

# Macromolecular Engineering of Poly( $\epsilon$ -Caprolactone) Based on Macrocyclic Units

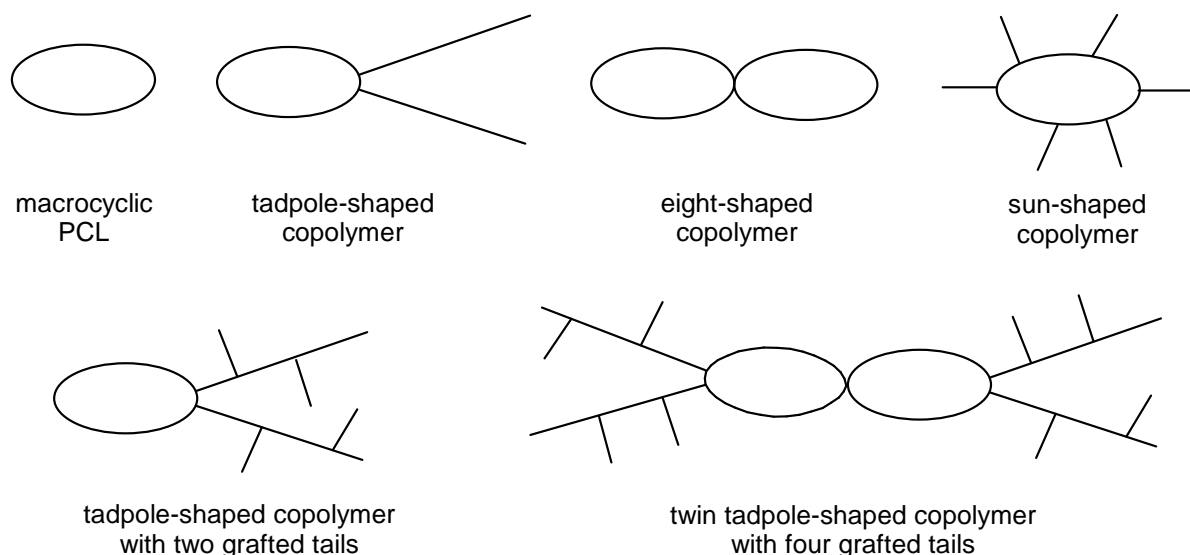
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The usual routes towards well-defined macrocycles relies on the coupling of the two chain-ends of a linear precursor under very high dilution ( $C < 10^{-5}$  M). Herein, we report on a novel strategy based on the sequential ring-opening polymerization of  $\epsilon$ -caprolactone followed by a few units (15-20) of an  $\epsilon$ -caprolactone  $\alpha$ -substituted by an acrylate, by using a cyclic tin dialkoxide as initiator. The key step relies on the intramolecular photo-cross-linking of pendant acrylates. Interestingly enough, after a final hydrolysis step, tin-free macrocyclic PCL is obtained.

Unlike the usual process based on the intramolecular coupling of chain-ends of a linear precursor, our strategy is particularly efficient to synthesize high molecular weight macrocycles (at least 20000 mol/g) because the probability of intramolecular cross-linking does not decrease when the chain length increases. Moreover, after photo-cross-linking, tin dialkoxides remain untouched and the addition of a fresh feed of a monomer ( $\epsilon$ -caprolactone or L-lactide) results in the resumption of polymerization leading to two-tail tadpole-shaped copolyesters.



In the frame of the macromolecular engineering of aliphatic polyesters based on macrocyclic units, our strategy was extended to the synthesis of eight-shaped, sun-shaped and twin tadpole-shaped copolymers. Finally, the synthesis of novel (twin) tadpole shaped copolymers with tails consisting of amphiphilic PCL-*graft*-PEO graft copolymers will be reported for the very first time.