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Synthesis of Eugenol-Based Polyols via Thiol–Ene Click Reaction and High-Performance Thermosetting Polyurethane Therefrom

Sauravkumar Patel
Pittsburg State University

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Sauravkumar Patel and Ram K. Gupta

Department of Chemistry, National Institute for Materials Advancement
Pittsburg State University, Pittsburg, KS 66762

Abstract

The thiol−ene click reaction to prepare biobased polyols is a strategy to promote the green and environmental protection of polyurethane. The excessive usage of thiol and low conversion of carbon−carbon double bonds (C=C) would severely limit the properties of polyurethane (PU). In this work, a set of eugenol-based polyols were prepared via the thiol−ene click reaction. Interestingly, the conversion of the C=C was nearly 100% at the eugenol and various thiol compounds (-SH) in a stoichiometric ratio without excess of -SH. Then, the prepared polyols were reacted with diphenylmethane-diisocyanate (MDI), followed by a series of structure adjustable thermosetting polyurethane networks with colorless transparency, high glass transition temperature (Tg), and good mechanical properties being obtained. In particular, the tensile strength was up to 54.88 MPa, and Tg can be adjusted from 36.45 to 77.21 °C. Moreover, it is revealed that the compounds with an allyl structure are conducive to the efficient click reaction, and its application in PU can be greatly extended.

Results

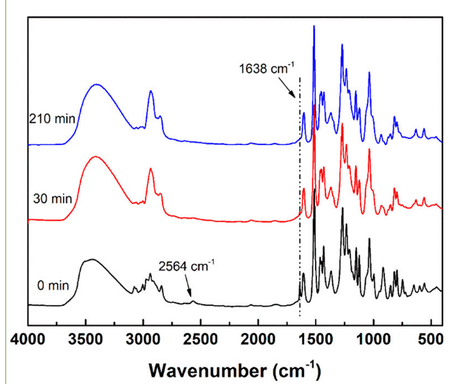


Figure 1. FTIR tracing of eugenol-based polyols (0.5%-initiator) with different irradiation times under UV-light.

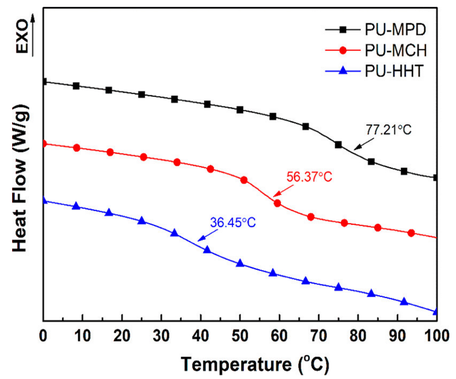


Figure 2. DSC curves of PU-MPD, PU-MCH, and PU-HHT.

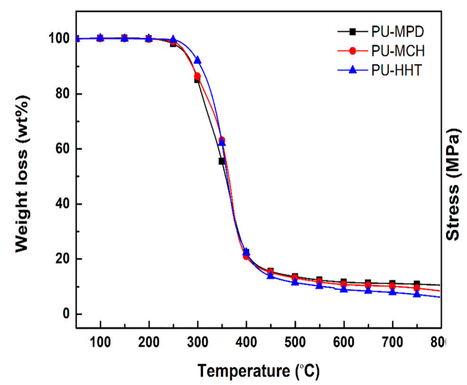


Figure 3. TGA curves of PU-MPD, PU-MCH, and PU-HHT.

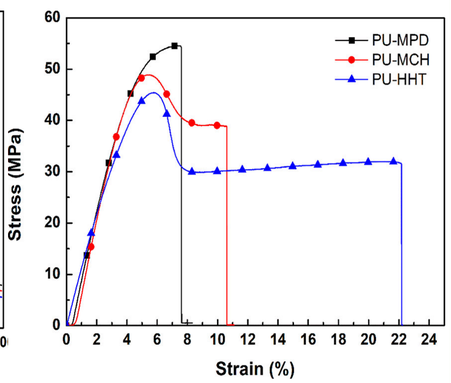
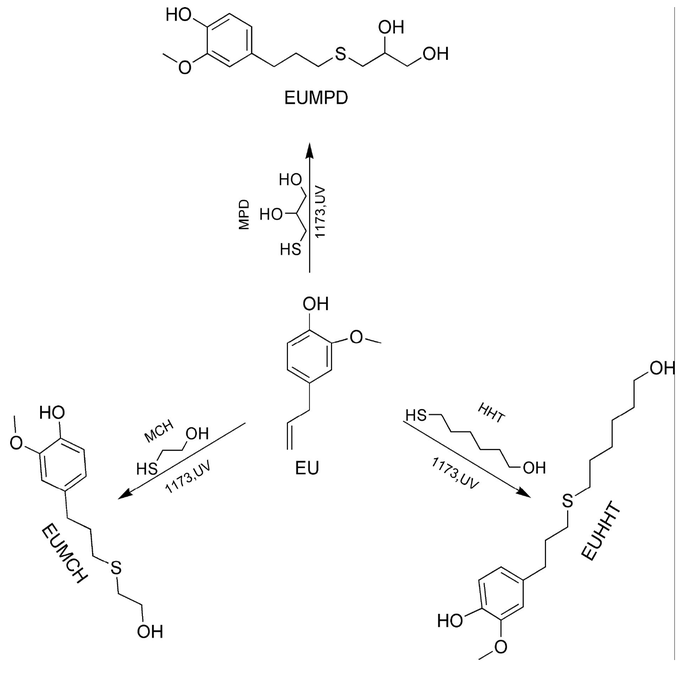
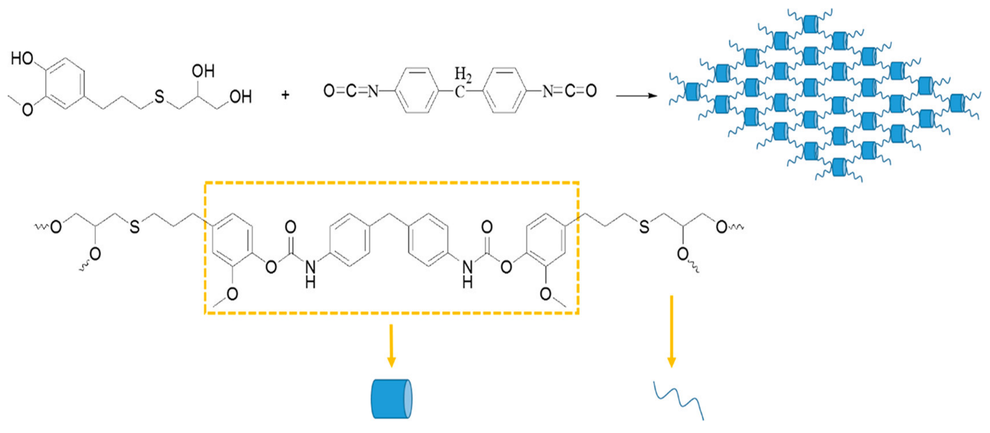


Figure 4. Typical stress−strain curves of PU-MPD, PU-MCH, and PU-HHT.

Experiment



Synthesis Route of Eugenol-Based Polyols via the Thiol–Ene Click Reaction



Schematic Diagram of the PU Networks of EUMPD/MDI

CONCLUSIONS

In this work, eugenol-based polyols and a series of colorless transparent thermosetting PU films with great comprehensive properties were successfully prepared via an effective and simple strategy. The eugenol-based polyols were prepared through the thiol−ene click reaction at room temperature, and more importantly, it can be directly used without purification. The target product was successfully obtained, and the conversion of C□C nearly approached 100%. The Tg's of PU-MPD, PU-MCH, and PU-HHT were 36.45, 56.37, and 77.21 °C, respectively. The PU-MPD demonstrated better mechanical properties (tensile strength of 54.88 MPa) than the others due to the higher cross-linking density and complete network. The transmittances of these PU films in the visible light region all were over 85%. This work may provide an environmental measurement for translating eugenol into varieties of polyols for PU, which will broaden the utilization of eugenol in the sustainability of the PU industry.

ACKNOWLEDGMENTS

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