SUPPORTING INFORMATION

Highly Cis/Trans-stereoselective (ONSO)CrCl-Catalyzed Ring-opening Copolymerization of Norbornene Anhydrides and Epoxides

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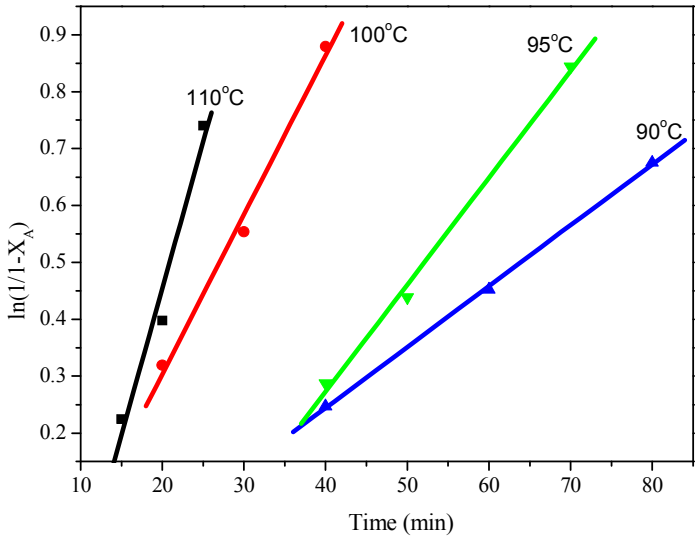


Figure S1a First-order liner fits of the kinetic data for the copolymerization of *endo*-NA and CHO. (X_A is conversion of *endo*-NA)

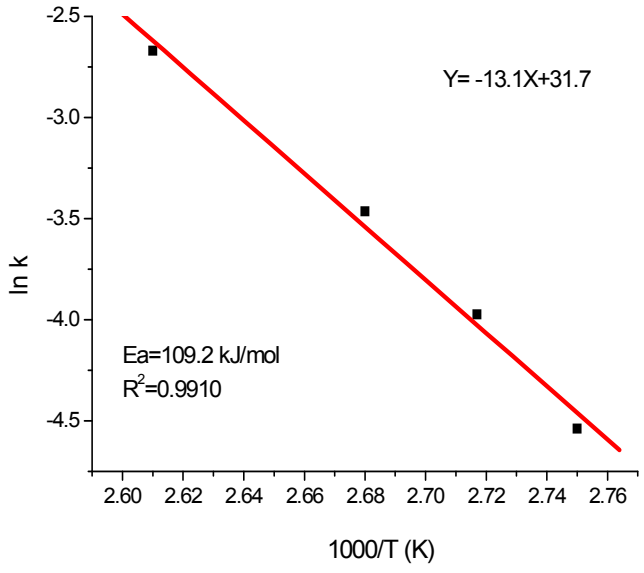


Figure S1b. Arrhenius plots for the formation of polyester. The equations for the linear fit are given in the top right corners, while the apparent activation energies are given in the bottom left corners as insets

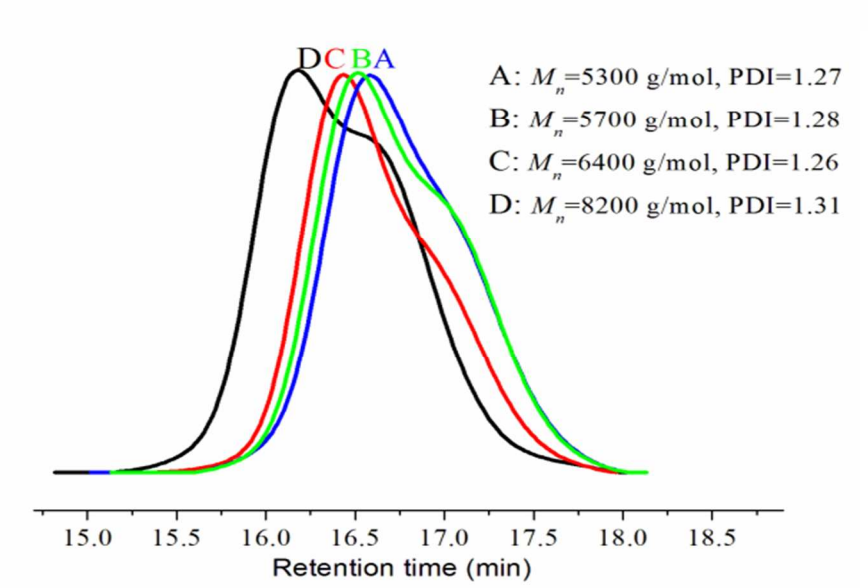


Figure S2. GPC curves of poly(*endo*-NA-*alt*-CHO) at different cocatalysts (Conditions: A: *N*-MeIm (Table 1, entry 4); B: TBACl (Table 1, entry 1); C: DMAP (Table 1, entry 5); D: DBU (Table 1, entry 6); [CHO]/[*endo*-NA]/[(ONSO)CrCl]/[cocatalysts] = 250:250:1:1 (molar ratio), 2.0 mL CHO as solvent in bulk copolymerization, 110 ^{o}C; 40 min)

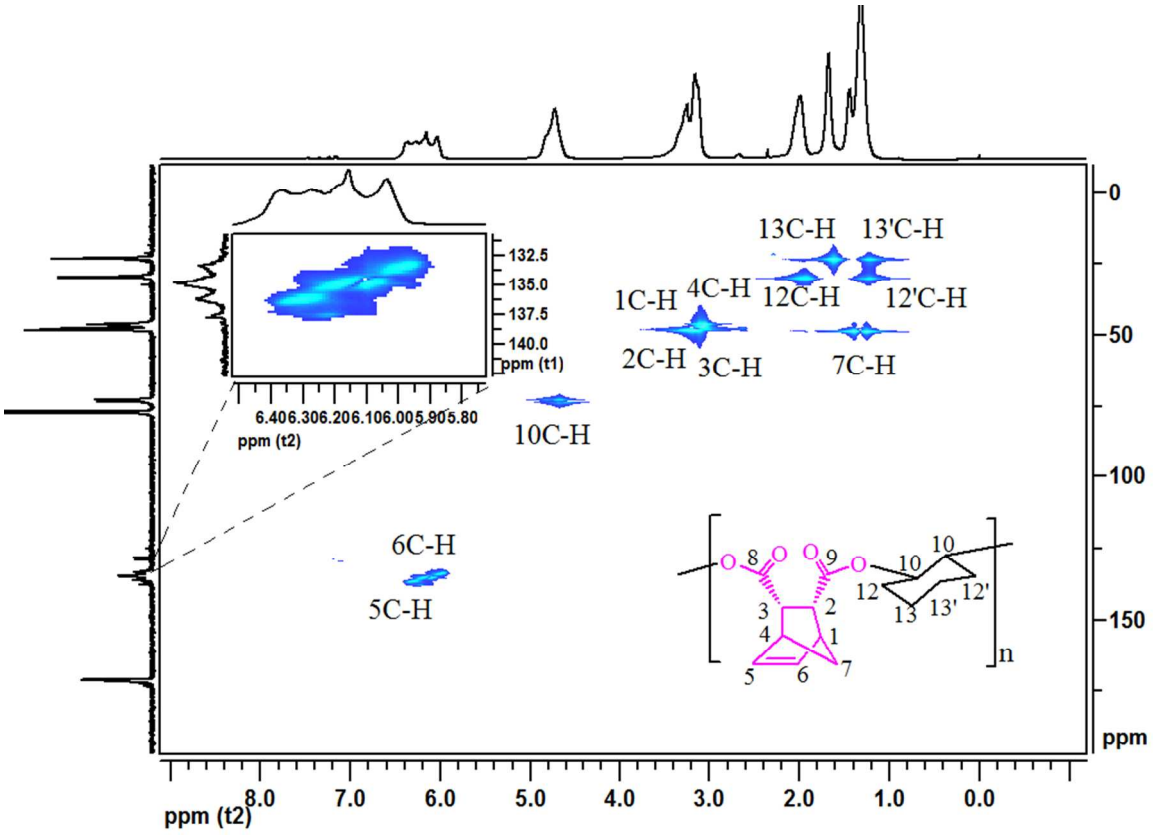
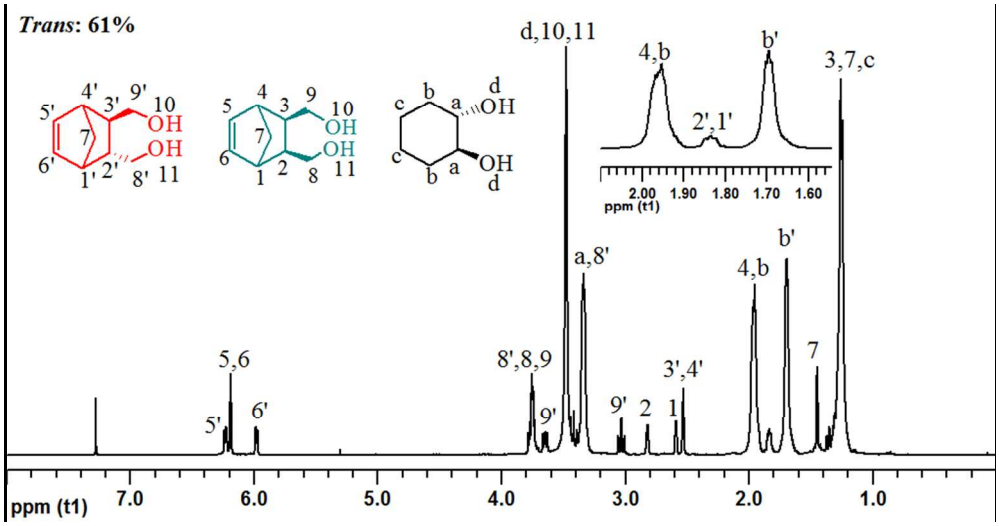
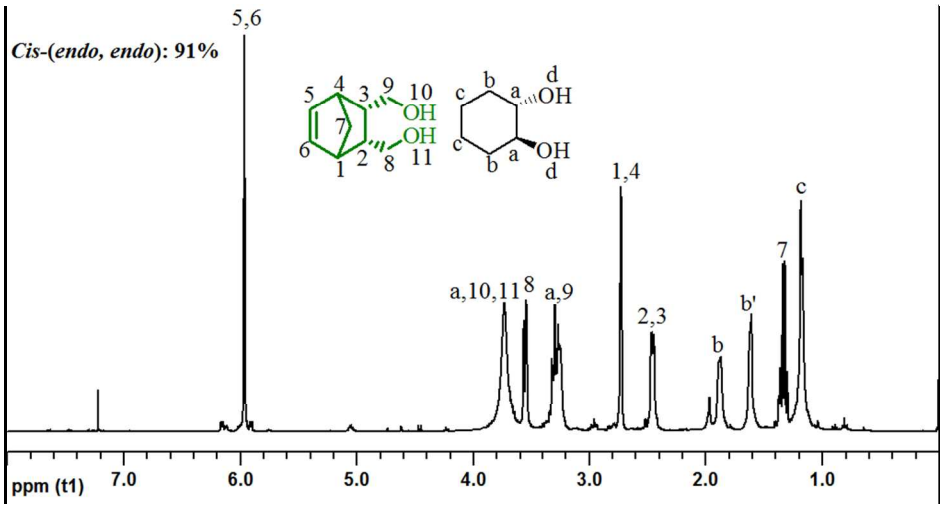


Figure S3. ^{1}H-^{13}C HMQC spectrum of poly(*endo*-NA-*alt*-CHO) (Table 1, entry 3)..



(A)



(**B**)

Figure S4. ^{1}H NMR spectra of the reductive degradation of polyester derived from (A) ROCOP of *exo*-NA and CHO, 30 min and (B) from ROCOP of *endo*-NA and CHO, 40 min. ([NA]/[CHO]/[(ONSO)CrCl]/[PPNCl]=250/250/1/1, in excess 2.0 mL CHO, 110 ^{o}C, NA: 1.64 g (10mmol)

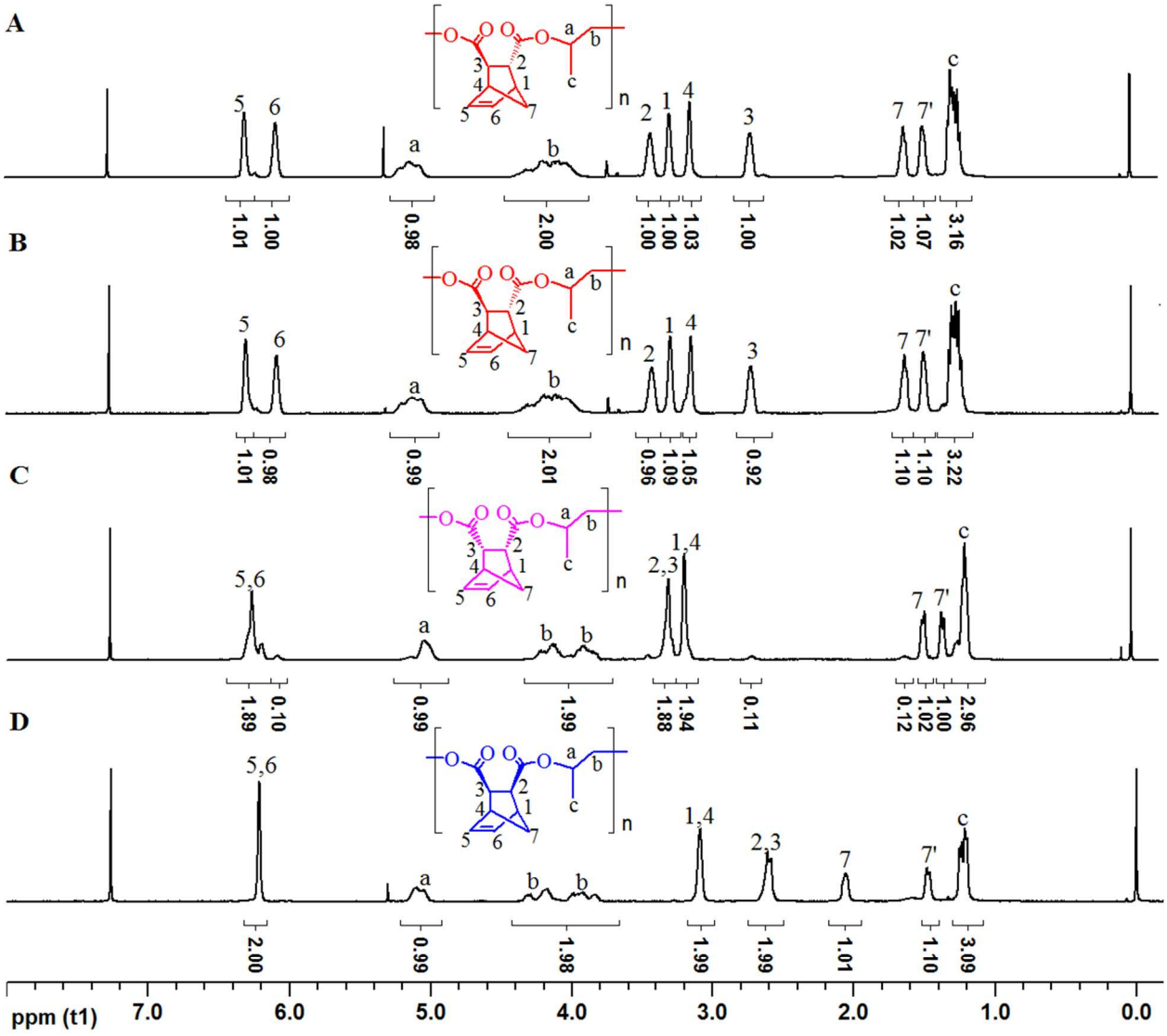


Figure S5. ^{1}H NMR spectra of poly(NA-*alt*-PO) with bulk/solvent copolymerization. (Conditions: A: [*exo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL PO, yield: 93%. B: [*endo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL PO, yield: 92%; C: [*endo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL toluene, yield: 71%; D: [*exo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL toluene, yield: 79%; 110^{o}C, 5.0 h, NA: 1.64 g, (10 mmol))

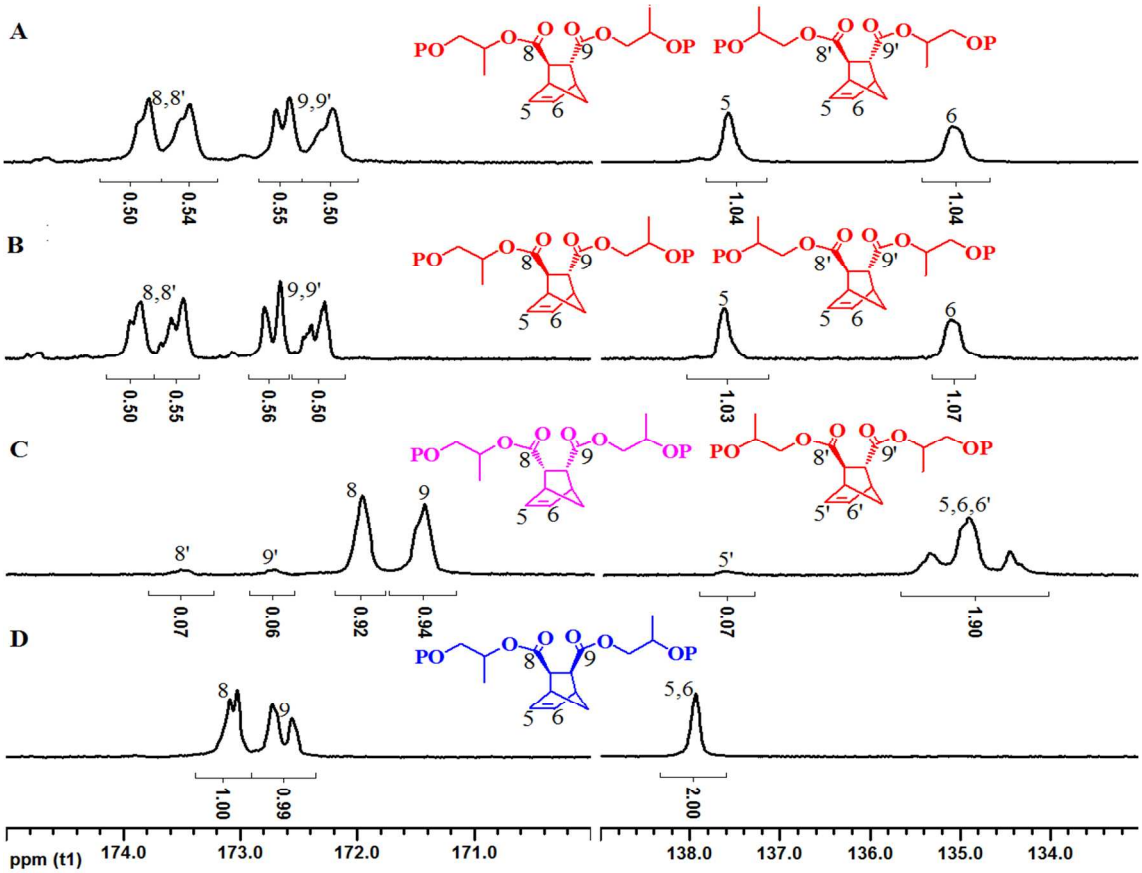


Figure S6. ^{13}C NMR spectra of poly(NA-*alt*-PO) with bulk/solvent copolymerization. (Conditions: A: [*exo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL PO, yield: 93%; B: [*endo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL PO, yield: 92%; C: [*endo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL toluene, yield: 71%; D: [*exo*-NA]/[PO]/[(ONSO)CrCl]/[PPNCl]=250:250:1:1, 2.0 mL toluene, yield:79%; 110 ^{o}C, 5.0 h, NA: 1.64 g, (10 mmol))

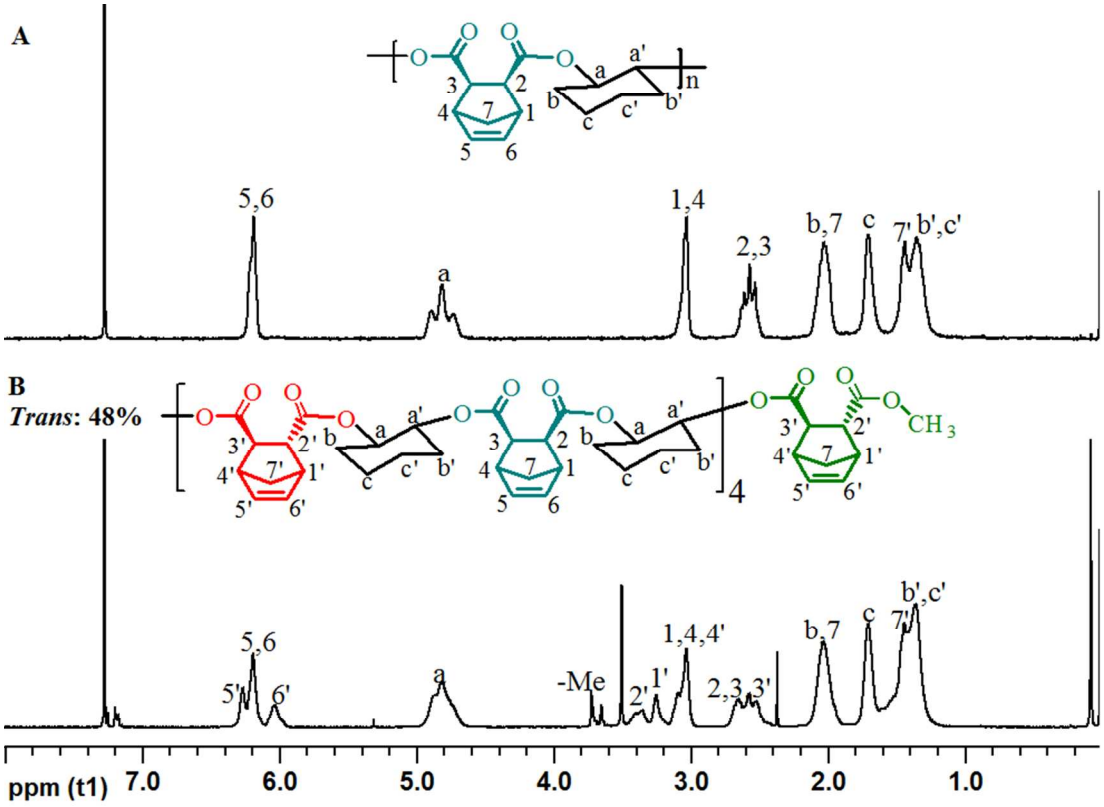


Figure S7. ^{1}H NMR spectra of *cis*-(*exo, exo*)-polyester. A: before isomerization, B: after isomerization. (Conditions: *cis*-(*exo, exo*)-polyester (1g, 3.7 mmol), CH_3ONa (0.2 mL, 1 mol/L), 100 ^{o}C, 50 min, 2.0 mL toluene)