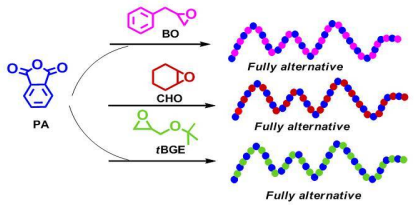
Perfectly Alternating and Regioselective Ring-Opening Copolymerization of Phthalic anhydride with Eoxides using Metal-Free Lewis Pairs

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Abstract

Recent work has been directed to the design of metal- free Lewis pair catalysts for ringopening alternating copolymerization (ROAP) reactions to enhance both activity and selectivity. While the simplest type of organic bases/Lewis bases (for example: PPN+Cl-, DMAP, DBU and TBD) are able to copolymerize anhydride-epoxide in a non-living and nonquantitative manner, the introduction of Lewis acids radically changes this behaviour. In this study, various Lewis acids (B(C2H5)3, Al(CH)3, Et2Zn and nBu2Mg), in combination with various Lewis bases (PPN+Cl-, DMAP, DBU and TBD), were tested as Lewis pair catalysts for anhydride-epoxide ring-opening copolymerization (ROCOP) studies. Based on the observed results, the B(C2H5)3/PPNCl pair stood out as the most active and effective Lewis pair for the perfectly alternating and regioselective controlled ROCOP of various epoxides (cyclohexene oxide, CHO; *tert*-butyl glycidyl ether, *t*BGE and 2-benzyloxirane, BO) with pthalic anhydride (PA). Medium to high molecular weight linear poly(ester-*co*-ether)s (*M*n up to 57.5 kg mol-1) were achieved, and most of them exhibit narrow molecular weight distributions (*M*w/*M*n as low as 1.02). However, in the presence of strong Lewis acids (Al(CH)3, Et2Zn and nBu2Mg) and neutral Lewis bases (DMAP/DBU/TBD) this broad applicability is offset by a lack of control over the polymerizations, including side reactions as a consequence of it's strong acidity/alkalinity. Hence, the ideally suitable acidity/alkalinity and matched size of the Lewis pair are considered crucial for the effective copolymerization of PA and epoxides. In addition, from PA/*t*BGE copolymers, hydroxyl-functionalized poly (ester-*co*-glycerol)'s were successfully synthesized by deprotection of the *t*-butyl groups.



Scheme 1. Fully alternating copolymerization of PA with Epoxides by Lewis pairs**.**

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Biography

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Notes / Comments: