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Enhanced aminolysis of cyclic carbonates by beta-hydroxyamines for the production of fully biobased polyhydroxyurethanes

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PURPOSE OF THE ABSTRACT

Polyurethanes (PUs), ranking 6th among all polymers based on annual worldwide production, are commonplace in everyday life as foams, coatings, adhesives, elastomers, insulation, composites, and so forth. They are present in a wide range of applications due to the numerous industrially available polyols, which allow to cover a large panel of properties.

However, their synthesis requires the use of isocyanates, known to be harmful for human health and for the environment.[1] In order to limit the use of isocyanates, the development of isocyanate-free PUs has emerged over the last decade and has gained increasing attention in both the academic and industrial communities. Hence, the aminolysis of 5-membered cyclic carbonates, which yields polyhydroxyurethanes (PHUs), is nowadays the most promising and described route to non-isocyanate polyurethanes (NIPUs).[2] This route has the advantage that these carbonates are easily obtained by the carbonation of commercial epoxides. Moreover, the valorization of CO2 as a cheap, renewable and non-toxic resource makes this pathway the least toxic and most eco-friendly route to PHUs.[3] However, 5-membered cyclic carbonates suffer from lower reactivity compared to isocyanates or larger cyclic carbonates. Therefore, the aminolysis of cyclic carbonates has been thoroughly investigated in order to understand and optimize the ring opening reaction.[4]

In this study,[5] we highlighted the higher reactivity of beta-hydroxyamines toward cyclic carbonate in comparison to classical alkylamines through the determination of their reaction rate constants. The key role of the beta-OH substituent in the aminolysis was enlighten by a DFT investigation. In addition to their higher reactivity, biobased beta-hydroxyamines were easily synthesized by a one-step process and used for the synthesis of fully biobased PHU thermosets. The higher reactivity of beta-hydroxyamines was also confirmed in the thermoset synthesis, the thermal and thermo-mechanical properties of PHUs were then compared.

FIGURES

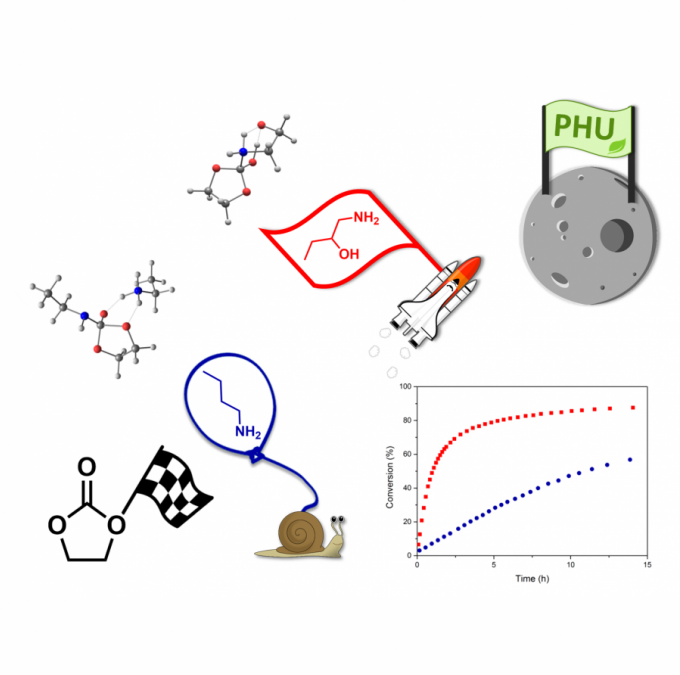

FIGURE 1
Graphical abstract

FIGURE 2

KEYWORDS
Non-isocyanate polyurethanes | Biobased | Beta-hydroxyamine | Reactivity

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