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ELECTRONIC SUPPLEMENTARY INFORMATION

Highly Thermally Stable and Robust Enantiopure NNN-Scorpionate Zirconium Initiators for the Controlled Ring-Opening Polymerization of *rac*-Lactide

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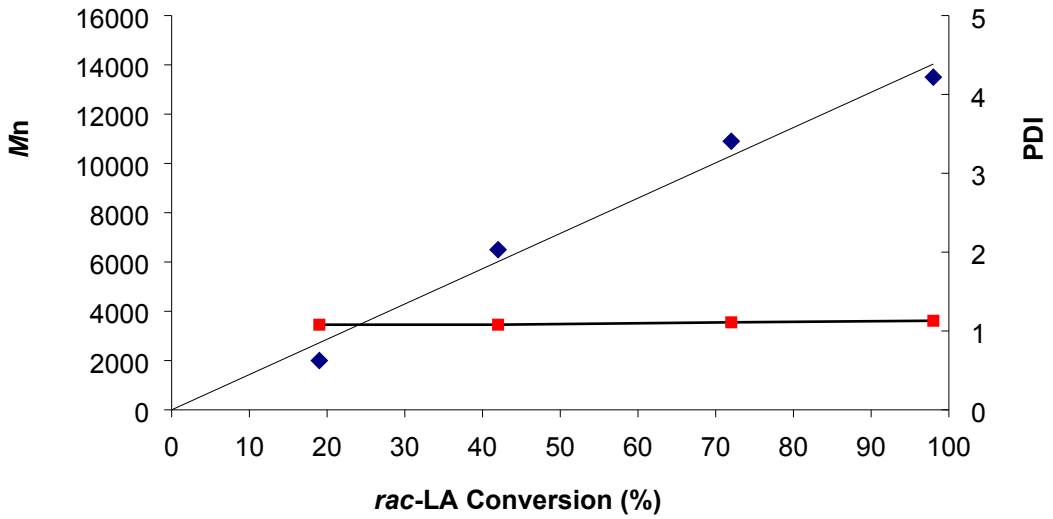
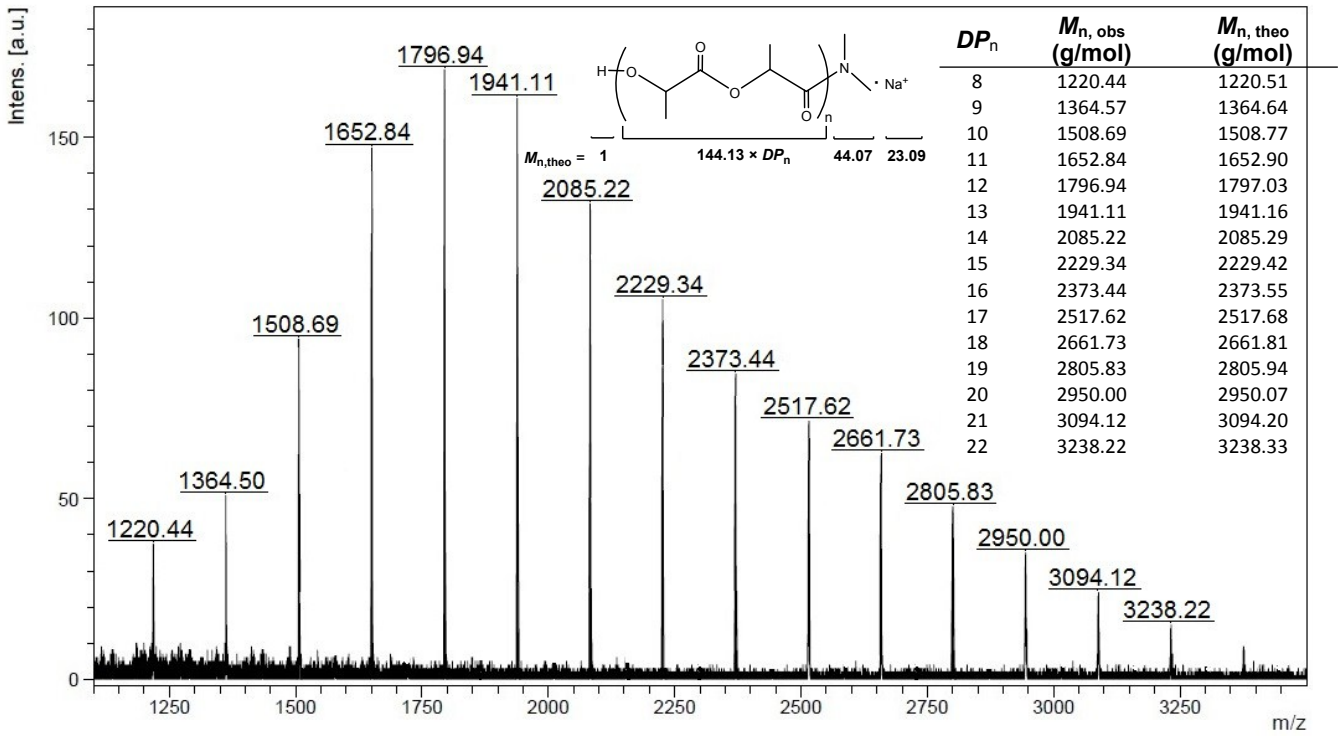


Figure S1. Plot of PLA M_n and molecular weight distribution values (PDI) as a function of monomer conversion (%) for the polymerization of *rac*-LA initiated by [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)]; [*rac*-LA]$_0$/[Zr]$_0$ = 100, toluene, 70 ºC (Table 2, entries 3–6, R^2 = 0.9894).



DP_n	$M_{n,obs}$ (g/mol)	$M_{n,theo}$ (g/mol)
8	1220.44	1220.51
9	1364.57	1364.64
10	1508.69	1508.77
11	1652.84	1652.90
12	1796.94	1797.03
13	1941.11	1941.16
14	2085.22	2085.29
15	2229.34	2229.42
16	2373.44	2373.55
17	2517.62	2517.68
18	2661.73	2661.81
19	2805.83	2805.94
20	2950.00	2950.07
21	3094.12	3094.20
22	3238.22	3238.33

Figure S2. Selected area of the MALDI-ToF mass spectrum of a PLA sample obtained on using [$Zr(NMe_2)_3(\kappa^3$-*R*,*R*-fbpza)] with [*rac*-LA]$_0$/[Zr]$_0$ = 30, 77% conversion; theoretical molecular weights calculated according to the equation: $M_n = (DP_n \times M_{wLA}) + M_w{}^tBuH + M_{wNa}$, where DP_n is the degree of polymerization, M_{wLA} = 144.13 g·mol^{-1}, M_{wHNMe2} = 45.07 g·mol^{-1} and M_{wNa} = 23.09 g·mol^{-1}.

The distribution in the spectrum indicates the existence of a single family of polymer chains capped by –$CH(CH_3)OH$ and $(CH_3)_2$–N–OC(O)– *termini*, corresponding to oligomers of formula $H(OCHMeCO)_{2n}(N\text{-}(CH_3)_2)\cdot Na^+$ (n = 8 to 23) with consecutive peaks separated by increments of 144 Da. Moreover, neither intermolecular ester-exchange (transesterification) reactions nor cyclic oligomers were detected.

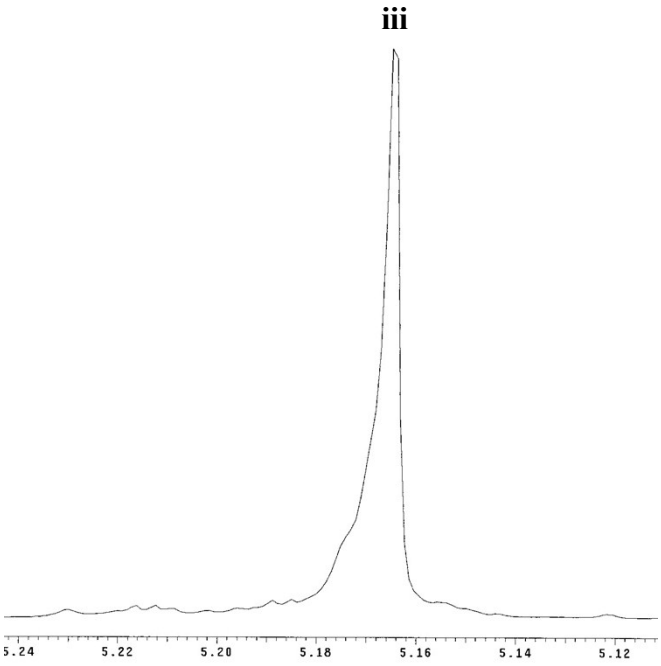


Figure S3. ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of the homodecoupled C*H* resonance of poly(L-lactide) prepared using [Zr(OCHMeEt)$_3$(κ^3-*R*,*R*-fbpza)] (**2**) ([Zr]$_0$ = 90 μmol and [L-LA]$_0$/[Zr]$_0$ = 300, 130 ºC, 1 min). The tacticity of the polymer was assigned using the

methine signals with homonuclear decoupling, as described by Hillmyer and co-workers.[1]

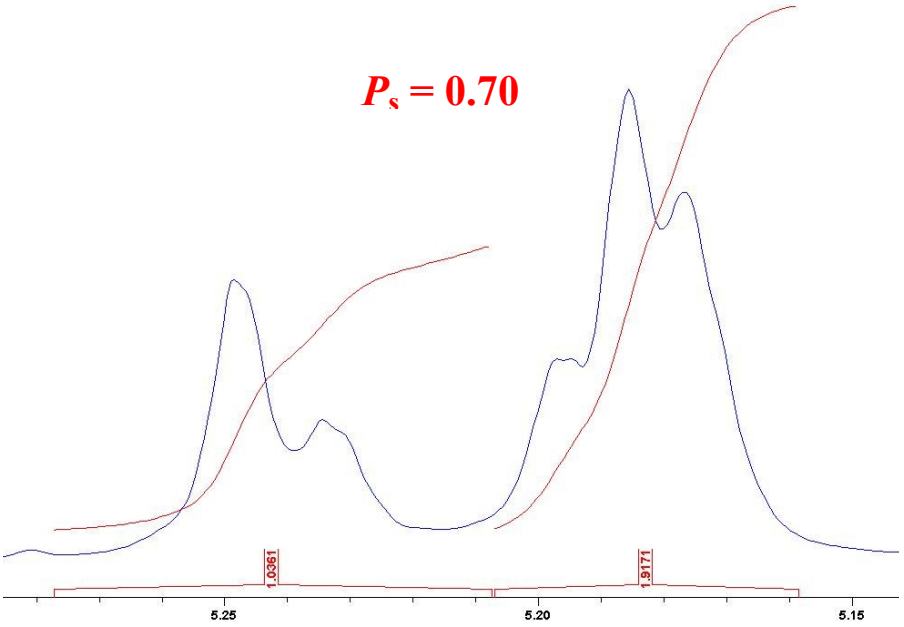


Figure S4. ^{1}H NMR spectra (400 MHz, 298 K, $CDCl_3$) of the homodecoupled C*H* resonance of poly(*rac*-lactide) prepared employing [Zr(S4-^{t}BuPh)$_3$(κ^3-*R*,*R*-fbpza)] (**6**) in toluene at 70 ºC for 24 h (Table 2 entry 17). The tacticity of the polymer was assigned using the methine signals with homonuclear decoupling, as described by Hillmyer and co-workers.[1]

Table S1. Crystal data and structure refinement for **6×0.25C_4H_8O**.

Empirical formula	$C_{59}H_{71}FN_5O_{0.50}S_3Zr$
Formula weight	1064.60
Temperature (K)	240(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	P 2_1
a(Å)	9.9418(3)
b(Å)	28.5201(8)
c(Å)	10.9256(3)
β(°)	102.641(2)
Volume(Å^3)	3022.8(1)
Z	2
Density (calculated) (g/cm^3)	1.170
Absorption coefficient (mm^{-1})	0.328
F(000)	1122
Crystal size (mm^3)	0.19 x 0.15 x 0.12
Index ranges	$-11 \le h \le 11$, $-33 \le k \le 33$, $-12 \le l \le 11$
Reflections collected	15981
Independent reflections	9418 [R(int) = 0.1104]
Data / restraints / parameters	9418 / 58 / 631
Goodness-of-fit on F^2	1.001
Final R indices [$I>2\sigma(I)$]	R1 = 0.0854, wR2 = 0.1767
Absolute structure parameter	0.12(11)
Largest diff. peak / hole, e.Å^{-3}	0.612 and -0.364

[a] $R = \Sigma||F_o|-|F_c|/\Sigma|F_o|$. [b] $wR = \{\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2\}^{1/2}$. [c] GOF = $\{\Sigma [w((F_o^2-F_c^2)^2)/(n-p)\}^{1/2}$, where n = number of reflections and p = total number of parameters refined.

References

(1) M. T. Zell, B. E. Padden, A. J. Paterick, K. A. M. Thakur, R. T. Kean, M. A. Hillmyer, E. J. Munson, *Macromolecules*, 2002, **35**, 7700–7707.