New methodologies for polyurethane synthesis by in-situ isocyanate generation from dioxazolones

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Résumé :

Polyurethanes, produced from polyols and isocyanates, are widely used due to their versatile properties[1,2]. However, the toxicity of isocyanates has led to strict EU regulation under REACH legislation[3], highlighting the need for safer alternatives. This work aims to develop a safer alternative to conventional polyurethane synthesis by enabling the in-situ generation of isocyanates from non-toxic precursors. Our approach involves the intra-molecular Lossen rearrangement of dioxazolones triggered by a reaction with an alcohol, leading to the formation of an isocyanate with CO_2 as unique co-product[2,4,5]. This isocyanate is immediately available for the formation of the urethane function with the same alcohol (Figure 1).

Herein, an efficient synthetic route to dioxazolone was developed using undecylenic acid, a biosourced compound derived from castor oil. The resulting undecylenyl dioxazolone was successfully utilized for the synthesis of urethanes via reactions with model alcohols in the presence of different catalysts combinations. To extend this technology toward polyurethane production, the design and synthesis of (bis)- and (tri)-dioxazolone monomers based on undecylenyl dioxazolone has also been developed. These new isocyanate precursors permitted to obtain respectively thermoplastic polyurethanes and thermoset foams by reaction with diols, using the previously described Lossen rearrangement of dioxazolone, generating the isocyanate moieties during the polymerization process.

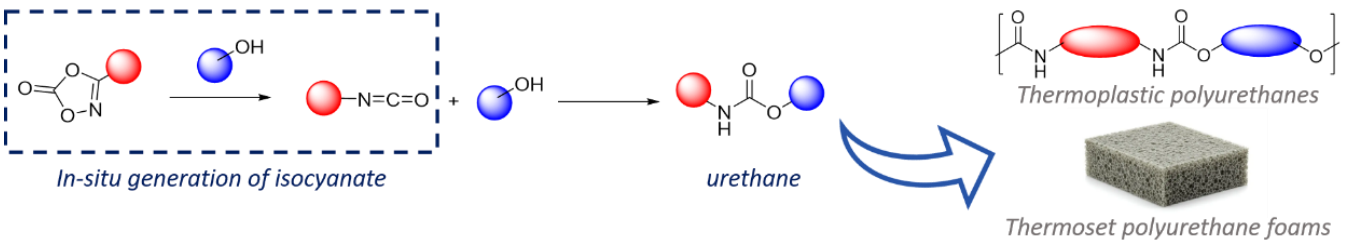

Figure 1: In-situ generation of isocyanates for polyurethane synthesis

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