150th Canadian Conference and Exhibition 2022 – June 13th – 17th – Calgary TELUS Convention Centre

Toronto Metropolitan University

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Applications of Bio-based Monomers for Novel Polyurethanes and Polyimines

SACRIPANTE RESEARCH GROUP

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Introduction

Polymers are ubiquitous in everyday life and have multiple applications including medical, transport, electrical, construction, coatings, and packaging. Increasing social awareness and public interest in environmental issues, global warming, limited fossil fuel resources, are driving the growth for sustainable and green chemistry.[1,2] The most prevalent commercial bio-based polymers are obtained from monomers such as diols, hydroxy-acids, and acids derived corn-, sugar-, or plant-based oils. However, these sources are food-based, and critics have suggested more sustainable monomers from non-food biomass.

The central focus of our research program is to advance the fundamental chemistries and applications of sustainable biomass resources that are abundant, inexpensive, and non-food based into commercial polymers

Cardanol is a phenolic material derived from cashew nutshell liquid as a food waste by-product of cashew nut processing.[3] In addition, this material is inexpensive with approximately 1-million-ton production in 2021 and utilized in formulations for surface coatings, paints and varnishes. Vanillin is a phenolic aldehyde derivative from lignin as a by-product from cellulose as a sulfite process.[4] This material has seen applications as bio-based fibers, surfactants and polymers.

Figure. 1. Vanillin from Lignin

Figure. 2. Cashew Nut Shell Liquid

Polyurethanes are produced from the polymerization reaction between polyols and/or organic diols with diisocyanates. Usually, the polyols are hydroxyl-terminated oligomers, such as poly (ethylene oxide or can be a polyester oligomer terminated with hydroxyl moiety. The diisocyanates are usually selected as toluene-diisocyanate, 4,4'-methylene diphenyl diisocyanate, isophorone diisocyanate and hexamethylene diisocyanate.

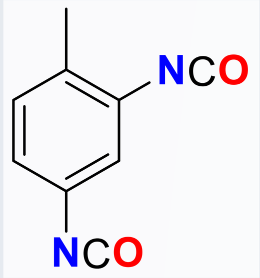
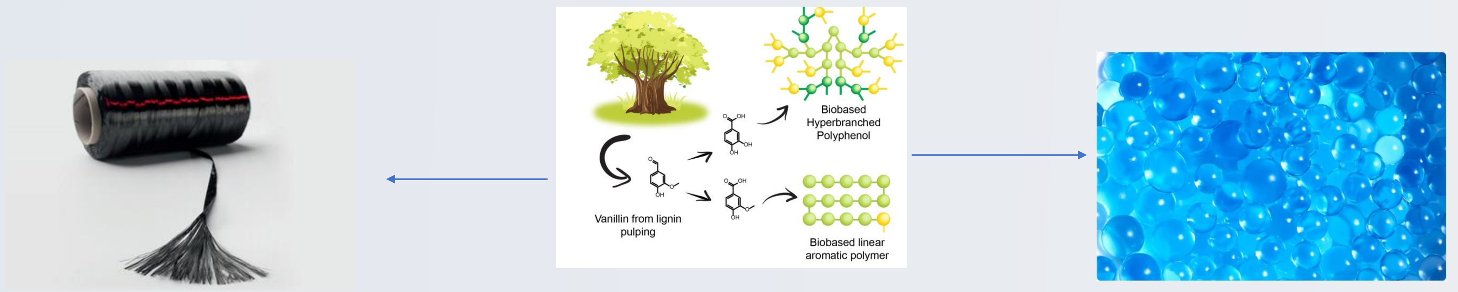


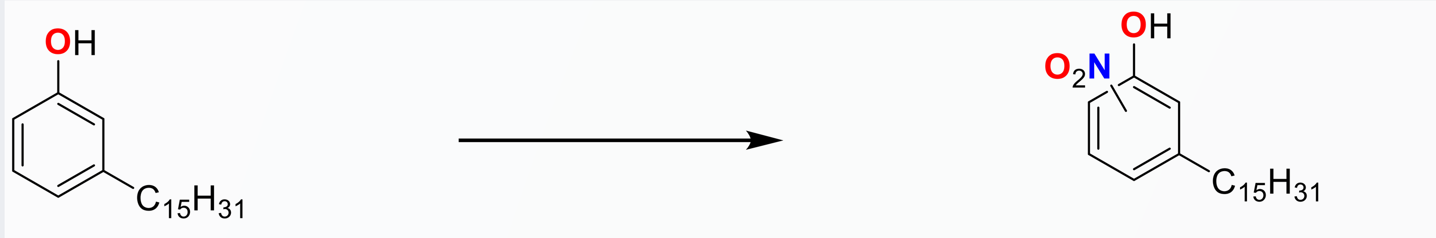
Figure 3. Toluene Diisocyanate (TDI)



Objectives

- The current strategy is to functionalize Cardanol to a novel Diamine using the 12 Principles of Green Chemistry
- Amines are good platform chemicals for the synthesis of Diisocyanates and Imines that will have wide applications in polyurethane foams and polyimine thermosets

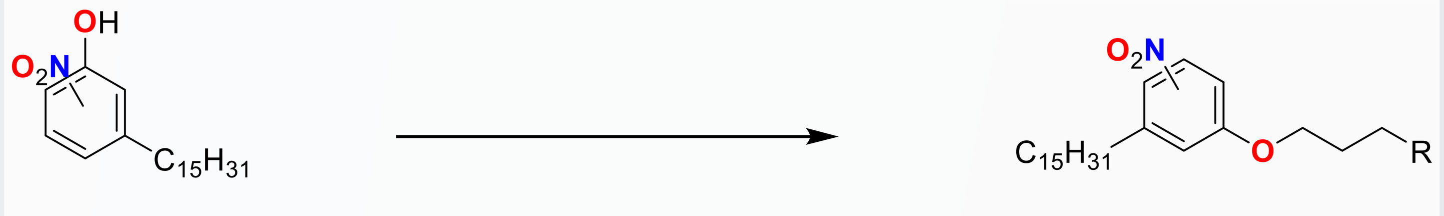
Reaction Schemes



62-98 % conversion

Scheme 1.

Conditions: 1.6 mol equiv. 65% HNO_3 in ACN or $CHCl_3$ for 4 hrs.

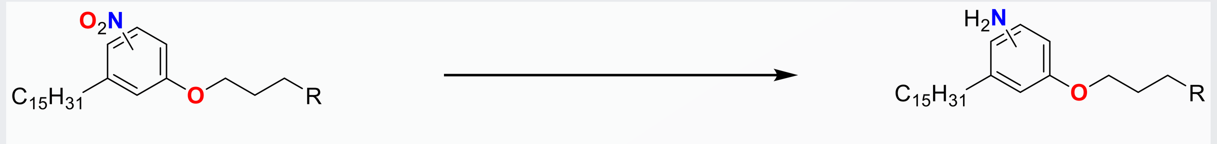


91% conversion

Scheme 2.

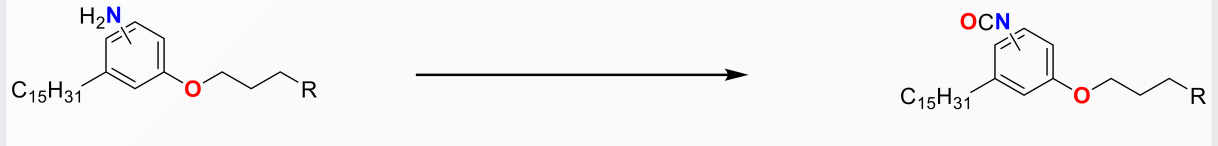
Conditions: 1 mol of 1,3-dibromopropane, 2% mol loading TBAI, 2 mol equiv K_2CO_3 in H_2O, reflux @ 110 °C for 24 hrs.

Future Work



Scheme 3.

Conditions: 14.5 mol equiv. Zn, 4 mol equiv. NH_4Cl, 15 mL of H_2O, 80 °C, 30 mins

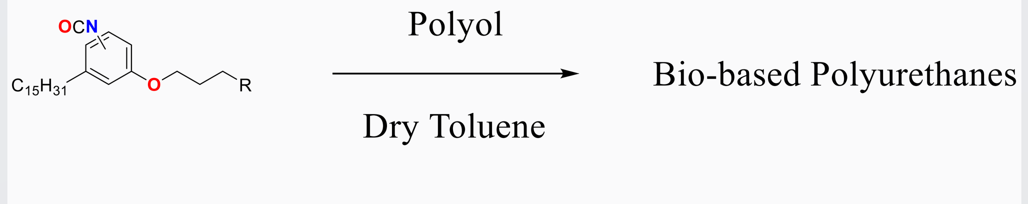


Scheme 4.

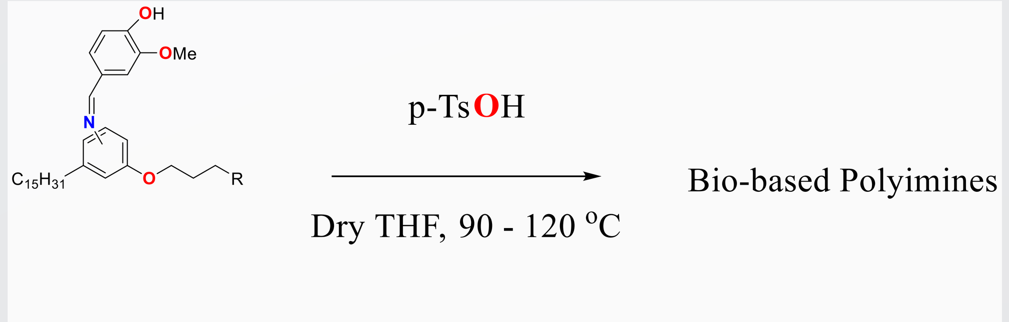
Conditions: 4 mol equiv. NEt_3, 1.5 mol equiv. Triphosgene, dry Toluene, 80 °C, 8 hrs

Scheme 5.

Conditions: 2.2 mol equiv. Vanillin, dry EtOH, 60 °C, 4-6 hrs.



Scheme 6.



Scheme 7.

- Attempt a reduction of the Dinitro using different catalysts.
- Initiate a hydrogenation reduction of 1,5-pentamethylene diisocyanate to Cadaverine.
- Perform tensile tests on the polyimines and compare if it has excellent mechanical properties

Acknowledgements

I'd like to formally thank my supervisors for their full support towards my research and guiding towards our synthetic goals.

Special thanks for TMU and NSERC for funding this research and generous lab space.

Huge appreciation to my lab mates in KHN 202: Foucher research group (Liam, Cristele, Nicola, Jenny and Lena), Gossage research group (Kathleen May) and Sacripante research group members (Rachele, Sidra and Alex)

Finally, thank you to the many restaurants around Toronto for improving my tastebuds.

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Funding Support

NSERC CRSNG
evoco
Mitacs