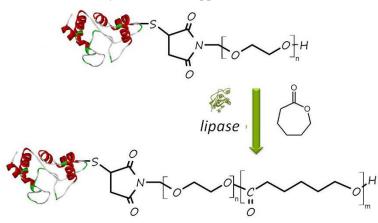
Synthesis of Giant Amphiphiles by Enzyme Catalyzed Ring Opening Polymerization

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Amphiphilic protein-polymer chimeras -the so-called *Giant Amphiphiles*- are designed to mimic the hierarchical self-assembly displayed in biological and synthetic material systems over a range of lengths. During the last years we synthesized several such protein-polymer amphiphilic bioconjugates using different synthetic approaches varying from the direct coupling of end-functionalized polymers to proteins, to the *grafting* of polymers *from* protein macroinitiators.^{1,2,3} Interestingly, *Giant Amphiphiles* have shown to assemble into well-defined, functional superstructures suitable for a variety of materials applications.



Scheme 1. Synthesis of Giant Amphiphiles by Enzyme Catalyzed ROP.

Herein we present a novel synthetic approach involving the Ring Opening Polymerization (ROP) grafting of ε -caprolactone from protein biomacroinitiators (Scheme 1). It will be shown that this method proceeds under mild reaction conditions with the high yields and reaction rates and is characterized by the absence of toxic monomers/catalysts/by-products that are intrinsic to enzymatic catalysis. This the first report of the "grafting from", in situ, formation of biocompatible and biodegradable giant soaps with interesting assembling properties that will be comparatively discussed.

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