Abstract: The preparation of perfectly alternating and regioselective copolymers derived from the copolymerization of carbonyl sulfide (COS) and epoxides via metal-free Lewis pair catalysts composed of a Lewis base (amidine, guanidine, or quaternary onium salts) and a Lewis acid (triethyl boron) is demonstrated. CO2-soluble and highly transparent copolymers of poly(monothiocarbonate) were successfully obtained with >99% tail-to-head content and high molecular weight (up to 92.5 kg/mol). In most instances, oxygen-sulfur exchange reactions (O/S ERs), which would generate random thiocarbonate and carbonate units, were effectively suppressed. The turnover frequencies (TOF) of these Lewis pairs catalyzed processes were as high as 119 h⁻¹ at ambient temperature.

Active Lewis pairs for copolymerization

Considering the similarity of Frustrated Lewis Pairs (FLPs) and binary metal/base catalyst systems, we developed a perfectly alternating and perfectly regioselective COS/epoxide copolymerization process catalyzed by the Lewis pair of TEB with various Lewis bases, including amidine, quinidine, quaternary onium salts to provide colorless and highly transparent well-defined poly(monothiocarbonate).

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