Electronic Supplementary Material (ESI) for Polymer Chemistry

Activation of Carbonyl Bonds by Quaternary Ammoniums and a (Na^+:Crown-Ether) Complex: Investigation of the Ring-Opening Polymerization of Cyclic Esters

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Contents

Materials: DL-Lactide was recrystallized three times in toluene and freshly sublimated. Lactones and dichloromethane were dried over calcium hydride and distilled. 4-biphenylmethanol was purified by precipitation in pentane. Commercially available 15-crown-5, (-)-sparteine, DABCO, TMEDA, DMAP, DBU, MTBD, $LiNTf_2$ and NaBARF were used as received.

1/ Procedure for the synthesis of ionic organocatalysts:

Quaternary ammonium Iodide: The tertiary amine/pyridine/amidine/guanidine (~ 2 g), an excess of iodomethane and dry toluene (5 mL) were introduced into a sealed reactor. The mixture was stirred at room temperature for 3 h. The resulting precipitate was filtered, washed with pentane, and dried under vacuum.

Complexation of sodium(I) in crown ether [15-c-5]: The crown ether [15-c-5] (1 g, 4.5 mmol) and sodium iodide (682 mg, 4.5 mmol) were dissolved in methanol (2 mL). The mixture was stirred for 12 h at room temperature. After concentration under vacuum, a white solid was obtained.

Anion Exchanges:

- *NTf_2 Counterion:*

Iodide quaternary ammoniums or iodide [15-c-5]Na (500 mg) were dissolved in deionized water (2 mL) and a solution of $LiNTf_2$ (1.1 eq. per iodide to be exchanged) in deionized water (2 mL) was added dropwise. A precipitate was instantaneously formed. The reaction mixture was stirred at room temperature for 1h. After filtration and washing (deionized water 3x1 mL), the precipitate was dried under vacuum.

- *BARF Counterion:*

Iodide quaternary ammoniums or iodide [15-c-5]Na (500 mg) were dissolved in a deionized water/ethanol (1:1, 2 mL). A solution of NaBARF (1.1 equivalents per iodide to be exchanged) in deionized water / ethanol (1:1, 2 mL) was added dropwise. A precipitate was instantaneously formed. The suspension was stirred at room temperature for 1h. After filtration and washing (ethanol, 3x1 mL), the solid was dried under vacuum.

Table S1. Synthesis of ionic catalysts (X = I, NTf_2, BARF)

Salt	**Yield** (%)		
	X = I	X = NTf_2	X = BARF
DBU-Me.X	99	98	73
MTBD-Me.X	100	98	89
DMAP-Me.X	96	95	89
DABCO-Me_2.X_2	96	88	46
TMEDA-Me_2.X_2	99	87	49
[15-c-5]Na.X	100	71	90

*Methyl-1,8-diazabicyclo[5.4.0]undec-7-enium.**X***$^-$ (DBU-Me.X$^-$)

X = NTf_2
White solid, yield: 98 %
RMN ^{1}H ($CDCl_3$, 300 MHz): δ (ppm) = 3.64 (m, 2H); 3.51 (m, 4H); 3.27 (s, 3H); 2.84 (m, 2H); 2.14 (m, 2H); 1.76 (m, 6H)
RMN ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 19.8, 22.2, 26.2, 28.7, 28.8, 41.2, 48.8, 48.9, 55.4, 120.0 (q, $^1J_{C-F}$ = 319.5 Hz, NTf_2), 166.9
IR (ν_{max}, cm^{-1}): 2987, 1595, 1552, 1472, 1403, 1372, 1348, 1335, 1222, 1173, 1139, 1102, 1051
M. p.: 72.9 °C
HRMS (ESI) *m/z* calcd for $C_{10}H_{19}N_2$ 167.1542, found 167.1536

X = BARF
White solid, yield: 73 %
RMN ^{1}H ($CDCl_3$, 300 MHz): δ (ppm) = 7.69 (bs, 8H); 7.54 (s, 4H); 3.46 (m, 2H); 3.31 (t, J = 5.9 Hz, 2H); 3.25 (t, J = 5.9 Hz, 2H); 3.06 (s, 3H); 2.63 (m, 2H); 1.96 (quintuplet, J = 6.0 Hz, 2H); 1.75 (m, 2H); 1.62 (m, 4H).
RMN ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 19.7, 22.2, 26.1, 28.3, 28.7, 41.0, 48.8, 48.9, 55.6, 117.7 (bs, *para*-CH, BARF), 124.7 (q, $^1J_{C-F}$ = 270.9 Hz, CF_3), 129.1 (q, $^2J_{C-F}$ = 31.2 Hz, C-CF_3, BARF), 134.9 (bs, *ortho*-CH, BARF), 161.8 (quartet, $^1J_{C-B}$ = 49.4 Hz, BARF), 166.0
IR (ν_{max}, cm^{-1}): 2949, 1633, 1612, 1534, 1452, 1421, 1355, 1330, 1272, 1163, 1112
M. p. : 133.4 °C
HRMS (ESI) *m/z* calcd for $C_{10}H_{19}N_2$ 167.1542, found 167.1540

*4-(dimethylamino)-N'-methylpyridinium.**X***$^-$ (DMAP-Me.X$^-$)

X = NTf_2
White solid, yield: 95 %
RMN ^{1}H (acetone-d_6, 400 MHz): δ (ppm) = 8.16 (d, J = 7.7 Hz, 2H); 7.02 (d, J = 7.7 Hz, 2H); 4.05 (s, 3H); 3.27 (s, 6H)
RMN ^{13}C (acetone-d_6, 100 MHz): δ (ppm) = 40.1, 44.9, 108.4, 120.8 (q, $^1J_{C-F}$ = 319.3 Hz, NTf_2), 143.5, 157.1
IR (ν_{max}, cm^{-1}): 3090, 1656, 1573, 1440, 1403, 1346, 1332, 1176, 1136, 1052
M. p. : 55.5 °C
HRMS (ESI) *m/z* calcd for $C_8H_{13}N_2$ 137.1073, found 137.1070

X = BARF
White solid, yield: 89 %
RMN ^{1}H ($CDCl_3$, 400 MHz): δ (ppm) = 7.70 (bs, 8H), 7.50 (s, 4H), 7.34 (d, J = 7.8 Hz, 2H), 6.43 (d, J = 7.8 Hz, 2H), 3.64 (s, 3H), 3.03 (s, 6H)
RMN ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 40.1, 44.7, 107.8, 117.7 (bs, *para*-CH, BARF), 124.6 (q, $^1J_{C-F}$ = 270.9 Hz, CF_3), 129.2 (q, $^2J_{C-F}$ = 31.3 Hz, C-CF_3, BARF), 134.8 (bs, *ortho*-CH, BARF), 141.5, 156.0, 161.8 (quartet, $^1J_{C-B}$ = 49.5 Hz, BARF)
IR (ν_{max}, cm^{-1}): 2960.22, 1659.74, 1609.61, 1574.73, 1446.18, 1398.57, 1353.53, 1272.89, 1185.69, 1160.53, 1107.45, 1088.54
M. p. : 126.7 °C
HRMS (ESI) *m/z* calcd for $C_8H_{13}N_2$ 137.1073, found 137.1073

*1,4-Dimethyl-1,4-diazoniabicyclo[2.2.2]octane.2**X***$^-$ (DABCO-Me$_2$.2X$^-$)

X = NTf$_2$

White solid, yield: 88 %

RMN ^{1}H (acetone-*d*$_6$, 400 MHz): δ (ppm) = 4.47 (s, 12H) ; 3.69 (s, 6H)

RMN ^{13}C (acetone-*d*$_6$, 100 MHz): δ (ppm) = 53.5, 54.6, 121.0 (q, $^1J_{C\text{-}F}$ = 319.2 Hz, NTf$_2$)

IR (ν_{max}, cm^{-1}): 3038, 1478, 1346, 1279, 1229, 1185, 1128, 1054

M. p.: 228.3 °C

HRMS (ESI) *m/z* calcd for $C_{10}H_{18}N_3O_4F_6S_2$ (M + NTf$_2$) 422.0637, found 422.0649

X = BARF

White solid, yield: 46 %

RMN ^{1}H (acetone-*d*$_6$, 400 MHz): δ (ppm) = 7.79 (bs, 16H); 7.67 (s, 8H); 4.56 (s, 12H); 3.75 (s, 6H)

RMN ^{13}C (acetone-*d*$_6$, 100 MHz): δ (ppm) = 53.6, 55.3, 118.4 (bs, *para*-CH, BARF), 125.4 (q, $^1J_{C\text{-}F}$ = 270.1 Hz, CF_3), 130.0 (q, $^2J_{C\text{-}F}$ = 31.5 Hz, C-CF_3, BARF), 135.5 (bs, *ortho*-CH, BARF), 162.6 (quartet, $^1J_{C\text{-}B}$ = 49.5 Hz, BARF).

IR (ν_{max}, cm^{-1}): 2961, 1610, 1471, 1354, 1273, 1112, 1058

M. p.: 194.4 °C

HRMS (ESI) *m/z* calcd for $C_8H_{18}N_2$ 71.0729, found 71.0727

*5,7-Dimethyl-1,5,7-triazabicyclo[4.4.0]dec-5-enium.**X***$^-$ (MTBD-Me.X$^-$)

X = NTf$_2$

White solid, yield: 98 %

RMN ^{1}H ($CDCl_3$, 400 MHz): δ (ppm) = 2.07 (quintuplet, J = 5.9 Hz, 4H), 2.99 (s, 6H); 3.27 (t, J = 5.9 Hz, 4H); 3.40 (t, J = 5.9 Hz, 4H);

RMN ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 21.1, 40.9, 48.1, 48.3, 120.0 (q, $^1J_{C\text{-}F}$ = 319.5 Hz, NTf$_2$), 157.9

IR (ν_{max}, cm^{-1}): 2948, 2883, 1607, 1575, 1451, 1411, 1400, 1350, 1335, 1322, 1170, 1139, 1051

M. p.: 96 °C

HRMS (ESI) *m/z* calcd for $C_9H_{18}N_3$ 168.1495, found 168.1495

X = BARF

White solid, yield: 89 %

RMN ^{1}H ($CDCl_3$, 300 MHz): δ (ppm) = 7.69 (bs, 8H); 7.54 (s, 4H); 3.20 (t, J = 6.3 Hz, 4H); 3.10 (t, J = 6.3 Hz, 4H); 2.83 (s, 6H); 1.90 (quintuplet, J = 6.3 Hz, 4H)

RMN ^{13}C ($CDCl_3$, 100 MHz) : δ (ppm) = 21.0, 40.7, 48.1, 48.3, 117.6 (bs, *para*-CH, BARF), 124.6 (q, $^1J_{C\text{-}F}$ = 270.8 Hz, CF_3), 129.1 (q, $^2J_{C\text{-}F}$ = 31.5 Hz, C-CF_3, BARF), 134.8 (bs, *ortho*-CH, BARF), 157.6, 161.7 (quartet, $^1J_{C\text{-}B}$ = 49.7 Hz, BARF).

IR (ν_{max}, cm^{-1}): 2984, 1595, 1553, 1472, 1403, 1372, 1350, 1335, 1274, 1222, 1173, 1138

M. p.: 158.5 °C

HRMS (ESI) *m/z* calcd for $C_9H_{18}N_3$ 168.1495, found 168.1487

*N,N,N',N',N'',N''-hexamethylethylenediammonium.2**X***$^-$ (TMEDA-Me$_2$.2X$^-$)

X = NTf$_2$

White solid, yield: 87 %

RMN ^{1}H (acetone-*d*$_6$, 400 MHz): δ (ppm) = 4.45 (s, 4H); 3.57 (s, 18H)

RMN ^{13}C (acetone-*d*$_6$, 100 MHz): δ (ppm) = 54.8, 59.2, 120.9 (q, $^1J_{C\text{-}F}$ = 319.2 Hz, NTf$_2$)

IR (ν_{max}, cm^{-1}): 3060, 1495, 1482, 1423, 1347, 1184, 1138, 1054

M. p.: 207.4 °C

HRMS (ESI) *m/z* calcd for $C_{10}H_{22}N_3O_4F_6S_2$ (M + NTf$_2$) 426.0950, found 422.0945

X = BARF
White solid, yield: 49 %
RMN ^{1}H (acetone-d_6, 400 MHz): δ (ppm) = 7.79 (bs, 16H); 7.67 (s, 8H); 4.59 (s, 4H); 3.65 (s, 18H)
RMN ^{13}C (acetone-d_6, 100 MHz): δ (ppm) = 55.0, 59.5, 118.5 (bs, *para*-CH, BARF), 125.5 (q, $^{1}J_{C\text{-}F}$ = 270.1 Hz, CF_3), 130.1 (q, $^{2}J_{C\text{-}F}$ = 31.0 Hz, C-CF_3, BARF), 135.7 (bs, *ortho*-CH, BARF), 162.7 (quartet, $^{1}J_{C\text{-}B}$ = 49.5 Hz, BARF).
IR (ν_{max}, cm^{-1}): 2983, 1611, 1480, 1354, 1274, 1112
M. p.: 235.1 °C
HRMS (ESI) *m/z* calcd for $C_7H_{19}N_2$ 73.0886, found 73.0884

*[15-c-5]Na.**X***$^{-}$

X = NTf_2
White solid, yield: 71 %
RMN ^{1}H ($CDCl_3$, 400 MHz): δ (ppm) = 3.64 (s, 20H)
RMN ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 68.8, 119.9 (q, $^{1}J_{C\text{-}F}$ = 318.7 Hz, NTf_2),
IR (ν_{max}, cm^{-1}): 2903, 2881, 1479, 1470, 1345, 1331, 1295, 1243, 1226, 1184, 1128, 1098, 1051
M. p.: 135.4 °C
HRMS (ESI) *m/z* calcd for $C_{10}H_{20}O_5Na$ 243.1202, found 243.1202

X = BARF
White solid, yield: 90 %
RMN ^{1}H ($CDCl_3$, 400 MHz): δ (ppm) = 7.72 (bs, 8H); 7.56 (s, 4H); 3.56 (s, 20H)
RMN ^{13}C ($CDCl_3$, 100 MHz): δ (ppm) = 68.8, 117.7 (bs, *para*-CH, BARF), 124.7 (q, $^{1}J_{C\text{-}F}$ = 270.8 Hz, CF_3), 129.1 (q, $^{2}J_{C\text{-}F}$ = 33.4 Hz, C-CF_3, BARF), 134.9 (bs, *ortho*-CH, BARF), 161.8 (quartet, $^{1}J_{C\text{-}B}$ = 49.6 Hz, BARF).
IR (ν_{max}, cm^{-1}): 2927, 2885, 1609, 1479, 1354, 1275, 1111, 1047
M. p.: 186.8 °C
HRMS (ESI) *m/z* calcd for $C_{10}H_{20}O_5Na$ 243.1202, found 243.1205

2/ Molecular modelling

The structures of all compounds were optimized at the B3LYP level[1] in conjunction with the 6-31G** basis set[2]. Then, vibrational frequency calculations were performed at the same level of calculation using the standard approximations: rigid rotator and harmonic approximation and we checked that all the frequencies are positive, confirming the fact that theses structures are minima of the potential energy surface. Charges were calculated using the natural population analysis. All the calculations were performed using Gaussian09.[3] Interaction energies were also computed using the counterpoise method and the values indicated in the text are all corrected from BBSE (basis set superposition error).[4]

We also performed a few additional calculations at the B97D/6-31G** level of calculation.[5] The structures were quite similar as well as the association energy and association free energy. It confirms the greater contribution of the electrostatic part compared to the dispersion contribution for the formation of these complexes.

References :

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Table S2 : Enthalpy and free energy corresponding to the formation of the complexes shown on Fig. 1. Interaction energy (ΔE_{int}) corrected from the BSSE. Energy in kcal/mol.

	Fig 1a	Fig. 1b	Fig 1c	Fig 1d
ΔH_{ass} (B3LYP)	-8.73	-8.32	-22.00	-17.18
ΔG_{ass} (B3LYP)	+0.27	+0.04	-11.11	-5.79
ΔE_{int} (B3LYP)	-7.63	-7.64	-22.39	-15.01
ΔH_{ass} (B97D)	-13.26	-11.98	-26.70	-20.01
ΔG_{ass} (B97D)	-3.31	-2.39	-12.99	-8.86

Table S3: B3LYP/6-31G, distance in Å, energy in kcal/mol**

	Fig 1a	Fig. 1b	Fig 1c
d(O1···H1)	2.72	2.37	2.42
d(O1···H2)	3.00	2.47	2.83
d(O1···H3)	3.03	2.72	2.23
d(O1···H4)	3.04	-	2.39
Additional Interaction	d(O1···C1) 2.97	-	-
ΔE_{int}	-7.63	-7.64	-22.39
ΔH	-8.73	-8.32	-22.00
ΔG	+0.27	+0.04	-11.11

	Fig 1d
d(Na^{+}···O1)	2.27
d(Na^{+}···O2)	2.53
d(Na^{+}···O3)	2.51
d(Na^{+}···O4)	2.52
d(Na^{+}···O5)	2.53
d(Na^{+}···O6)	2.52
ΔE_{int}	-15.01
ΔH	-17.18
ΔG	-5.79

	Fig 2
d(N1···H1)	2.13
d(N2···H1)	2.84
d(N2···H2)	2.64
ΔE_{int}	-20.06
ΔH	-17.73
ΔG	-6.32

Table S4 : Charges (NPA) in e, within (LA: catalyst) complexes.

	Fig 1a	**Fig. 1b**	**Fig 1c**	**Fig 1d**	**Fig 2**
H1	+0.265	+0.272	+0.282	-	+0.316
H2	+0.249	+0.258	+0.287	-	+0.263
H3	+0.286	+0.272	+0.297	-	-
H4	+0.256	-	+0.282	-	-
O1	-0.616 (-0.529 for 2nd O=C of LA)	-0.621 (-0.532 for 2nd O=C of LA)	-0.684 (-0.504 for 2nd O=C of LA)	-0.644 (-0.530 for 2nd O=C of LA)	**N1** : -0.550 **N2** : -0.541
Additional Atom	**C1**: + 0.582	-	-	-	-
Carbon of C=O (complexed LA)	+0.826 (+0.797 for 2nd O=C of LA)	+0.830 (+0.799 for 2nd O=C of LA)	+0.849 (+0.794 for 2nd O=C of LA)	+0.850 (+0.799 for 2nd O=C of LA)	-

(*L*-Lactide:DBU-Me) Complex (Figure 1a)

SCF Done: E(RB3LYP) = -1036.22146462 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	2.814476	0.266736	-0.628947
6	2.155404	0.330180	0.533130
6	2.697581	1.400267	-1.570943
6	2.904696	2.706014	-0.818901
6	1.861478	2.791255	0.281677
7	1.685412	1.502388	0.984858
6	0.797615	1.582142	2.157454
1	1.704609	1.358217	-2.032069
1	3.443634	1.267449	-2.354124
1	2.799060	3.562094	-1.490410
1	3.916181	2.734974	-0.401455
1	0.886108	3.080424	-0.127482
1	2.144458	3.537962	1.028837
1	-0.177741	1.136813	1.940685
1	1.241891	1.100610	3.029750
1	0.653409	2.635402	2.395218
6	3.689164	-0.844786	-1.093225
6	4.300946	-1.720092	-0.000157
6	3.347845	-2.800540	0.522810
6	1.924230	-2.262831	0.689962
6	1.851468	-0.894381	1.379934
1	4.498960	-0.349640	-1.635186
1	3.139266	-1.448372	-1.825747
1	4.650497	-1.074068	0.814252
1	5.200361	-2.184600	-0.416775
1	3.723165	-3.184046	1.478068
1	3.331167	-3.651513	-0.166848
1	1.332540	-2.964324	1.286346
1	1.416773	-2.190039	-0.278099
1	2.478785	-0.872561	2.281224

1	0.823882	-0.758114	1.720342
6	-1.606722	-0.071771	-0.659017
6	-2.680044	-0.083910	-1.737680
8	-2.009987	-0.248601	0.611046
6	-3.400544	-0.621513	0.876008
6	-4.365652	0.165708	-0.013081
8	-3.925271	0.461775	-1.260716
8	-5.457776	0.506889	0.352546
8	-0.429869	0.096194	-0.906345
6	-3.661552	-0.396650	2.352628
6	-2.868829	-1.468293	-2.364992
1	-3.538531	0.658045	2.609698
1	-2.976780	-1.000217	2.952403
1	-4.688413	-0.683785	2.582952
1	-3.175724	-2.218928	-1.631420
1	-1.933800	-1.796236	-2.826660
1	-3.639152	-1.405756	-3.136564
1	-3.503657	-1.686375	0.631537
1	-2.349445	0.617865	-2.505741

DBU-Me (Figure 1a)

SCF Done: E(RB3LYP) = -501.836004872 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-0.005247	-0.877570	-0.260504
6	0.255534	0.418684	-0.053948
6	1.114278	-1.779722	-0.612581
6	2.293695	-1.509395	0.308849
6	2.699441	-0.054418	0.151259
7	1.523397	0.845587	0.068430
6	1.863879	2.279563	0.145843
1	1.386182	-1.613158	-1.661765
1	0.762255	-2.806587	-0.521684
1	3.138366	-2.155110	0.055802
1	2.008992	-1.726553	1.343131
1	3.296667	0.093407	-0.755955
1	3.302757	0.274195	1.002148
1	1.612657	2.802755	-0.780582
1	1.368719	2.766264	0.988587
1	2.939918	2.358633	0.292658
6	-1.331219	-1.552080	-0.121738
6	-2.335301	-0.886824	0.818804
6	-3.093818	0.283930	0.182274
6	-2.172327	1.153120	-0.677454
6	-0.831920	1.480173	-0.002080
1	-1.093005	-2.543336	0.270246
1	-1.756801	-1.698989	-1.121523
1	-1.811430	-0.572983	1.729728
1	-3.041829	-1.659924	1.137010
1	-3.554950	0.888411	0.970827
1	-3.913524	-0.092193	-0.438875
1	-2.666126	2.101159	-0.909972
1	-1.978403	0.674591	-1.644234
1	-0.982419	1.772372	1.046257
1	-0.418514	2.362747	-0.492647

(*L*-Lactide:MTBD-Me) Complex (Figure 1b)

SCF Done: E(RB3LYP) = -1052.26549228 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-4.051800	0.790740	0.469369
6	-4.656538	0.266386	-0.834248
6	-3.147568	-1.611048	-0.557332
6	-2.162030	-0.685086	0.141224
1	-4.532547	0.263964	1.303803
1	-2.572055	-2.166568	-1.300283
6	-4.228370	2.288795	0.627146
1	-5.291493	2.531194	0.596828
1	-3.810598	2.616543	1.581428
1	-3.733235	2.821632	-0.187895
6	-3.813947	-2.595283	0.408081
1	-4.489099	-3.243736	-0.154440
1	-3.052826	-3.213109	0.891825
1	-4.391842	-2.086301	1.184340
8	-2.619562	0.508719	0.543965
8	-4.120214	-0.877510	-1.327270
8	-1.001379	-0.988983	0.330473
8	-5.559293	0.818048	-1.403800
6	1.573890	2.480989	-0.271116
6	2.823812	0.037044	0.221556
6	3.092422	2.385450	-0.378522
1	1.123036	2.083017	-1.186032
1	3.580832	2.822013	0.502747
6	4.509634	0.564640	-1.466628
6	4.454411	-1.700780	-0.475982
6	5.356826	-0.520813	-0.811126
1	4.066760	0.209523	-2.406588
1	4.938162	-2.382394	0.233000
1	5.828477	-0.115985	0.090226
7	3.459591	0.968955	-0.521091

7	1.861691	0.420294	1.087856
7	3.164977	-1.270193	0.098608
1	5.105962	1.450610	-1.690686
1	6.154144	-0.852629	-1.481339
1	4.238219	-2.275875	-1.384886
1	3.462119	2.909087	-1.261565
1	1.255414	3.521912	-0.170495
6	1.120097	1.690050	0.948533
1	0.053899	1.447429	0.897838
1	1.293034	2.272217	1.862024
6	1.542979	-0.328000	2.309238
1	0.573710	-0.823890	2.224023
1	2.323895	-1.054652	2.525419
1	1.504855	0.385617	3.138018
6	2.180723	-2.350962	0.260836
1	2.376212	-2.946569	1.157956
1	1.168626	-1.951073	0.293291
1	2.258870	-3.010290	-0.609275

MTBD-Me (Figure 1b)

SCF Done: E(RB3LYP) = -517.880659492 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-2.358962	-1.170845	0.596811
6	-0.000007	0.201967	-0.000126
6	-1.260148	-1.885254	-0.180928
1	-2.108765	-1.170546	1.662632
1	-1.509498	-1.960693	-1.247303
6	1.260487	-1.885103	0.180675
6	2.484631	0.248988	-0.062324
6	2.359494	-1.170336	-0.596441
1	1.509386	-1.960818	1.247139
1	3.056758	0.883732	-0.748067
1	2.109778	-1.169960	-1.662373
7	0.000155	-1.145934	-0.000327
7	-1.165437	0.877757	-0.155668
7	1.165244	0.878060	0.155520
1	1.101409	-2.895354	-0.199518
1	3.315912	-1.686724	-0.481070
1	3.013903	0.245346	0.898476
1	-1.100725	-2.895588	0.198890
1	-3.315312	-1.687439	0.481814
6	-2.484622	0.248499	0.062876
1	-3.056464	0.883159	0.748944
1	-3.014410	0.244850	-0.897640
6	-1.232035	2.188664	-0.816596
1	-1.503463	2.985176	-0.117461
1	-0.282655	2.428316	-1.291300
1	-1.998495	2.139456	-1.595692
6	1.231307	2.189049	0.816393
1	1.502284	2.985666	0.117209
1	0.281870	2.428261	1.291216
1	1.997886	2.140209	1.595387

(*L*-Lactide:TMEDA-Me_2) Complex (Figure 1c)

SCF Done: E(RB3LYP) = -427.032912590 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-3.507017	0.855728	0.027709
6	-4.157301	-0.344514	-0.666380
6	-2.523182	-1.684889	0.522571
6	-1.547076	-0.525645	0.415830
1	-3.882960	0.913866	1.055407
1	-1.979981	-2.582232	0.219122
6	-3.759540	2.156619	-0.705749
1	-4.836767	2.312518	-0.783067
1	-3.320714	2.994669	-0.159728
1	-3.352962	2.118378	-1.719035
6	-3.060610	-1.879371	1.945287
1	-3.756136	-2.721305	1.940498
1	-2.239745	-2.108061	2.630256
1	-3.589759	-0.998685	2.317806
8	-2.040710	0.673908	0.125144
8	-3.575125	-1.554179	-0.446322
8	-0.336295	-0.655452	0.577239
8	-5.121352	-0.241331	-1.369414
7	2.049227	2.097693	0.251405
6	3.331016	2.897370	0.278463
1	3.133052	3.850792	0.768428
1	4.092682	2.358692	0.841299
1	3.664199	3.072763	-0.744947
6	2.237880	0.756357	-0.454107
1	1.230507	0.377284	-0.626854
1	2.724400	0.988252	-1.403493
6	1.008725	2.868108	-0.543085
1	0.059895	2.333607	-0.481623
1	0.911920	3.862560	-0.107565

1	1.341530	2.949493	-1.578405
6	1.524899	1.917816	1.662475
1	2.314188	1.511554	2.294722
1	1.234422	2.897244	2.042268
1	0.667063	1.245932	1.625000
6	3.023958	-0.272981	0.372216
1	2.422100	-0.592757	1.223522
1	3.977467	0.117041	0.734775
7	3.362642	-1.550293	-0.392323
6	3.912592	-2.542684	0.616583
1	4.223922	-3.440555	0.083211
1	4.768953	-2.098169	1.124566
1	3.129220	-2.788329	1.333652
6	4.421101	-1.304765	-1.445113
1	5.320920	-0.919530	-0.964460
1	4.643840	-2.252517	-1.935512
1	4.050029	-0.598541	-2.186587
6	2.129760	-2.153201	-1.038204
1	1.319642	-2.175623	-0.308312
1	1.841688	-1.548536	-1.897732
1	2.380925	-3.158856	-1.374932

TMEDA-Me$_2$ (Figure 1c)

E (RB3LYP)= -427.032912590 Hartrees

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	-1.974135	0.006493	0.000001
6	-2.258842	0.833209	-1.238220
1	-3.317135	1.094629	-1.238500
1	-1.667894	1.748180	-1.218617
1	-2.028316	0.240804	-2.124541
6	-0.548035	-0.540515	-0.000137
1	-0.477502	-1.174278	0.885727
1	-0.477713	-1.174393	-0.885934
6	-2.910923	-1.193120	0.000162
1	-2.729436	-1.786637	0.896524
1	-3.937212	-0.826748	-0.000155
1	-2.729098	-1.787152	-0.895793
6	-2.258610	0.833335	1.238212
1	-1.668153	1.748609	1.218050
1	-3.317060	1.094123	1.239012
1	-2.027373	0.241220	2.124545
6	0.547983	0.540426	-0.000365
1	0.477401	1.174570	0.885225
1	0.477611	1.173860	-0.886469
7	1.974119	-0.006507	0.000006
6	2.910820	1.193166	-0.000468
1	3.937141	0.826875	-0.000374
1	2.729119	1.786594	-0.896848
1	2.729128	1.787241	0.895481
6	2.258851	-0.833808	-1.237838
1	2.027763	-0.242013	-2.124420
1	3.317272	-1.094705	-1.238278
1	1.668367	-1.749068	-1.217538
6	2.258754	-0.832703	1.238619
1	2.027845	-0.239999	2.124641
1	1.668196	-1.747917	1.219115
1	3.317172	-1.093629	1.239308

(*L*-Lactide: [15-c-5]Na) Complex (Figure 1d)

SCF Done: E(RB3LYP) = -1465.78502898 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	4.169690	0.711028	-0.620420
6	5.000140	-0.121100	0.358775
6	3.315927	-1.837831	0.046498
6	2.288083	-0.743404	-0.193664
1	4.416596	0.386243	-1.639165
1	2.870599	-2.525319	0.767981
6	4.418131	2.199337	-0.470064
1	5.478295	2.403233	-0.626427
1	3.831134	2.752791	-1.206011
1	4.149879	2.533616	0.534758
6	3.669038	-2.601184	-1.233580
1	4.398991	-3.376724	-0.991945
1	2.773025	-3.075442	-1.642561
1	4.098200	-1.949399	-1.999536
8	2.734849	0.486837	-0.434725
8	4.491147	-1.328902	0.705755
8	1.090514	-0.969818	-0.165646
8	6.051478	0.254647	0.801972
11	-1.021714	-0.154685	-0.043539
8	-1.364106	2.019628	-1.261178
8	-1.059116	1.838387	1.508628
8	-1.862126	-0.718346	2.260442
8	-2.568481	-2.137475	-0.030803
8	-2.272934	-0.434571	-2.222350
6	-3.102779	-1.421383	2.235822
1	-3.349959	-1.802854	3.236670
1	-3.923698	-0.763189	1.911648
6	-2.926765	-2.586812	1.278323
1	-3.838523	-3.196177	1.248049
1	-2.101457	-3.215117	1.625597

6	-3.648744	-1.994782	-0.950891
1	-4.207615	-2.937381	-1.038750
1	-4.351039	-1.214585	-0.619154
6	-3.035359	-1.641852	-2.294617
1	-2.335658	-2.430109	-2.586801
1	-3.815609	-1.567049	-3.062345
6	-2.972367	0.755920	-2.579539
1	-3.398394	0.664124	-3.588864
1	-3.798083	0.955246	-1.879059
6	-1.957544	1.884757	-2.555216
1	-2.426375	2.824268	-2.872289
1	-1.144458	1.652150	-3.249355
6	-2.037138	1.692695	2.536816
1	-1.939624	2.498988	3.277834
1	-3.056485	1.733888	2.122875
6	-1.776269	0.353576	3.202970
1	-2.473239	0.201259	4.036019
1	-0.756233	0.340882	3.598228
6	-1.918184	3.039516	-0.432274
1	-1.880496	4.012966	-0.941616
1	-2.970604	2.824579	-0.191124
6	-1.068039	3.093496	0.825156
1	-1.416613	3.897165	1.485945
1	-0.030429	3.298524	0.546982

Lactide (Figure 1d)

SCF Done: E(RB3LYP) = -534.369427869 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
6	-1.037514	0.521681	0.493782
6	-1.096998	-0.828722	-0.221753
6	1.322301	-0.696761	-0.263274
6	1.229673	0.825104	-0.283946
1	-0.825686	0.323071	1.554415
1	2.019911	-0.967833	-1.057711
6	-2.337741	1.295574	0.365880
1	-3.159200	0.699541	0.765783
1	-2.264385	2.235414	0.917110
1	-2.547249	1.513961	-0.683773
6	1.843910	-1.225642	1.074500
1	1.928299	-2.313866	1.027703
1	2.830367	-0.799657	1.274395
1	1.180527	-0.965231	1.904702
8	0.019485	1.366526	-0.022275
8	0.083509	-1.342824	-0.634030
8	2.184415	1.520686	-0.522470
8	-2.125455	-1.428490	-0.407945

(Sparteine:TMEDA-Me$_2$) Complex (Figure 2)

SCF Done: E(RB3LYP) = -1123.85500683 A.U. after 1 cycles

Atomic Number	Coordinates (Angstroms) X	Y	Z
7	1.216998	1.785673	0.666294
6	0.240723	2.824945	1.026351
1	0.743084	3.704866	1.472533
1	-0.416946	2.423565	1.810029
6	-0.581262	3.291196	-0.179483
1	-1.259465	4.094749	0.129086
1	-1.218019	2.461310	-0.535861
6	0.330138	3.754964	-1.321192
1	-0.253800	3.993186	-2.216977
1	0.826834	4.685560	-1.019995
6	1.395188	2.693233	-1.623452
1	0.921840	1.800943	-2.056412
1	2.103001	3.068362	-2.370547
6	2.161606	2.299872	-0.353181
1	2.629697	3.230927	0.028531
6	3.344498	1.336576	-0.601365
1	3.999803	1.841561	-1.321474
6	4.086375	1.133187	0.723174
1	5.010635	0.568234	0.574301
1	4.372496	2.097195	1.157920
6	3.110264	0.398862	1.652031
1	3.570888	0.251325	2.635969
6	1.892387	1.309499	1.890258
1	1.144814	0.789829	2.506111
1	2.245986	2.167891	2.491618
6	2.800985	-1.014399	1.103386
1	1.968953	-1.436134	1.693661
6	4.012664	-1.956484	1.310509
1	4.910814	-1.518719	0.860676
1	4.211156	-2.031919	2.385725

6	3.790609	-3.349155	0.709316
1	4.692980	-3.958062	0.819509
1	2.993793	-3.871199	1.259176
6	3.393335	-3.223759	-0.764254
1	3.160670	-4.202621	-1.198541
1	4.226106	-2.812382	-1.347186
6	2.164434	-2.311379	-0.879812
1	1.866650	-2.201261	-1.932269
1	1.337110	-2.816466	-0.348926
7	2.301234	-0.962593	-0.301275
6	3.028060	-0.044803	-1.206784
1	2.422024	0.063628	-2.115595
1	3.989427	-0.472777	-1.533335
7	-1.754639	-1.122588	-0.921918
6	-1.163564	-0.613435	-2.223956
1	-1.086569	0.472316	-2.173589
1	-0.168655	-1.042197	-2.330867
1	-1.802176	-0.921393	-3.052913
6	-1.767472	-2.632116	-0.967007
1	-0.740079	-2.971806	-1.092514
1	-2.157302	-3.028557	-0.030150
1	-2.376246	-2.963425	-1.809523
6	-0.869834	-0.639975	0.220281
1	-1.026044	0.428460	0.354787
1	-1.123709	-1.199286	1.121216
1	0.195849	-0.772439	-0.043021
6	-3.162147	-0.554311	-0.823373
1	-3.047318	0.524515	-0.940426
1	-3.709724	-0.944031	-1.684152
6	-3.876125	-0.888153	0.495970
1	-3.978049	-1.965895	0.634808
1	-3.327277	-0.479822	1.346030
7	-5.292217	-0.325384	0.605082
6	-5.822712	-0.711024	1.975953
1	-5.184956	-0.268619	2.741532

1	-6.838678	-0.328753	2.073180
1	-5.825732	-1.797770	2.064499
6	-5.304188	1.185125	0.496396
1	-6.314486	1.535140	0.708384
1	-4.609560	1.600850	1.227141
1	-5.026642	1.486046	-0.512845
6	-6.211271	-0.915180	-0.444339
1	-5.902413	-0.585765	-1.435427
1	-6.182515	-2.003047	-0.373196
1	-7.224028	-0.561590	-0.250514

Sparteine (Figure 2)

SCF Done: E(RB3LYP) = -696.791483666 A.U. after 1 cycles

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
7	1.541395	0.568240	-0.543551		
6	2.822262	0.711441	-1.231169		
1	3.453356	1.489850	-0.748590		
1	2.622163	1.060652	-2.251265		
6	3.595975	-0.607223	-1.272352		
1	4.562212	-0.450224	-1.766439		
1	3.032244	-1.328928	-1.876060		
6	3.788281	-1.159609	0.143571		
1	4.272765	-2.142756	0.116941		
1	4.456927	-0.493526	0.707156		
6	2.433809	-1.245547	0.856514		
1	1.809100	-1.990246	0.350071		
1	2.563468	-1.573893	1.895503		
6	1.703209	0.106657	0.843333		
1	2.344436	0.827060	1.403358		
6	0.359770	0.074393	1.615474		
1	0.606571	-0.176313	2.655744		
6	-0.292276	1.460501	1.553055		

1	-1.201398	1.488292	2.164440
1	0.384182	2.229408	1.947065
6	-0.592983	1.733329	0.073043
1	-1.059489	2.720650	-0.039864
6	0.745755	1.785470	-0.679229
1	0.569691	1.952613	-1.749923
1	1.302199	2.674677	-0.309960
6	-1.585966	0.692515	-0.494765
1	-1.576193	0.793294	-1.592739
6	-3.042037	0.965167	-0.039854
1	-3.104698	0.944620	1.055963
1	-3.339692	1.974496	-0.352277
6	-4.009007	-0.078628	-0.620311
1	-5.024949	0.087062	-0.242691
1	-4.058357	0.043964	-1.712378
6	-3.530008	-1.501284	-0.297952
1	-4.168591	-2.247430	-0.787154
1	-3.605700	-1.680644	0.782943
6	-2.070415	-1.677072	-0.756592
1	-1.696995	-2.674195	-0.495396
1	-2.038635	-1.604676	-1.854627
7	-1.147990	-0.683549	-0.216017
6	-0.679318	-0.956960	1.137289
1	-0.252132	-1.966705	1.140419
1	-1.488637	-0.968827	1.896406

3/ General procedures for polymerization

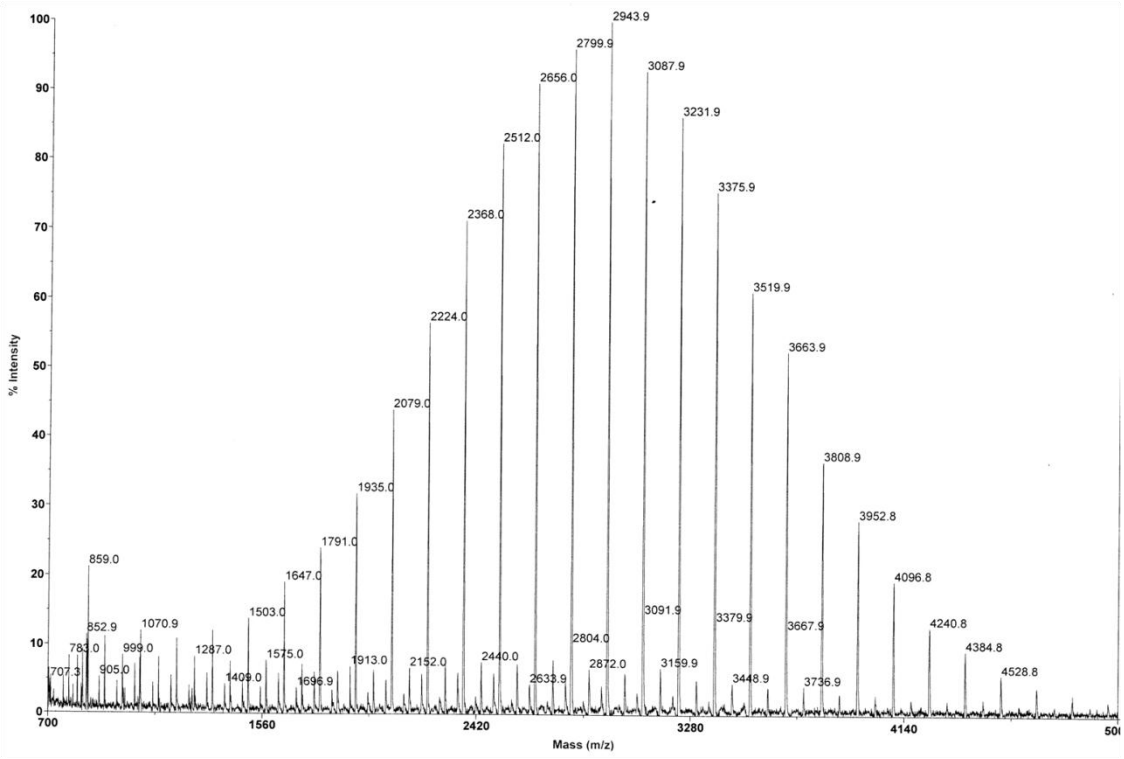
Polymer molar masses and dispersity were determined by SEC on apparatus equipped with Tosoh GSK4000, GSK3000 and GSK2000 columns (Eluent: THF, flow rate 1.0 mL/min, 40 °C), either with RI and UV detectors and a calibration with polystyrene standards.

Procedure for the ring-opening polymerization (Table 1-2): Under nitrogen, in a dry Schlenk tube, were successively introduced dry dichloromethane (0.5 mL), monomer (LA, VL or CL, 2 mmol), ionic organocatalyst (5 % mol), the H-bond acceptor cocatalyst (Sp or DBU, 5 % mol), 4-biphenylmethanol (5 % mol), and 4Å molecular sieves (5 beads). The reaction mixture was stirred at 20 °C under nitrogen for 24 h. The reaction was quenched mixture by benzoic acid (10 mg) and the reaction mixture was filtered and concentrated *in vacuo*. Conversion was determined by ^{1}H NMR, integrating the signals of the methine proton (adjacent to the carbonyl group) in both the residual monomer and the polymer. Molar masses and dispersity of the crude products were measured by Size Exclusion Chromatography (SEC).

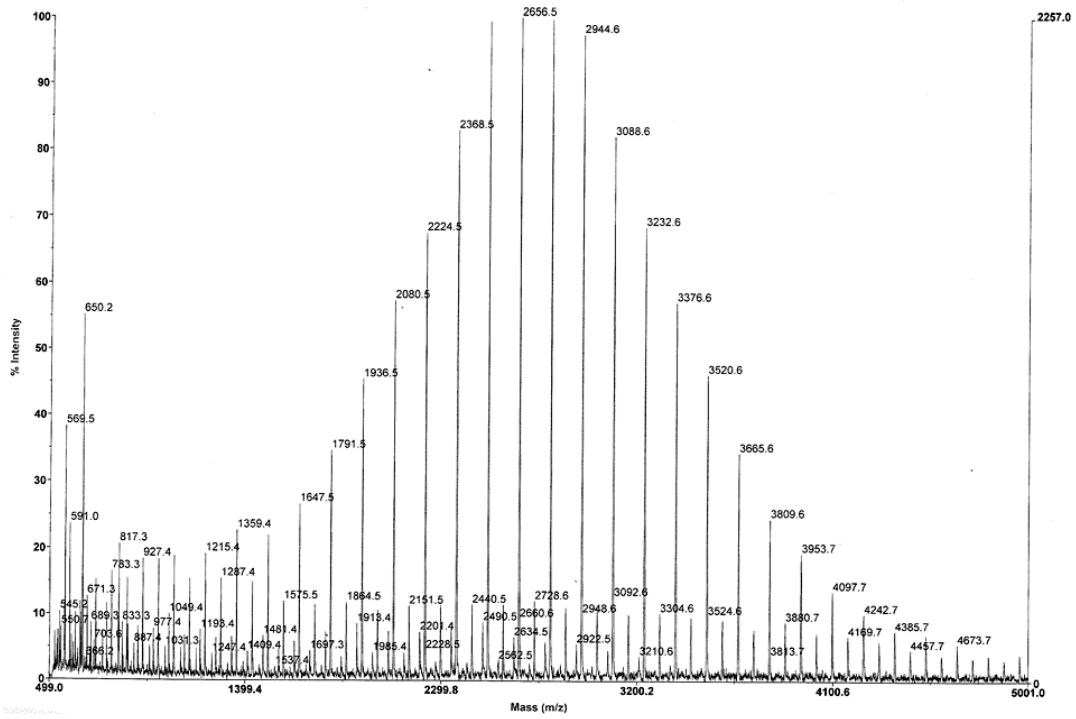
Procedure for chain extension of lactide and δ-valerolactone (Table 3): Under nitrogen, in a dry Schlenk tube, were successively introduced dry dichloromethane (0.5 mL), monomer (LA or VL, 2 mmol), ionic organocatalyst (5 % mol), the H-bond acceptor cocatalyst (Sp or DBU, 5 % mol), 4-biphenylmethanol (5 % mol), and 4 Å molecular sieves (5 beads). The reaction mixture was stirred at 20 °C under nitrogen for 24 h. After 24h and 48h, the same quantity of monomer was added to the reaction. After 72 h, the reaction was quenched by benzoic acid (10 mg) and the reaction mixture was filtered and concentrated *in vacuo*. Conversion was determined by ^{1}H NMR, integrating the signals of the methine proton (adjacent to the carbonyl group) in both the residual monomer and the polymer. Molar masses and dispersity of the crude products were measured by Size Exclusion Chromatography (SEC).

4/ Mass Spectra of representative PLA, PVL and PCL obtained from the general procedure (Tables 1-2, monomer 4M, CH_2Cl_2)

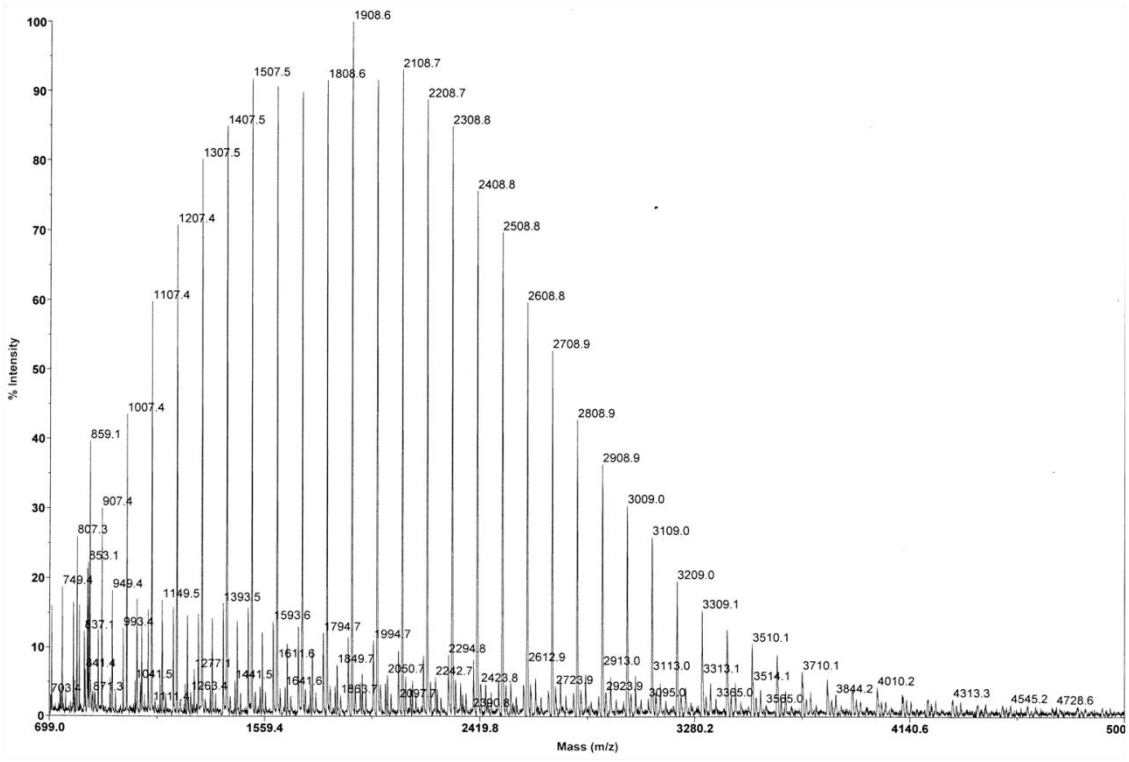
a) PLA using DBU-Me.NTf_2/Sp/BPM (5:5:5)



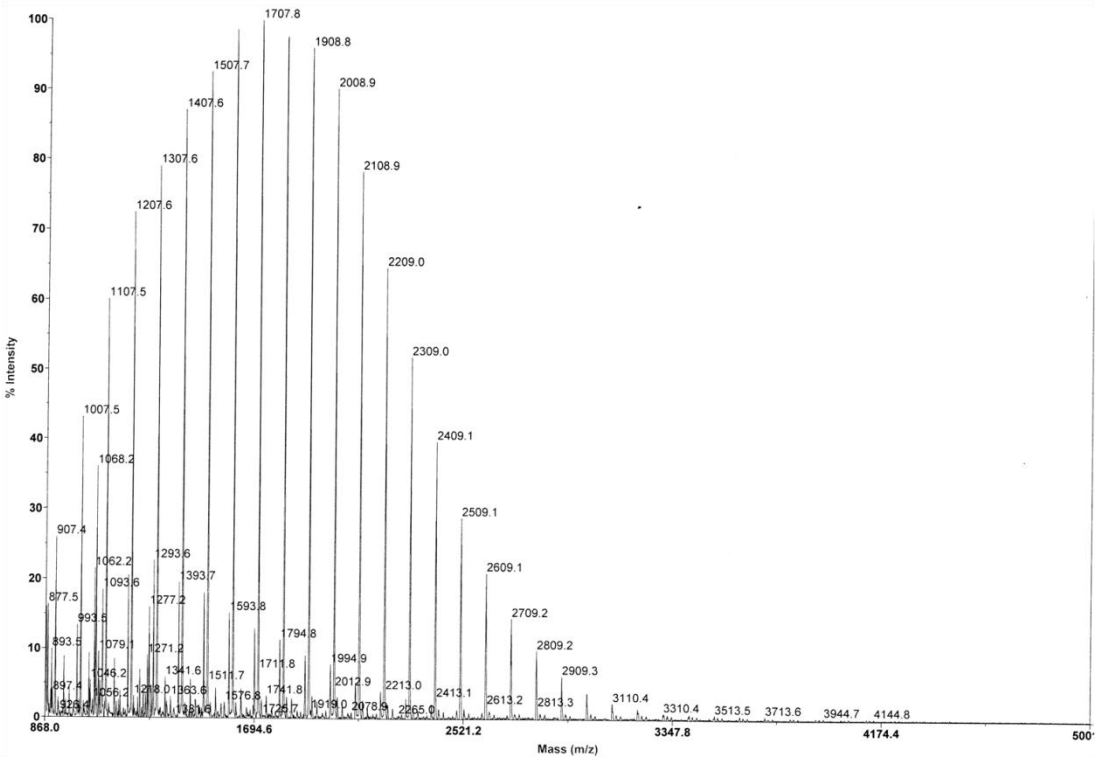
b) PLA using [15-c-5]Na.BARF/Sp/BPM (5:5:5)



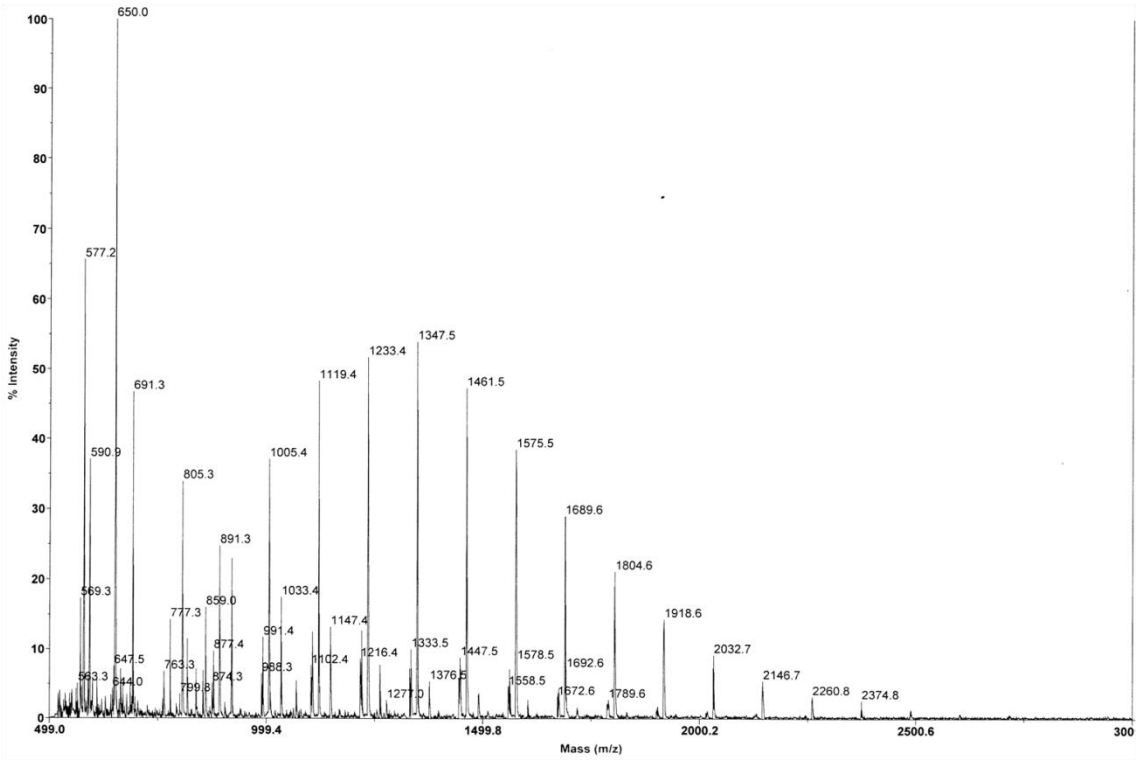
c) PVL using DBU-Me.NTf$_2$/DBU/BPM (5:5:5)



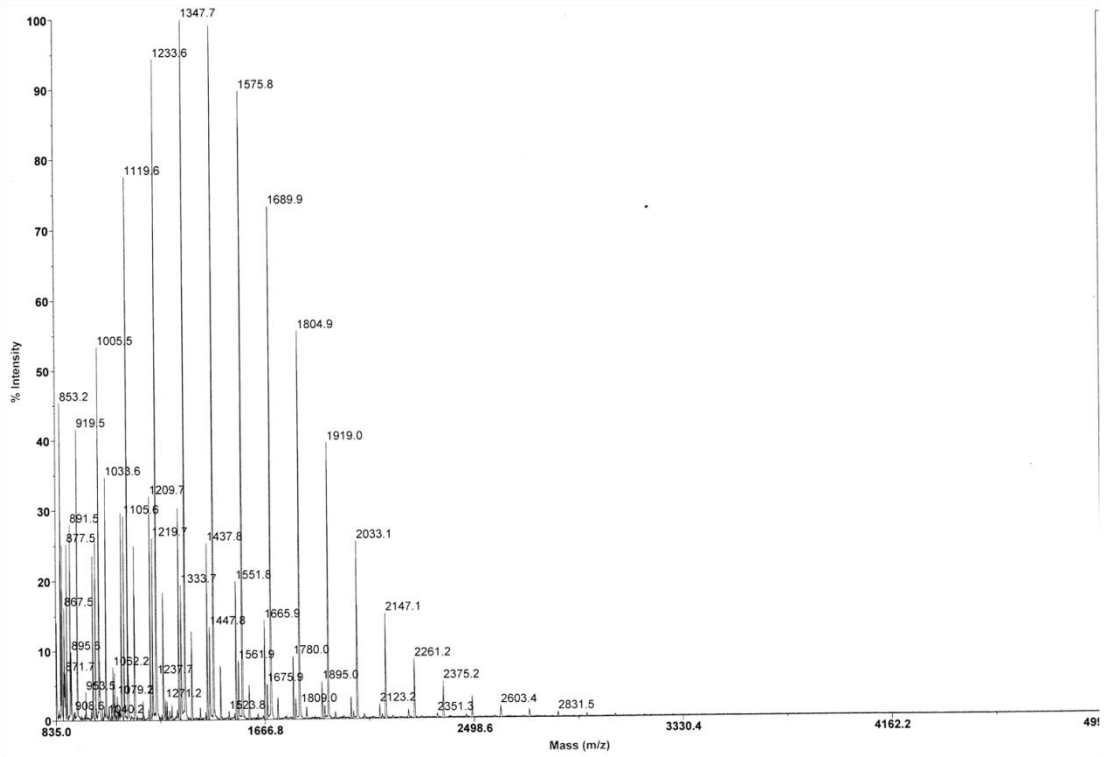
d) PVL using [15-c-5]Na.BARF/DBU/BPM (5:5:5)



e) PCL using DBU-Me.NTf$_2$/DBU/BPM (5:5:5)



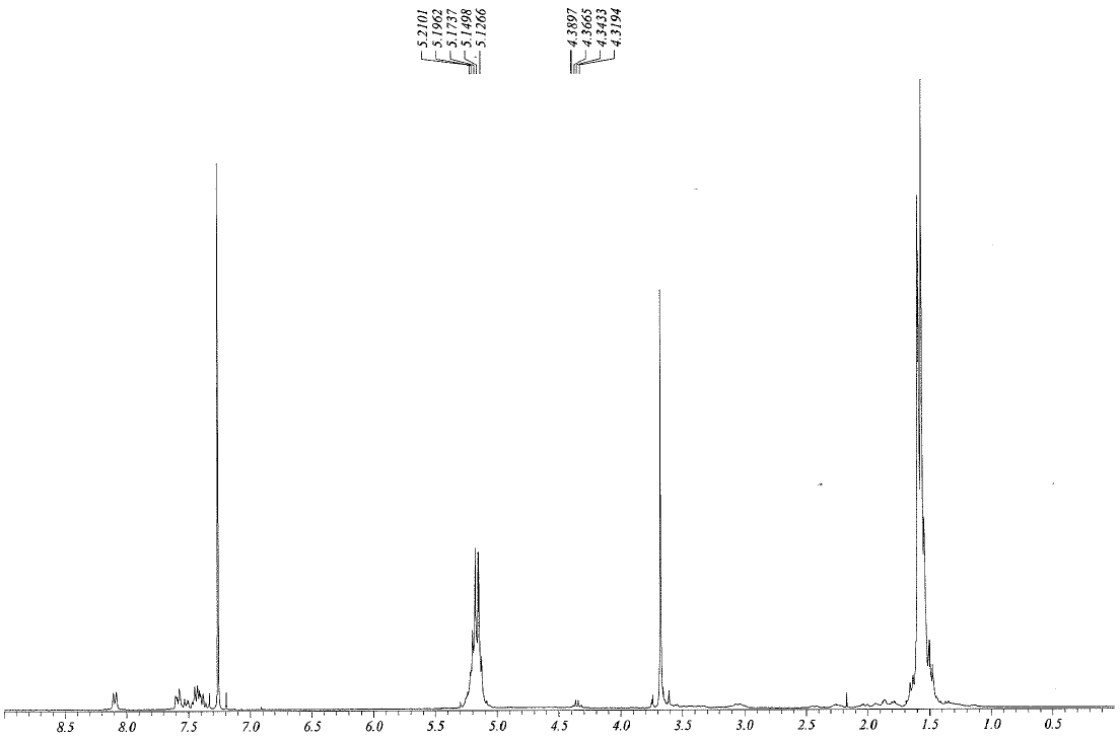
f) PCL using [15-c-5]Na.BARF/DBU/BPM (5:5:5)



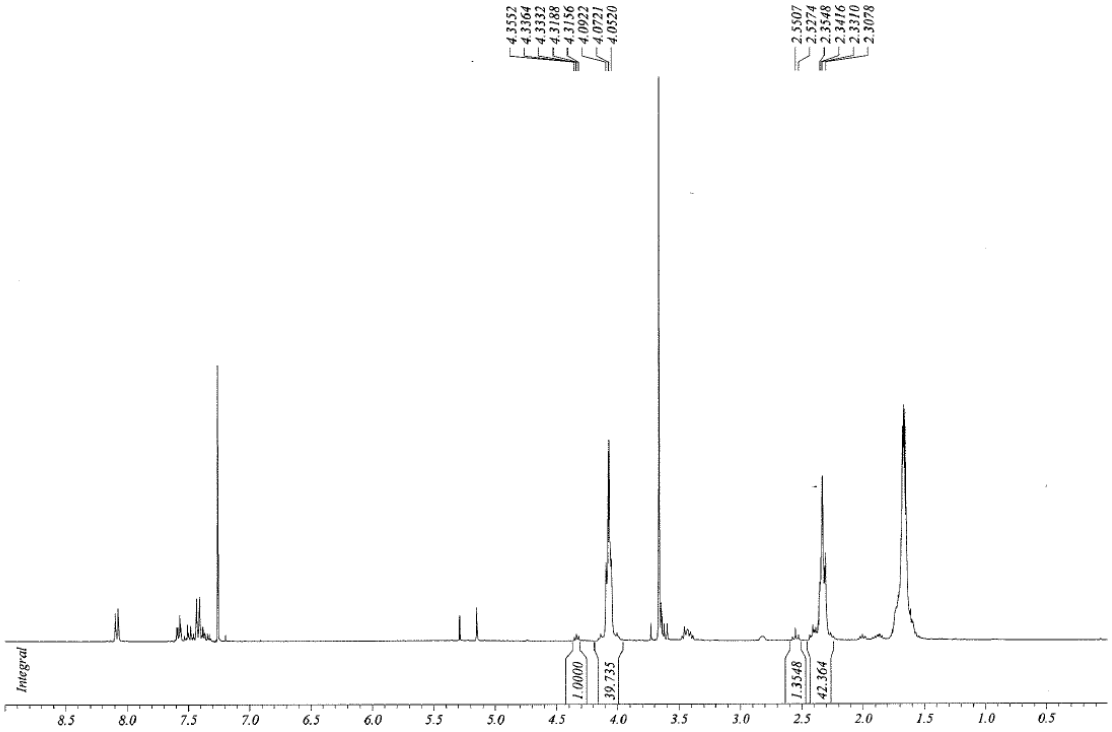
5/ Proton NMR Spectra of representative PLA and PVL (Table 1-2)

Experiments were quenched by benzoic acid (seen in the aromatic region)

a) Polylactides ([15-c-5]Na.NTf$_2$/Sp/BPM: 5/5/5, 100% conv.)

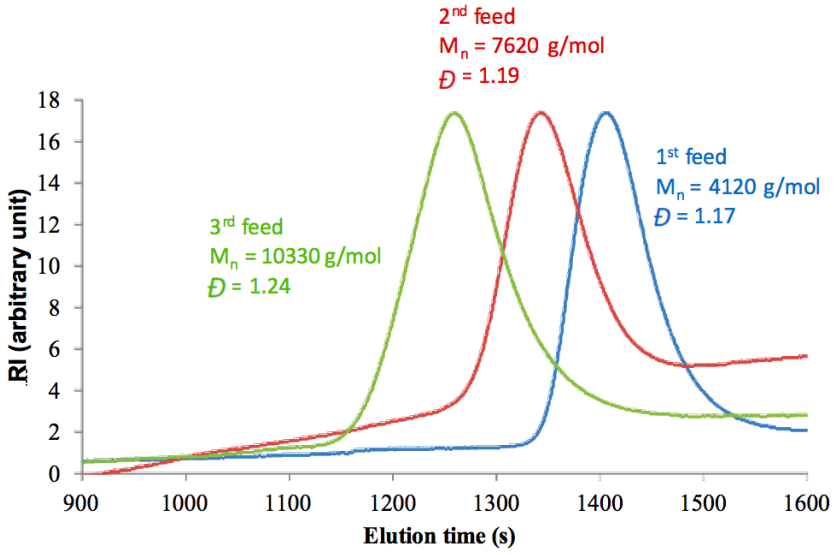


b) PVL ([15-c-5]Na.NTf$_2$/DBU/BPM: 5/5/5, 99% conv.)

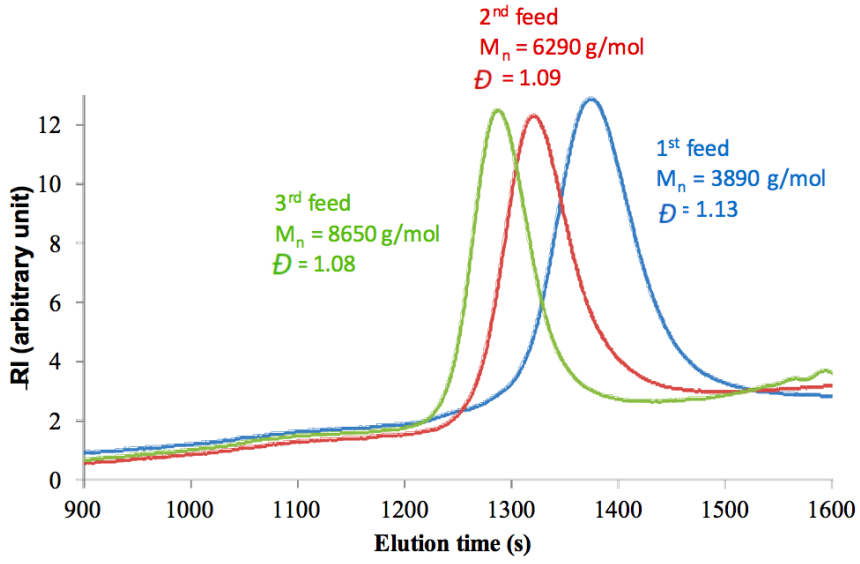


6/ SEC Traces of representative PLA and PVL – Chain extension experiments (Table 3)

a) Polylactides

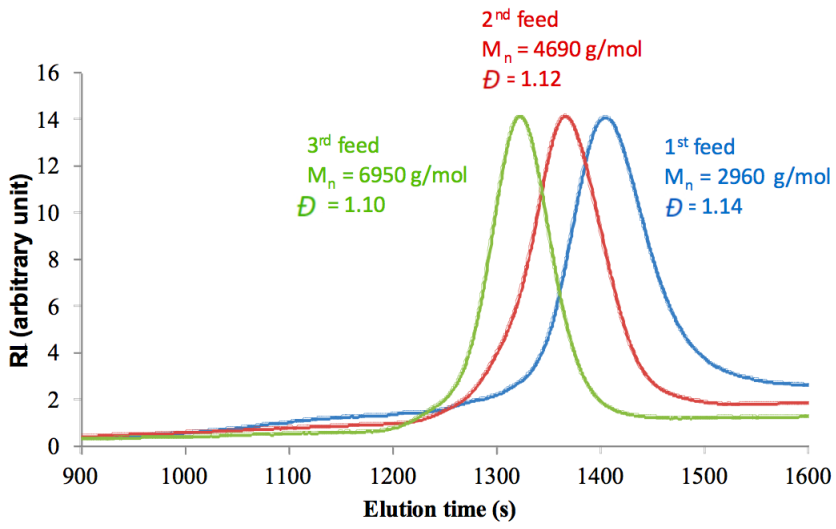


DBU-Me.NTf$_2$/Sp/BPM (5:5:5)

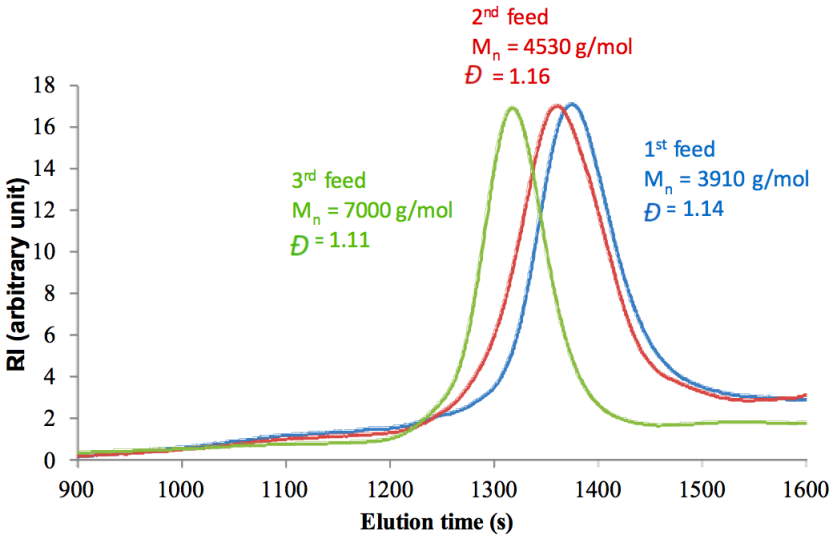


[15-c-5]Na.NTf$_2$/Sp/BPM (5:5:5)

b) PVL



DBU-Me.NTf$_2$/DBU/BPM (5:5:5)



[15-c-5]Na.NTf$_2$/DBU/BPM (5:5:5)