

A new route for the preparation of enriched *iso*-polylactide from *rac*-lactide via a Lewis acid catalyzed ring-opening of an epoxide

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Supporting Information

Table S1: Ring opening polymerization data for PLA obtained from *rac*-LA catalyzed by TPPAICI with different ratios of PPN⁺Cl⁻ in *rac*-PO at room temperature.

Catalyst	ratio ^a	Time (h)	% Conversion ^b	M _n ^c	PDI ^c
TPPAICI	100:1:1	1	92	4210	1.09
TPPAICI	100:1:5	0.5	98	1480	1.24
TPPAICI	100:1:25	0.5	97	730	1.36

^a [*rac*-lactide]₀/[initiator]₀: PPN⁺Cl⁻ ratio, All the polymerization reactions were carried out at room temperature. ^b Percentage conversion was obtained by ¹H NMR spectroscopy. ^c Determined by GPC relative to polystyrene standards in tetrahydrofuran. The experimental M_n was calculated considering Mark-Houwink's corrections for M_n (M_n(obsd) = 0.58[M_n(GPC)]).

Estimation of Pi and the related issues with the calculations

The assessment of the isotacticity is compared by the tetrads unit resonance obtained by the homo-decoupled $^1\text{H-NMR}$ data values. The Pi values were calculated by Bernoullian Statistics predicted by Coundae *et.al*. The percentages of *iii*, *isi*, *iis*, *sii* and *sis* were determined by peak deconvolution method. In the linear PLAs we always observed a PO unit in the end of the polymer chain with Cl- and 2 or more PO units in cycles. This leads to the complication on tacticity analysis. We have not considered the interference of methine and methylene peak of PO units with lactide methine in this estimation. Certainly there will be a **significant error on the Pi values** and the efforts on the actual Pi analysis is in progress by collaborators.

Table S2: Estimation of Pi for the PLA obtained from *rac*-LA catalyzed by TPPAlCl with different ratios of PPN⁺Cl⁻ in *rac*-PO at room temperature in 1 h $[[rac\text{-lactide}]_0/[initiator]_0]$: PPN⁺Cl⁻ = 100:1:1.

Tetrad /Peak	% by peak deconvolution	Pi/100	Pi
<i>sis</i>	5.5	$(1-Pi)^2/2$	0.67
<i>sii</i>	11.7	$Pi(1-Pi)/2$	0.75
<i>iis</i>	4.6	$Pi(1-Pi)/2$	0.90
<i>iii</i>	55.7	$Pi(Pi+1)/2$	0.67
<i>isi</i>	22.5	$(1-Pi)/2$	0.55
	Average Pi		0.71

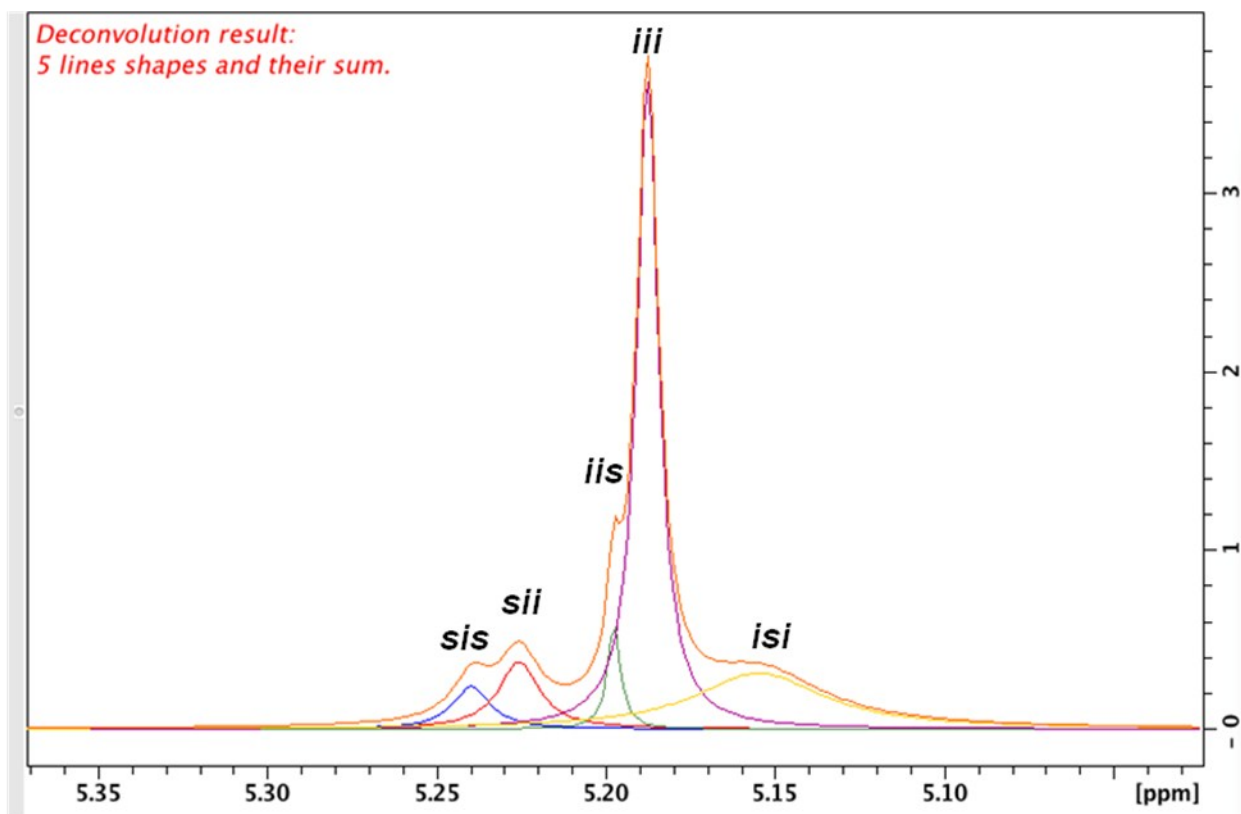


Figure S1: Homodecoupled ^1H -NMR of the PLA obtained from the reaction of *rac*-LA and TPPAICl/PPN $^+\text{Cl}^-$ in *rac*-PO ($M_w = \sim 3200$ Daltons, PDI = 1.11)

MHC2(PLA)2ESP_gpc (7#586 RT: 8.93 AV: 1 NL: 1.63E6
T: FTMS + p ESI Full ms [200.00-3000.00])

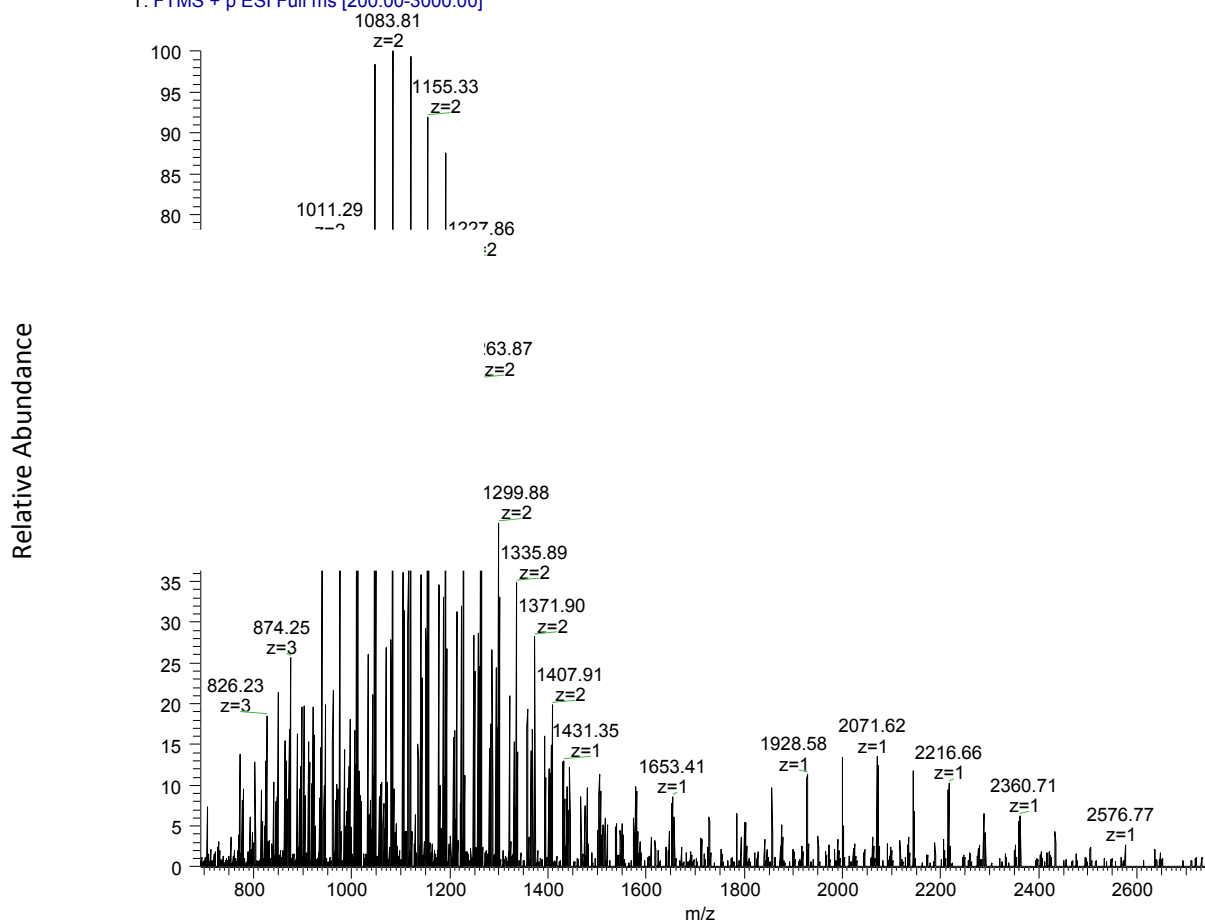


Figure S2: Positive electrospray ionization spectrum of narrow molecular weight fraction taken from a Gel Permeation Chromatographic separation of polylactide obtained from the reaction of *rac*-LA catalyzed by TPPAlCl/PPN⁺Cl⁻ in *rac*-PO at room temperature in 1 h. Detailed assignments are included in Figure S3.

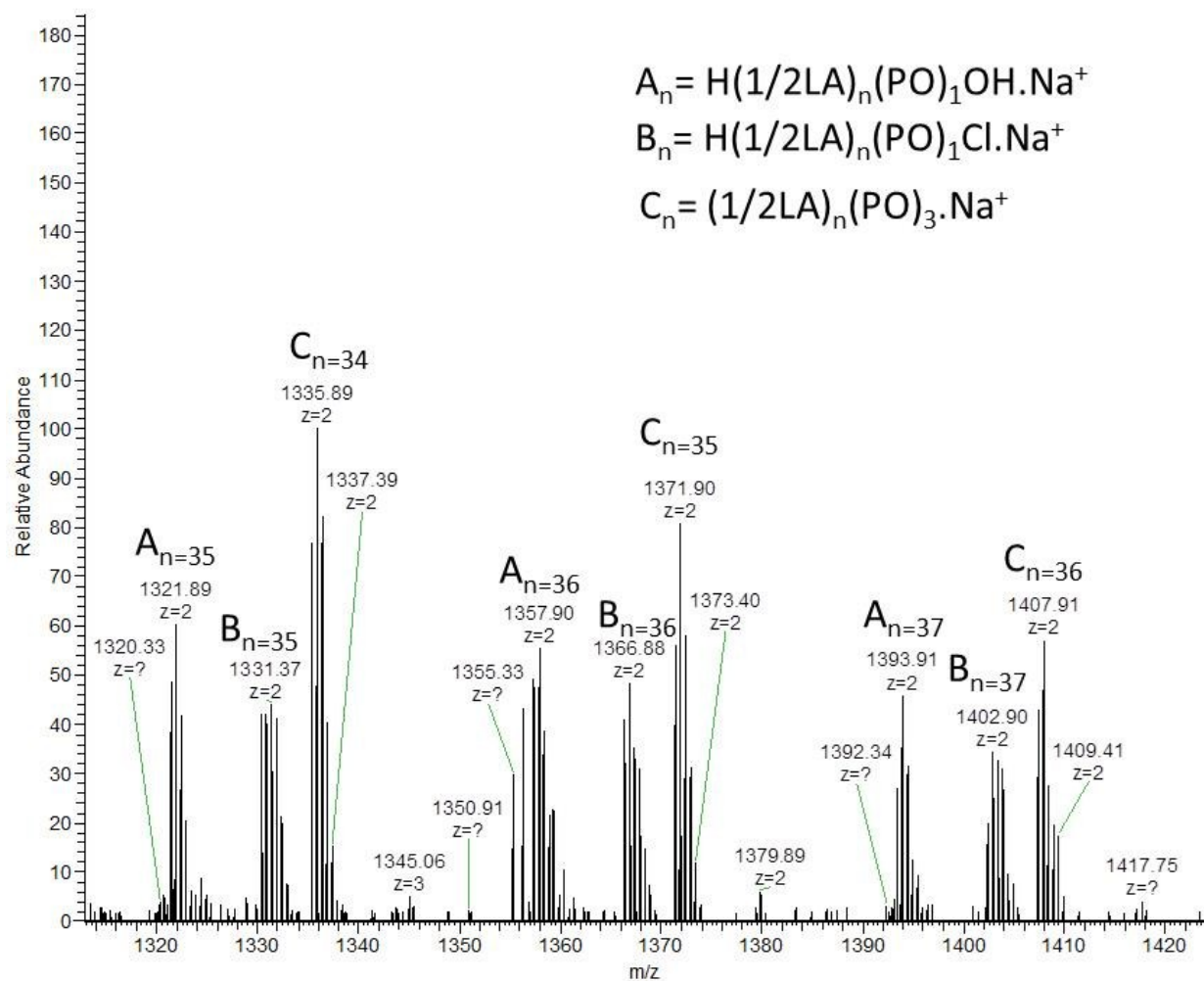


Figure S3: Detailed assignments of an electrospray ionization mass spectrum of a narrow molecular weight fraction obtained from a GPC separation of polylactide obtained from the reaction of *rac*-LA catalyzed by TPPAICl/PPN⁺Cl⁻ in *rac*-PO at room temperature in 1 h.

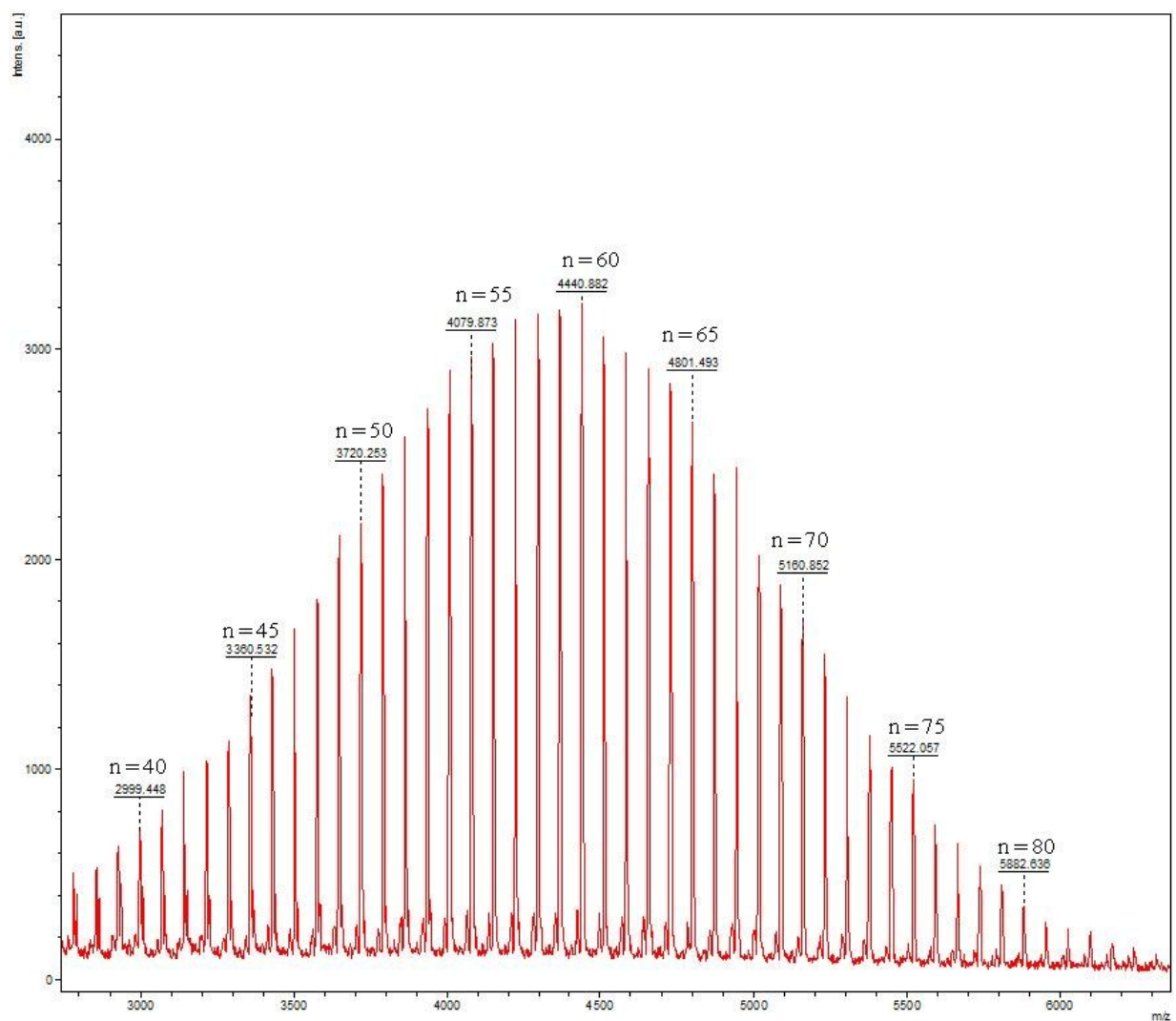


Figure S4: MALDI spectrum of polyactide obtained from the reaction of *rac*-LA catalyzed by TPPAICl/PPN⁺Cl⁻ in *rac*-PO at room temperature. [Major polyactide pattern is $(\text{PO})_2(\text{LA}_{1/2})_n\text{H}^+$ and minor series are $(\text{PO})_3(\text{LA}_{1/2})_n$ and $\text{H}(\text{LA}_{1/2})_n\text{POCl}$]

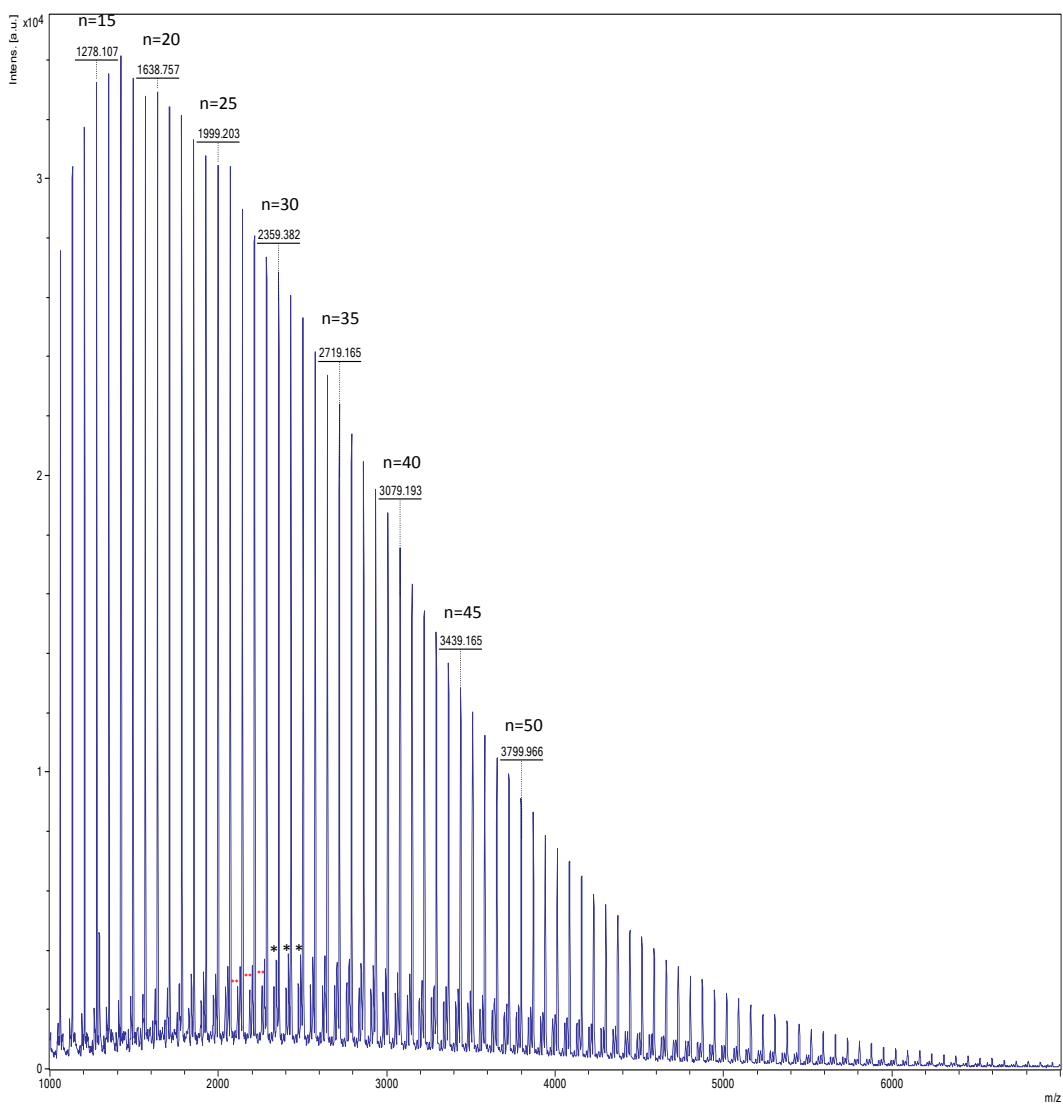


Figure S5: MALDI spectrum of polylactide obtained from the reaction of *rac*-LA catalyzed by TPPAICI/PPN⁺Cl⁻ in *rac*-PO at room temperature. [Major polylactide pattern is (PO)₃(LA_{1/2})_n.Na⁺ and minor series are * (PO)₄(LA_{1/2})_n and ** (PO)₅(LA_{1/2})_n]