Fully bio-based non-isocyanate polyurethanes (NIPU) via cyclic carbonate/amine route

Thermoplastic poly(hydroxyurethane)s (PHUs) raised industrial and academic research curiosity, since their synthesis is achieved via the ring-opening of bis-cyclic carbonates with diamines, enabling the replacement of phosgene and isocyanates employed in the classical polyurethane (PU) manufacture. Due to fossil fuel depletion and environmental concerns, the use of building-blocks from renewable resources is highly investigated. Combining PHUs synthesis and bio-based compounds, a large platform of fatty acid-based cyclic carbonates as poly(hydroxyurethane) precursors was synthesized by epoxidation/carbonation routes. However, such monomers exhibited a slow polymerization rate towards amines, due to the electron-releasing alkyl chains, which deactivate the cyclic carbonates. An alternative route consists in inserting a heteroatom nearby the cyclic carbonate to improve/activate its reactivity. Herein, the synthesis of new activated lipidic cyclic carbonates from glycerol carbonate and epichlorohydrin has been achieved, leading respectively to an ester or an ether linkage in β position of the carbonate. After kinetic investigations of the cyclic carbonate aminolysis on model compounds, the corresponding activated bis-cyclic carbonates were polymerized with two diamines and exhibited enhanced reactivities. A specific focus on the side reactions that could occur in both model reaction and polymerization is also discussed. On the other hand, a new route to access bio-based diamines using mild and green conditions has been set up through an optimization of aliphatic alcohol oxidation into the corresponding nitriles, followed by an hydrogenation. The resulting diamines were subsequently polymerized with activated cyclic carbonates in order to obtain fully bio-based poly(hydroxy urethane)s.

Biography

Etienne Grau was trained in chemistry and physical chemistry at the ENS Cachan (France) and then undertook a PhD in polymer chemistry at CPE Lyon (France), where he studied the radical and catalytic polymerization of ethylene and its copolymerization with polar monomers in the C2P2 laboratory under the supervision of Dr. Vincent Monteil, Dr. Christophe Boisson and Dr. Roger Spitz (2007-2010). During a first post-doctoral stay, he studied Ziegler-Natta catalysis merging theoretical (with Prof. Phillipe Sautet at the ENS Lyon), surface (Prof. Christophe Copéret at ETH Zurich) and polymer chemistry (with Dr. Vincent Monteil at C2P2). Then in 2012, he moved to the group of Prof. Stefan Mecking in Konstanz (Germany) to work on Pd catalysis of the synthesis of monomers from lipids and terpenes. He was recruited by LCPO in 2013 as Assistant Professor in the group of Prof. Henri Cramail for his expertise in polymer chemistry and catalysis. He published around 30 articles and 10 patents. He received the best 2011 thesis prize of the French polymer group (GFP).

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