Supporting information

Bimetallic Schiff-base Aluminum Complex Based on Pentaerythrityl Tetramine and Their Stereoselective Polymerization of Racemic Lactide

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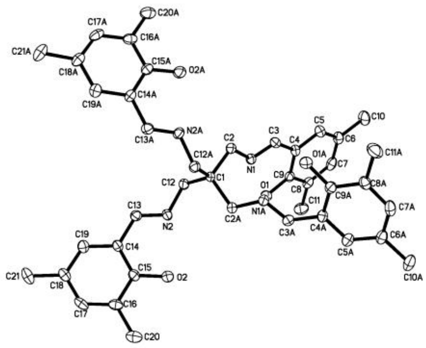

Figure S1 Crystal structure of **ligand 2**. CCDC 908777

Table S1. Summary of crystallographic data for **ligand 2**.

	Ligand 2
Formula	$C_{41}H_{48}N_4O_4$
F_w	660.83
crystal system	Monoclinic
space group	C2/c
a (Å)	19.779(2)
b (Å)	9.9011(13)
c (Å)	18.960(2)
α (deg)	90.00
β (deg)	102.300(2)
γ (deg)	90.00
v (Å^3)	3627.8(8)
Z	4
μ (mm^{-1})	0.078
$R_{(int)}$	0.0702
GOOF	0.954
R_1 [I>2sigma(I)]	0.0573
wR_2[I>2sigma(I)]	0.1474

Calculation of the entropy and enthalpy difference between homo-propagation and cross-propagation

In a first-order Markovian statistics, PLA derived from *rac*-lactide could exhibit up to five tetrad sequences (mmm, mmr, rmm, mrm, rmr) in relative ratios determined by the ability of initiators to control racemic [r-diad] and meso [m-diad] connectivity of the monomer units. According to first-order Markovian statistics, the probability for *meso* linkages could be determined as

$P_m = k_m/(k_m + k_r) = k_{S/SS}/(k_{S/SS} + k_{S/RR}) = k_{R/RR}/(k_{R/SS} + k_{R/RR})$ (S1)

where $k_{S/SS}$ and $k_{R/RR}$ were the rate constants of homopropagation, $k_{S/RR}$ and $k_{R/SS}$ were the rate constants of cross propagation. If $k_{S/SS} > k_{S/RR}$ or $k_{R/RR} > k_{R/SS}$, the formation of isotactic sequences were favored, otherwise syndiotactic sequences were formed. The following equations could be deduced according to absolute reaction rate theory:

$k_{S/SS} = k_{R/RR} = k_m = (KT/h)\exp[(\Delta S^{\neq}_m/R) - (\Delta H^{\neq}_m/RT)]$ (S2)

$k_{R/SS} = k_{S/RR} = k_r = (KT/h)\exp[(\Delta S^{\neq}_r/R) - (\Delta H^{\neq}_r/RT)]$ (S3)

Further deduction of equation S4 could be obtained from equation S2 and equation S3:

$P_m/(1 - P_m) = k_m/k_r = \exp[(\Delta S^{\neq}_m - \Delta S^{\neq}_r)/R - (\Delta H^{\neq}_m - \Delta H^{\neq}_r)/RT]$ (S4)

where $(\Delta S^{\neq}_m - \Delta S^{\neq}_r)$ was the entropy difference between homopropagation and cross propagation, and $(\Delta H^{\neq}_m - \Delta H^{\neq}_r)$ was the enthalpy difference between homopropagation and cross propagation. To determine the values of $(\Delta S^{\neq}_m - \Delta S^{\neq}_r)$ and $(\Delta H^{\neq}_m - \Delta H^{\neq}_r)$, $\ln P_m/(1 - P_m)$ was plotted versus the 1/T (Figure S2). From this plot, the entropy difference $(\Delta S^{\neq}_m - \Delta S^{\neq}_r)$ of –23.23 cal/K·mol and activation enthalpy difference $(\Delta H^{\neq}_m - \Delta H^{\neq}_r)$ of –9.42 kcal/K·mol were obtained, which may explain the preference of isotactic stereosequence.

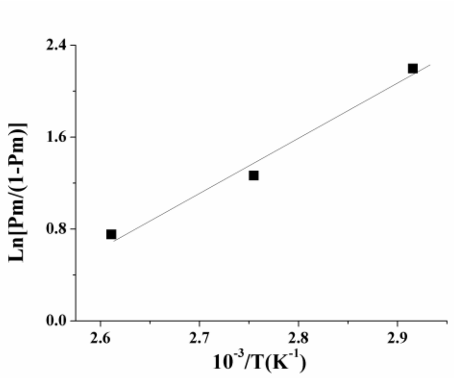

Figure S2 Relationship between polymerization temperature and stereochemistry of the resulting poly(rac-LA)s by using **3a**.