Electronic Supplementary Material (ESI)

Enzymatic Ring-Opening Polymerization (ROP) of Lactides and Lactone in Ionic Liquids and Organic Solvents: Digging the Controlling Factors

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Table S1 Comparison of enzymatic ROP of lactides under different reaction conditions

#	Lactide	Lipase [a]	Solvent [b]	Water (%)	T (°C)	t/d	Conversion (%)	Yield (%)	M_w	PDI	Ref.
1	DL	N435, 3 wt%	–	unknown	80	7	0	0	–	–	[1]
2	L	N435, 6 wt%	–	unknown	100	10	91	–	2,440	2.6	[2]
3	L	Free CALB	–	unknown	130	1	–	54.1	45,200	1.13	[3]
4	L	Free CALB	toluene (1/1, w/w)	unknown	120	1	100	17.3	49,800	1.17	[3]
5	L	Free CALB	[BMIM][BF_4] (1/1, w/w)	unknown	110	1	96.2	24.3	68,300	1.25	[3]
6	L	N435, 10 wt%	[BMIM][PF_6] (7/10, w/w)	unknown	65	11	–	29.5	700	1.2	[4]
7	L	N435, 10 wt%	[BMIM][PF_6] (7/10, w/w)	unknown	90	5	–	–	23,500	1.2	[5]
8	L	N435, 10 wt%	[HMIM][PF_6] (7/10, w/w)	unknown	90	7	–	63.2	49,100	1.3	[6]
9	L	N435, 10 wt%	[HMIM][PF_6] (7/10, w/w)	unknown	65	9	–	51.1	1,800	1.2	[6]
10	L	N435, 15 wt%	$scCO_2$	$a_w < 0.16$	65	3	35.2	5.16	11,900	1.25	[7]
11	L	N435, 12.5 wt%	toluene (1/2, g/mL)	unknown	70	3	0	0	–	–	[8]
12	D	N435, 12.5 wt%	toluene (1/2, g/mL)	unknown	70	3	33	25	4,000	1.2	[8]
13	L	N435, 10 wt%	toluene	unknown	70	2	23	23	–	–	[9]
14	DL	N435, 10 wt%	toluene	unknown	70	2	5	–	–	–	[9]
15	D	N435, 10 wt%	toluene	unknown	70	2	98	90	4,600	1.3	[9]
16	D	PS, 3 wt%	–	unknown	100	7	96	5	59,000	1.2	[1]
17	DL	PS, 3 wt%	–	unknown	100	7	82	8	69,000	1.2	[1]
18	L	PS, 3 wt%	–	unknown	100	7	82	8	48,000	1.2	[1]
19	D	PS, 5 wt%	toluene	unknown	90	2	14	5	–	–	[9]
20	DL	PS, 5 wt%	toluene	unknown	90	2	20	10	550	1.1	[9]
21	L	PS, 5 wt%	toluene	unknown	90	2	80	65	770	1.1	[9]
22	L	PPL, 1wt%	–	unknown	100	7	–	–	17,600	1.9	[10]
23	D	PPL, 1wt%	–	unknown	100	7	–	–	27,000	1.4	[10]
24	DL	PPL, 1wt%	–	unknown	100	7	–	–	26,600	2.1	[10]

Note: [a] N435 = Novozym 435; PS = lipase PS from *Burkholderia cepacia*; lipase concentration (wt%) based on monomer; [b] the number in parenthesis indicates the substrate/solvent ratio.

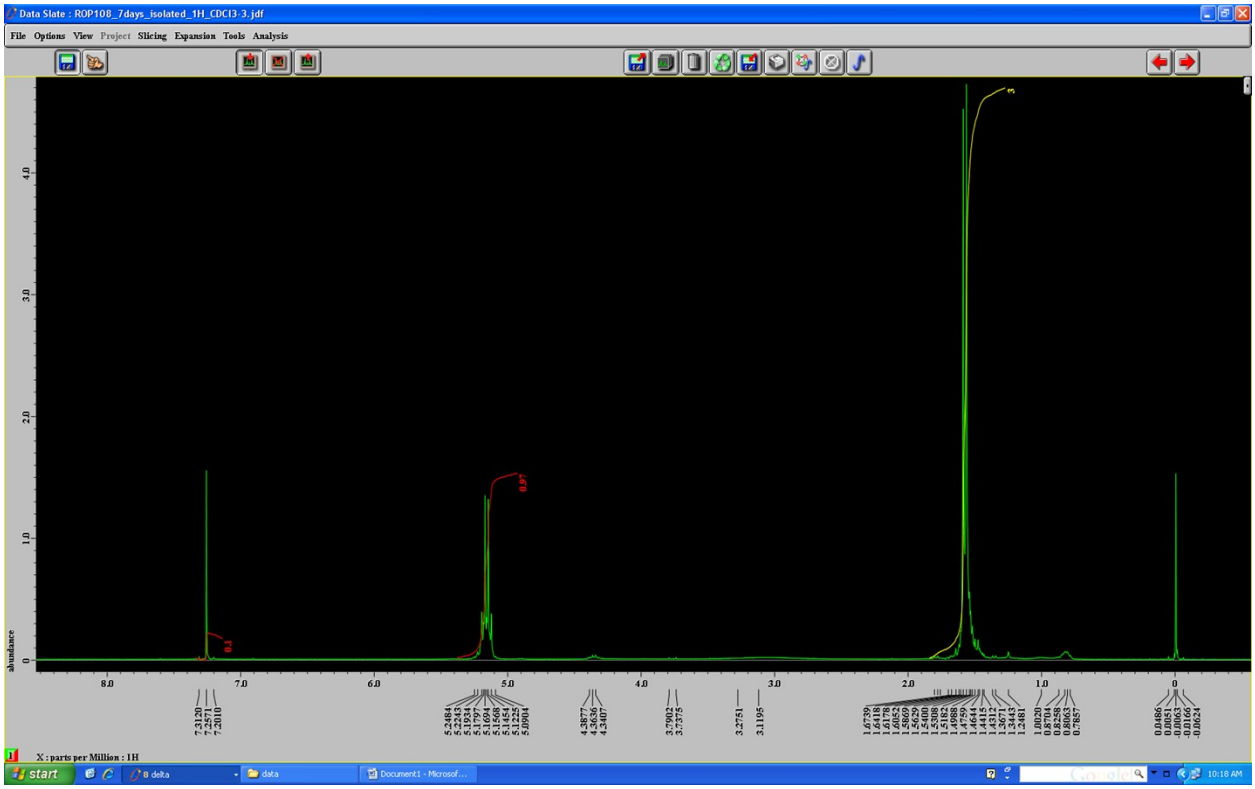
Table S2 Water contents in monomers, enzymes, and solvents

Name	Manufacturer and catalog number	Lot number	Water content (wt%)
L-(−)-lactide	Sigma 367044	STBF8444V	0.16
L-(−)-lactide	TCI L0115	KFISL-NP	0.08
D-(−)-lactide	Ark Pharm AK-57455	WG0123247-170118001	0.22
DL-lactide	Sigma 303143	BCBR2168V	0.12
DL-lactide	TCI L0091	OLMDE-DH	0.08
Novozym 435 (05/2009)	Sigma L4777	097K1155	0.77
Novozym 435 (09/2009)	Sigma L4777	067K3522	1.09
Novozym 435 (03/2016)-electrostatic	Sigma L4777	SLBP0766V	1.09
Novozym 435 (03/2017)	Sigma L4777	SLBS9524	1.94
Novozym 435 (05/2017)-electrostatic	Sigma L4777	SLBT3895	1.97
Novozym 435 (03/2016) dried over P_2O_5	Sigma L4777	SLBP0766V	1.26
Novozym 435 (05/2009), a_w = 0.11 (KCl)	Sigma L4777	097K1155	2.62
Novozym 435 (09/2009), a_w = 0.11 (KCl)	Sigma L4777	067K3522	2.52
Novozym 435 (03/2016), a_w = 0.11 (KCl)	Sigma L4777	SLBP0766V	2.26
Novozym 435 (03/2017), a_w = 0.11 (KCl)	Sigma L4777	SLBS9524	2.38
Novozym 435 (05/2009), a_w = 0.33 ($MgCl_2$)	Sigma L4777	097K1155	3.62
Novozym 435 (03/2016), a_w = 0.33 ($MgCl_2$)	Sigma L4777	SLBP0766V	3.49
Novozym 435 (03/2017), a_w = 0.33 ($MgCl_2$)	Sigma L4777	SLBS9524	2.77
CALB on Immobead 150	Sigma 54326	BCBN4171V	1.27
CALB on Immobead 150, a_w = 0.11	Sigma 54326	BCBN4171V	2.39
Free CALB	Sigma 62288	BCBP3380V	4.14
CALB-CLEA, 2.7 U/mg	Sigma 16698	BCBQ6594V	14.04
Amano lipase PS from *Burkholderia cepacia*	Sigma 534641	MKBV0029V	3.26
Amano lipase PS	Amano	LPSAC0750102	1.78
lipase from porcine pancreas (PPL), type II	Sigma L3126	074K0610	4.44
lipase from porcine pancreas (PPL), type II	Sigma L3126	SLBL2143V	3.51
lipase PS-C Amano I	Amano	ILPSAC0350403R	1.16
lipase PS-D Amano I	Amano	ILPSAB0152305R	1.22
Amano lipase A from *Aspergillus niger*	Aldrich 53478-1	KI07922HI	5.05
lipase from *Pseudomonas cepacia* immobilized in sol-gel-AK	Sigma 62279	047096/1	0.74
lipase from *Candida Cylindracea* immobilized in sol-gel-AK	Fluka 62278	046989/1	2.94
Amano lipase from *Pseudomonas fluorescens*	Aldrich 534730	MKCB1125V	3.30

[BMIM][PF_6]	Merck KGaA	0.02
[BMIM][PF_6], a_w = 0.11 (KCl)	Merck KGaA	0.46
tetraglyme, a_w = 0.11 (KCl)	Sigma-Aldrich	2.33

Note: CALB = *Candida antarctica* lipase B; CLEA = Cross-Linked Enzyme Aggregate.

(a)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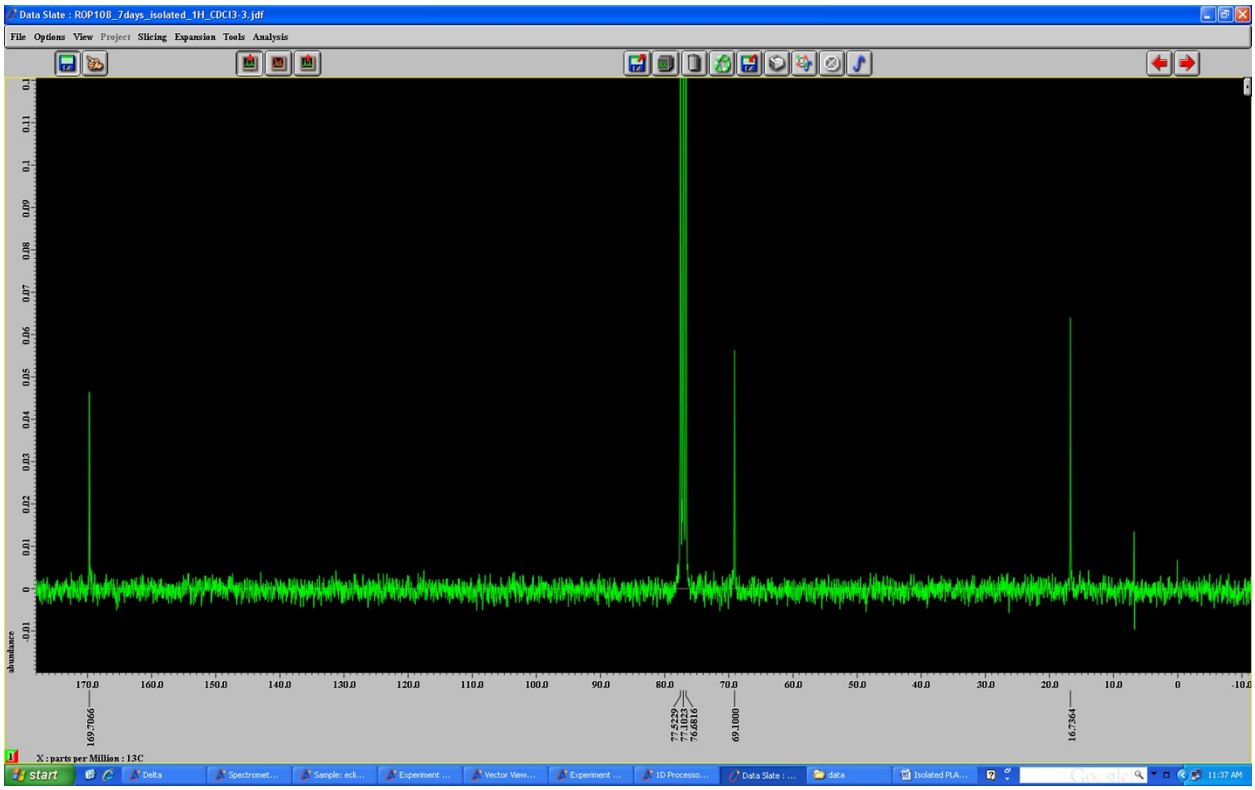
(b)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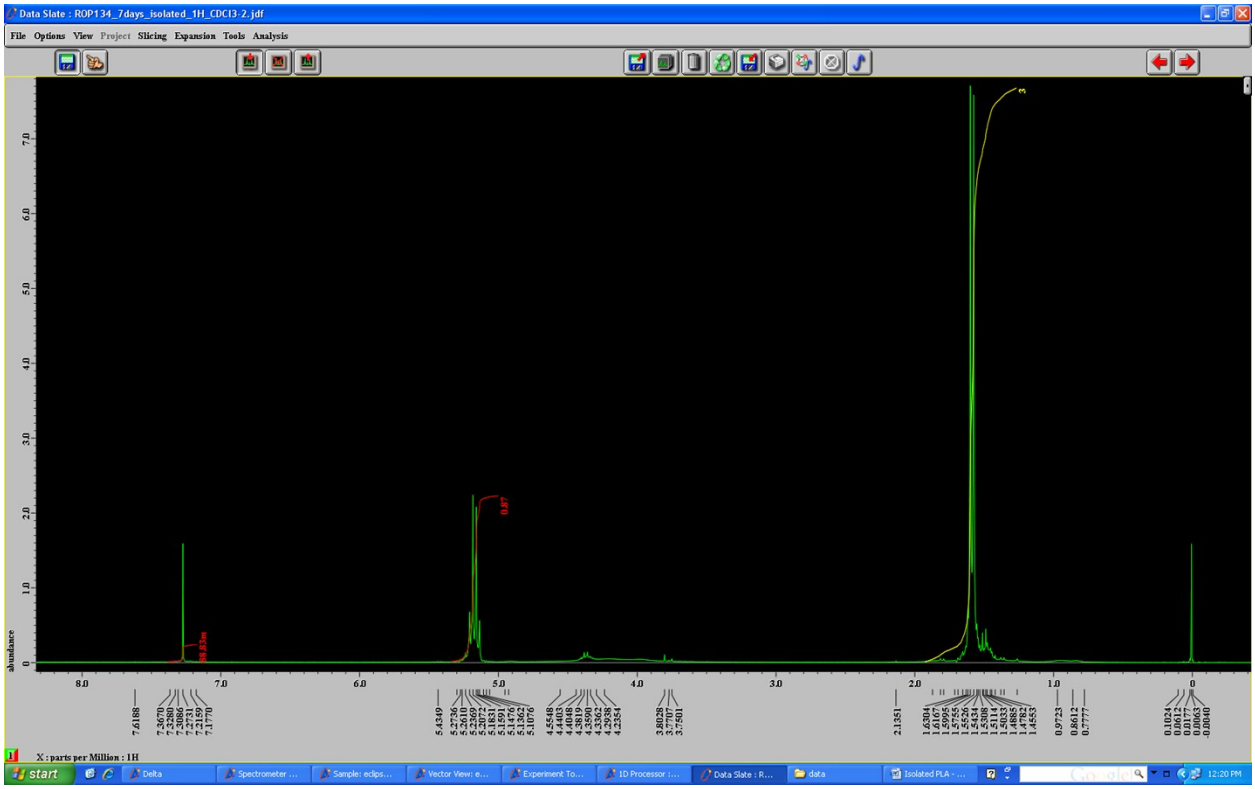
(c)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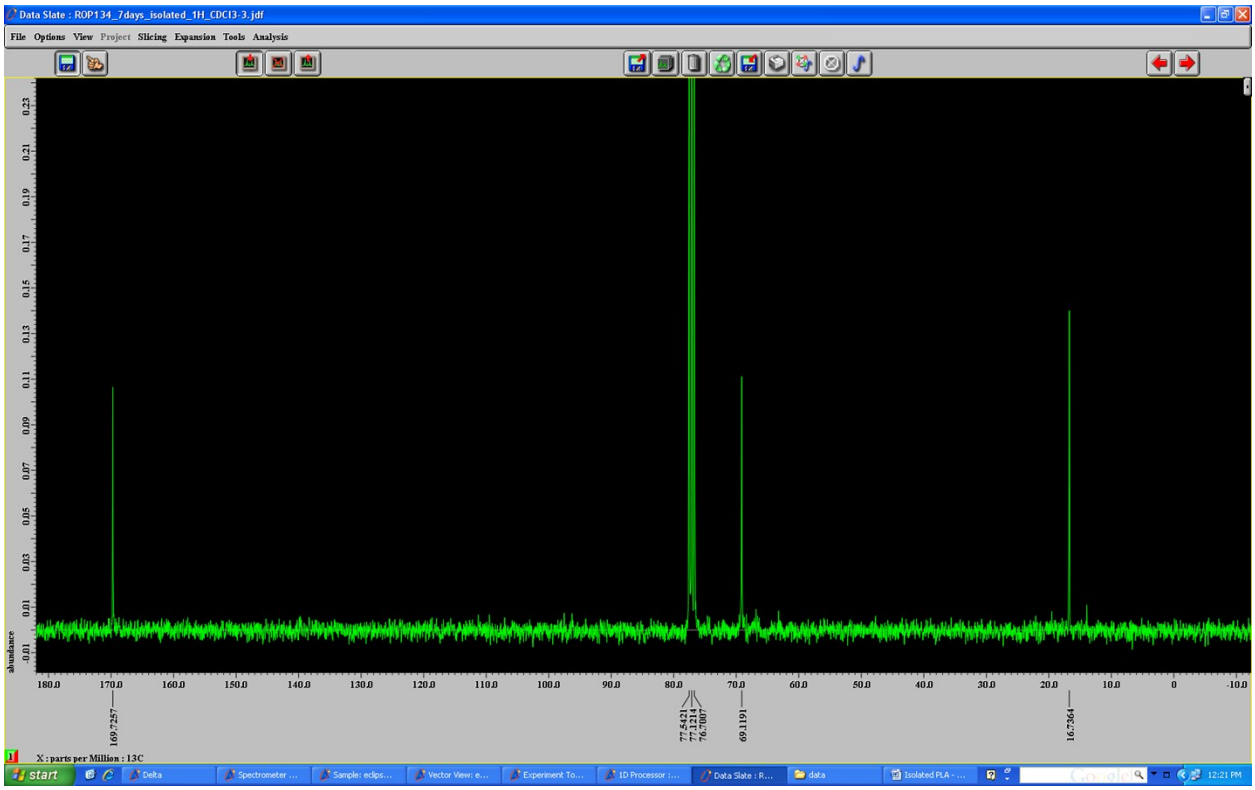
(d)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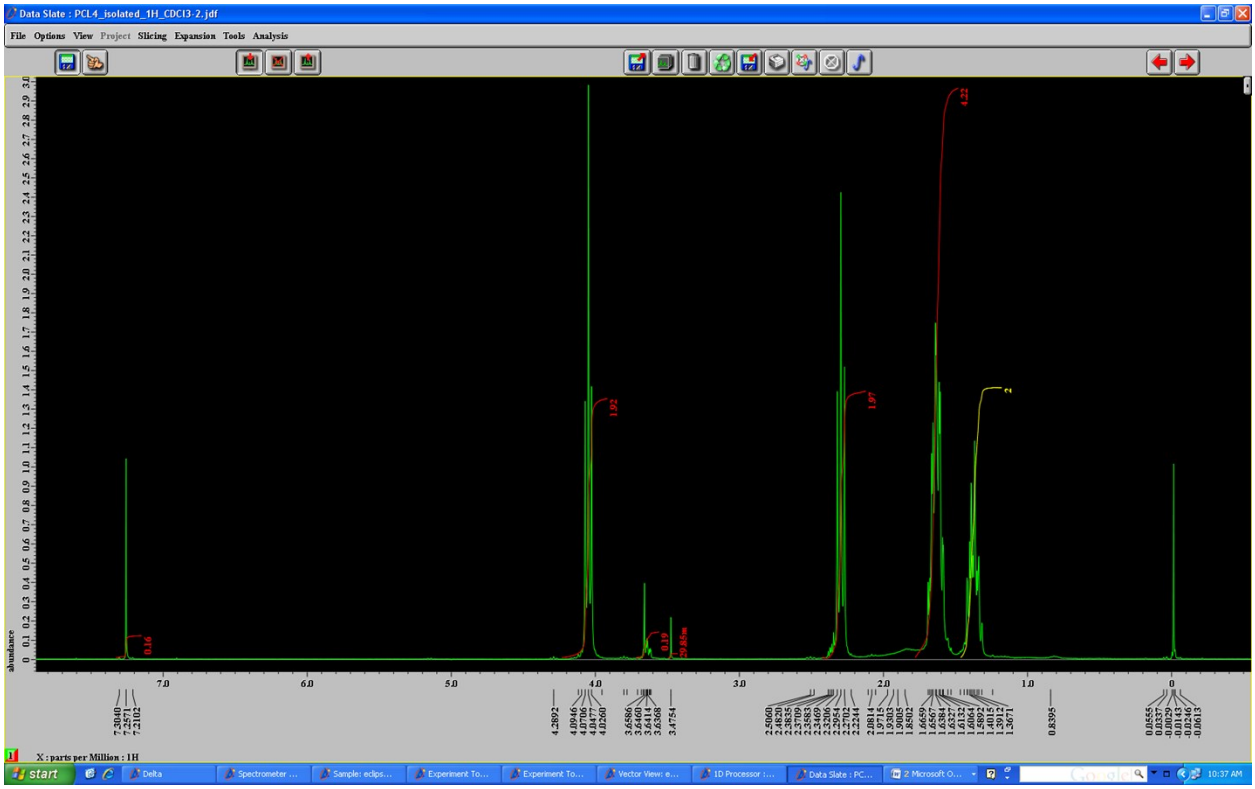
(e)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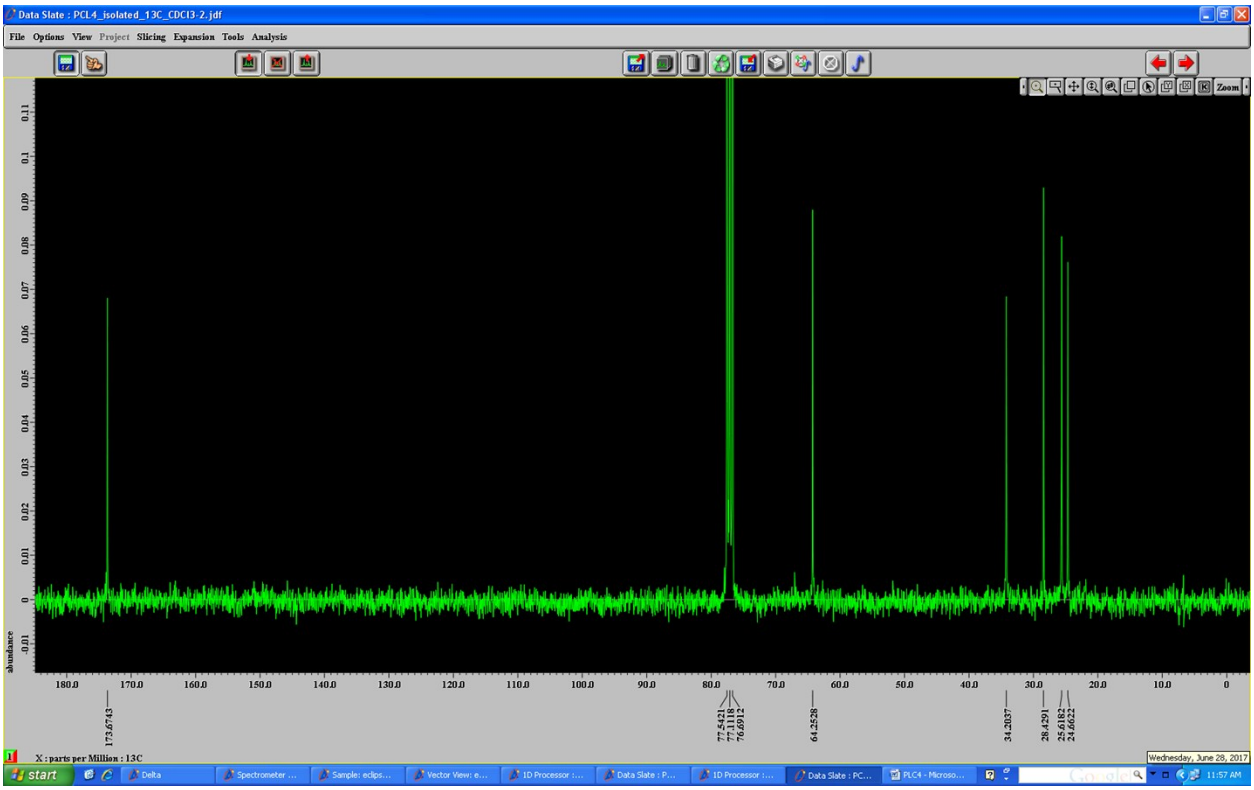
(f)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X : parts per Million : 13C

Figure S1 ^{1}H and ^{13}C NMR spectra of polyesters: (**a**) ^{1}H NMR of PLLA (trial 1 in Table 1); (**b**) ^{13}C NMR of PLLA (trial 1 in Table 1); (**c**) ^{1}H NMR of PDLA (trial 37 in Table 2); (**d**) ^{13}C NMR of PDLA (trial 37 in Table 2); (**e**) ^{1}H NMR of PCL (trial 3 in Table 3); (**f**) ^{13}C NMR of PCL (trial 3 in Table 3).

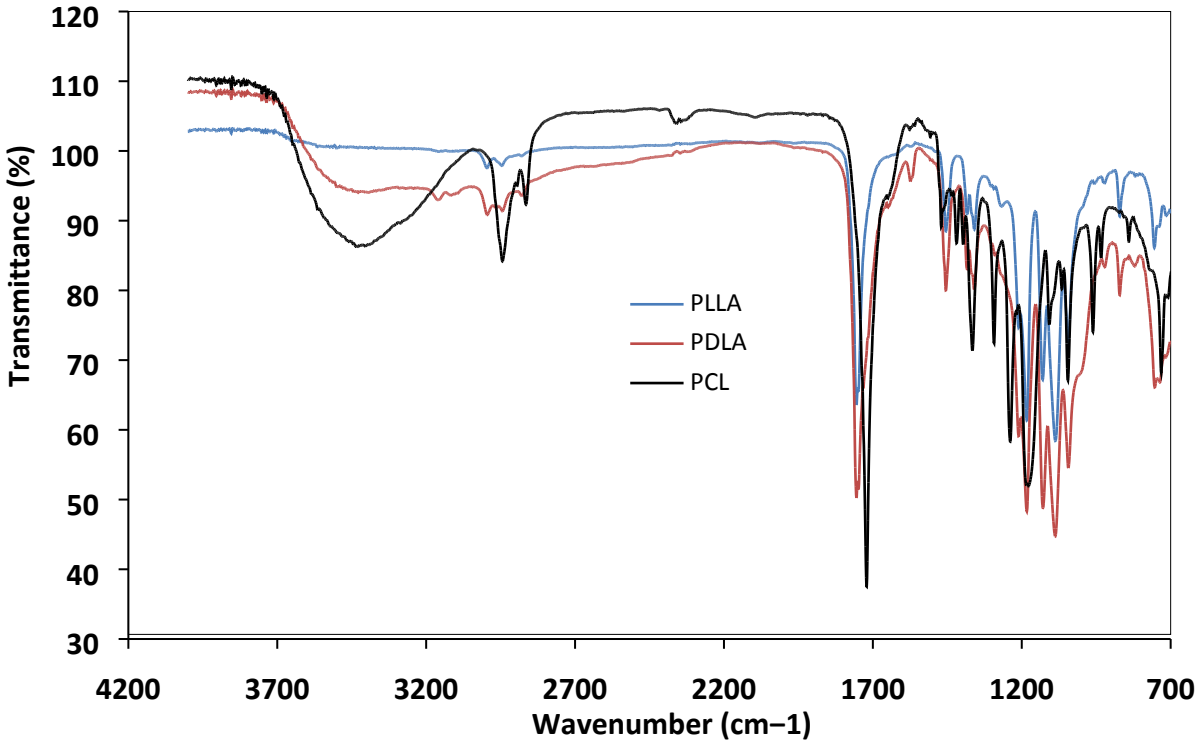

Figure S2 FT-IR spectra of polyesters.

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