; White, S.R.; Moore, J.S. "Mechanically-Induced Chemical Changes in Polymeric Materials." *Chem. Rev.* **2009**, *109*, 5755–5798. DOI: 10.1021/cr9001353
- [2] Dowding, P.J.; Atkin, R.; Vincent, B.; Bouillot, P. *Langmuir* **2004**, *20*, 11374-11379.