

单脒基铝络合物催化己内酯聚合及己内酯/丙交酯共聚

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摘要 将单脒基铝络合物用于催化 ϵ -己内酯 (ϵ -CL) 开环聚合反应, 结果表明, 该类铝络合物表现出很高的催化活性: 25 °C 时络合物 $[\{\text{PhC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{AlMe}_2]$ (C1) 催化 ϵ -CL 聚合 1 h, 单体转化率为 91%; 70 °C 时络合物 $[\{\text{PhC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)-(\text{N}-2,6\text{-Me}_2\text{C}_6\text{H}_3)\}\text{AlMe}_2]$ (C2) 催化 ϵ -CL 聚合 15 min, 单体转化率达 100%。脒基 *N*-芳环上取代基的引入能明显提高催化剂活性, *N*-芳环邻位双取代的单脒基铝络合物的催化活性高于邻位单取代的。所得聚合物的分子量大于理论值, 且分子量分布较宽 (PDI = 1.43~1.85), 说明聚合的可控度不高。单脒基铝络合物可通过先催化 ϵ -CL 聚合, 再引发外消旋丙交酯聚合, 得到聚己内酯和聚丙交酯的两嵌段共聚物。

关键词: 脒基铝络合物 ϵ -己内酯 外消旋丙交酯 开环聚合 共聚

Abstract: Mono(amidinate) aluminum complexes showed high catalytic activity for the ring-opening polymerization of ϵ -caprolactone in toluene at ambient temperature. Monomer conversion up to 91% could be reached within 1 h when using $[\{\text{PhC}(\text{N}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)_2\}\text{AlMe}_2]$ (C1) as initiator at 25 °C. The electron-donating groups on the ortho-positions of the N-substituted phenyl ring were superior to the electron-withdrawing groups for the enhancement of the catalytic activity, but both brought an increase in activity when compared with the un-substituted complex C7. The complexes bearing two ortho-substituents on one of the N-phenyl rings were more active than the analogues bearing one ortho-substituent. Although high molecular weight poly(ϵ -caprolactone)s were obtained by using these aluminum catalysts, the polymerization of ϵ -caprolactone was not well controlled as indicated by the broad molecular weight distributions (PDI = 1.43~1.85) and the deviation of the number average molecular weight from the theoretical values. Sequential copolymerization of ϵ -caprolactone and rac-lactide using mono(amidinate) aluminum complexes afforded poly(ϵ -caprolactone)-poly(rac-lactide) diblock copolymer, which was characterized well by NMR spectroscopy and gel permeation chromatography analysis.

Keywords: aluminum amidinate complex, ϵ -caprolactone, rac-lactide, ring-opening polymerization, copolymerization

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