

Stereoselective Ring-Opening Polymerization of a Racemic Lactide by Using Achiral Salen- and Homosalen-Aluminum Complexes

Nobuyoshi Nomura,^{*,[a]} Ryohei Ishii,^[a] Yoshihiko Yamamoto,^[b] and Tadao Kondo^[a]

Abstract: Highly isotactic polylactide or poly(lactic acid) is synthesized in a ring-opening polymerization (ROP) of racemic lactide with achiral salen- and homosalen-aluminum complexes (salenH₂ = *N,N'*-bis(salicylidene)ethylene-1,2-diamine; homosalenH₂ = *N,N'*-bis(salicylidene)trimethylene-1,3-diamine). A systematic exploration of ligands demonstrates the importance of the steric influence of the Schiff base moiety on the degree of isotacticity and the backbone for high activity. The complexes prepared in situ are pure enough to apply to the polymerizations without purification. The crystal structures of the key complexes are elucidated by X-ray diffraction, which confirms that they are chiral. However, analysis of the ¹H and ¹³C NMR spec-

tra unambiguously demonstrates that their conformations are so flexible that the chiral environment of the complexes cannot be maintained in solution at 25 °C and that the complexes are achiral under the polymerization conditions. The flexibility of the backbone in the propagation steps is also documented. Hence, the isotacticity of the polymer occurs due to a chain-end control mechanism. The highest reactivity in the present system is obtained with the homosalen ligand with 2,2-dimethyl substituents in the backbone (ArCH=NCH₂CMe₂CH₂N=CHAr),

Keywords: aluminum • homogeneous catalysis • lactides • polymers • ring-opening polymerization

whereas *t*BuMe₂Si substituents at the 3-positions of the salicylidene moieties lead to the highest selectivity ($P_{meso} = 0.9_8$; $T_m = 210^\circ\text{C}$). The ratio of the rate constants in the ROPs of racemic lactide and L-lactide is found to correlate with the stereoselectivity in the present system. The complex can be utilized in bulk polymerization, which is the most attractive in industry, although with some loss of stereoselectivity at high temperature, and the afforded polymer shows a higher melting temperature ($P_{meso} = 0.9_2$, T_m up to 189 °C) than that of homochiral poly(L-lactide) ($T_m = 162\text{--}180^\circ\text{C}$). The “livingness” of the bulk polymerization at 130 °C is maintained even at a high conversion (97–98%) and for an extended polymerization time (1–2 h).

[a] Dr. N. Nomura, Dr. R. Ishii, Prof. Dr. T. Kondo
Laboratory of Polymer Chemistry
Graduate School of Bioagricultural Sciences
Nagoya University
Nagoya 464-8601 (Japan)
Fax: (+81)52-789-4012
E-mail: nnomura@nagoya-u.jp.

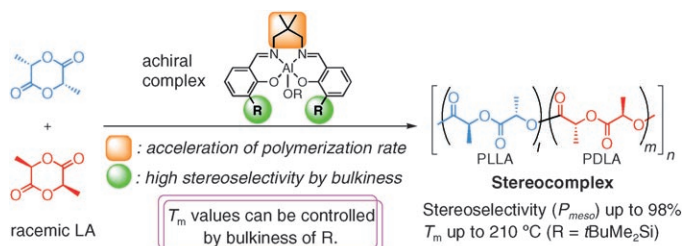
[b] Dr. Y. Yamamoto
Department of Applied Chemistry
Graduate School of Science and Engineering
Tokyo Institute of Technology
Meguro, Tokyo 152-8552 (Japan)

Supporting Information for this article is available on the WWW under <http://www.chemeurj.org/> or from the author. Crystal structures of **8**, **9**, **10**, and **11**; ¹H, ¹³C, and ¹H-¹H COSY NMR of complexes **9** and **11**, and homonuclear decoupled ¹H NMR spectra of the methine regions of poly(*rac*-LA) prepared with Al(O*i*Pr)₃, **8**, and **9**; plots of time versus ln[*rac*-LA]₀/[*rac*-LA]_t and plots of ln[Al]₀ versus ln*k*_{(rac)app} in the polymerization of *rac*-LA with complex **9**.

Polymerization

N. Nomura,* R. Ishii, Y. Yamamoto,
T. Kondo

Stereoselective Ring-Opening Polymerization of a Racemic Lactide by Using Achiral Salen- and Homosalen-Aluminum Complexes



Highly isotactic poly(racemic lactide) is generated by the ring-opening polymerization of a racemic lactide with achiral homosalen-aluminum complexes (see picture).