Supplementary Material (ESI) for Polymer Chemistry

Ring-Opening Polymerization of L-Lactide using N-Heterocyclic Molecules: Mechanistic, Kinetics and DFT Studies

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Supporting Information:

Appendix A: Experimental Details of ROP of L-lactide

Table A1. Extended experimental details for ROP of L-lactide.

Entry	Cat: [L]/[I]	T (ºC)	t (min)	M_n	DP_n	M_w	M_w/M_n	Conv.(%)
1	PDP-50	120	10	5.6×10^3	39	6.5×10^3	1.15	42
2	PDP-50	120	20	9.6×10^3	67	1.2×10^4	1.27	69
3	PDP-50	120	30	1.2×10^4	85	1.5×10^4	1.28	75
4	PDP-50	120	40	1.4×10^4	95	1.8×10^4	1.29	83
5	PDP-50	120	50	1.5×10^4	105	1.9×10^4	1.35	89.7
6	PDP-50	120	60	1.6×10^4	112	2.3×10^4	1.40	91
7	PDP-50	120	120	1.9×10^4	133	2.8×10^4	1.43	99
8	PDP-50	140	20	1.3×10^4	87	1.7×10^4	1.36	70
9	PDP-50	140	30	1.4×10^4	95	1.9×10^4	1.46	-
10	PDP-50	140	40	1.6×10^4	110	2.4×10^4	1.47	83.4
11	PDP-50	140	50	1.6×10^4	110	2.3×10^4	1.4	94
12	PDP-50	140	60	1.6×10^4	114	2.3×10^4	1.40	96
13	PDP-50	160	10	1.1×10^4	76	1.5×10^4	1.4	49
14	PDP-50	160	30	1.3×10^4	88	1.7×10^4	1.31	84
15	PDP-50	160	40	1.4×10^4	100	1.9×10^4	1.3	93.3
16	PDP-50	160	50	1.3×10^4	90	1.8×10^4	1.4	99
17	PDP-50	160	60	1.5×10^4	101	2.1×10^4	1.4	99.6
18	PDP-100	120	30	8.9×10^3	62	1.1×10^4	1.24	69.3
19	PDP-100	120	50	1.2×10^4	81	1.5×10^4	1.28	83
20	PDP-100	120	60	1.3×10^4	90	1.7×10^4	1.30	87
21	PDP/ BA -50	120	10	5.9×10^3	41	6.9×10^3	1.16	96.3
22	PDP/ BA -50	120	30	8.5×10^3	59	9.9×10^3	1.16	98.7
23	PDP/ BA -50	120	50	8.3×10^3	57	9.9×10^3	1.18	99.5
24	PDP/ BA -50	120	60	8.7×10^3	61	1.1×10^4	1.28	99.7

Appendix B: ^{1}H NMR of organically initiated ROP of L-lactide

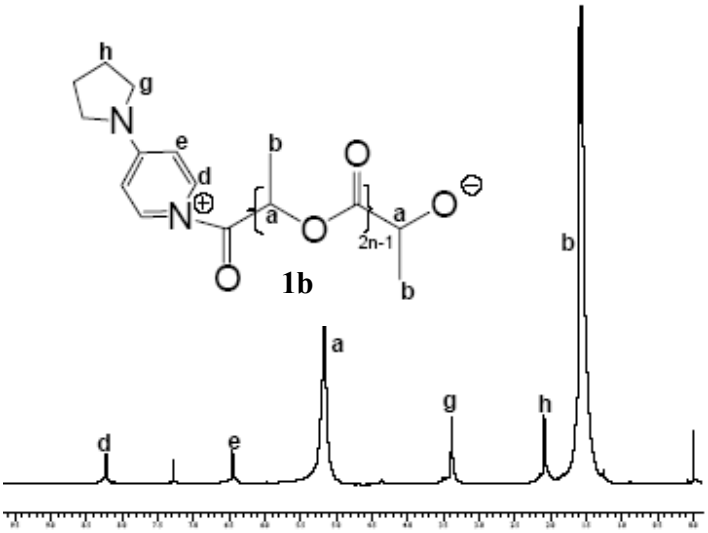

Figure B1. ^{1}H NMR spectrum (400 MHz) of PLA via PDP initiated ROP, in $CDCl_3$. Conditions: [L]/[I]=25 at 120°C, ROP time= 90 min.

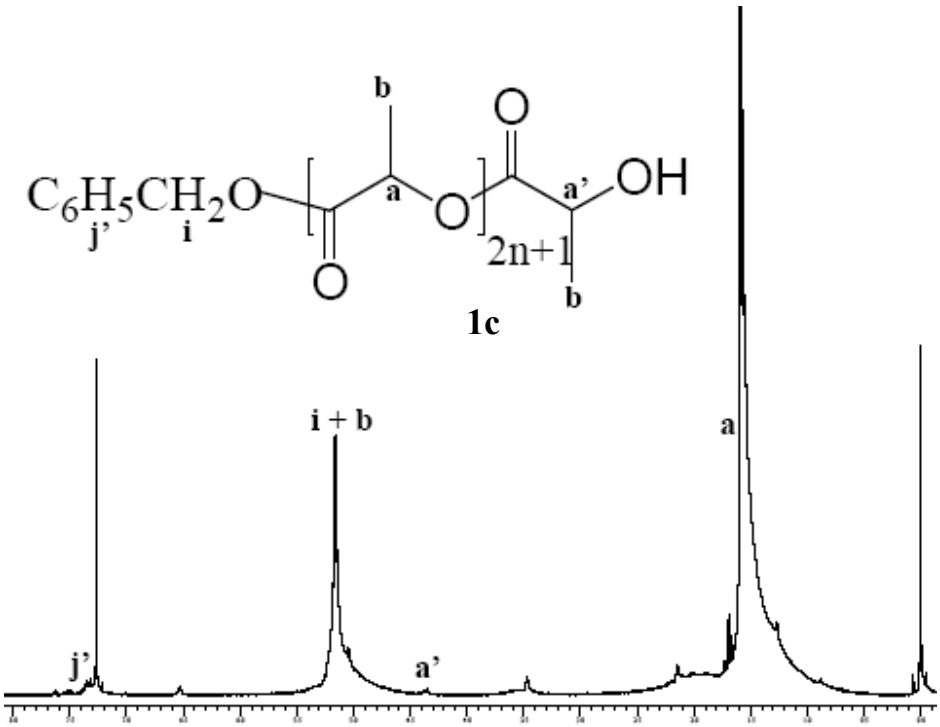

Figure B2. ^{1}H NMR spectrum (400 MHz) of PLA via PDP + BA (molar ratio =1) initiated ROP, in $CDCl_3$. Conditions: [L]/[I]=50 at 120°C, ROP time= 90 min.

Appendix C: DFT Calculations

*B3LYP/6-31+G** optimized coordinates of the N-heterocycles and their protonated forms.*

PDP				**PDP-H$^+$**			
GSEE = -459.716629 hartree.particle^{-1}				GSEE =-460.118012 hartree.particle^{-1}			
C	2.670722	1.132236	-0.080538	C	-2.596907	1.183369	0.076250
C	1.281225	1.197590	-0.086510	C	-1.230925	1.217423	0.077277
C	0.531233	0.000073	-0.000421	C	-0.474107	-0.000014	-0.000087
C	1.281174	-1.197586	0.086138	C	-1.230950	-1.217426	-0.077445
C	2.670545	-1.132407	0.080871	C	-2.596939	-1.183342	-0.076196
N	3.386899	-0.000018	0.000360	N	-3.267342	0.000006	0.000125
H	3.245185	2.054596	-0.148494	H	-3.202723	2.079208	0.138480
H	0.794224	2.162415	-0.167016	H	-0.739530	2.177933	0.149691
H	0.793904	-2.162296	0.166402	H	-0.739597	-2.177943	-0.150041
H	3.245095	-2.054660	0.149202	H	-3.202762	-2.079182	-0.138380
N	-0.837065	0.000018	-0.000860	N	0.859477	-0.000012	-0.000022
C	-1.649636	1.218912	0.003586	C	1.693737	1.226596	0.006324
C	-3.067890	0.708120	0.299762	C	3.104693	0.707613	-0.299241
C	-3.068022	-0.708171	-0.299156	C	3.104616	-0.707625	0.299441
C	-1.649616	-1.218796	-0.003583	C	1.693746	-1.226596	-0.006454
H	-1.599936	1.729633	-0.970913	H	1.639441	1.701526	0.994217
H	-1.295287	1.923212	0.765566	H	1.332374	1.936013	-0.743527
H	-3.227227	0.659587	1.383188	H	3.261792	0.665937	-1.382259
H	-3.840116	1.356035	-0.123991	H	3.875459	1.353183	0.126858
H	-3.840033	-1.356113	0.124960	H	3.875496	-1.353223	-0.126407
H	-3.227790	-0.659705	-1.382520	H	3.261416	-0.665893	1.382505
H	-1.599387	-1.728685	0.971373	H	1.639654	-1.701338	-0.994455
H	-1.295882	-1.923845	-0.765145	H	1.332286	-1.936185	0.743187
				H	-4.280026	0.000022	0.000186

2-Methylpyridine	**2-Methylpridine-H^+**
GSEE = -287.627802 hartree.particle^{-1}	GSEE =-288.002999 hartree.particle^{-1}
C 0.879336 0.007478 -0.000076	C 0.903168 0.074259 -0.009155
C 0.157533 1.210415 -0.000073	C 0.149198 1.247293 -0.007036
C -1.236859 1.170700 0.000012	C -1.244657 1.188083 0.001716
C -1.873538 -0.070206 0.000066	C -1.899473 -0.050972 0.006407
C -1.073716 -1.215682 -0.000015	C -1.134529 -1.200117 0.001259
N 0.264196 -1.189237 -0.000063	N 0.217833 -1.100397 -0.006453
H -1.813621 2.091460 0.000072	H -1.823049 2.106683 0.003302
H 0.684925 2.159693 -0.000167	H 0.664761 2.200719 -0.012546
H -2.955698 -0.154154 0.000194	H -2.980471 -0.123964 0.011380
H -1.529094 -2.204290 -0.000040	H -1.546483 -2.202222 0.000330
C 2.387218 -0.013815 0.000075	C 2.399407 0.018721 0.007213
H 2.758815 -0.548747 -0.880346	H 2.819537 0.993122 -0.245016
H 2.806911 0.995774 -0.000026	H 2.762542 -0.256388 1.004974
H 2.758547 -0.548417 0.880822	H 2.782589 -0.715753 -0.708711
	H 0.757054 -1.963012 -0.010968
Pyridine	**Pyridine-H^+**
GSEE = -248.303368 hartree.particle^{-1}	GSEE = -248.671793 hartree.particle^{-1}
C -1.144618 -0.722712 -0.000218	C -0.667517 1.190710 -0.000197
C -1.199699 0.673841 -0.000119	C 0.717234 1.212295 -0.000130
C 0.000263 1.386658 0.000090	C 1.416816 0.000057 0.000061
C 1.199954 0.673404 0.000214	C 0.717335 -1.212237 0.000202
C 1.144345 -0.723127 0.000130	C -0.667418 -1.190764 0.000136
N -0.000268 -1.420904 -0.000098	N -1.310165 -0.000053 -0.000065
H 0.000439 2.472991 0.000166	H 2.502227 0.000106 0.000129
H -2.060770 -1.309693 -0.000374	H -1.285914 2.080376 -0.000352
H -2.158489 1.182969 -0.000231	H 1.234651 2.164713 -0.000233
H 2.158956 1.182138 0.000358	H 1.234826 -2.164615 0.000363
H 2.060271 -1.310456 0.000186	H -1.285742 -2.080480 0.000227
	H -2.327589 -0.000096 -0.000106

Imidazole			**Imidazole-H^+**		
GSEE = -226.235385 hartree.particle^{-1}			GSEE = -226.6081 hartree.particle^{-1}		
C	-0.610054	0.987599	0.000091	C	0.680192	0.979704	0.000046
C	-1.139456	-0.280743	0.000064	C	-0.683871	0.977127	0.000081
N	-0.136243	-1.226722	-0.000011	N	-1.073939	-0.350666	0.000009
C	0.989079	-0.543631	-0.000054	C	0.002199	-1.143349	-0.000067
N	0.759200	0.805260	-0.000091	N	1.075305	-0.346620	-0.000059
H	1.458607	1.532330	-0.000073	H	2.034371	-0.676655	-0.000126
H	-1.060701	1.968029	0.000138	H	1.386770	1.794747	0.000083
H	-2.181513	-0.566715	0.000153	H	-1.394040	1.789051	0.000151
H	1.985493	-0.962756	-0.000116	H	0.004080	-2.223040	-0.000131
				H	-2.031862	-0.683994	0.000020
Pyrrole			**Pyrrole-H^+**		
GSEE = = -210.188174 hartree.particle^{-1}			GSEE =-210.500286 hartree.particle^{-1}		
C	0.332492	-1.126604	-0.000029	C	0.248696	1.182584	0.000060
C	-0.984967	-0.713365	-0.000127	C	-1.013040	0.734809	0.000047
C	-0.984929	0.713416	0.000083	C	-1.013124	-0.734694	-0.000045
C	0.332550	1.126588	0.000006	C	0.248560	-1.182613	-0.000063
N	1.123581	-0.000030	0.000050	N	1.150190	-0.000064	0.000000
H	2.131080	-0.000060	0.000193	H	1.766608	-0.000059	-0.826440
H	0.766419	-2.115533	-0.000071	H	0.691242	2.168079	0.000113
H	-1.850028	-1.361743	-0.000238	H	-1.896585	1.360030	0.000085
H	-1.849954	1.361843	0.000141	H	-1.896740	-1.359814	-0.000083
H	0.766542	2.115488	0.000030	H	0.690995	-2.168158	-0.000124
				H	1.766588	-0.000142	0.826456

GSEE: Ground state electronic energy

Table C2: Absolute proton affinity of the N-heterocycles calculated at the B3LYP/6-31+G** level of theory

N-heterocycle	Proton Affinity ($kcal.mol^{-1}$)
PDP	235.33
2-Methypyridine	219.31
Pyridine	215.03
Imidazol	217.92
Pyrole	181.15