

Sustainable Synthesis of Non-Isocyanate Polyurethanes from Biobased Phenols and N,N-disubstituted Formamides via Copper Catalysis

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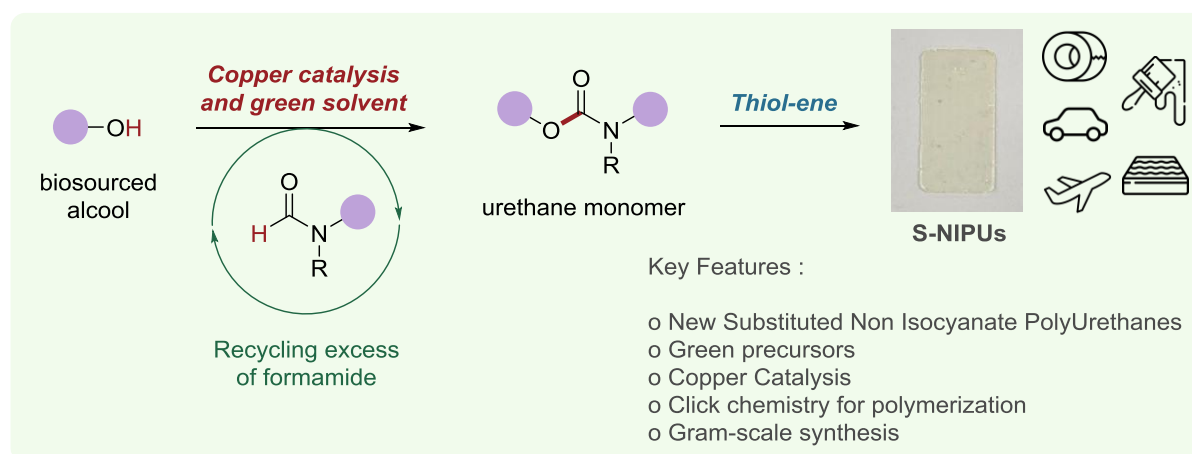
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Keywords : Catalysis, Non Isocyanate Polyurethane, Click Chemistry, Green Chemistry

Abstract :

Polyurethanes (PUs) are among the most versatile and widely used polymer families, with applications spanning foams, coatings, adhesives, sealants, elastomers, and high-performance materials.^[1] Their industrial success stems from the robustness of the isocyanate route, which enables structural diversity and tunable properties. However, the use of toxic isocyanates and their phosgene-derived precursors raises major environmental, health, and safety concerns, motivating the search for greener synthetic pathways.^[2] In this work, a sustainable route to *N*-substituted non-isocyanate polyurethanes (s-NIPUs) was developed, combining a copper-catalyzed synthesis of alkene-functionalized urethane monomers with thiol-ene click polymerization under solvent-free conditions. This strategy enabled the preparation of hydroxyl-free crosslinked thermosets that are structurally distinct from both conventional isocyanate-derived polyurethanes and polyhydroxyurethanes. Comprehensive characterization (HRMAS NMR, DSC, GC, swelling index, DMA, and TGA) confirmed efficient curing, high gel content, tunable network densities, and excellent thermal stability. Compared to a reference polyurethane synthesized via the classical isocyanate route, the S-NIPUs exhibited a lower modulus, due to the absence of hydrogen-bonding interactions, but superior thermal resistance, as the lack of such interactions also prevents the reversibility typically associated with urethane linkages.^[3] These results highlight the potential of s-NIPUs as a new class of sustainable polyurethane materials with properties complementary to those of established systems.



Access to non isocyanate polyurethane through copper catalysis and click chemistry

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