Electronic Supplementary Material (ESI) for RSC Advances

Ring-Opening Polymerization of Lactones using Supramolecular Organocatalysts, Under Simple Conditions

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Contents

1/ Optimization of the H-bond Acceptor Catalyst

To define the appropriate amine that could activate together with the phenol catalyst, preliminary ROP were achieved with δ-VL (2M in CH_2Cl_2), with a 5 mol % catalytic loading, in the presence of BPM as an initiator (5 mol %), in 6 h (except Sp in 24 h) (Table S1).

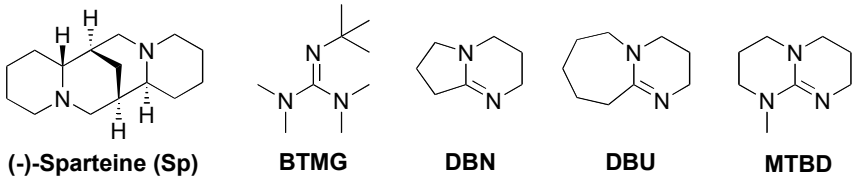


Table S1. Screening of the catalytic system (H-bond Donor + Acceptor) on the ROP of δ-VL, based on the percentage of conversion after 6 h.[a,b]

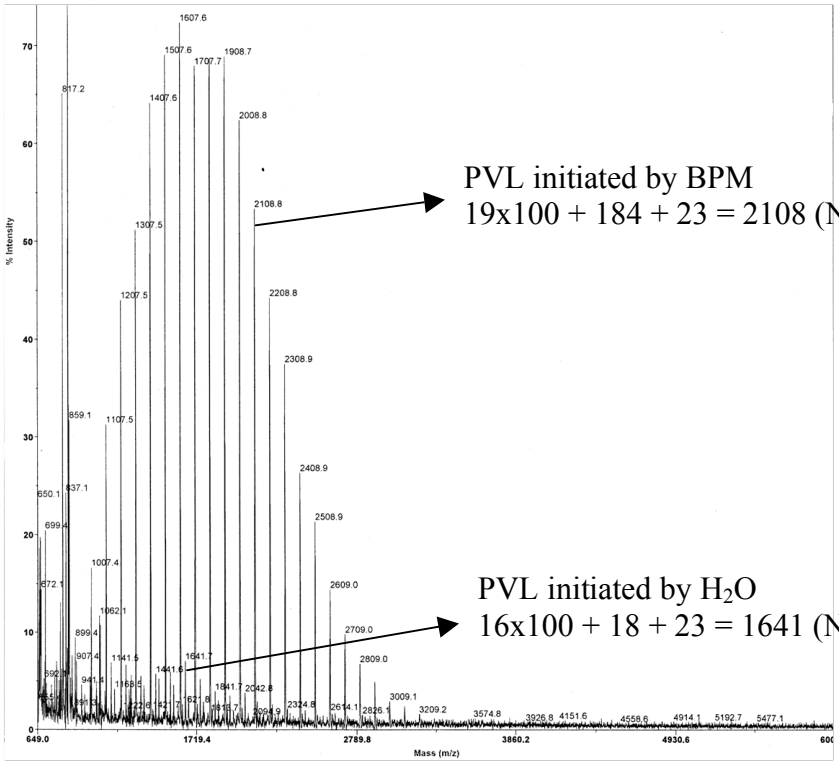
Run	H-Bond Donor	Sp[c]	BTMG	DBN	DBU	MTBD
1	None, no BPM	12	26	23	24	10
2	None	15	30	26	34	24
3	**TU**	42	66	80	100	75
4	**TUS**	28	41	35	59	30
5	**1d**	12	43	17	73	50
6	**1f**	18	37	21	73	45
7	**1g**	12	52	21	54	48
8	**2a**	30	31	29	73	43
9	**2b**	30	40	39	78	53
10	**2c**	45	38	19	70	42
11	**3a**	26	48	22	84	40
12	**3b**	26	50	29	84	45

[a] Conditions of ROP: δ-Valerolactone (2 M in dichloromethane), H-bond donor catalyst (5 mol %), amine/amidine/guanidine cocatalyst (5 mol %), 4-biphenylmethanol as an initiator (5 mol %), 4 Å molecular sieves, 20 °C, 6 h. [b] Determined by ^{1}H NMR ($CDCl_3$). [c] Reaction during 24 h.

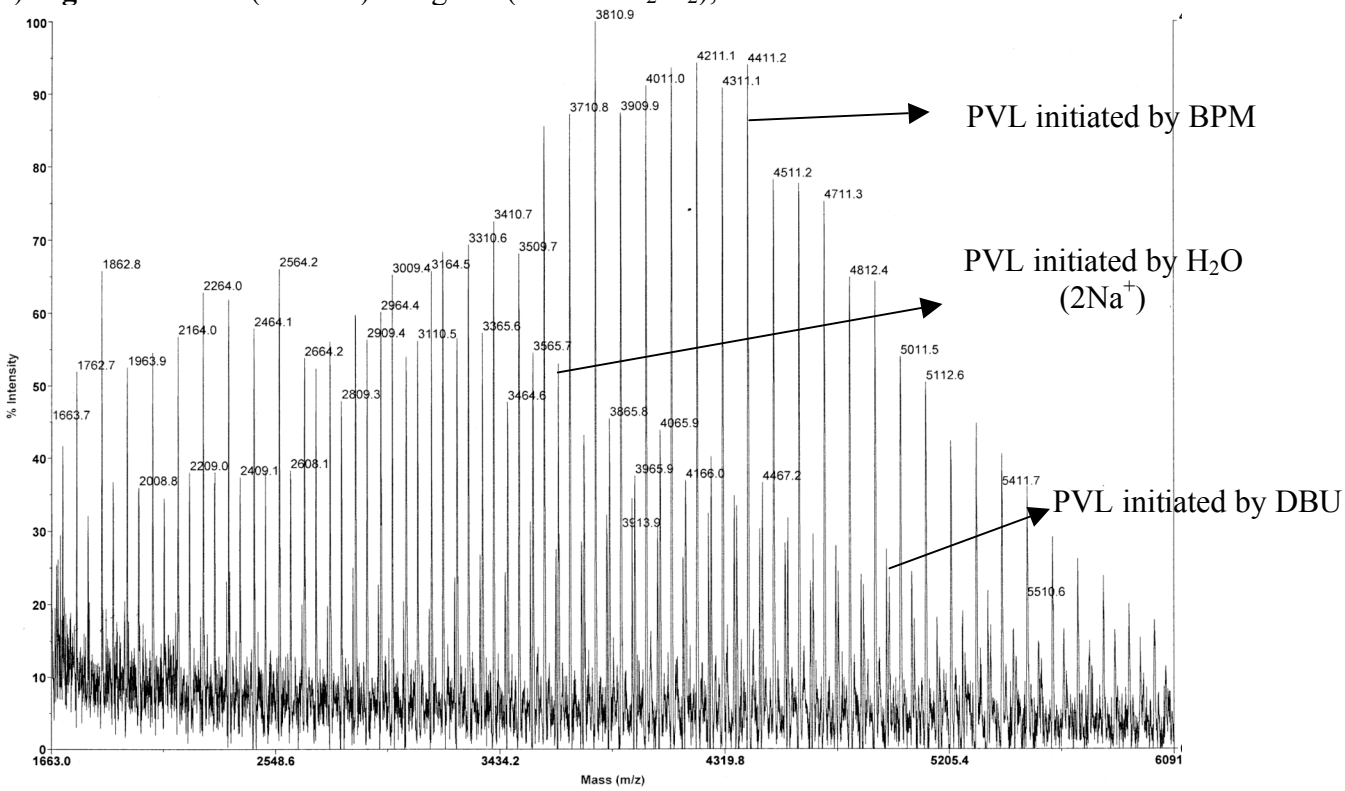
Note: $pK_{A\ CH3CN}$ values: Sp (21.7), BTMG (23.6), DBN (23.9), DBU (24.3), MTBD (25.4) and phenols (26-28).

2/ Mass Spectra of representative polylactones obtained from the general procedure (Tables 1 and 2)

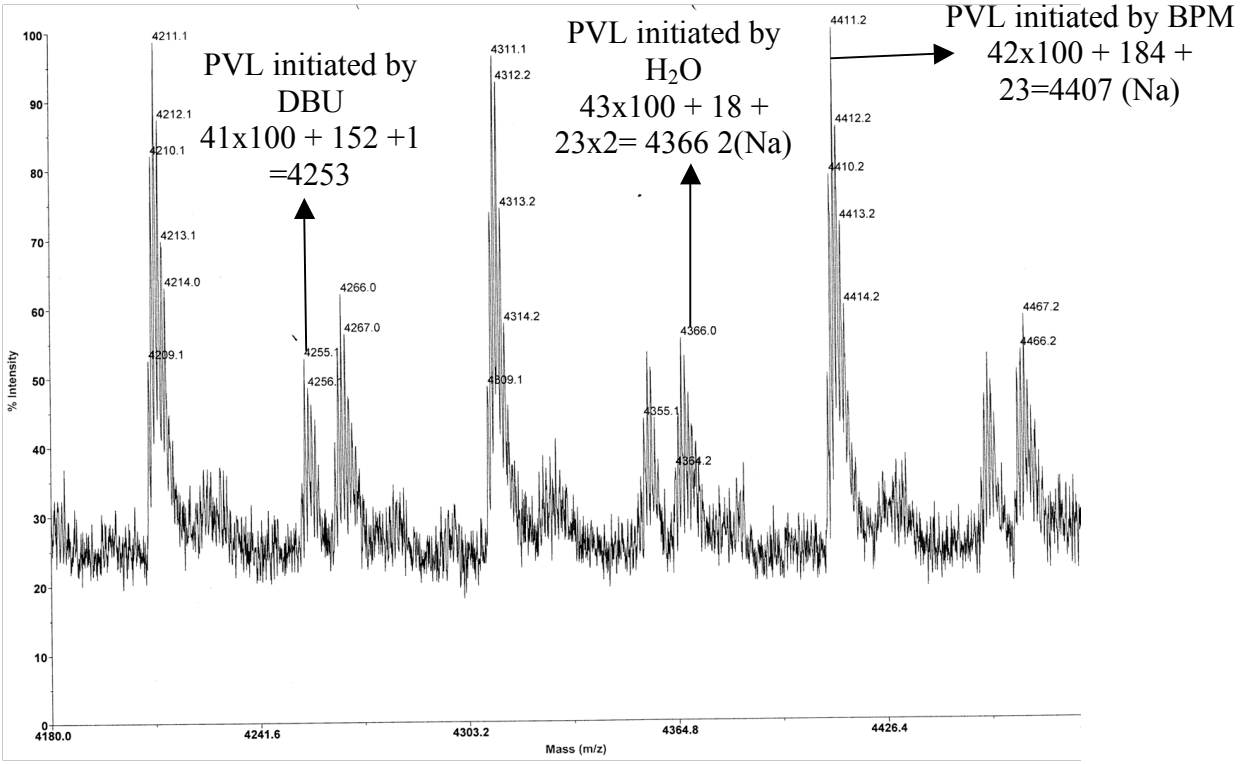
a) **Figure S1**: PVL (**Run 31**) using VL (4M in CH_2Cl_2), DBU/5-methoxyresorcinol/BPM 5:5:5



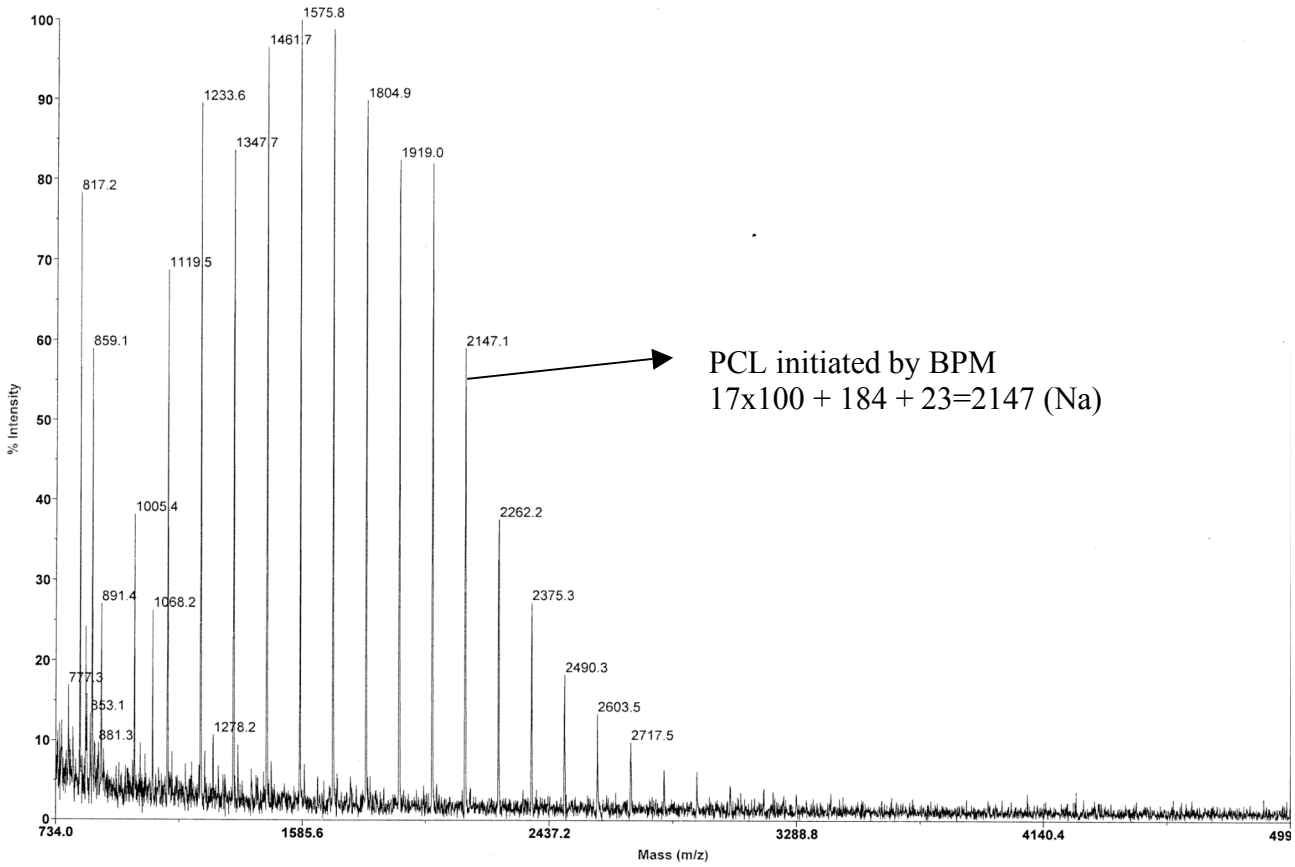
b) **Figure S2**: PVL (**Run 22**) using VL (4M in CH_2Cl_2), DBU/Catechol/BPM 5:5:1



Enlargement Figure S2



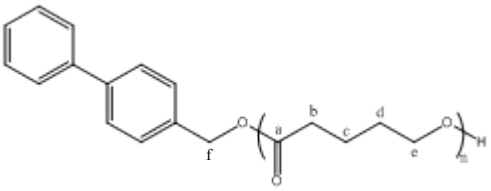
c) **Figure S3**: PCL using CL (4M in CH_2Cl_2), DBU/4-*tert*-butylcatechol/BPM 5:5:5



3/ ^{13}C NMR and ^{1}H NMR ($CDCl_3$)

of representative polymers PVL and PCL (Tables 1 and 2)

Figure S4:
^{13}C NMR of PVL (**Run 31**) from VL (4M, CH_2Cl_2), DBU/5-methoxyresorcinol/BPM 5:5:5



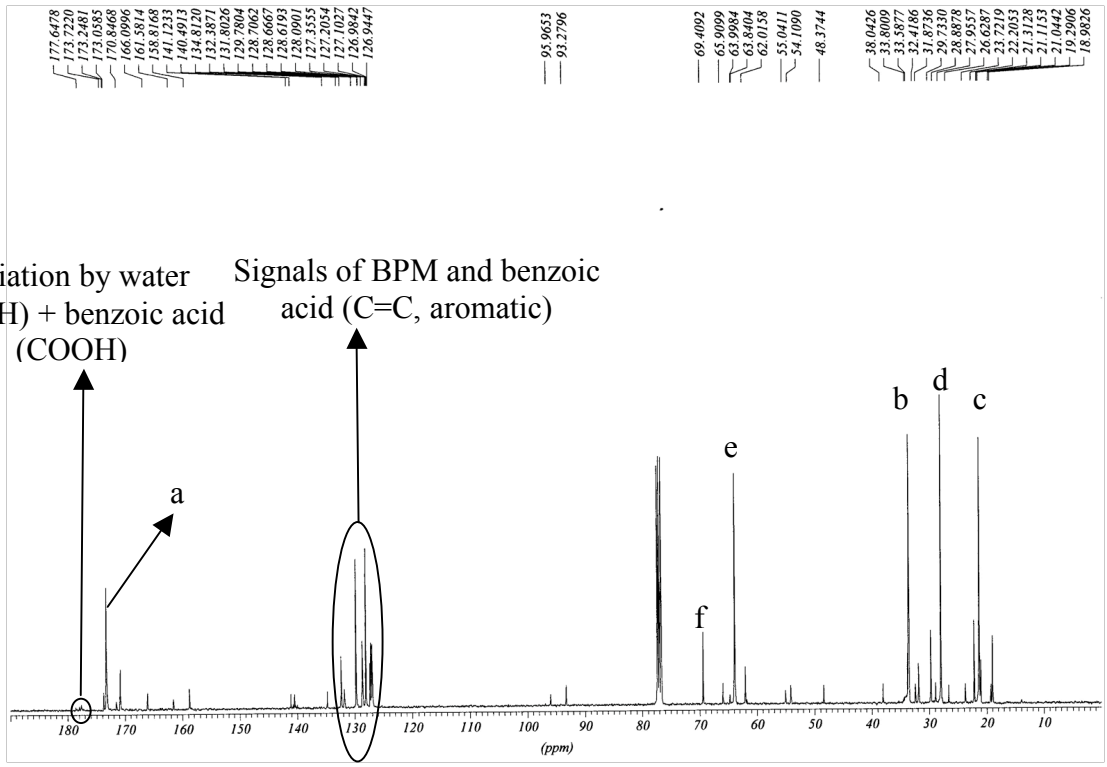


Figure S5:
^{1}H NMR of PVL (**Run 31**) from VL (4M, CH_2Cl_2), DBU/5-methoxyresorcinol/BPM 5:5:5

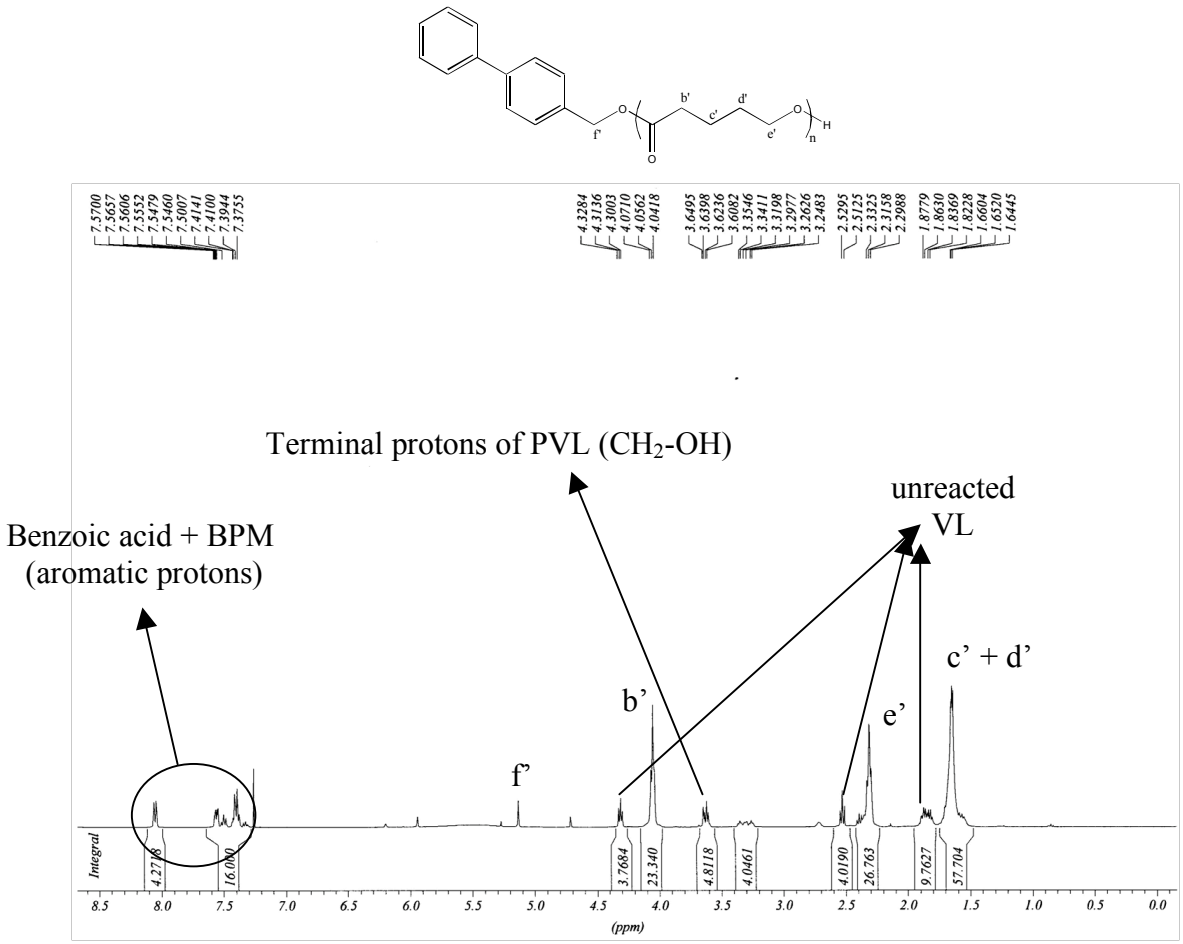


Figure S6: ^{13}C NMR of PCL from CL (4M in CH_2Cl_2), DBU/4-*tert*-butylcatechol/BPM 5:5:5

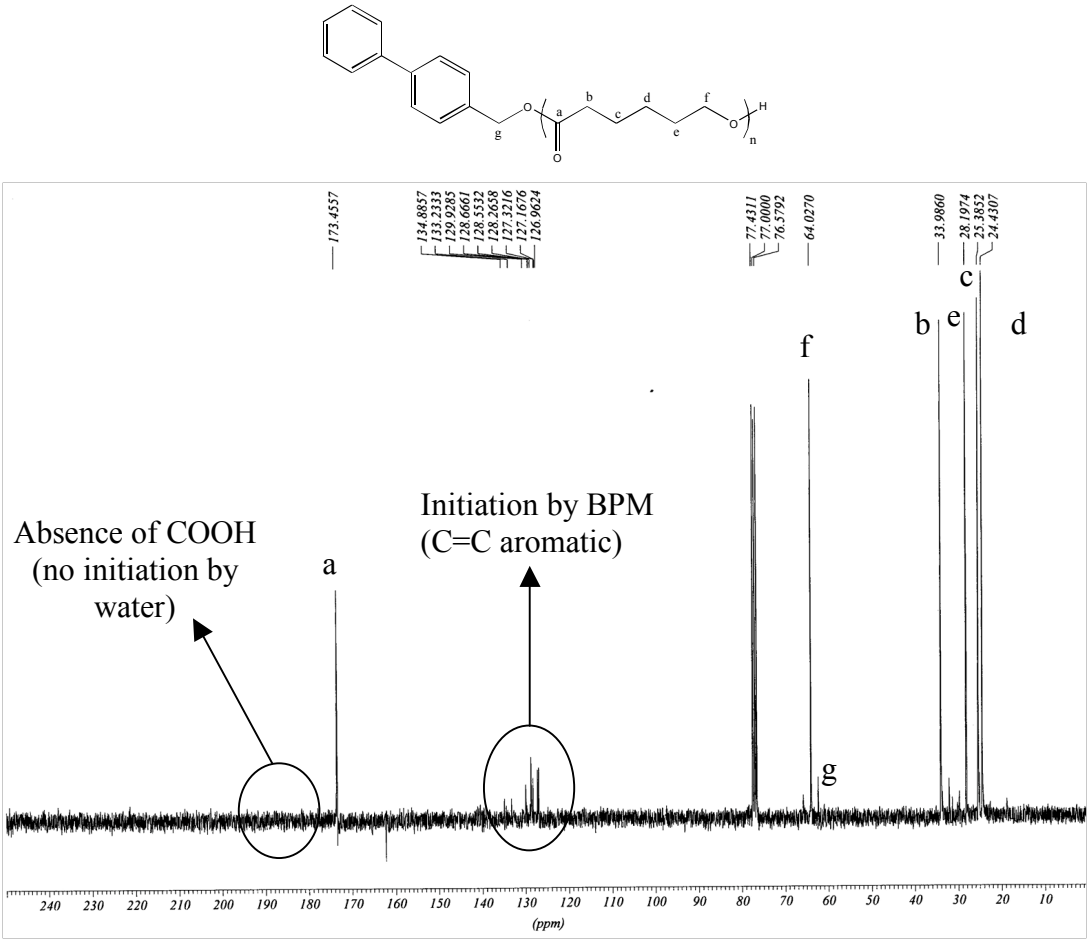
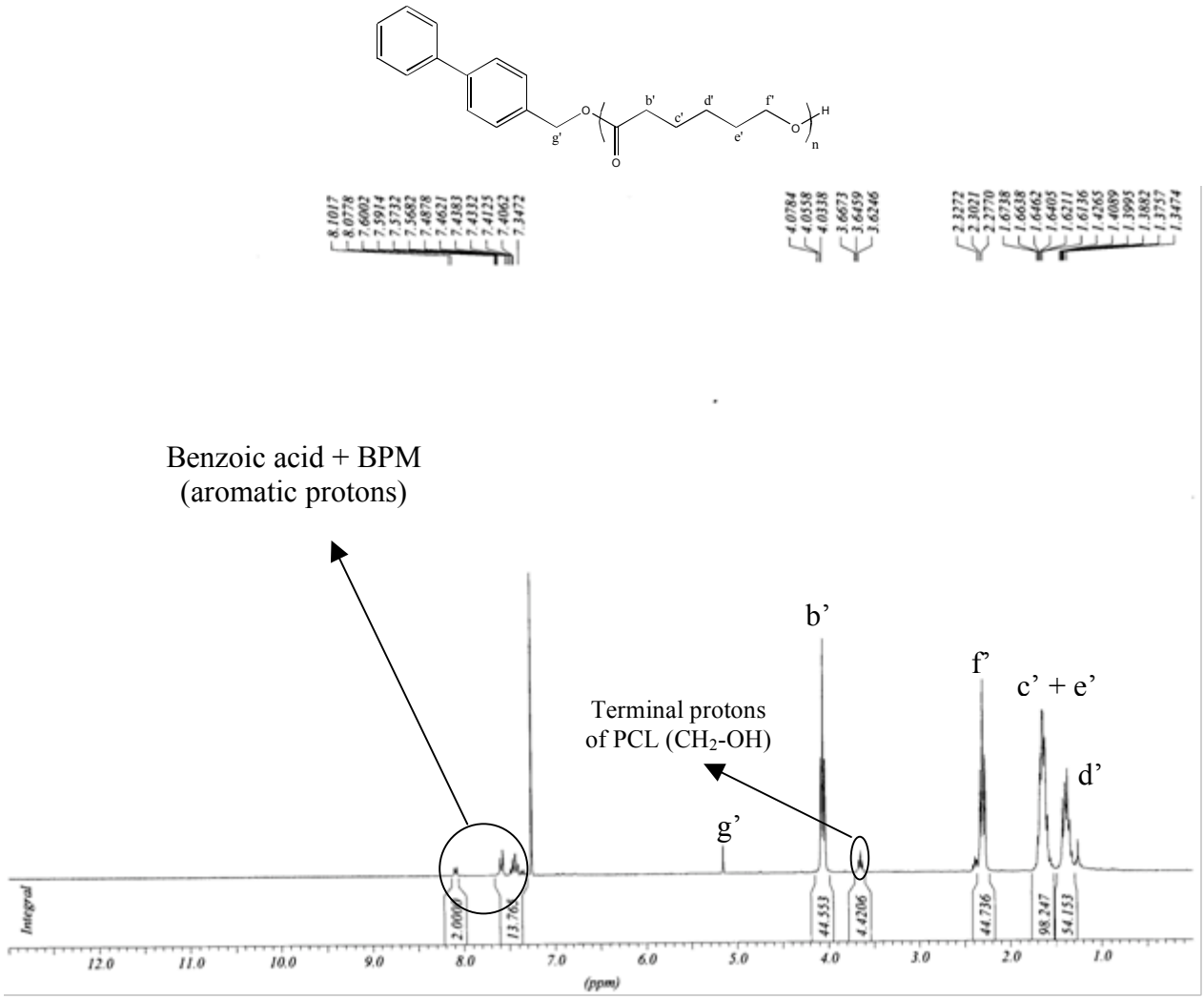
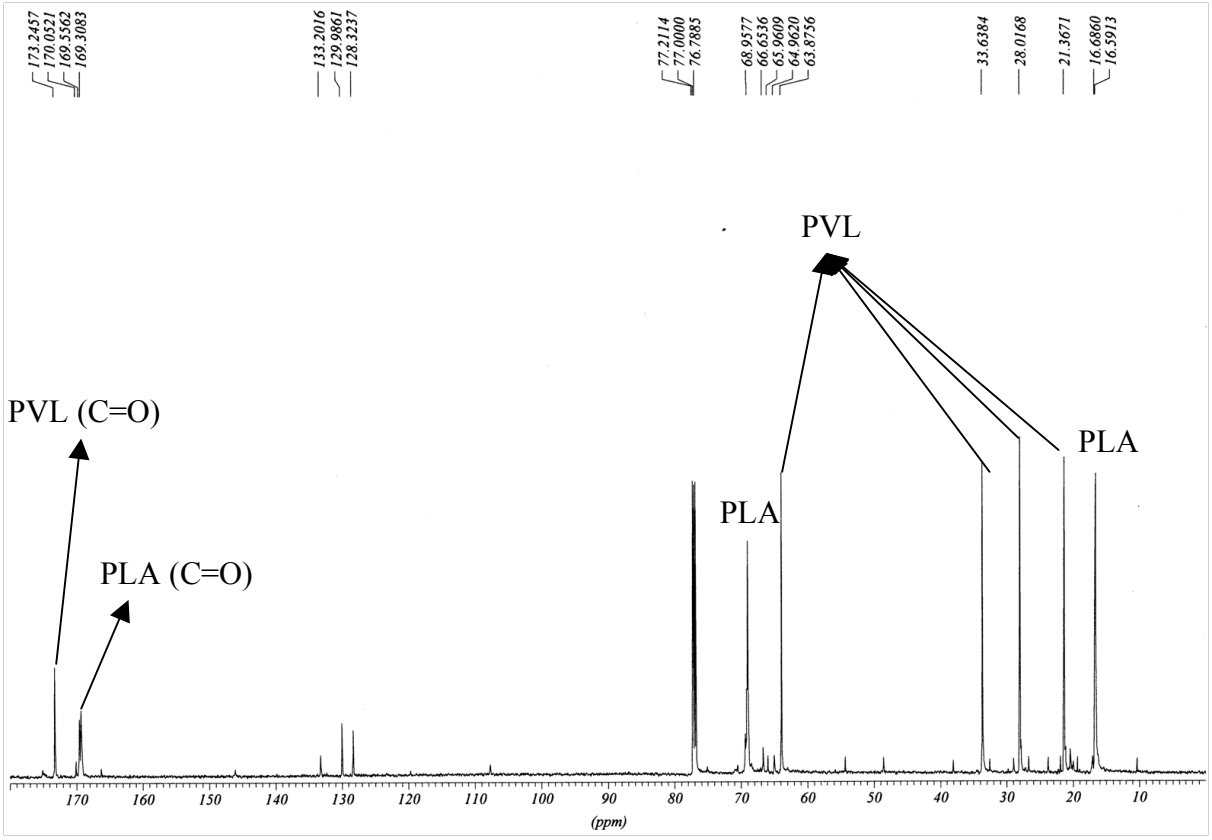


Figure S7: ^{1}H NMR of PCL from CL (4M in CH_2Cl_2), DBU/4-*tert*-butylcatechol/BPM 5:5:5



4/ ^{13}C NMR and ^{1}H NMR ($CDCl_3$) of representative copolymers (PVL-b-PLA) and (PCL-b-PLA) (Table 3)

Figure S8: ^{13}C NMR of copolymer (PVL-b-PLA), from ROP in the presence of propan-1-ol /2-(trifluoromethyl)phenol/DBU 5:5:5, **with ZOOM**



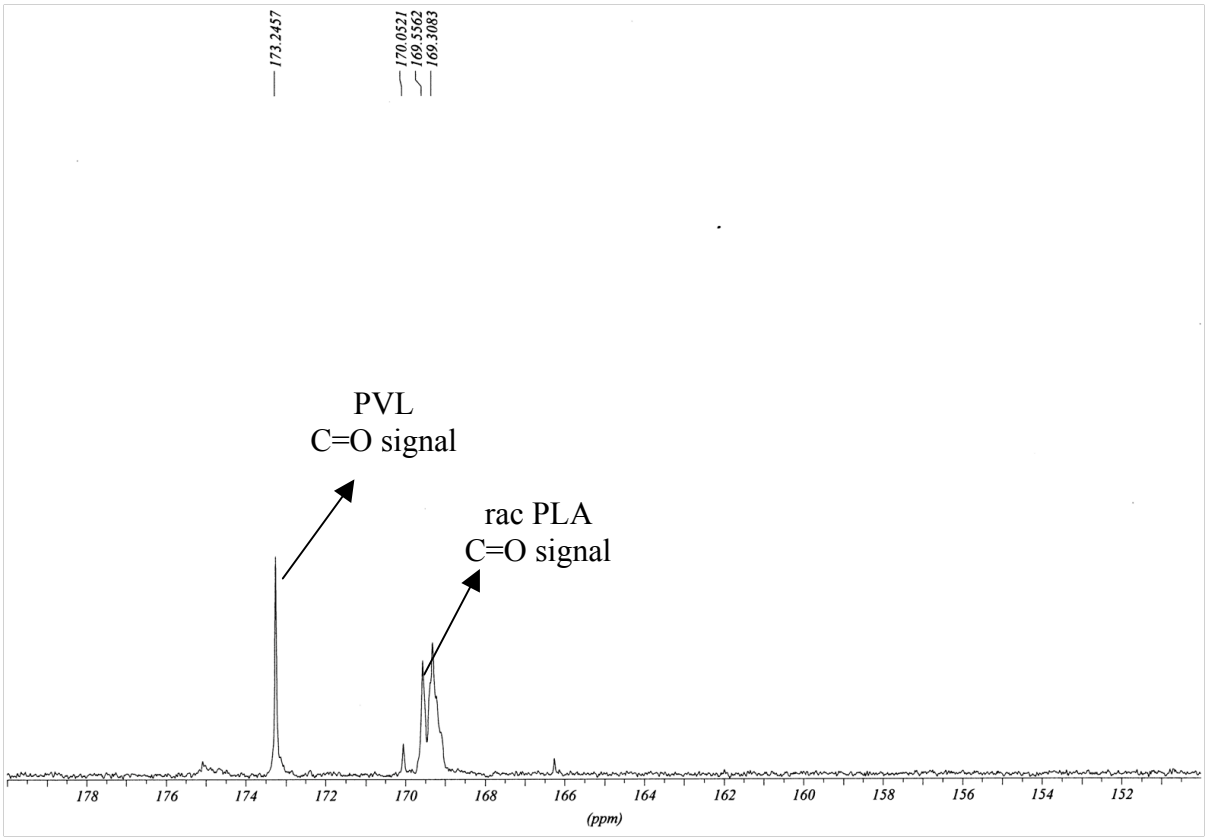


Figure S9: ^{1}H NMR of copolymer (PVL-b-PLA),
from ROP in the presence of propan-1-ol/2-(trifluoromethyl)phenol/DBU 5:5:5

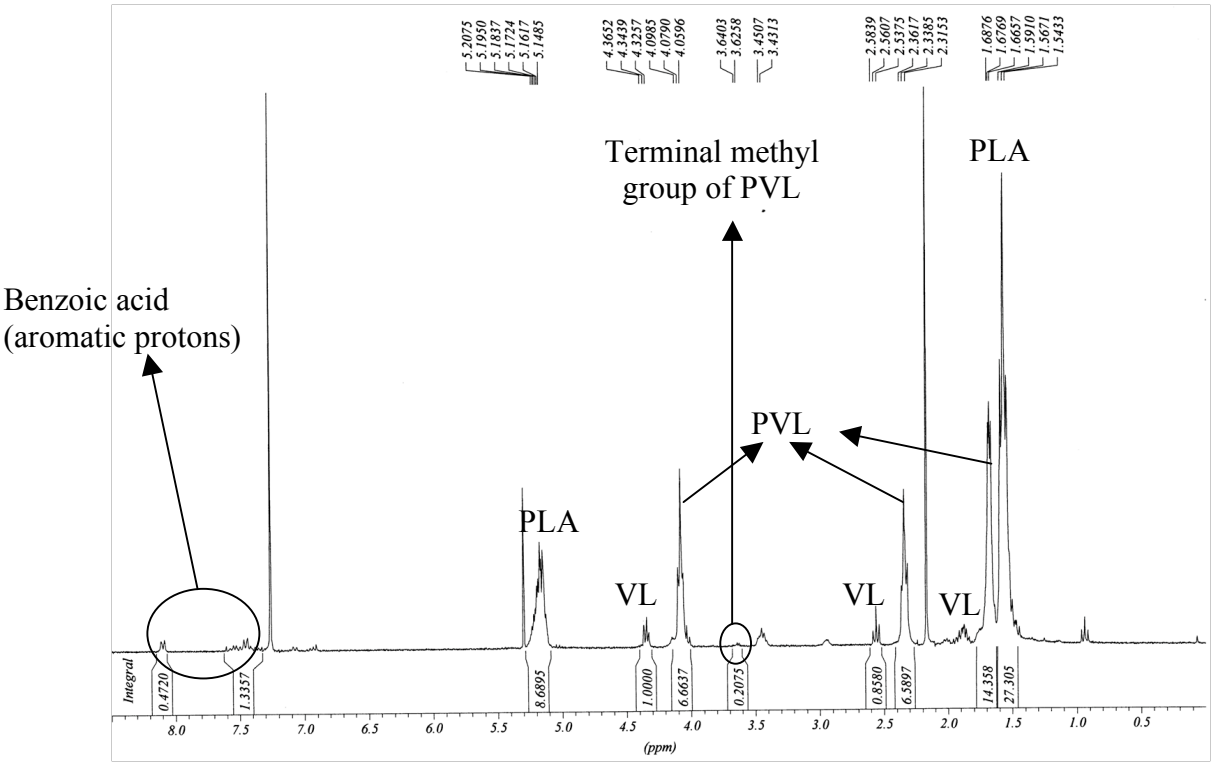


Figure S10: ^{1}H NMR of copolymer (PVL-b-PLA),
from ROP in the presence of propan-1-ol/4-*tert*-butylcatechol /DBU 5:5:5

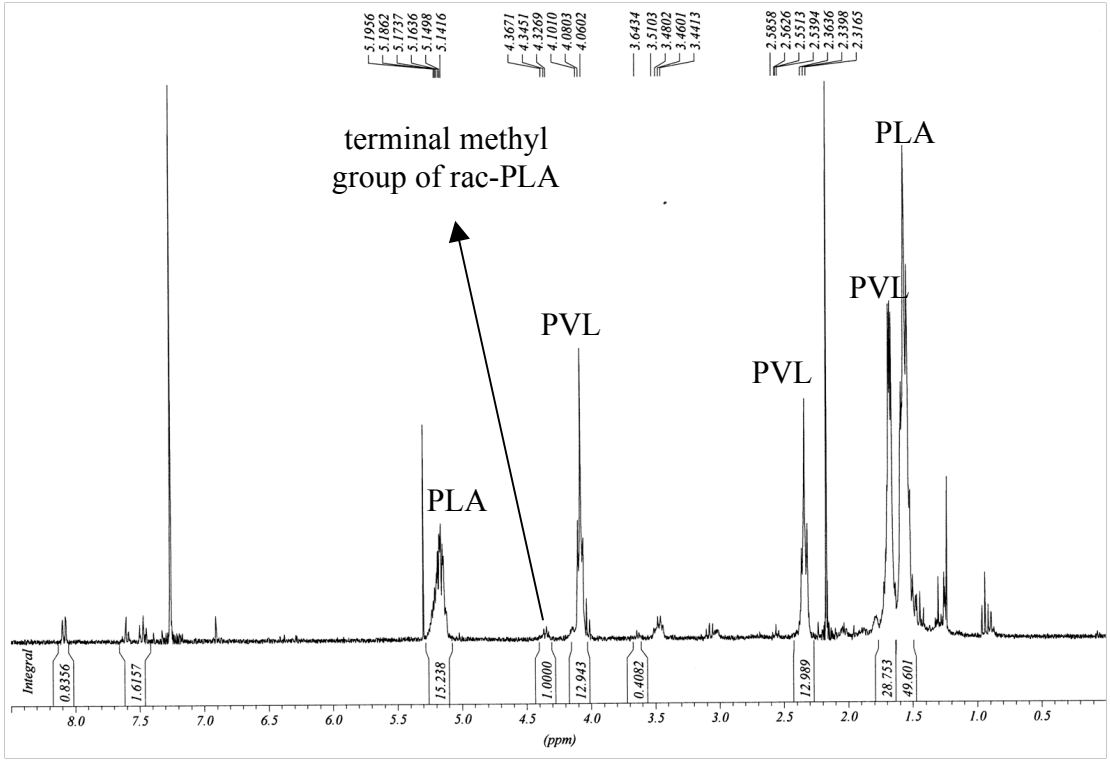
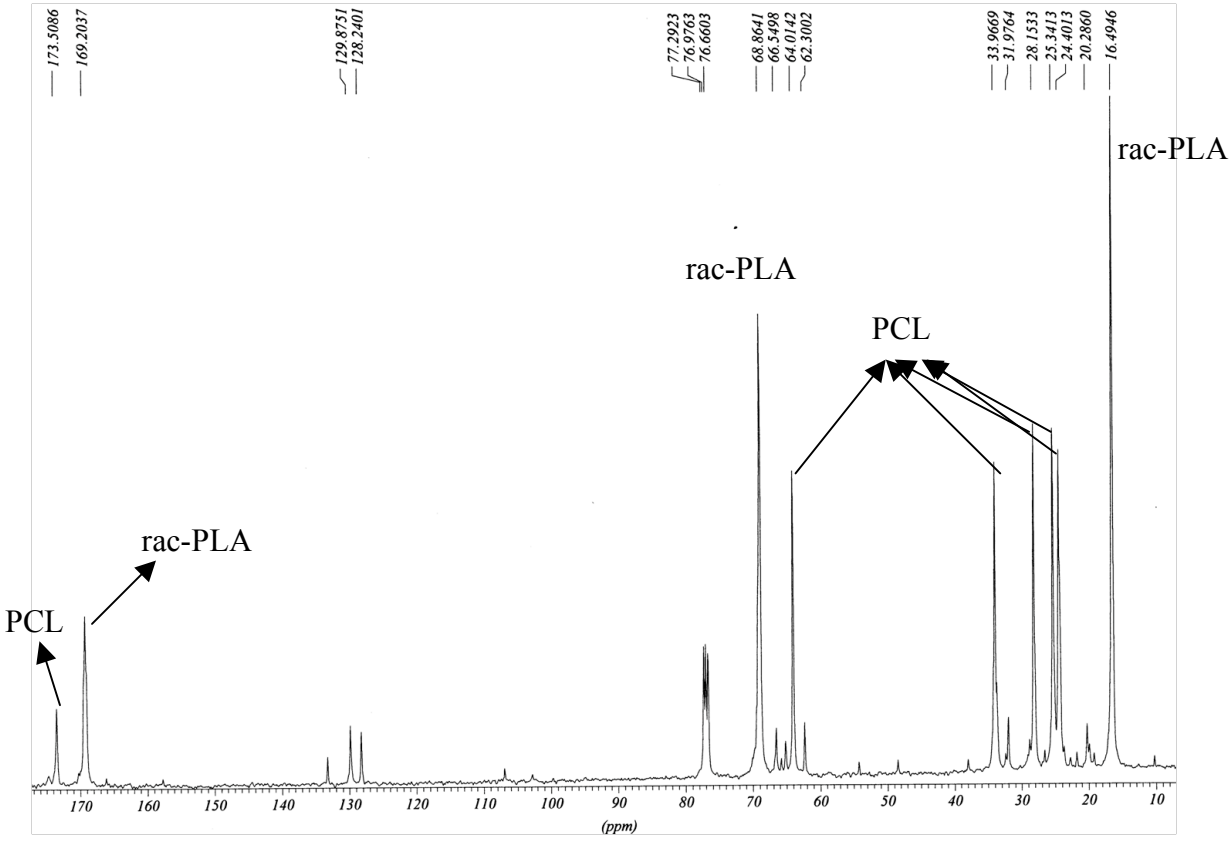


Figure S11: ^{13}C NMR of copolymer (PCL-block-PLA)
from ROP in the presence of propan-1-ol /4-*tert*-butylcatechol/DBU 5:5:5, **with ZOOM**



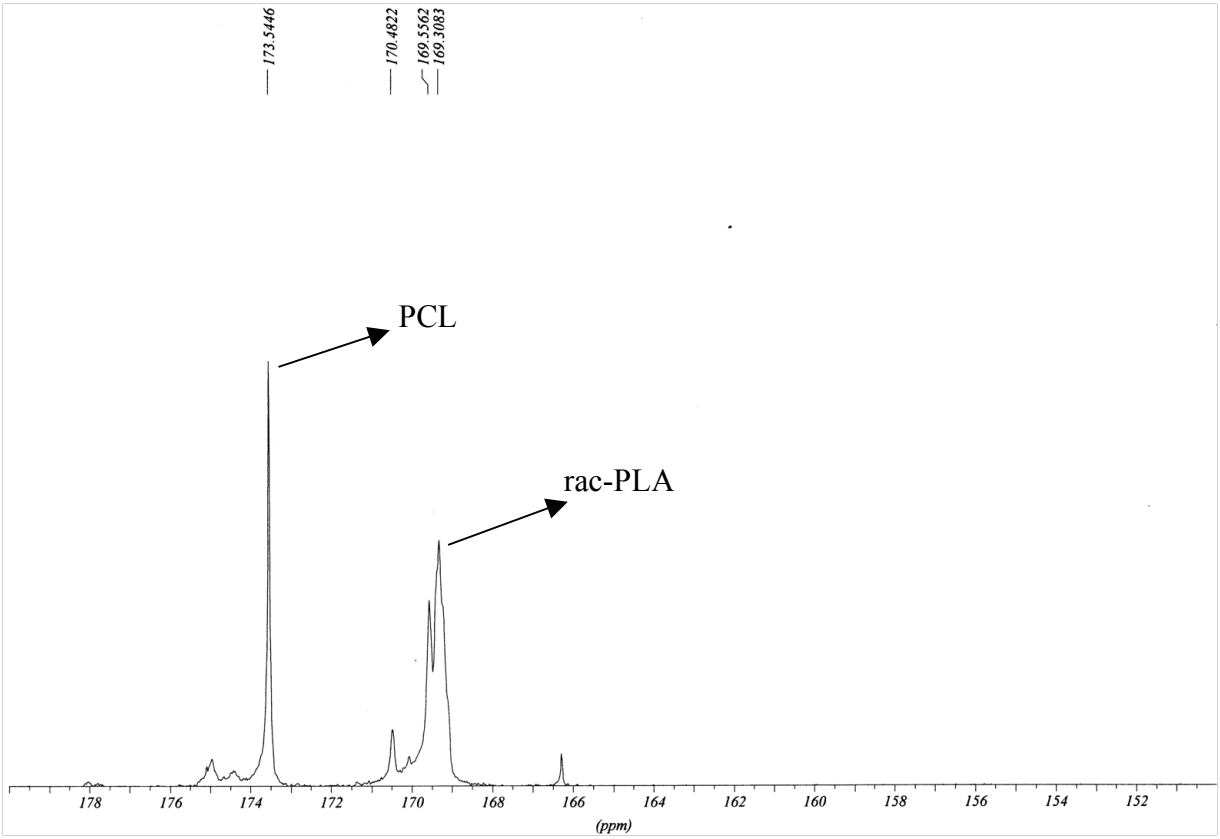
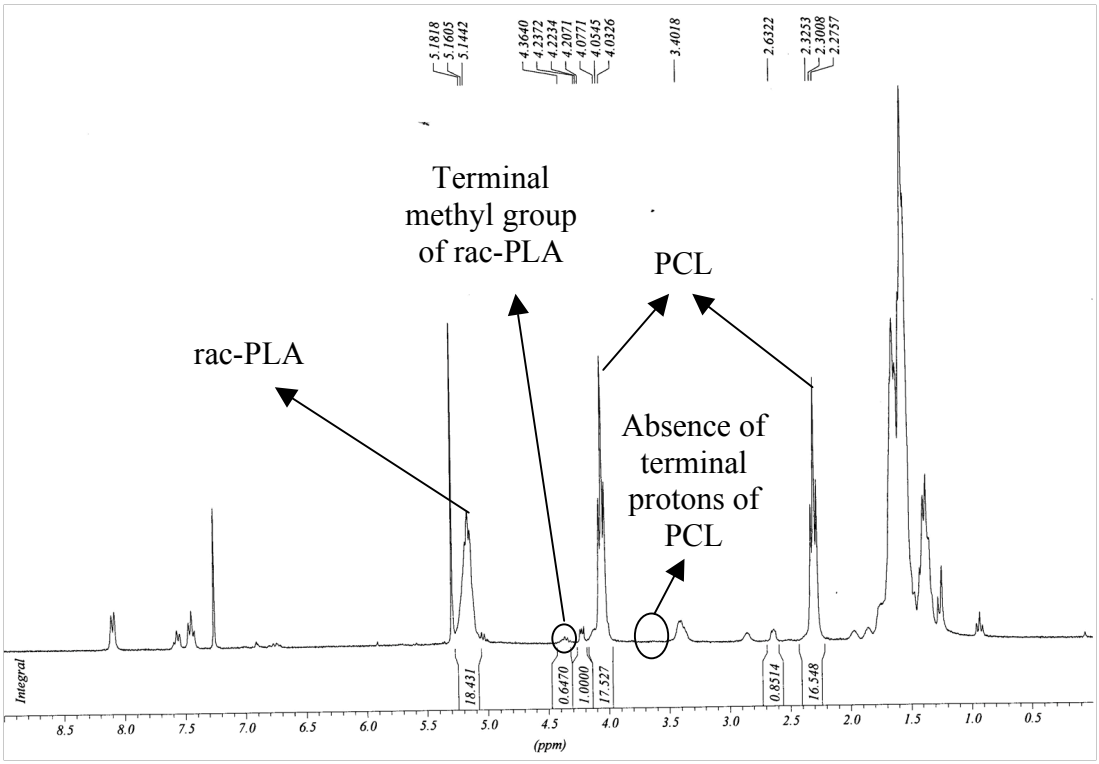
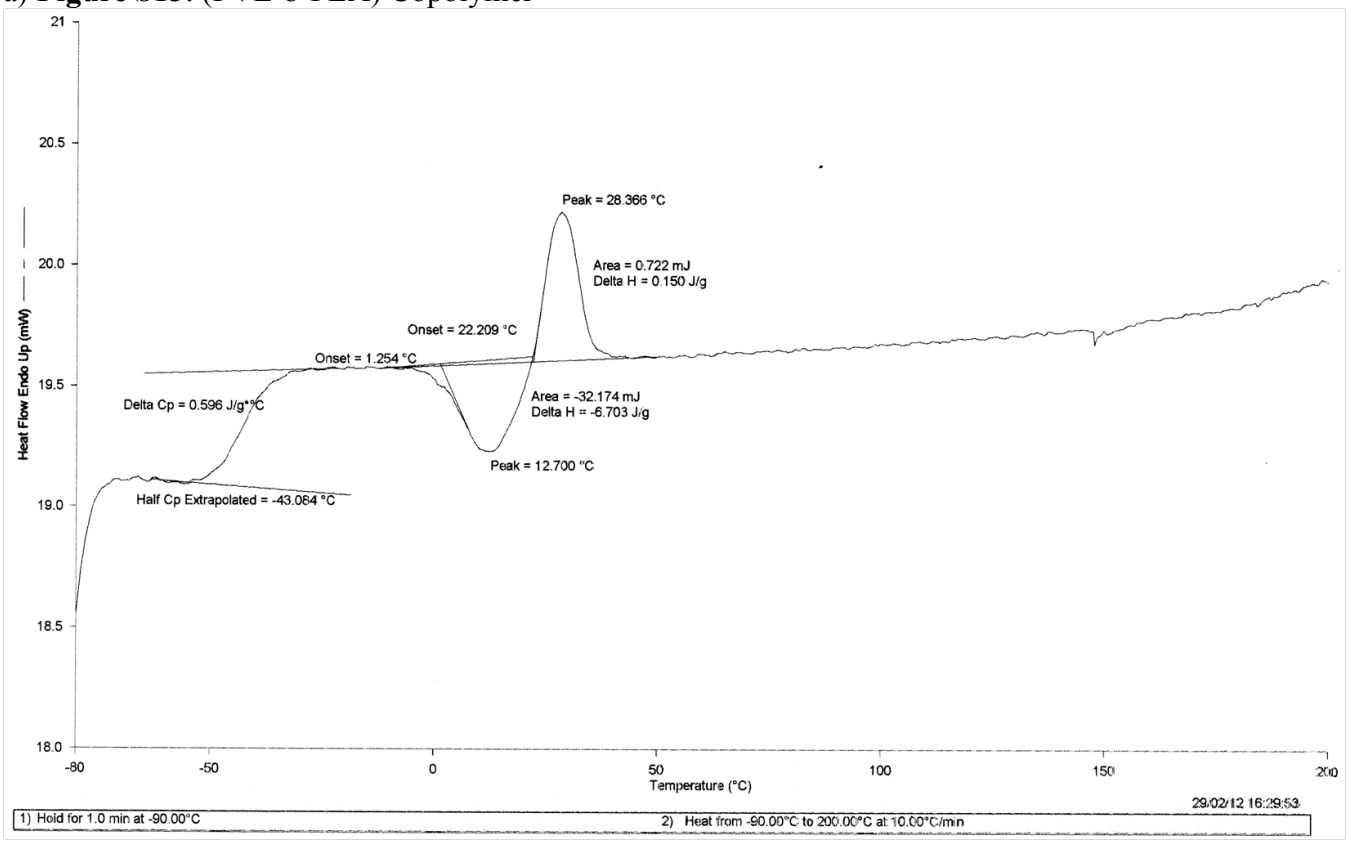


Figure S12: ^{1}H NMR of copolymer (PCL-block-PLA)
from ROP in the presence of propan-1-ol /resorcinol/DBU 5:5:5

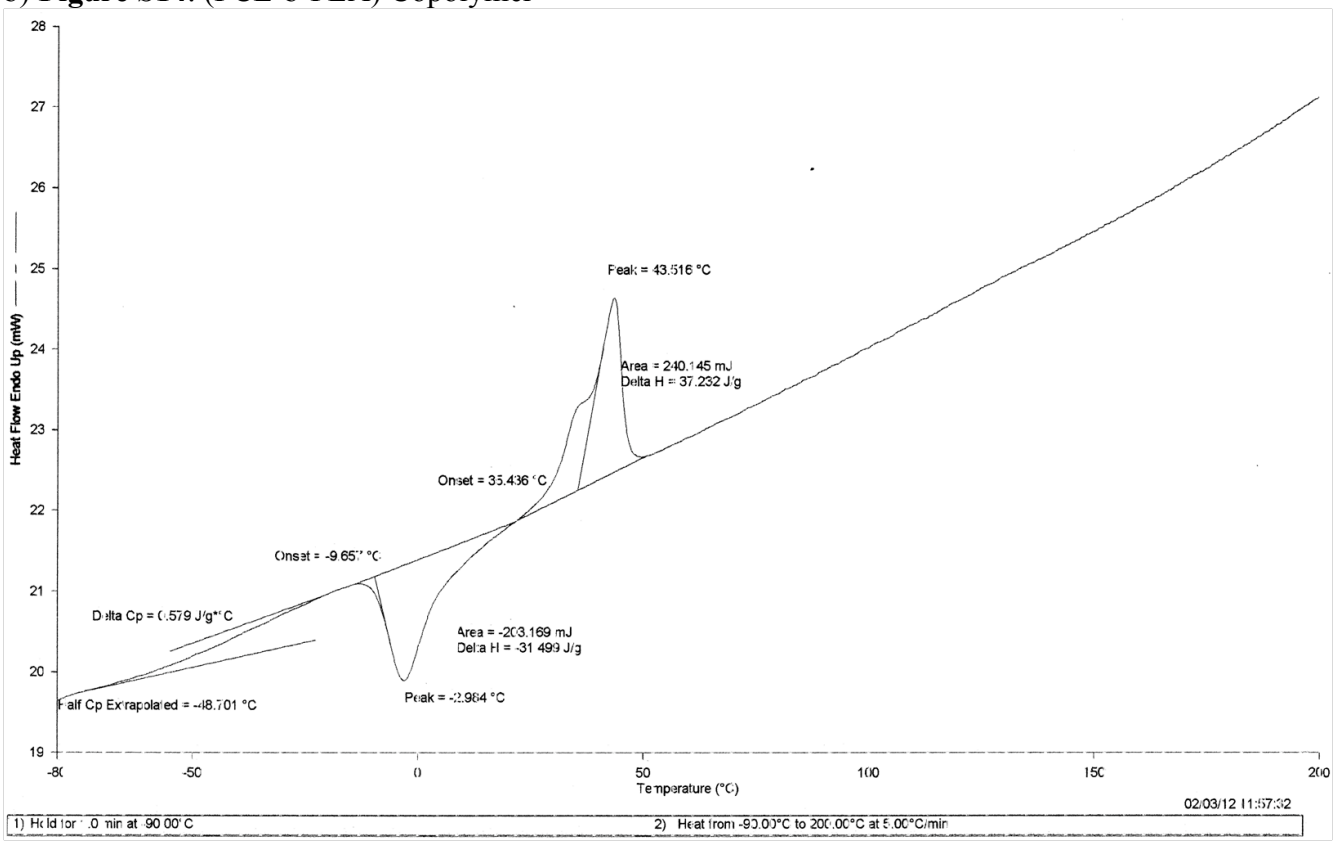


5/ DSC Analyses of representative copolymers (PVL-b-PLA) and (PCL-b-PLA)

a) **Figure S13**: (PVL-b-PLA) Copolymer

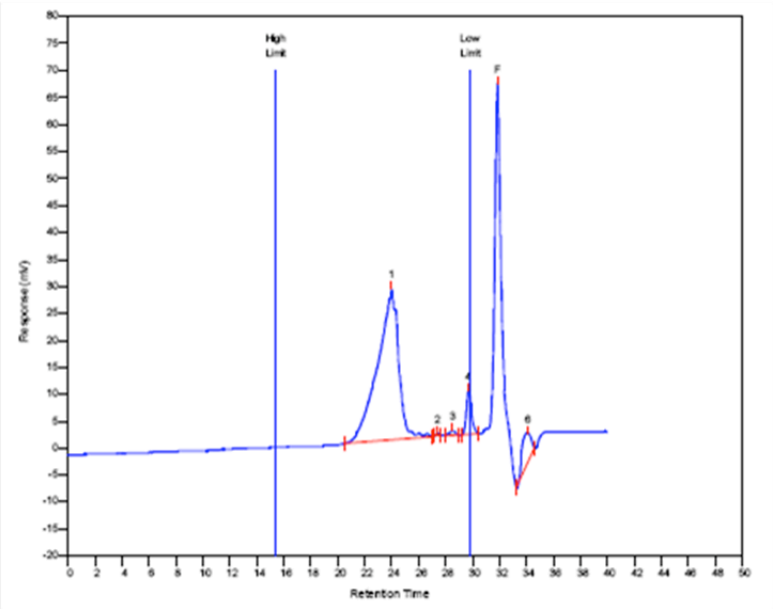


b) **Figure S14**: (PCL-b-PLA) Copolymer



6 / SEC Analyses of representative polymers PVL, PCL, (PVL-*b*-PLA) and (PCL-*b*-PLA)

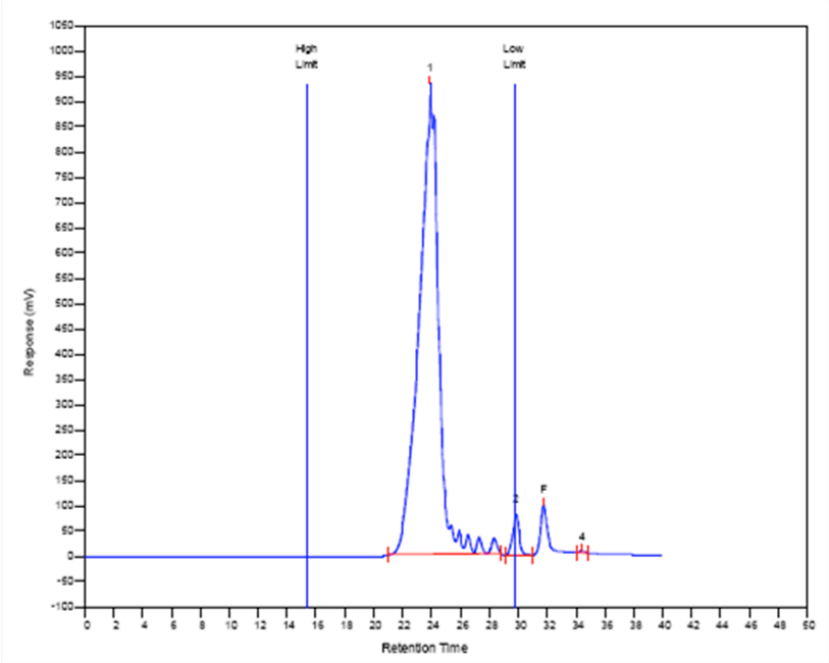
Figure S15: SEC (RI) of PVL from ROP in the presence of BPM /5-methoxyresorcinol/DBU 5:5:5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1444	1618	1792	2013	2291	1762	1.10754

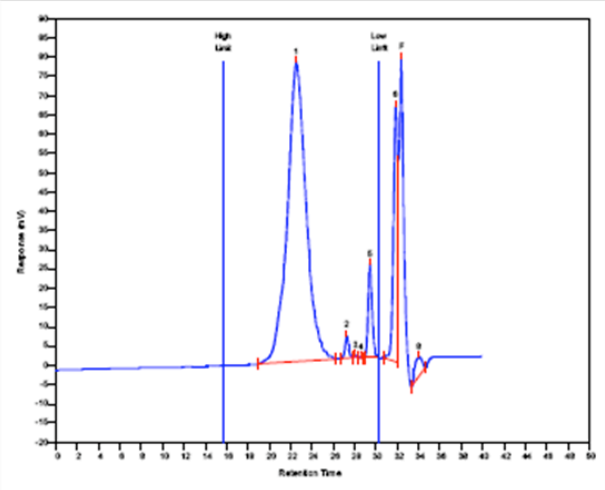
Figure S16: SEC (UV) of PVL from ROP in the presence of BPM /5-methoxyresorcinol/DBU 5:5:5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	1442	1401	1572	1712	1855	1551	1.12206

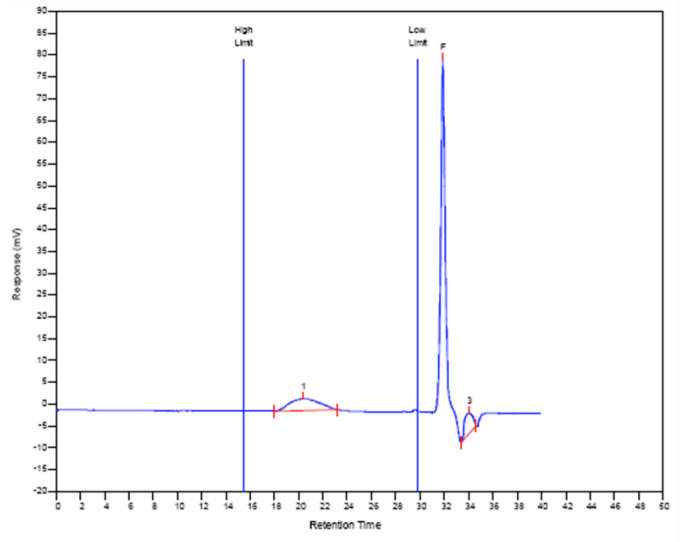
Figure S17: SEC (RI) of first block PVL
from ROP in the presence of propan-1-ol/2-(trifluoromethyl)phenol/DBU 5:5:5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	2877	2680	3099	3685	4578	3027	1.15634

Figure S18: SEC (RI) of copolymer (PVL-b-PLA)
from ROP in the presence of propan-1-ol/2-(trifluoromethyl)phenol/DBU 5:5:5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6684	5550	7358	9741	12336	7043	1.32577

Figure S19: SEC (UV) of copolymer (PVL-b-PLA)
from ROP in the presence of propan-1-ol/2-(trifluoromethyl)phenol/DBU 5:5:5

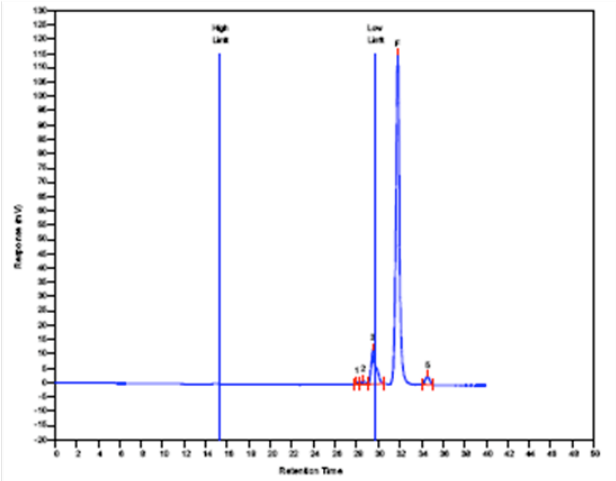
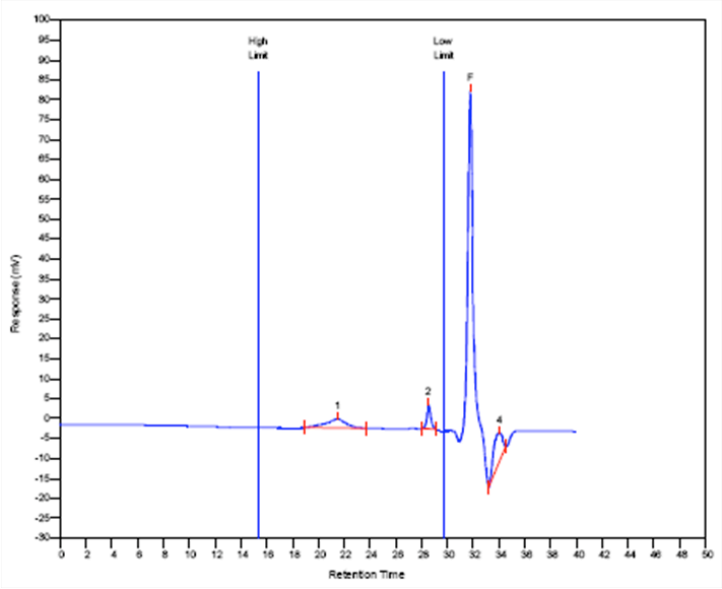


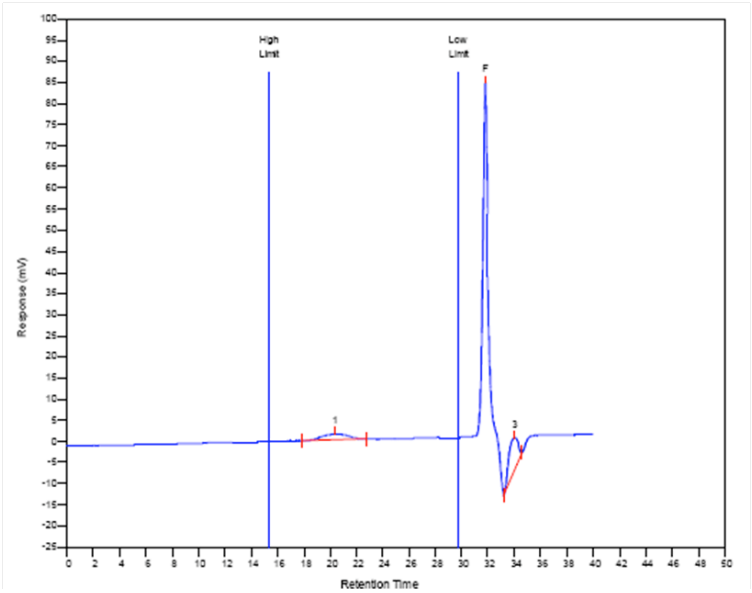
Figure S20: SEC (RI) of first block PCL
from ROP in the presence of propan-1-ol/4-*tert*-butylcatechol/DBU 5:5:5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	3750	3948	4577	5436	6499	4466	1.15932
2	272	269	270	272	273	270	1.00372
3	0	0	0	0	0	0	0
4	8	7	7	8	8	7	1

Figure S21: SEC (RI) of copolymer (PCL-*b*-PLA)
from ROP in the presence of propan-1-ol/4-tert-butylcatechol/DBU 5:5:5



MW Averages

Peak No	Mp	Mn	Mw	Mz	Mz+1	Mv	PD
1	6407	6051	7434	9296	11577	7193	1.22856
2	0	0	0	0	0	0	0
3	8	7	7	8	8	7	1

Figure S22: SEC (UV) of copolymer (PCL-b-PLA)
from ROP in the presence of propan-1-ol/4-tert-butylcatechol /DBU 5:5:5