

# Cyclic carbamates from (*R*)-(+)-limonene as monomers for isocyanate-free polyurethanes

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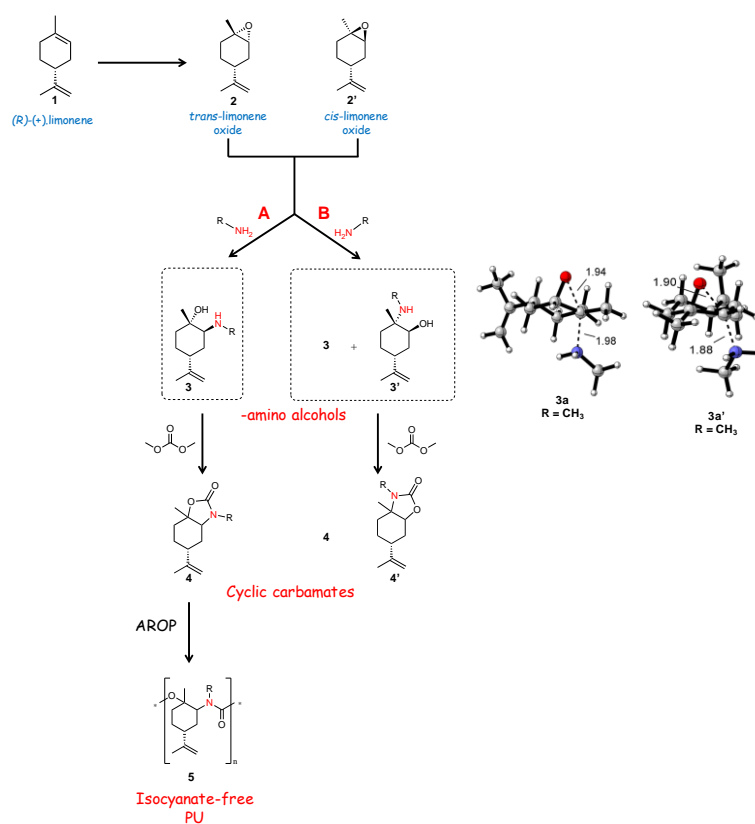
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## Abstract

A novel synthetic pathway for synthesizing polyurethanes without using toxic reagents, i.e. isocyanates, was designed and performed starting from limonene as a natural source [1]. In particular, (*R*)-(+)-limonene-oxide was selected. A library of  $\beta$ -amino alcohols was efficiently synthesized from the aminolysis of the epoxide ring of (*R*)-(+)-limonene-oxide with different primary amines as nucleophiles and hot water as catalyst. (*R*)-(+)-limonene-oxide exists as a mixture of *cis* and *trans* isomers. It is reported that the aminolysis reaction of limonene epoxide is regio- and diastereoselective [2]. A rational investigation was done in order to understand the mechanistic pathways that determine the formation of the  $\beta$ -amino alcohols only from the *trans* isomer or from both *cis* and *trans* isomers of (*R*)-(+)-limonene-oxide. The regio- and diastereoselectivities of the epoxide ring-opening of (*R*)-(+)-limonene-oxide by primary amines in water was studied. An *in-silico* study was performed with two nucleophiles: methylamine and benzylamine. The  $\beta$ -amino alcohols obtained were then used for the synthesis of cyclic carbamates by using the dialkyl carbonate (DAC) chemistry [3]. A library of cyclic carbamates deriving from (*R*)-(+)-limonene was synthesized. The synthesis of cyclic carbamates from (*R*)-(+)-limonene is not yet explored in the current scientific literature. Cyclic carbamates are known to be suitable monomers for the Cationic Ring-Opening Polymerization (CROP) to yield isocyanate-free polyurethanes [4]. One of the cyclic carbamate derived from (*R*)-(+)-limonene was used as monomer, and Anionic Ring-Opening Polymerization (AROP) was performed. The AROP of cyclic carbamates is another novelty of this work. An oligo-urethane was obtained, thus validating the synthetic pathway designed. The PU was characterized through <sup>1</sup>H, <sup>13</sup>C NMR spectroscopies, and GPC analysis.

## Solvent-free routes for the synthesis of isocyanate-free PU



## References

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