Protic Compounds Mediated Living Cross-Chain-Transfer Polymerization of *rac*-Lactide: Synthesis of Isotactic(crystalline)-Heterotactic(amorphous) Stereomultiblock Polylactide

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Supporting information

General Methods. All reactions were carried out under a dry and oxygen-free argon atmosphere by using Schlenk techniques or under a nitrogen atmosphere in an MBraun glovebox. Solvents were purified by an MBraun SPS system. The phenols, amines and poly(ethylene glycol) (MPEG5K and PEG2K) were purchased from Aldrich or Fluka. All liquids were dried over activated 4 Å molecular sieves for a week and distilled before use, and solid materials were used as received. *rac*-Lactide (Aldrich) was recrystallized three times from the dry ethylacetate. The synthesis of fluorescent primary alcohol followed the established method with minor alteration.[1] Triethanolamine was dried over calcium hydride prior to distillation under vacuum. Ligands and their corresponding aluminum complexes **1**[2] and **2**[3] were prepared according to literature procedures.

Instruments and Measurements. Organometallic samples for NMR spectroscopic measurements were loaded into NMR tubes in a glovebox and then the tubes were sealed by paraffin film. ^{1}H, ^{13}C NMR spectra were recorded on a Bruker AV400 (FT, 400 MHz for ^{1}H; 100 MHz for ^{13}C) spectrometer. NMR assignments were confirmed by ^{1}H-^{1}H (COSY), ^{1}H-^{13}C (HMQC), and ^{13}C NMR (DEPT) experiments when necessary. Polymer characterizations were carried out by combining a Waters 515 GPC instrument with multiangle laser light scattering (MALLS) apparatus at 25 °C. The system included Styragel HMW6E column, a 515 HPLC pump, an OPTILAB DSP RI detector, and a DAWN EOS multiangle laser-light scattering (MALLS) detector at a laser wavelength of 690 nm (from Wyatt Technology). One guard column and three 30 cm columns were used for polymer fractionation. HPLC-grade DMF was used as the mobile phase at a flow rate of 0.5 mL/min. The whole system, including columns and detectors, was maintained at 25 °C. Polymers solutions with a concentration between 8.0 and 10.0 mg/mL were injected into the columns at an injection volume of 200 μL. Astra software from Wyatt Technology was used to collect and analyze the data from the detectors. The differential refractive index (DRI) increment (dn/dc) value of 0.027 mL/g was used for all obtained star polylactide. Differential scanning calorimetry (DSC) measurements were performed on a TA Instrument Q100 DSC equipped with a refrigerated cooling system (RCS) under a N_2 atmosphere. The instrument was operated in the standard DSC mode and was calibrated with an indium standard. A N_2 purging flow of 50 mL/min was used. Samples (about 8 mg) were heated from 25 °C to 250 °C at 10 °C/min, hold for one minute and then cooled to 25 °C at 10 °C/min, the data were then collected in the second heating ramp from 25 °C to 250 °C at 10 °C/min. Glass transition temperatures (T_g) were read as the middle of the change in heat capacity and the melting temperatures (T_m) were read as the maximum of the endothermic peaks. Wide-angle X-ray diffraction (WAXD) measurements were performed using a Rigaku D/Max 2500V PC X-ray diffractometer (Cu $K_{\alpha,\lambda}$ = 1.5406Å). The diffraction patterns were collected during continuous scan at a speed of 4°/min between the angles of 10° and 30°.

Typical polymerization procedure. A typical procedure for polymerization of *rac*-LA was performed in a 25 mL ampule in a Braun Labmaster glovebox. To a vigorously stirred solution of complex **1** and/or complex **2** in 3 mL of THF was added triethanolamine in 2 mL of THF; after 10 min, *rac*-LA was added quickly, and the ampule was then taken out of the glovebox and heated to 70°C in a pre-equilibrated oil bath to start the polymerization. After the measured time interval, a small amount of aliquot (several drops) was taken from the reaction mixture via syringe and quickly quenched into ethanol; after removing volatiles, the residue was analyzed by ^{1}H NMR ($CDCl_3$) for determing monomer conversion by integration of the monomer vs. polymer methine or methyl resonances . The residue solution was quenched with an excess amount of ethanol, filtered, washed with ethanol, and then dried at 40°C for 24 h in vacuo to give the polymer product. The molecular weight and the molecular weight distribution of the resulting polymer were determined by SEC-MALLS. The tacticity of the PLA was calculated according to the methine region homonuclear decoupling ^{1}H NMR spectrum.[4] Melting temperature and glass transition temperaturewas determined by DSC analysis at a heating rate of 10 °C/min.

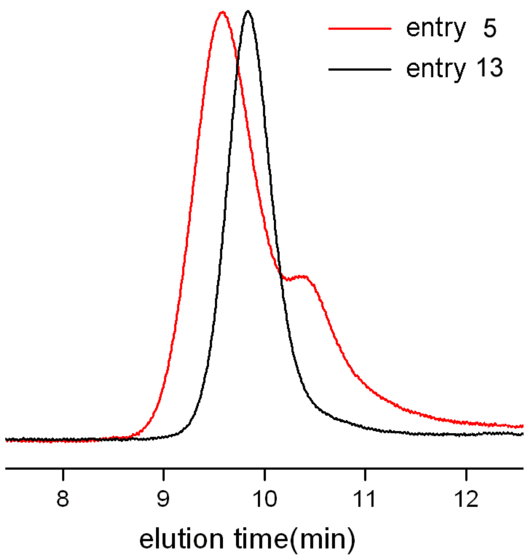

Figure S1. GPC profiles of representative samples, entries 5 and 13, Table 1.

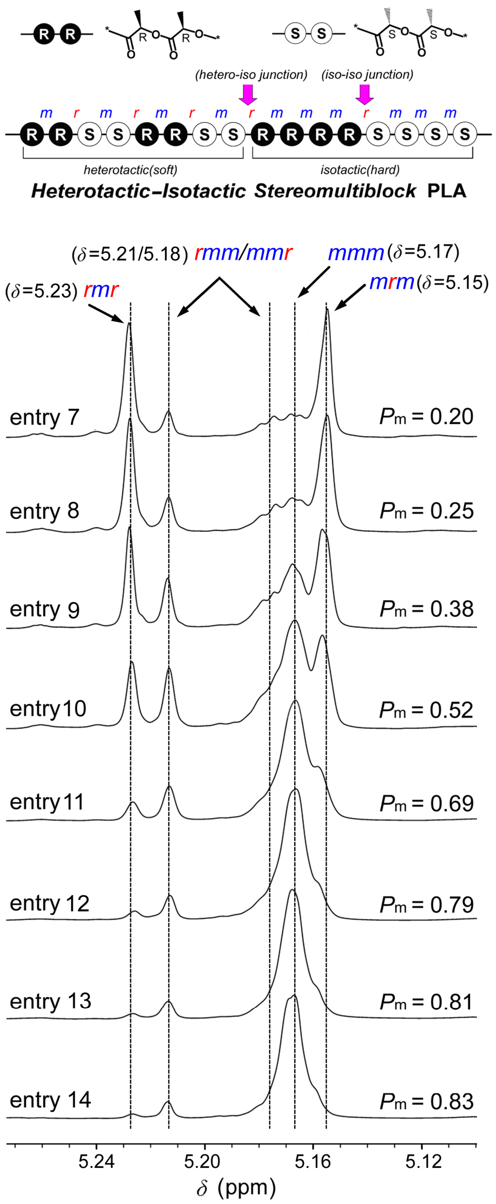

Figure S2. Homonuclear decoupled ^{1}H NMR spectra of the methine region of it-ht stereomultiblock PLA (600M, 25°C, $CDCl_3$).

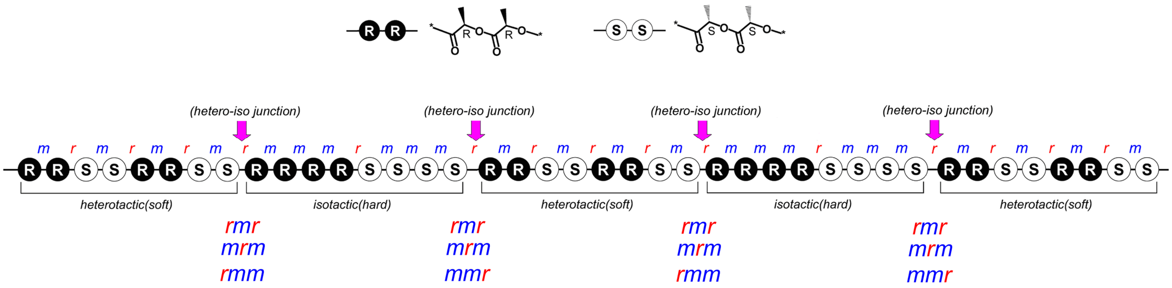

Figure S3. Relationship between the *hetero-iso* junction and the intensities of tetrads (the increase of *heterotactic-isotactic* block junctions leads to an increase in the intensities of *rmr, rmm, mmr,* and *mrm* tetrads and relative decrease of *mmm* which caused a decrease of P_m values of obtained PLA).

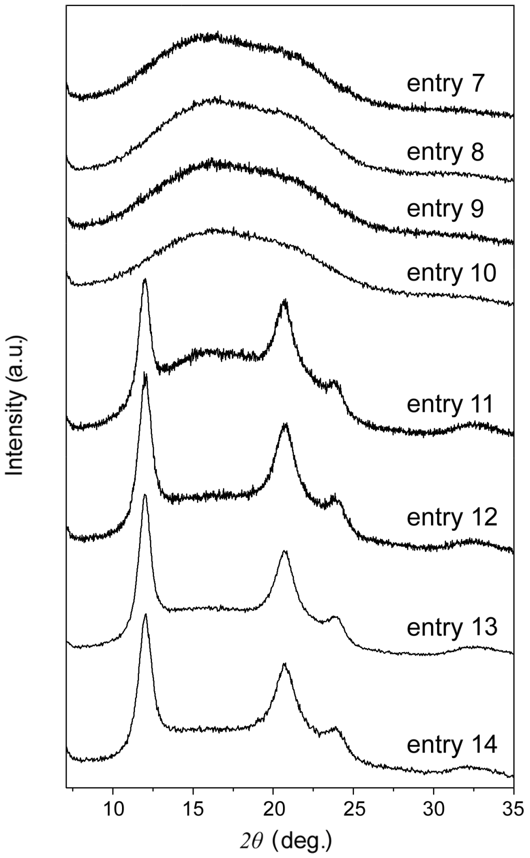

Figure S4. Wide-angle X-ray diffraction (WAXD) spectra of representative PLA samples in Table 1.

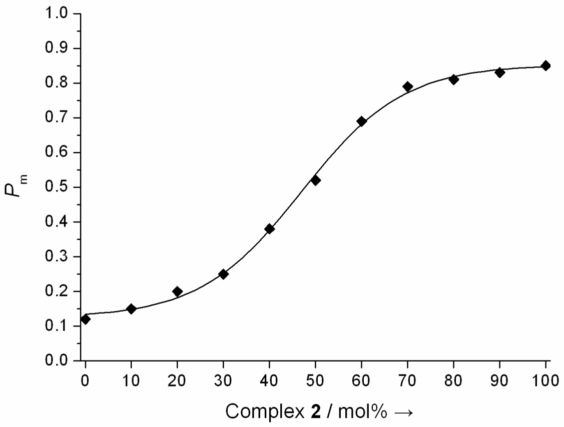

Figure S5. Experimental P_m values vs. molar percentage of complex **2** in catalytic system ($P_m + P_r = 1$, complex **1** + complex **2** = 100%).

References

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