Upcycling of Rubber into Adhesives

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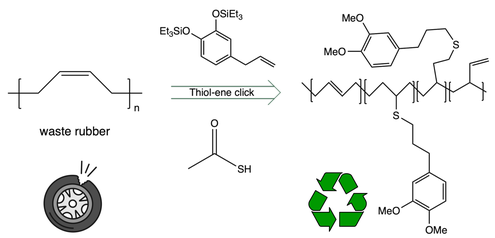
Abstract



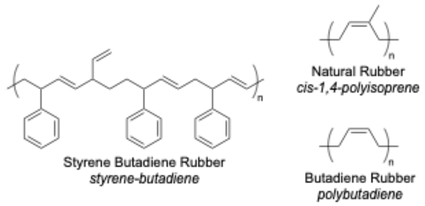
The synthesis of a polycatechol was carried out by subjecting polybutadiene (PB) to a thiol-ene click reaction to reduce end of life tire waste.

Synthetic rubbers are not amenable to modern recycling methods, and the tire industry is the largest market segment. Polymer upcycling, which uses polymer waste to create new products of higher value, provides a promising incentive to recycle these discarded tires and give them new purposes. Our research transformed PB into a polycatechol product with adhesive properties greater than scotch tape. Polycatechols derived from PB simultaneously reduce environmental pollution and produce value-added products from the abundant feedstock of end-of-life tires.

Justification & Motivation

Importance of Recycling Polybutadiene

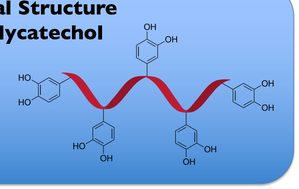
4 billion tires sit in landfills around the world.[1-2]



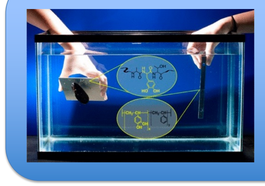
Types of rubbers used in tires.[3]

Versatility of Polycatechol

General Structure of Polycatechol

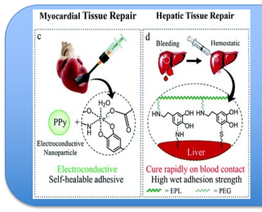


Material Adhesives



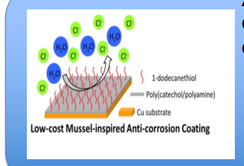
Mussel mimic adhesive that can bind things underwater.[4]

Tissue Repair



Bioadhesive hydrogel used to close wounds and promote tissue healing.[5]

Anti-Corrosion Coatings



Poly(catechol/amine) anti-corrosion coating on copper substrate.[6]

1. Agency, A. Environmental disaster: World's biggest tire graveyard in Kuwait. Daily Sabah. Aug 13, 2021. (accessed 2024-04-23).
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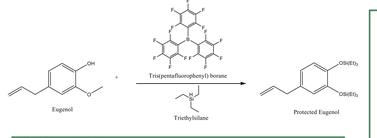
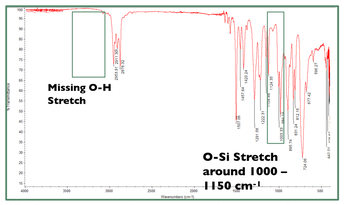
3. Fazli, A.; Rodrigue, D. Recycling Waste Tires into Ground Tire Rubber (GTR)/Rubber Compounds: A Review. J. Compos. Sci. 2020, 4(3), 103. DOI: 10.3390/jcs4030103
4. North, M. A.; Grosso, C. A. D.; Wilker, J. J. High Strength Underwater Bonding with Polymer Mimics of Mussel Adhesive Proteins. ACS Appl. Mater. Interfaces 2017, 9(8), 7866–7872. DOI: 10.1021/acsami.7b00270
5. Zhang, W.; Wang, R.; Sun, Z.; Zhou, Z.; Zhao, Q.; Zhang, T.; Cholewinski, A.; Yang, F.; Zhao, B.; Pinnaratip, R.; Forooshani, P.; Lee, B. P. Catechol-functionalized hydrogels: biomimetic design, adhesion mechanism, and biomedical applications. Chem. Soc. Rev. 2020, 49(2), 433-464. DOI: 10.1039/c9cs00285e
6. Wu, J.; Cai, C.; Zhou, Z.; Qian, H.; Zha, F.; Guo, J.; Feng, B.; He, T.; Zhao, N.; Xu, J. Low-cost mussel inspired poly(catechol/polyamine) coating with superior anti-corrosion capability on copper. Journal of Colloid and Interface Science 2016, 463, 214-221. DOI: 10.1016/j.jcis.2015.10.056

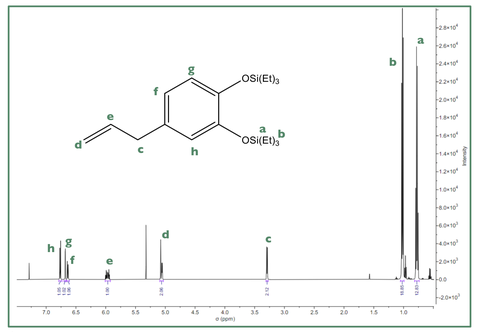
Synthesis of Catechol & Thioacetate Polybutadiene

Protection of Eugenol with Silyl Ethers:



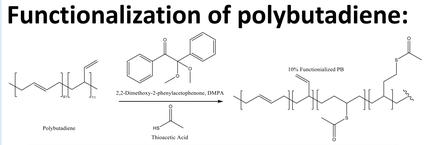


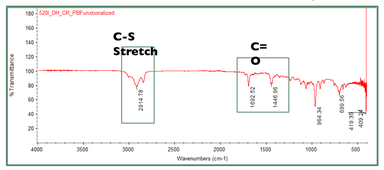
IR Spectrum of protected eugenol



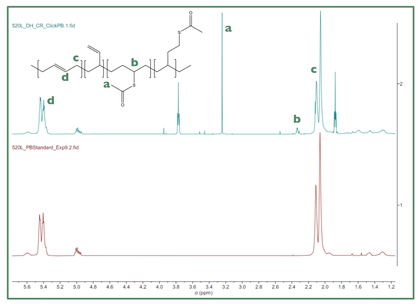
^{1}H NMR of protected eugenol

Functionalization of polybutadiene:



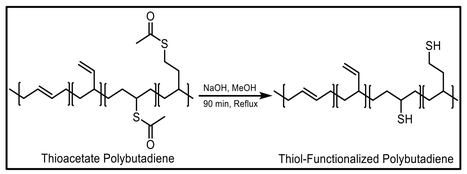


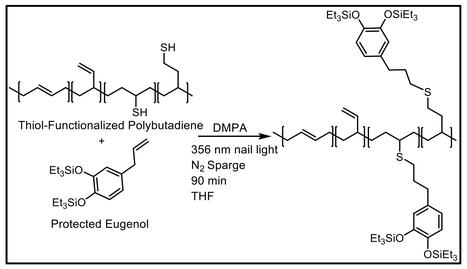
IR Spectrum of 10% functionalized polybutadiene



^{1}H NMR of polybutadiene stacked with 10% functionalized polybutadiene

Polymer Deprotection & Thiol-ene Reaction





- Thiol-ene reaction was unsuccessful
- Orange circles indicate protected eugenol alkene
- Alkene resonance should disappear from starting material to product, but doesn't

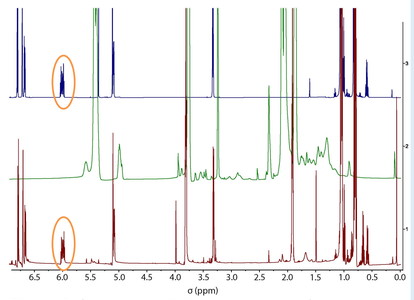
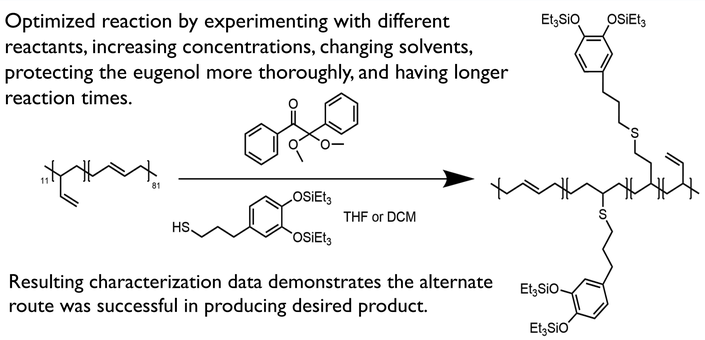


Figure 1. Stacked 1-H NMR spectra collected for protected eugenol (top), polybutadiene (middle), and the thiol-ene reaction product (bottom).

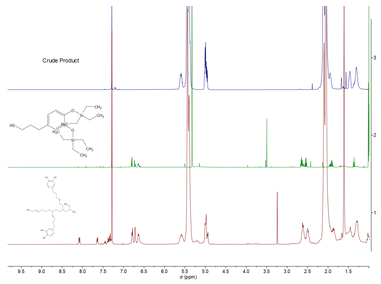
Alternative Route to Catechol Polymer

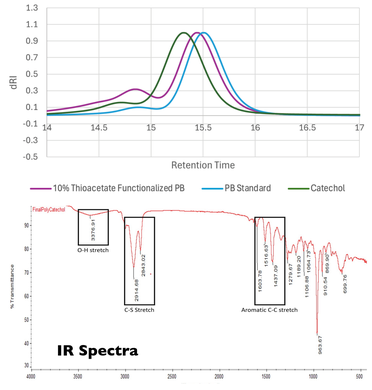
- Optimized reaction by experimenting with different reactants, increasing concentrations, changing solvents, protecting the eugenol more thoroughly, and having longer reaction times.



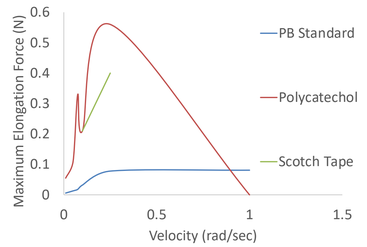
- Resulting characterization data demonstrates the alternate route was successful in producing desired product.

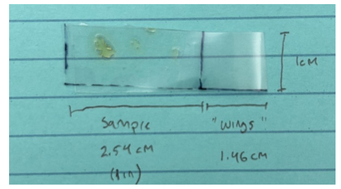
^{1}H NMR



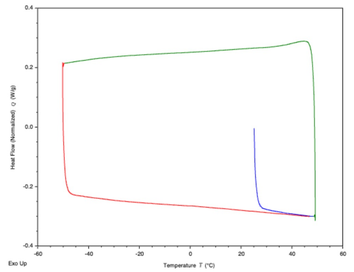


Polymer Properties & Adhesion Testing

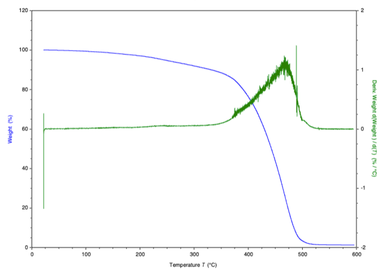




- Adhesion forces at a variety of velocities (peel-testing) on polyethylene rectangles were measured. Our novel polycatechol outperformed scotch tape at 0.25 rad/sec.



- Differential scanning calorimetry (DSC) indicates the polycatechol has a glass transition temperature (T_g) of -47.5 °C.



- Thermal gravimetric analysis (TGA) suggests that operating use of the polycatechol should not exceed 50 °C (when degradation begins).