

# Self-Switchable Copolymerization of Epoxides with Anhydrides Access to Block Polymeric Materials

He-Yuan Ji, Bin Wang\*, Yue-Sheng Li\*

School of Materials Science and Engineering, Tianjin University, Tianjin, 300350

**Abstract:** Poly(ester-*b*-ether)s, a kind of meaningful block polymeric materials for biomedicines and self-assembly, are typically synthesized *via* ring-opening polymerization of cyclic esters initiated by pre-prepared polyether macroinitiator. However, multi-step procedure is required in this traditional method. Herein, we detailed a one-step self-switchable copolymerization process of mixed monomers to precisely prepare poly(ester-*b*-ether) block copolymer materials. The strategy enables ring-opening alternating copolymerization of anhydrides with epoxides and ROP of epoxides sequentially in a closed system. Regioselective and living copolymerization is realized by cooperative organocatalysts to endow the poly(ester-*b*-ether) with controlled monomer sequence, high isotacticity and predictable molecular weight. A tandem copolymerization is developed by using lactide as an external trigger which could switch the hierarchically selective copolymerization to lactide polymerization. The study provides a new route to the facile synthesis of poly(ester-*b*-ether) block copolymer materials using a metal-free catalytic system.

**Key Words:** Switchable Polymerization; Block Copolymer; Polyester; Organocatalysis; Lewis Pair