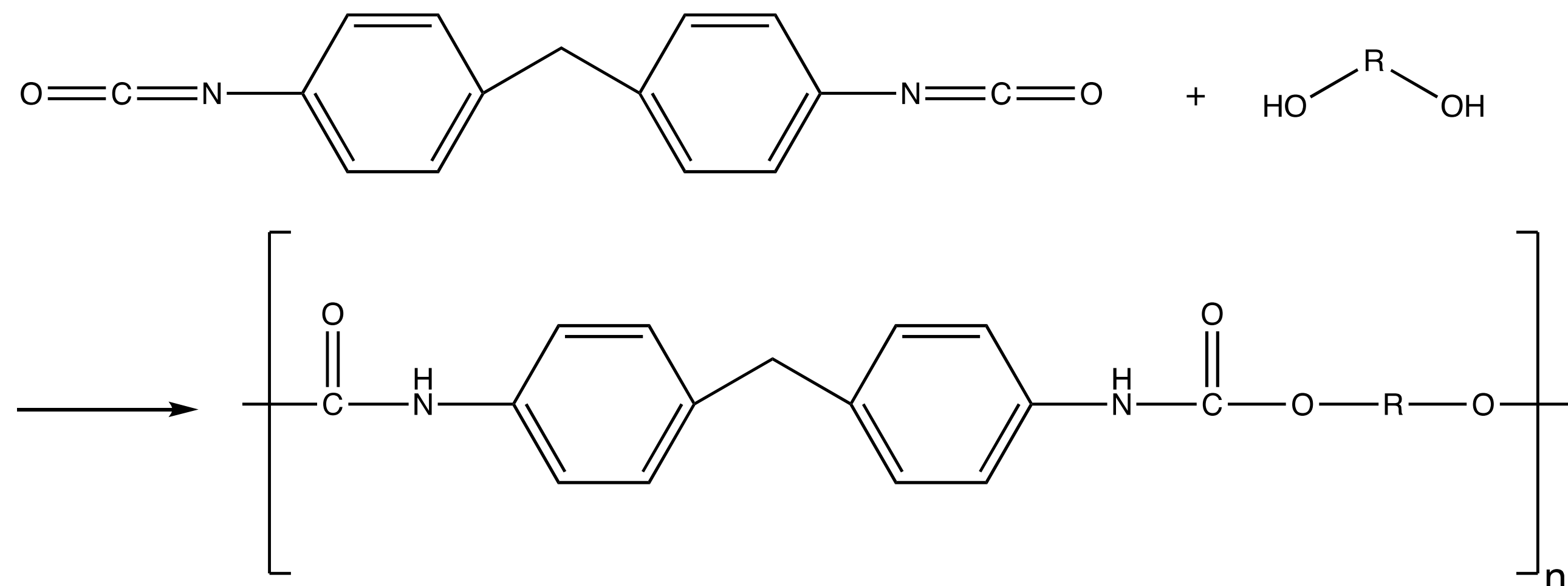


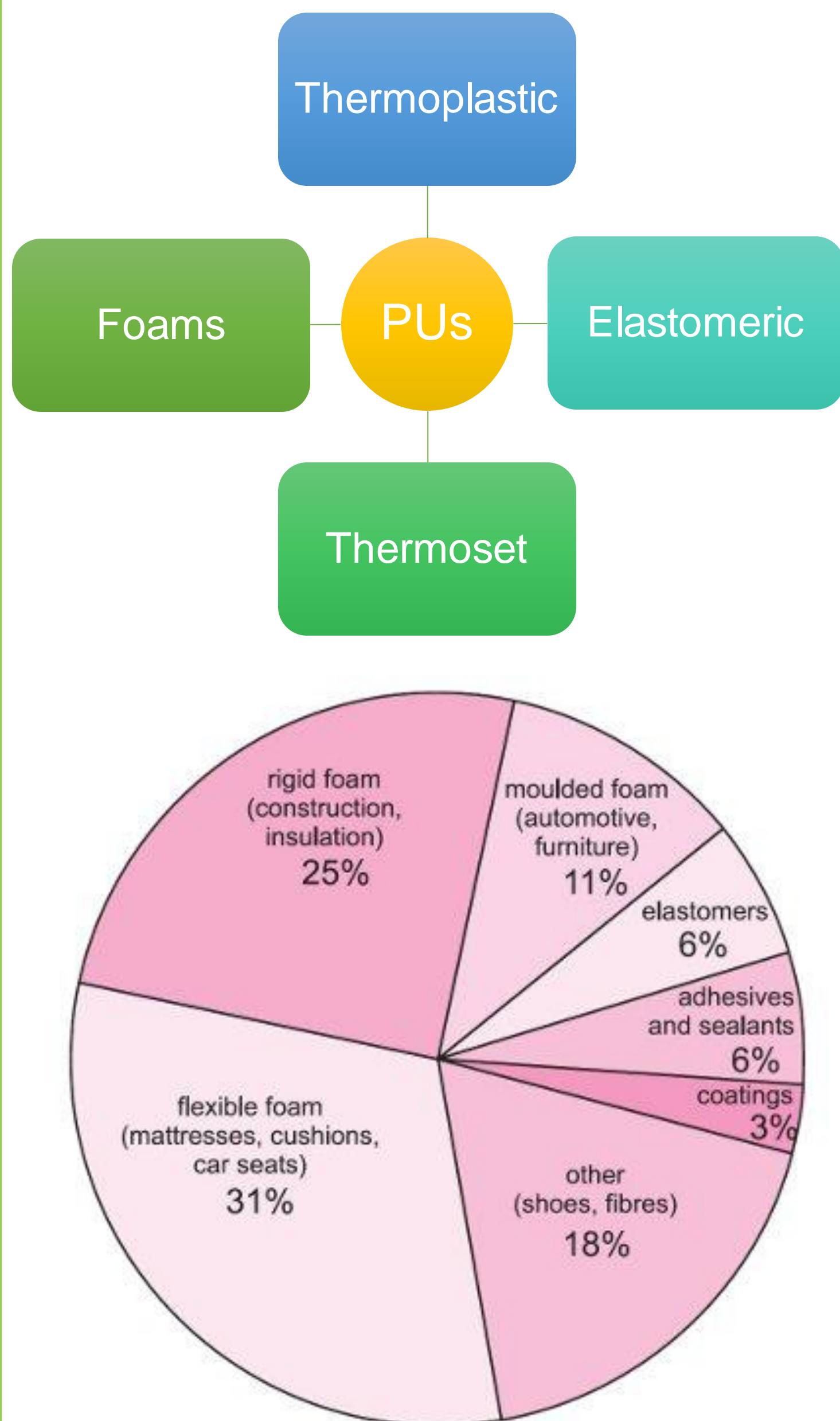
Objectives

Polyurethanes (PUs) represent an important class of polymers, with an annual production of more than 18 millions of tons, about 5 mass% of the total worldwide polymer production. PUs are versatile polymers and are suitable for a large variety of applications. The concern about PUs is that they are formed by chemical reaction between polyols and isocyanates. Isocyanates are known to be highly toxic for health and environment



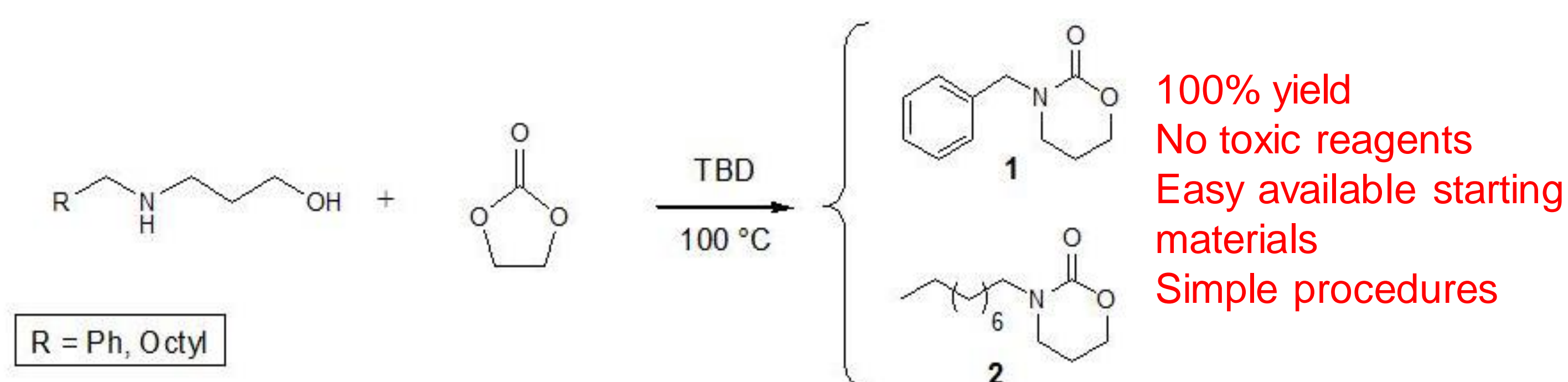
The present work is based on the synthesis of isocyanate-free polyurethanes. The strategies adopted for this goal are:

- Ring Opening Polymerization (ROP) of cyclic carbamates prepared via dialkyl carbonate chemistry
- Ring Opening of cyclic carbonates by amines

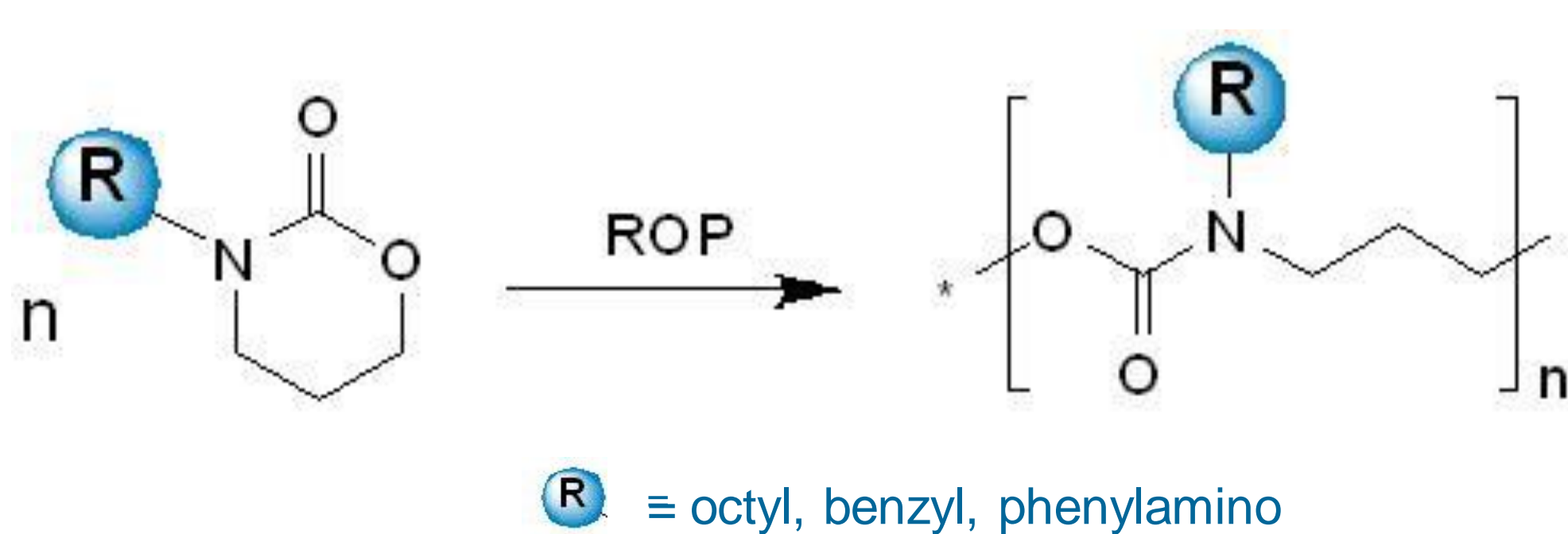


Synthesis of cyclic carbamates via DAC chemistry and ROP of cyclic carbamates to form PU oligomers

Substituted 1,3-amino alcohols + ethylene carbonate + bicyclic nitrogen base

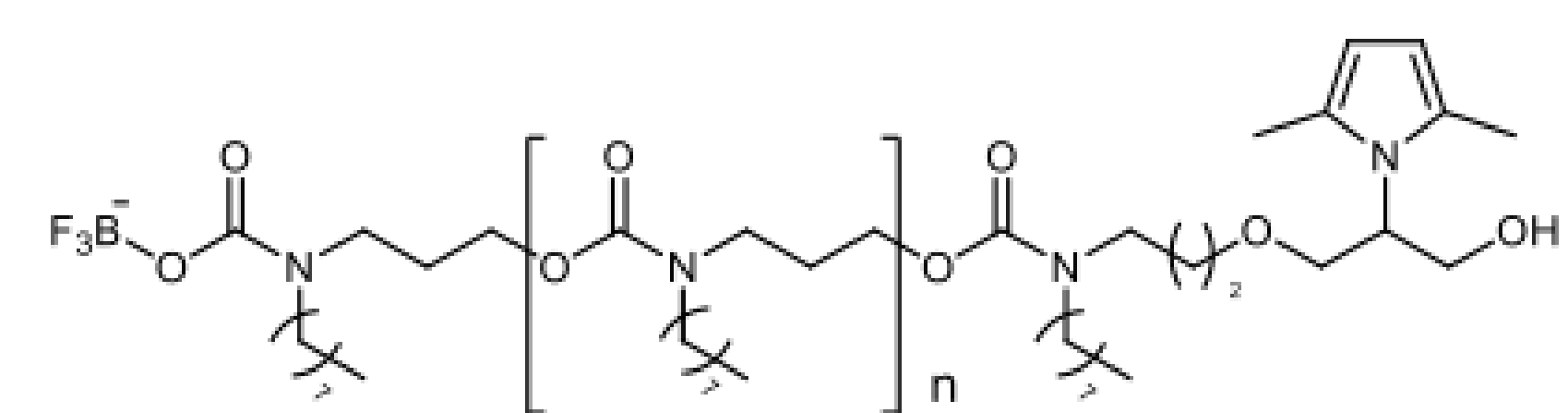


Base: 1,5,7-triazabicyclo[4.4.0]dec-5-ene (TBD)

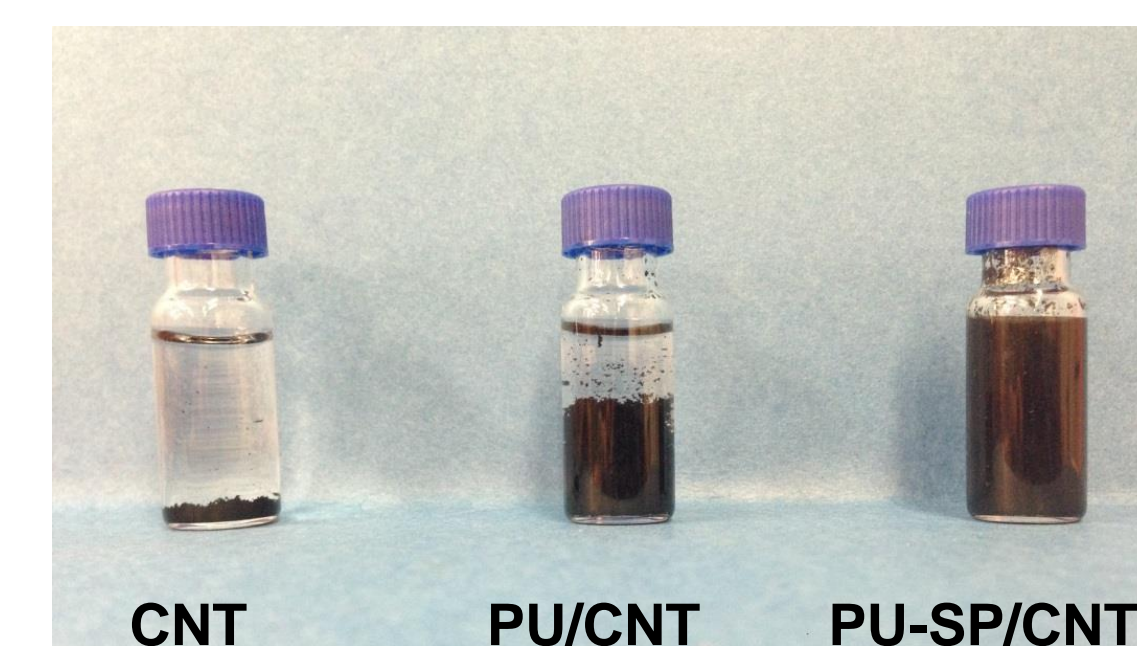


Cat: $\text{BF}_3\text{O}(\text{Et})_2$ Monomer / Cat = 1 / 0.015
T = 25 – 110°C, 12h, solvent free

Biobased molecule 2-(2,5-dimethyl-1H-pyrrol-1-yl)-1,3-propanediol (SP) as chain end of PU oligomers

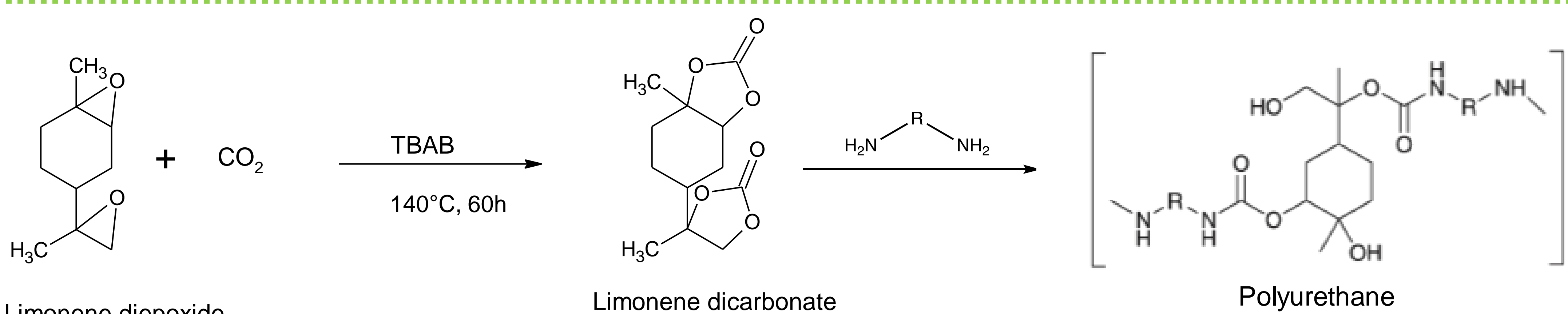


Adducts of PU and PU-SP with Carbon Nanotubes (CNT)



Stable dispersions in ethyl acetate were obtained with CNT adducts modified with PU-SP

Ring opening of cyclic carbonates by amines



Conclusions

Synthetic strategies to obtain isocyanate-free polyurethanes are here reported. Such PUs are obtained via ROP of cyclic carbamates and ring opening of cyclic carbonates by amines, thus replacing the use of hazardous isocyanates. The formation of stable adducts of CNT with PU-SP appears of great interest for CNT based composites.

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- Bähr, M., Bitto, A., & Mülhaupt, R. (2012). Cyclic limonene dicarbonate as a new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes. *Green Chemistry*, 14(5), 1447-1454.