NON-ISOCYANATE POLYURETHANE CHEMISTRY AND MULTIFUNCTIONAL BIO-INSPIRED POLYHYDROXYURETHANES

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The quest for green and sustainable plastics is stimulating the development of isocyanate- and phosgene free routes to polyurethanes exploiting both biological and chemical fixation of carbon dioxide. Particularly, polyfunctional cyclic carbonates, readily available by carbonatization of bio-based polyols and epoxides, represent highly versatile intermediates for non-isocyanate polyhydroxyurethanes (NIPU). In our process starting from the same raw bio-based raw material such as limonene dioxide and biobased glycidylethers carbonatization with carbon dioxide affords multifunctional cyclic carbonates, whereas amination with ammonia produces the corresponding bio-based amine curing agents [3]. The incorporation of limonene dicarbonate derived from orange peels substantially improves NIPU stiffness [4]. For the first time NIPU formulations and rapid cure enable the fabrication of flexible NIPU foams [5]. The amine cure of carbonated POSS epoxy resins produces a new family of NIPU hybrid materials for scratch resistant coatings [6]. Going well beyond conventional polyurethane chemistry, the polyaddition of erythritol dicarbonate and sorbitol tricarbionate enables to produce linear, branched and crosslinked poly(carbohydrateurethanes) at ambient temperatures without using protective groups [7]. The prospect of NIPU chemistry ranges from engineering plastics and thermoplastic elastomers to a great variety of tailor-made functional polyhdyroxyurethane materials including biocompatible materials for biomedical applications, triple-shape memory NIPUs [8], nacre-like NIPU, and new polymeric systems for 3D and 4D printing. This presentation gives an overview on the basic structure property correlations and new approaches toward the development of bio-inspired NIPU materials.

^[1] L. Maisonneuve, O. Lamarzelle, E. Rix, E. Grau, H. Cramail, Chem. Rev. 2015, 115, 12407-12439, Isocyanate-Free Routes to Polyurethanes and Poly(hydroxy Urethane)s

^[2] H. Blattmann, M. Fleischer , M. Bähr , R. Mülhaupt, Macromol. Rapid Commun. 2014, 35, 1238–1254, Isocyanate- and Phosgene-Free Routes to Polyfunctional Cyclic Carbonates and Green Polyurethanes by Fixation of Carbon Dioxide

^[3] H. Blattmann, R. Mülhaupt, Green Chem. 2016,18, 2406-2415, Multifunctional β -amino alcohols as bio-based amine curing agents for the isocyanate- and phosgene-free synthesis of 100% bio-based polyhydroxyurethane thermosets.

^[4] M. Bähr, A, Bitto, R. Mülhaupt, Green Chem. 2012,14, 1447-1454, Cyclic limonene dicarbonate as a new monomer for non-isocyanate oligo- and polyurethanes (NIPU) based upon terpenes.

^[5] H. Blattmann, M. Lauth, R. Mülhaupt , Macromol. Mater. Eng. 2016, 301, 944–952, Flexible and bio-based nonisocyanate polyurethane (NIPU) Foams.

^[6] H. Blattmann, R. Mülhaupt, "Multifunctional POSS cyclic carbonates and non-isocyanate polyhydroxyurethane hybrid materials", Macromolecules 2016, 49, 742-751.

^[7] S. Schmidt, B. S. Ritter, D. Kratzert, B. Bruchman, R. Mülhaupt, Macromolecules 2016, 49, 7268–7276, Isocyanate-free route to poly(carbohydrate–urethane) thermosets and 100% bio-based coatings derived from glycerol feedstock

^[8] V. Schimpf, B. Heck, G. Reiter, R. Mülhaupt, "Triple-shape memory materials via thermoresponsive behavior of nanocrystalline non-isocyanate polyhdyroxyurethanes", Macromolecules, 2017, 50, 3598–3606