New Biocatalytic Routes to Monomers, Macromers and Polymers

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New and versatile biocatalytic methods were developed that offer mild and efficient options for macromer and polymer synthesis. Lipase B from *Candida antartica* (CALB), physically immobilized on hydrophobic macroporous resins, is a remarkable catalyst for both ring-opening and step-condensation reactions. CALB catalysis enabled the synthesis of aliphatic polyolpolyesters and polycarbonates by using a wide range of building blocks including sugar alcohols such as *glycerol* and *sorbitol.* Lipase regioselectivity enables direct copolymerizations of polyols with diols and diacids to give non-crosslinked high molecular weight materials with controlled branching. The mild reaction conditions (50 to 90 ^{o}C) allowed incorporation of chemically and/or thermally sensitive co-monomers such as silicones. For example, poly(ester-amides) were prepared containing silicone chain segments and carbohydrates were directly linked to silicones ("sweet silicones"), the latter giving materials with interesting surfactant properties.

Enzymatic routes to new monomers and their polymerization will also be discussed. For example, fatty acids were transformed by an engineered *Candida tropicalis* strain to their corresponding α,ω-dicarboxylic acids, α-carboxyl-ω-hydroxyl fatty acids, or a mixture of these products. Enzyme-catalyzed copolymerizations of these fatty acid derived monomers resulted in new functional copolyesters. Also, sophorolipids were prepared by microbial fermentation of *Candida bombicola* were converted by metathesis polymerization to functional biomaterials.

Cutinases from different micro-organisms have been evaluated for polymer synthesis and modification reactions. It was discovered that cutinases also possess impressive catalytic activity for lactone ring-opening and diacid/diol polycondensation reactions. In addition to polymer synthesis, cutinases have been revealed that have interesting activities for polymer modification and hydrolysis. As examples, the results of cutinase-catalyzed hydrolysis of PET and de-acetylation of poly(vinyl acetate) will be presented.

Keywords: Enzyme-catalysis, lipase, cutinase, polyesters, polycarbonates, immobilization

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