- SUPPORTING INFORMATION -

# Stereoselective ROP of *rac*- and *meso*-Lactides using Achiral TBD as Catalyst

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**Figure S1.** Mixture of *L*- and *D*-LA (1/1 molar ratio) at 23 °C ($[rac\text{-LA}]_0$ = 0.22 M)

**Figure S2.** Mixture of *L*- and *D*-LA (1/1 molar ratio) after 10 minutes at -75 ℃ ([*rac*-LA]$_0$ = 0.22 M)

A B

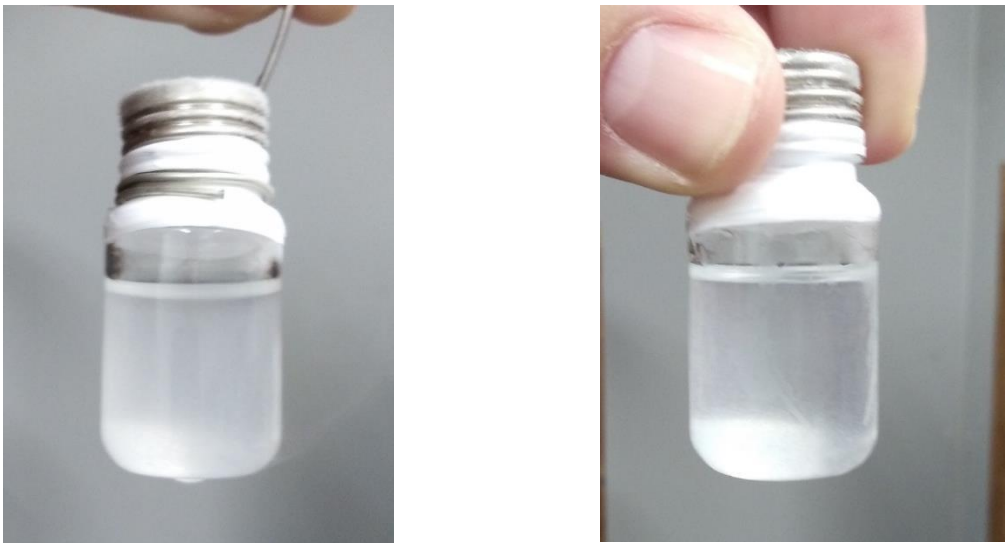

**Figure S3.** Mixture of *L*- and *D*-LA (1/1 molar ratio) after 20 (A) and 30 minutes (B) of polymerization at -75 ℃ (Table 1, entries 2 & 3)

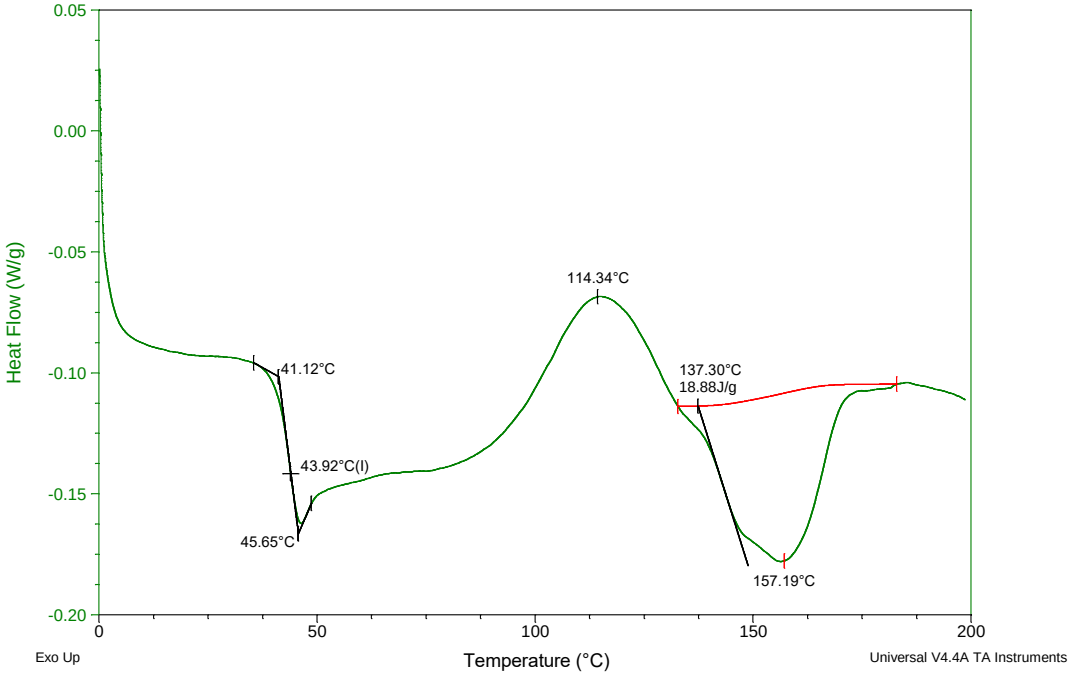


**Figure S4.** Differential Scanning Calorimetry Thermogram of poly(*rac*-LA) obtained by *rac*-LA ROP in toluene at -75 ℃, initiated by BnOH and catalyzed by TBD ($[LA]_0/[BnOH]_0/[TBD]_0$ = 100/1/0.1; $[rac\text{-}LA]_0$ = 0.08 M) – Entry 1, Table 1

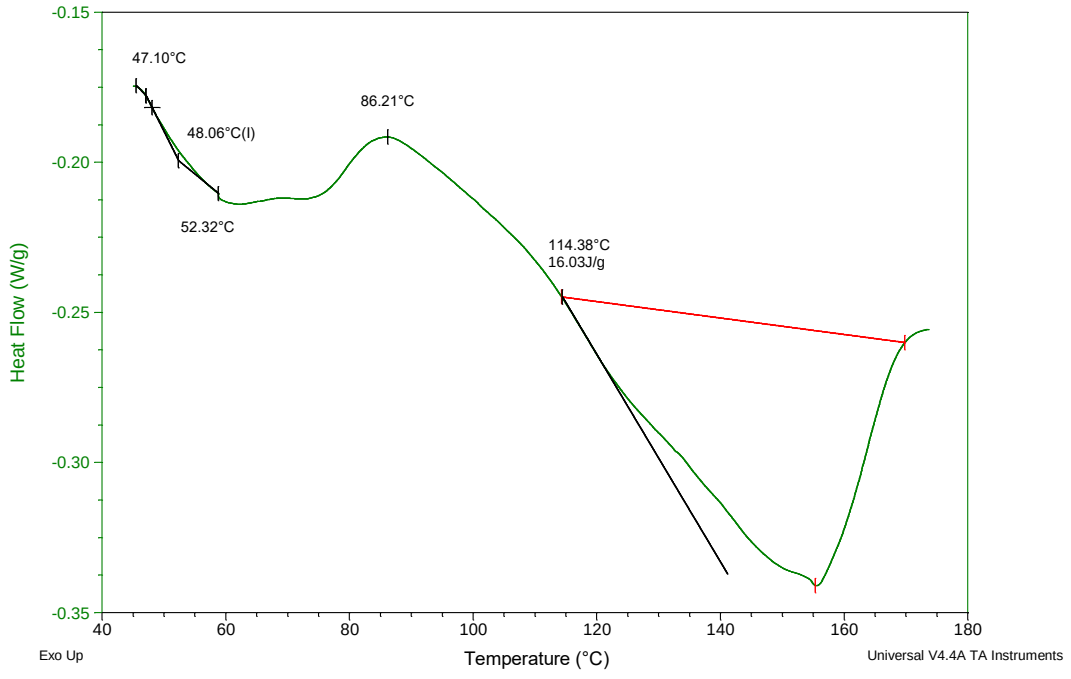


**Figure S5.** Differential Scanning Calorimetry Thermogram of poly(*rac*-LA) obtained by *rac*-LA ROP in toluene at -75 ℃, initiated by BnOH and catalyzed by TBD ($[LA]_0/[BnOH]_0/[TBD]_0$ = 100/1/0.1; $[rac\text{-}LA]_0$ = 0.08 M) – Entry 2, Table 1

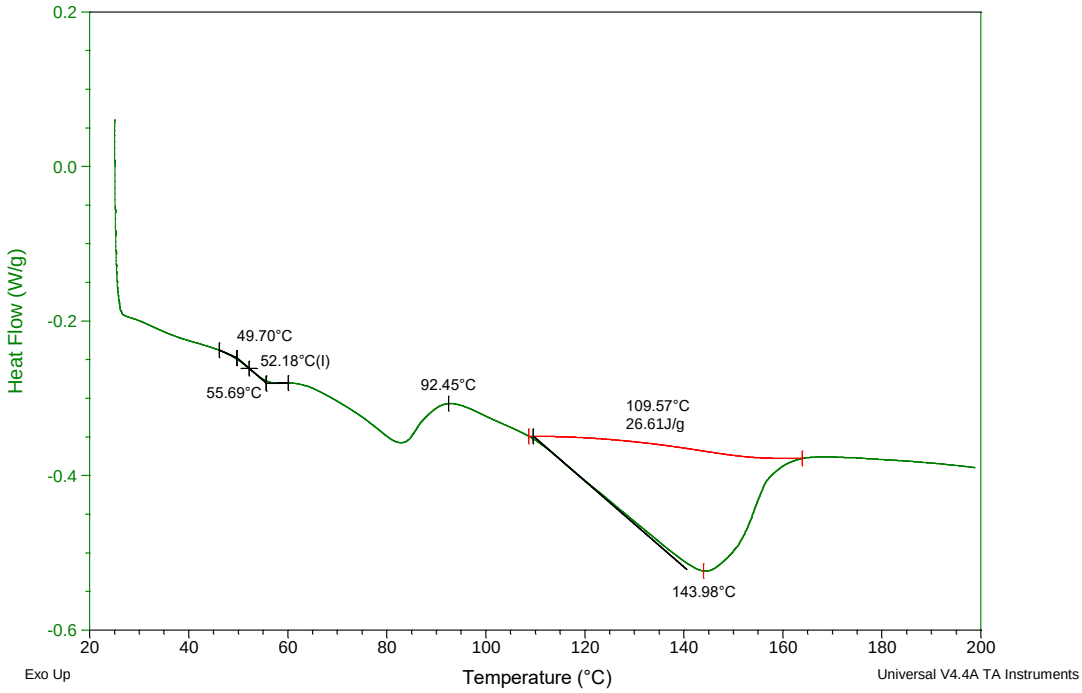


**Figure S6.** Differential Scanning Calorimetry Thermogram of poly(*rac*-LA) obtained by *rac*-LA ROP in toluene at -75 ℃, initiated by BnOH and catalyzed by TBD ($[LA]_0/[BnOH]_0/[TBD]_0$ = 100/1/1; $[rac\text{-}LA]_0$ = 0.22 M) – Entry 3, Table 1

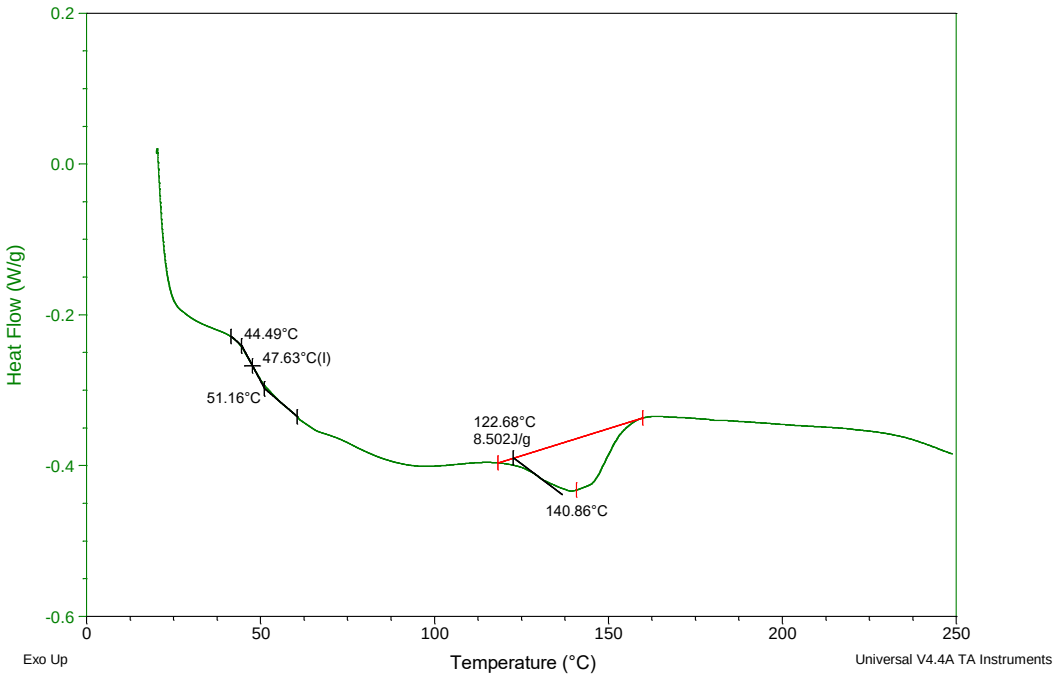


**Figure S7.** Differential Scanning Calorimetry Thermogram of poly(*rac*-LA) obtained by *rac*-LA ROP in toluene at -75 ℃, initiated by BnOH and catalyzed by TBD ($[LA]_0/[BnOH]_0/[TBD]_0$ = 100/1/1; $[rac\text{-}LA]_0$ = 0.22 M) – Entry 4, Table 1

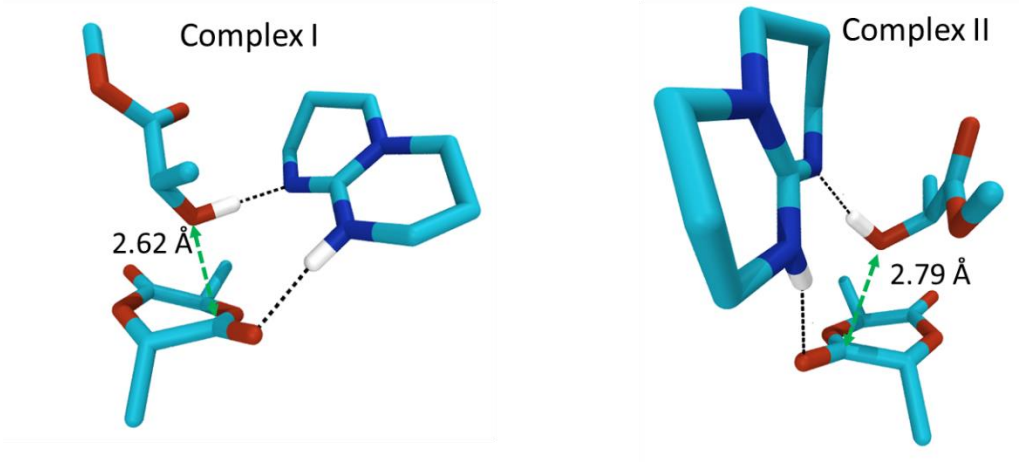


**Figure S8.** DFT-optimized (ωB97XD/6-31G**) reactants from IRC calculations of complex I (left) and complex II (right). The distance between the hydroxyl oxygen atom and the carbon atom of the carbonyl group is highlighted in green and is much shorter in complex I (2.62 Å vs 2.79 Å). Hydrogen atoms have been omitted for clarity, except those involved in hydrogen bonds.

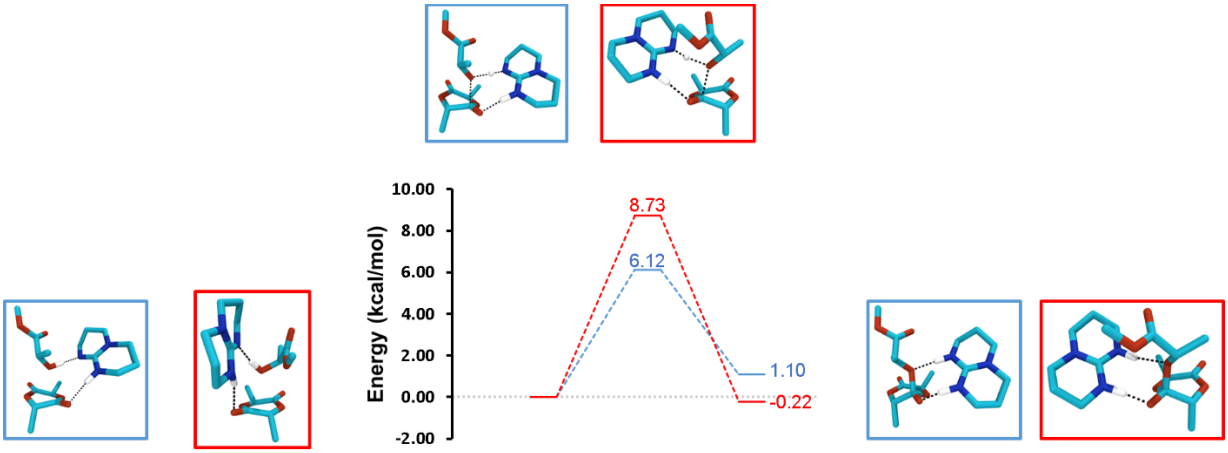


**Figure S9.** DFT-calculated (ωB97XD/6-31G**) energy profiles corresponding to the nucleophilic attack of the oxygen atom of the alcohol on the carbonyl carbon atom for complexes I (blue) and II (red). The energy barriers between reactants and transition states are relative to the reactants. The optimized geometries of the reactants (left), transition states (center) and products (right) for all the complexes are also displayed. Hydrogen atoms have been omitted for clarity, except those involved in hydrogen bonds.