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ACCEPTED MANUSCRIPT

Revisiting Monomer Synthesis and Radical Ring Opening

Polymerization of Dimethylated MDO Towards

Biodegradable Nanoparticles for Enzymes

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ABSTRACT

Radical ring opening polymerization is a powerful tool to achieve a polyester via radical polymerization. We used it to obtain a dimethylated version of poly(caprolactone) (PdmCL) from dimethylated MDO (DMMDO). First, we revisited monomer synthesis and achieved a milder synthetic protocol by introducing a cobalt-based catalyst. We also developed a new route towards DMMDO via a cyclic carbonate using the Petasis chemistry. Amphiphilic block-copolymers were then generated by free radical polymerization of DMMDO with a PEG-based macroinitiator. The resulting polyesters self-assembled into nanoparticles that

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