Electronic Supplementary Information

Lead calix[n]arenes (n=4, 6, 8): Structures and ring opening homo-/co-polymerization capability for cyclic esters.

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Crystallography

Figure S1. Two Pb-aryl interactions present result in the formation of the observed dimers for $[Pb_{12}(L^8)_2O_4]\cdot 8.7C_7H_8$ (**4**$\cdot 8.7C_7H_8$). The two Pb-aryl interactions shown are equivalent by symmetry. The Pb-centroid distance is 3.3608(1) Å.

Table S1. Crystal structure data for **1**·2.5MeCN, **2**·14MeCN, **3**·11MeCN, **4**$\cdot 8.7C_7H_8$, **5**, **6**·9.5MeCN, **7**·12MeCN.

ROP studies

Figure S2. Mass spectrum of PCL synthesized with **4**/BnOH (run 19, Table 1).

Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL synthesized with **2**/BnOH (run 17, Table 1).

Figure S4. Mass spectrum of PVL synthesized with **2**/BnOH (run 8, Table 2).

Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PVL synthesized with **3**/BnOH (run 9, Table 2).

Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL-PVL co-polymer synthesized with **3**/BnOH (run 3, Table 3).

Figure S7. Carbonyl range of ^{13}C NMR spectrum ($CDCl_3$, 25 ºC) of PCL-PVL co-polymer synthesized with **3**/BnOH (run 3, Table 3).

Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **1**/BnOH (run 1, Table 4).

Figure S9. Mass spectrum of PLA synthesized with **2**/BnOH (run 2, Table 4).

Figure S10. 2D J-resolved ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **1**/BnOH (run 1, Table 4).

Equation S1. Determination of number-average sequence length for CL

Equation S2. Determination of number-average sequence length for VL.

Equation S3. Determination of the Randomness Character (R).

Crystallography

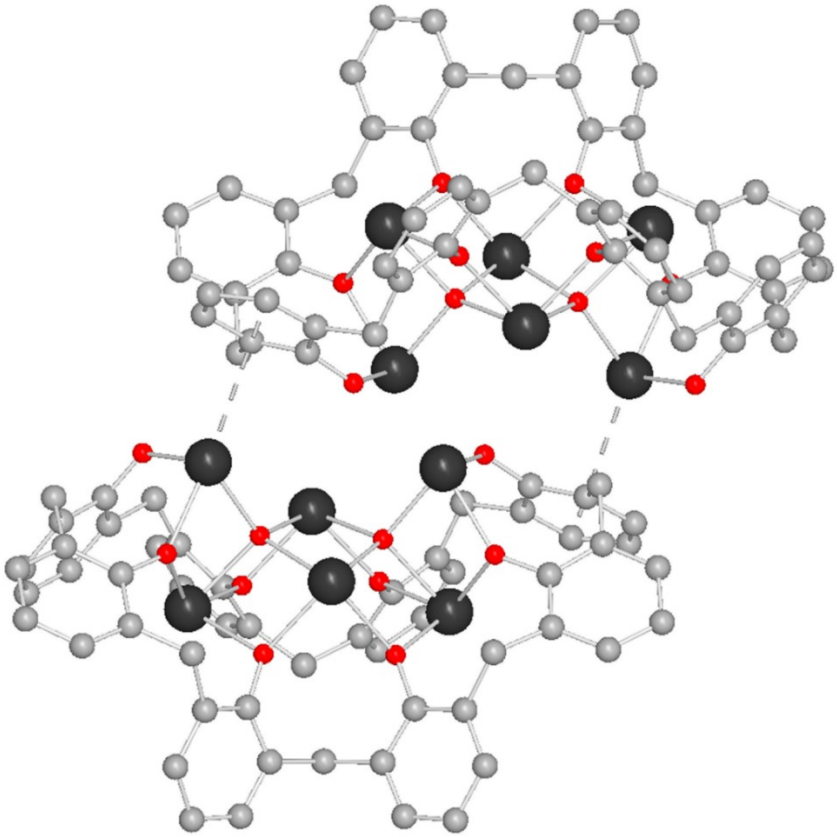

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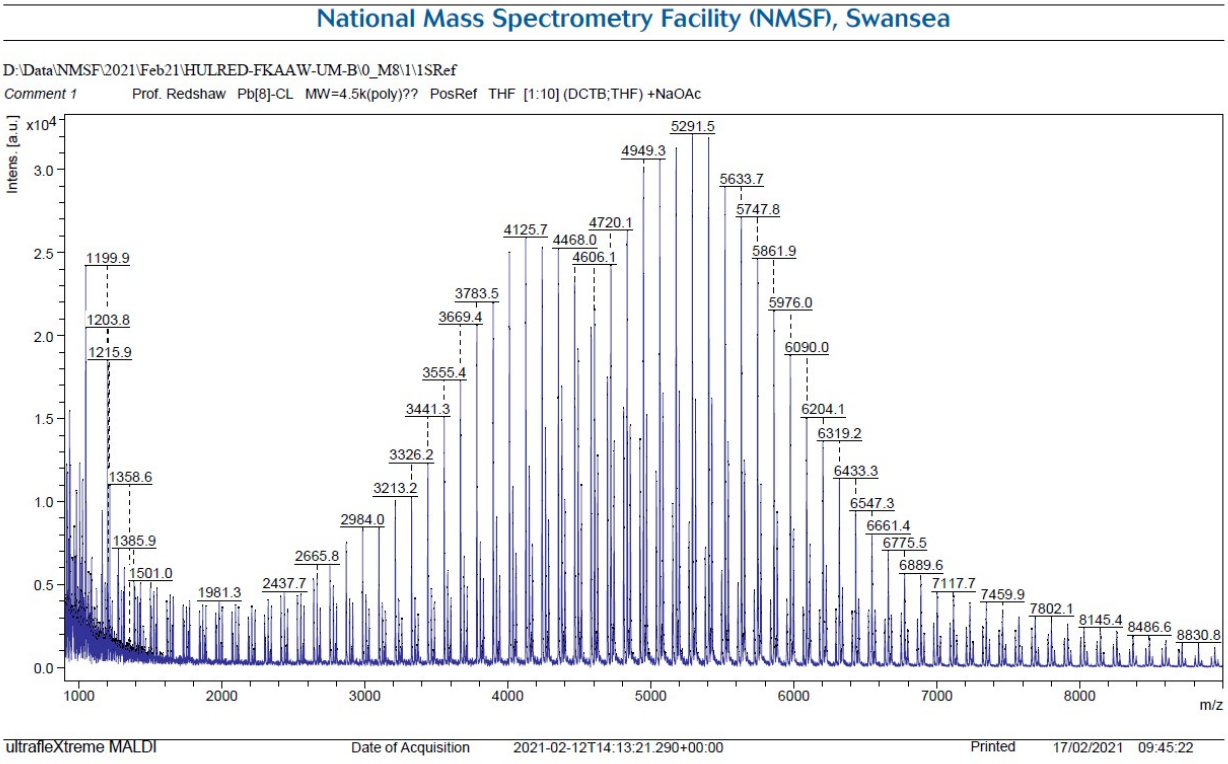
Table S1. Crystal structure data for **1**·2.5MeCN, **2**·14MeCN, **3**·11MeCN, **4**·$8.7C_7H_8$, **5**, **6**·9.5MeCN, **7**·12MeCN.

Compound	**1**·4.5MeCN	**2**·14MeCN	**3**·11MeCN	**4**·$8.7C_7H_8$
Formula	$C_{191}H_{236.5}Li_2N_{7.5}O_{17}Pb_4$	$C_{300}H_{371}Cl_2Li_{10}N_{18}O_{30}Pb_8$	$C_{229}H_{286}N_{11}O_{29}Pb_{13}$	$C_{236.9}H_{277.6}O_{20}Pb_{12}$
Formula weight	3753.16	6509.72	6357.82	5931.25
Crystal system	Triclinic	Triclinic	Triclinic	Triclinic
Space group	*P*–1	*P*–1	*P*–1	*P*–1
Unit cell				
a (Å)	13.7079(3)	23.1594(4)	19.2866(2)	17.5373(3)
b (Å)	15.0694(2)	25.7268(4)	23.0573(3)	17.9311(4)
c (Å)	22.7536(4)	28.7875(6)	29.8976(4)	21.0467(4)
α (°)	97.3001(15)	69.691(2)	72.2187(11)	67.965(2)
β (°)	100.2859(17)	72.882(2)	82.1388(10)	86.0380(10)
γ (°)	102.8843(16)	85.7680(10)	67.9805(11)	64.379(2)
V (Å^3)	4439.47(14)	15365.5(5)	11733.0(2)	5497.3(2)
Z	1	2	2	1
Temperature (K)	100(10)	100(2)	100(2)	100(2)
Wavelength (Å)	0.71075	0.71075	0.71075	0.71075
Calculated	1.365	1.326	1.710	1.792
Absorption	7.706	4.441	9.349	9.211
Transmission	0.828 and 1.000	0.682 and 1.000	0.587 and 0.595	0.809 and 1.000
Crystal size	0.04 × 0.04 × 0.01	0.25 × 0.18 × 0.1	0.104 × 0.061 × 0.053	0.04 × 0.01 × 0.01
θ(max) (°)	70.4	26.3	28.3	27.6
Reflections	74814	327875	256697	194208
Unique	16536	62724	57728	25401
R_{int}	0.0948	0.0644	0.0962	0.0809
Reflections with	14151	41423	37456	21078
Number of	961	3093	2358	1159
R_1 [$F^2 > 2\sigma(F^2)$]	0.0795	0.0679	0.0756	0.044
wR_2 (all data)	0.1279	0.2025	0.1628	0.114
GOOF, *S*	1.228	1.014	1.027	1.02
Largest	1.90 and -2.42	3.92 and -1.58	5.05 and -1.88	3.57 and –2.30

Compound	**5**	**6**·9.5MeCN	**7**·12MeCN
Formula	$C_{94}H_{122}Cl_2O_{10}Pb_6Si_2$	$C_{151}H_{185.5}N_{9.5}ClLi_2O_{17}Pb_{10}$	$C_{200}H_{242}N_{12}O_{20}Pb_{12}$
Formula weight	2782.13	4607.40	5620.32
Crystal system	Triclinic	Monoclinic	Triclinic
Space group	*P*–1	*I*2/*a*	*P*–1
Unit cell			
a (Å)	14.3597(5)	19.7928(2)	18.0913(3)
b (Å)	15.8609(8)	33.7801(3)	18.1443(3)
c (Å)	15.8791(6)	24.5621(3)	19.6341(3)

α (°)	66.795(5)	90	66.654(2)
β (°)	67.082(4)	105.5489(10)	73.896(2)
γ (°)	88.389(3)	90	89.9500(10)
V (Å^3)	3027.9(2)	15821.3(3)	5641.51(18)
Z	1	8	1
Temperature (K)	100(2)	100(2)	100.15
Wavelength (Å)	0.71075	0.71075	0.71075
Calculated	1.526	1.771	1.654
Absorption	8.376	10.668	8.972
Transmission	0.628 and 1.000	0.733 and 1.000	0.720 and 1.000
Crystal size	0.090 × 0.060 × 0.025	0.09 × 0.08 × 0.07	0.12 × 0.08 × 0.06
θ(max) (°)	25.0	31.97	25.7
Reflections	57186	211141	107191
Unique	10657	24791	21322
R_{int}	0.0600	0.0591	0.0701
Reflections with	6953	18155	17119
Number of	582	774	1101
R_1 [$F^2 > 2\sigma(F^2)$]	0.0816	0.0389	0.0571
wR_2 (all data)	0.2366	0.0897	0.1623
GOOF, S	1.035	1.059	1.042
Largest	4.36 and -2.20	2.79 and -1.34	5.46 and -3.10

ROP studies



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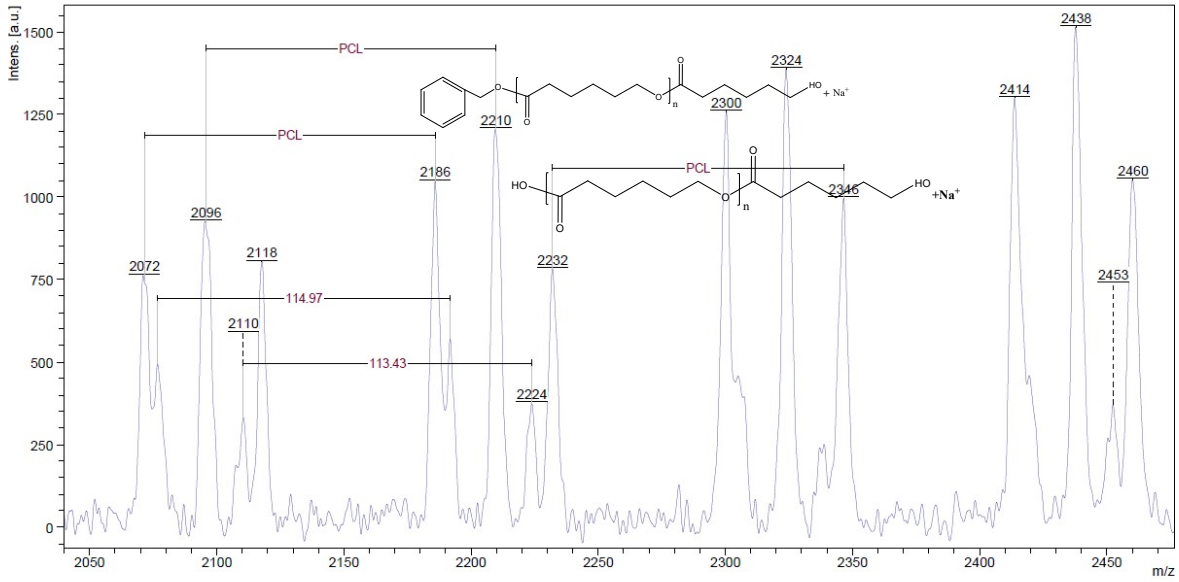

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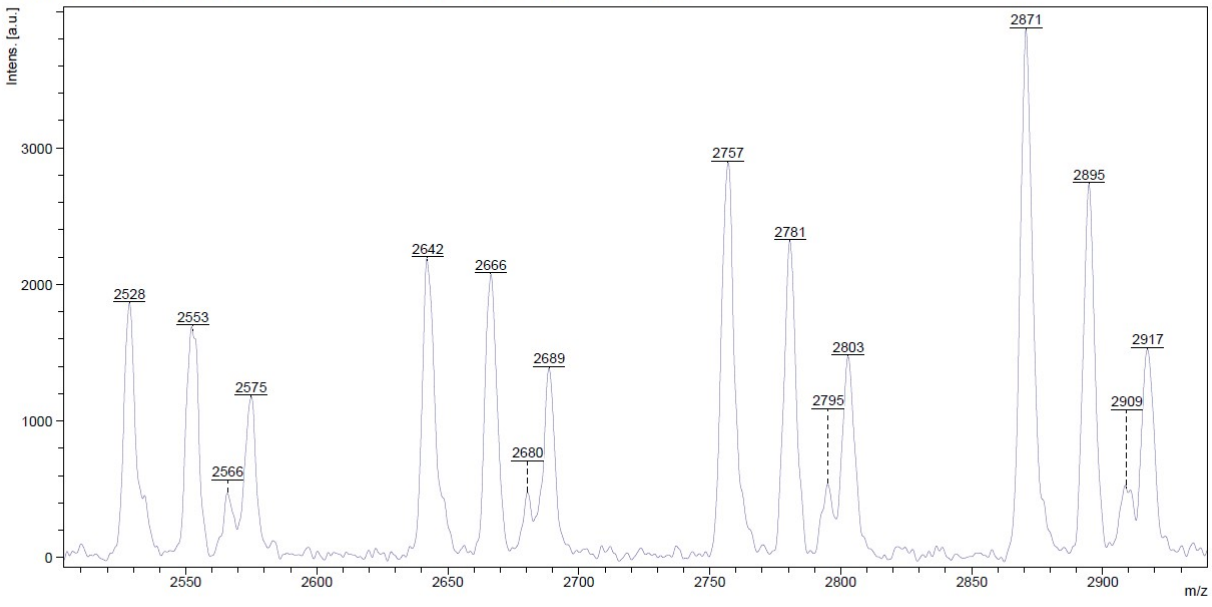

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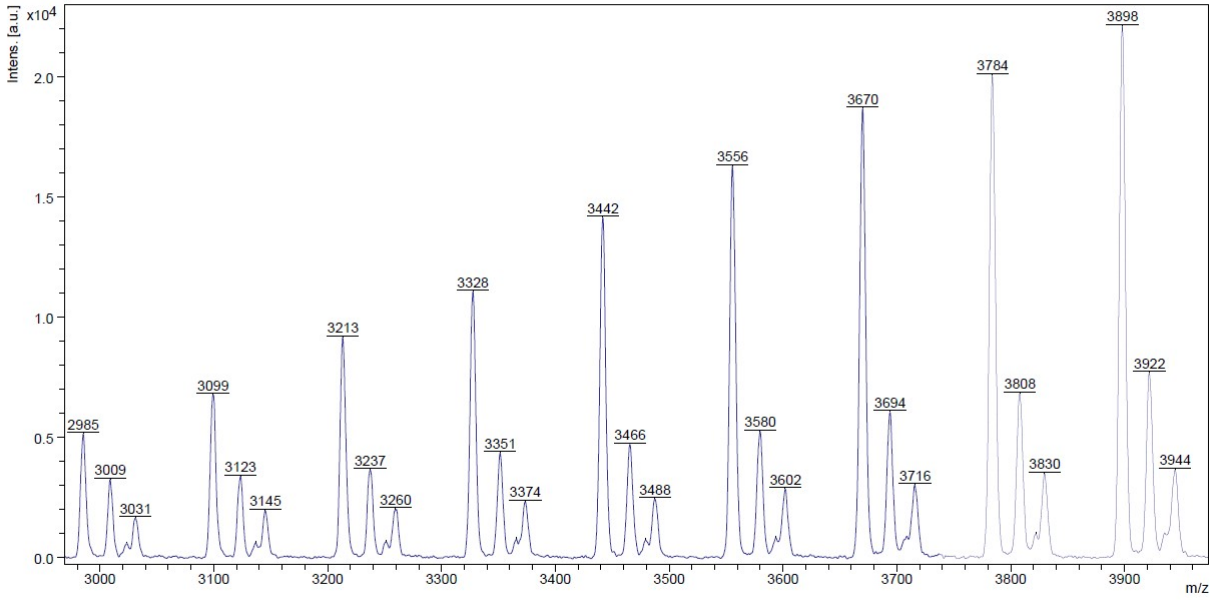

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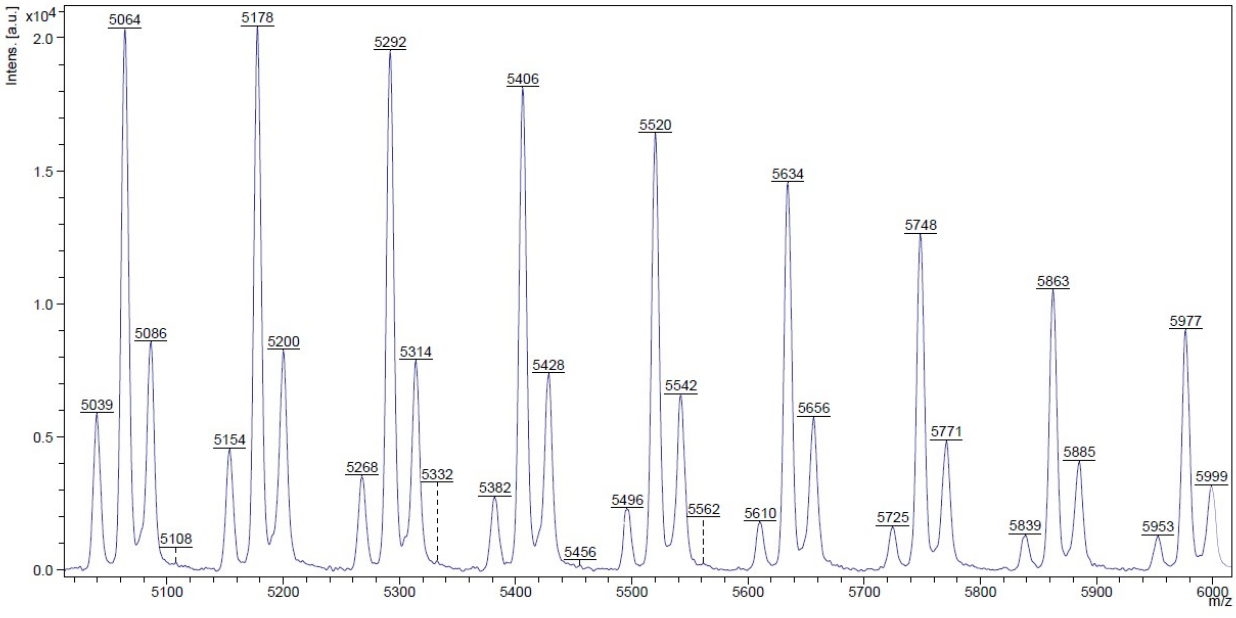

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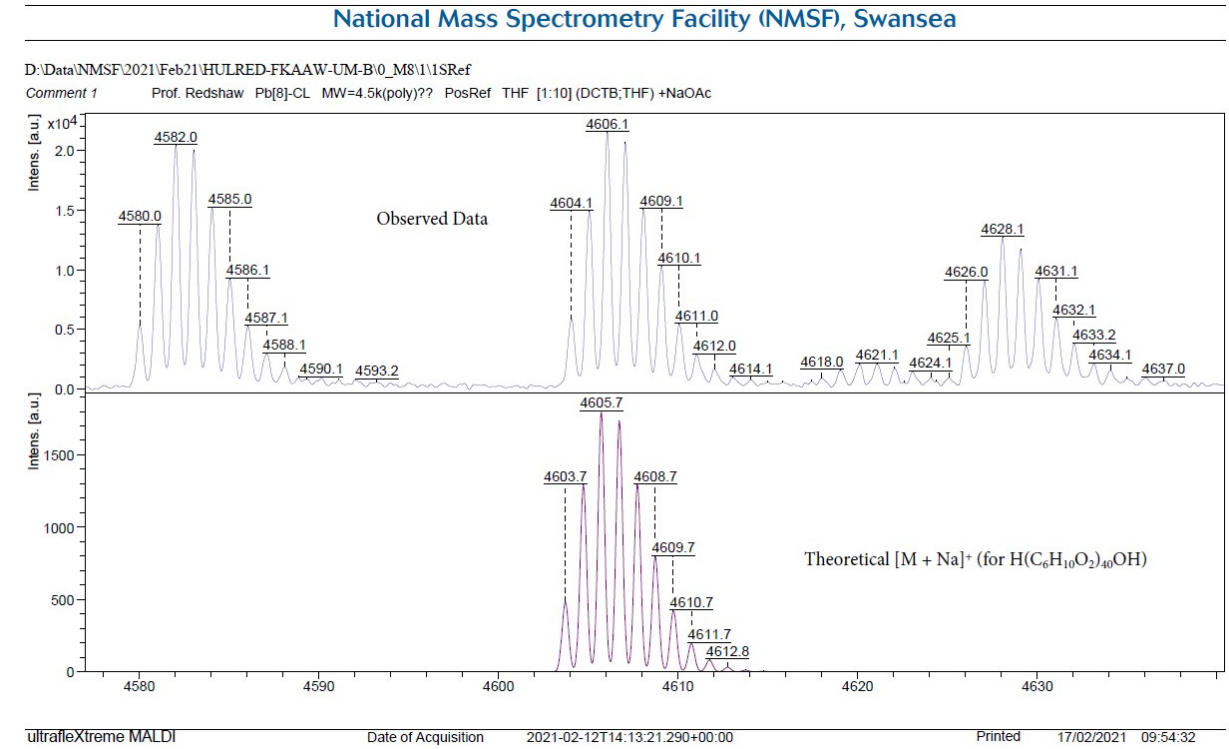


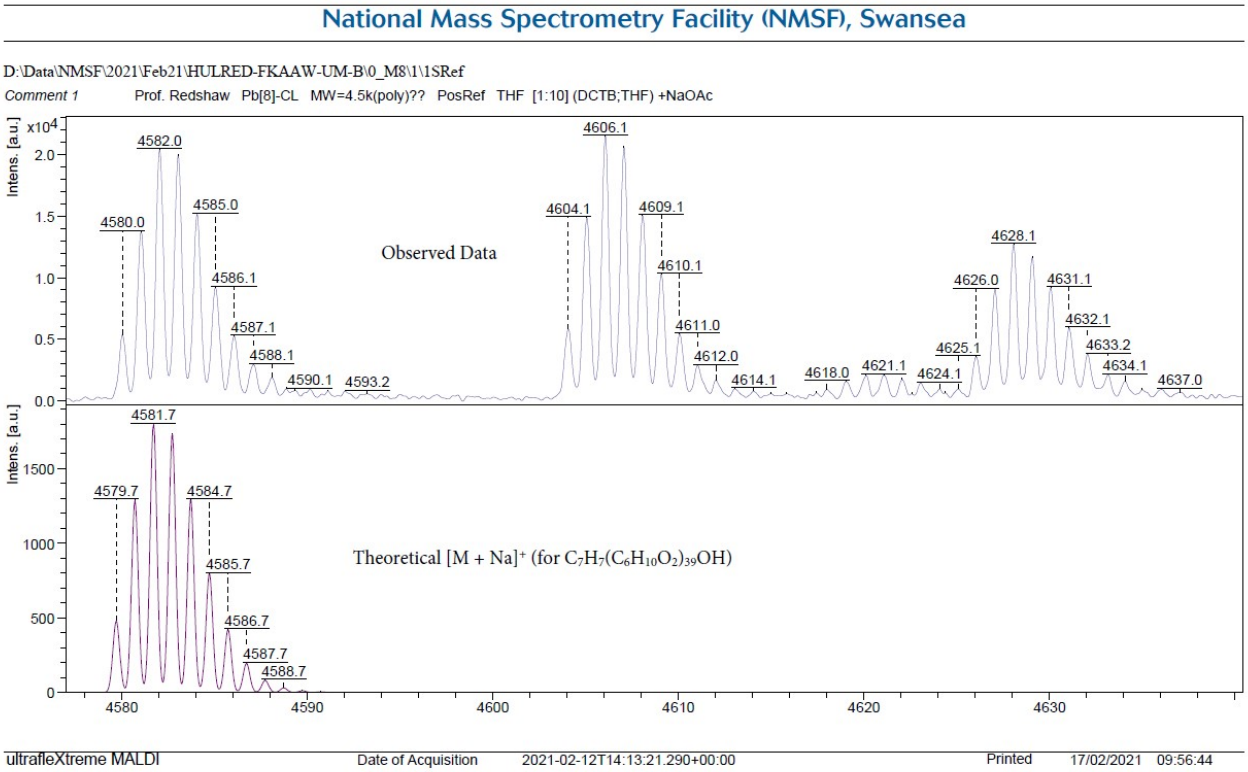


Figure S2. Mass spectrum of PCL synthesized with **4**/BnOH (run 19, Table 1).

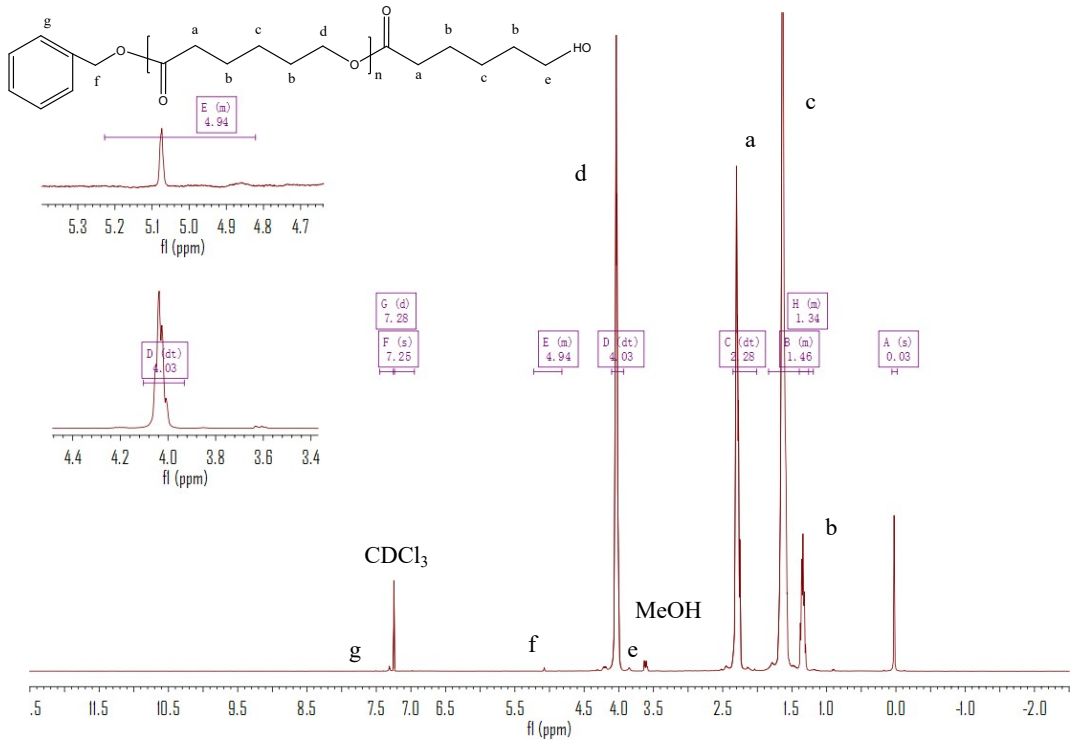
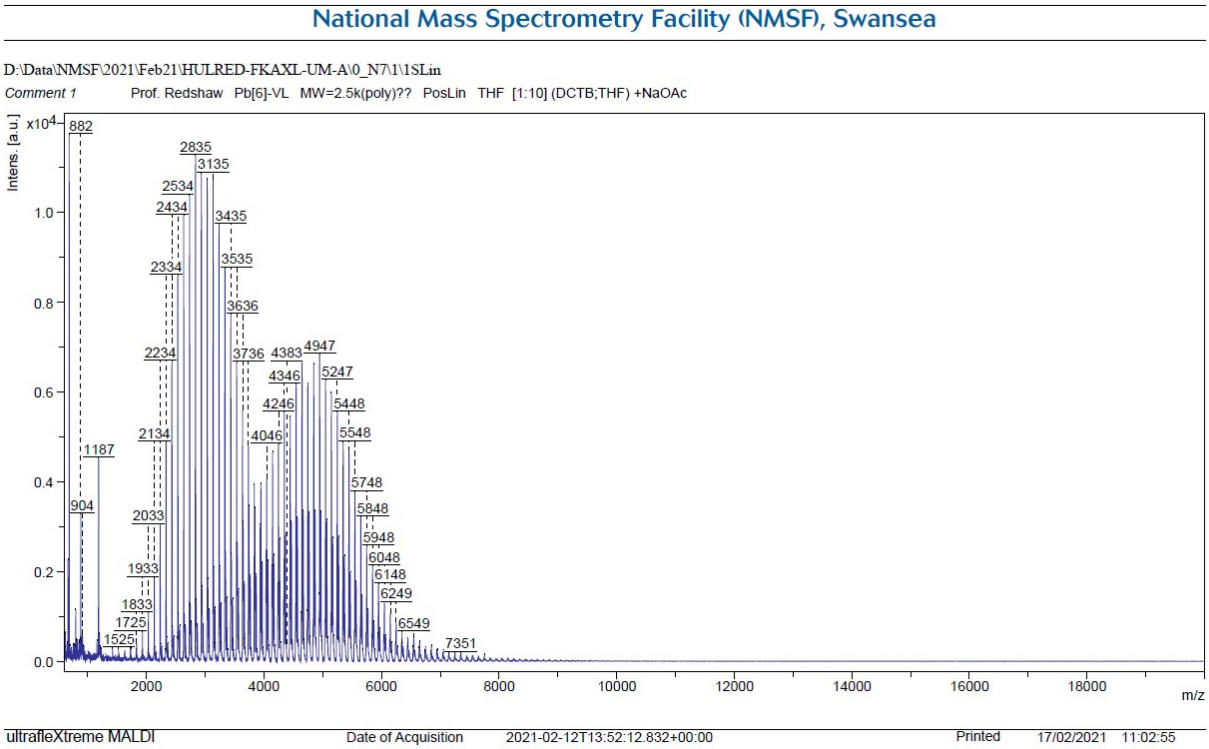


Figure S3. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL synthesized with **2**/BnOH (run 17, Table 1)



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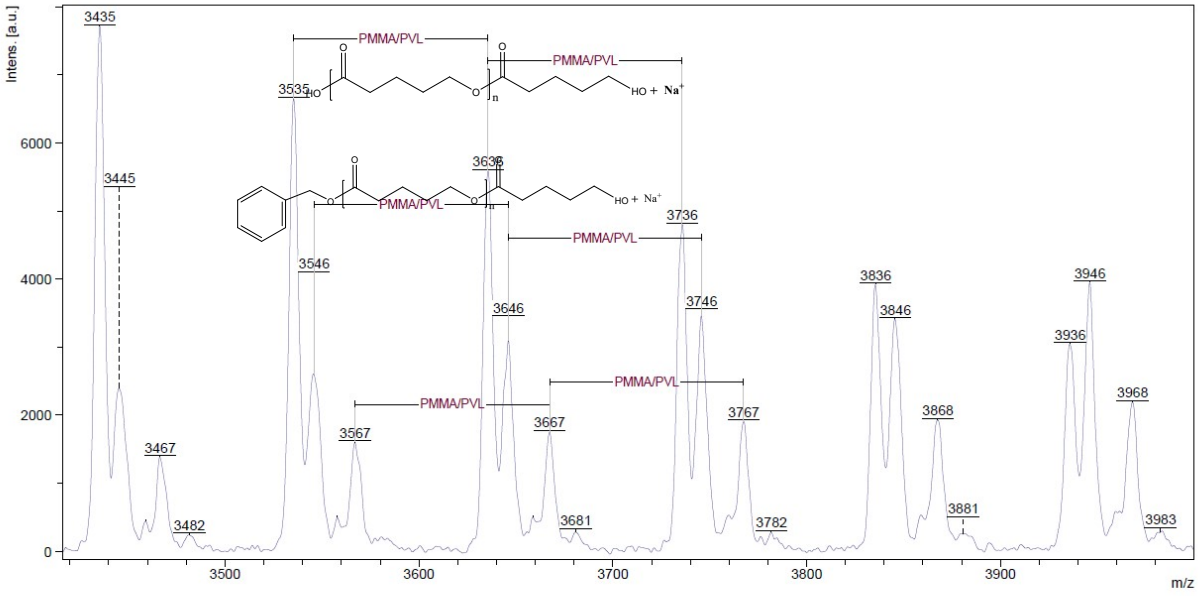

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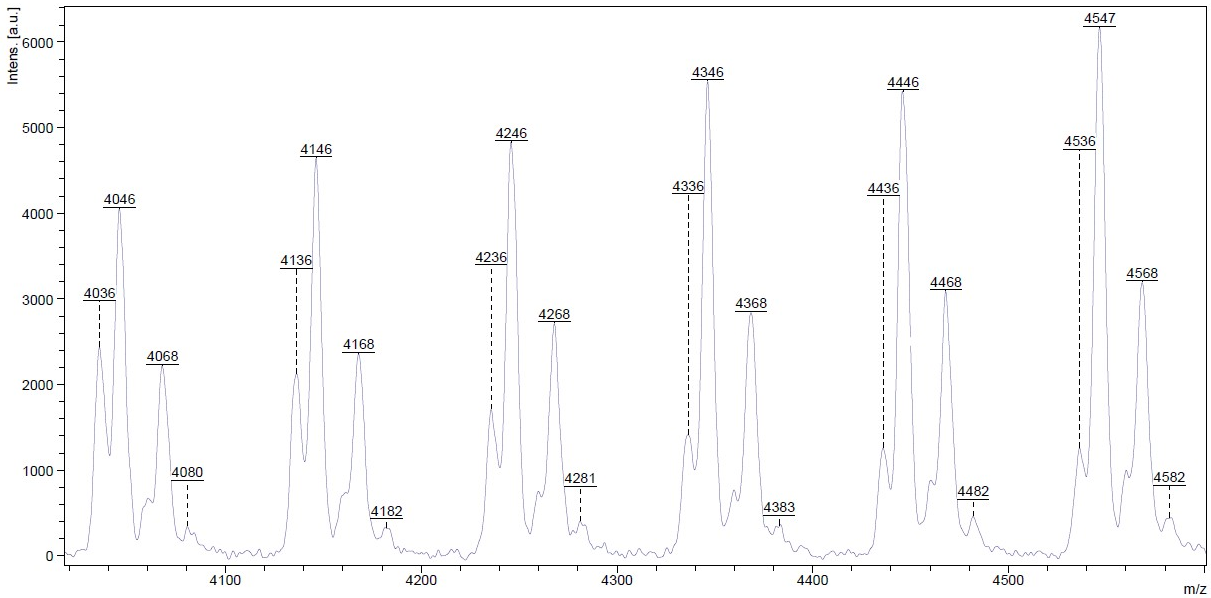

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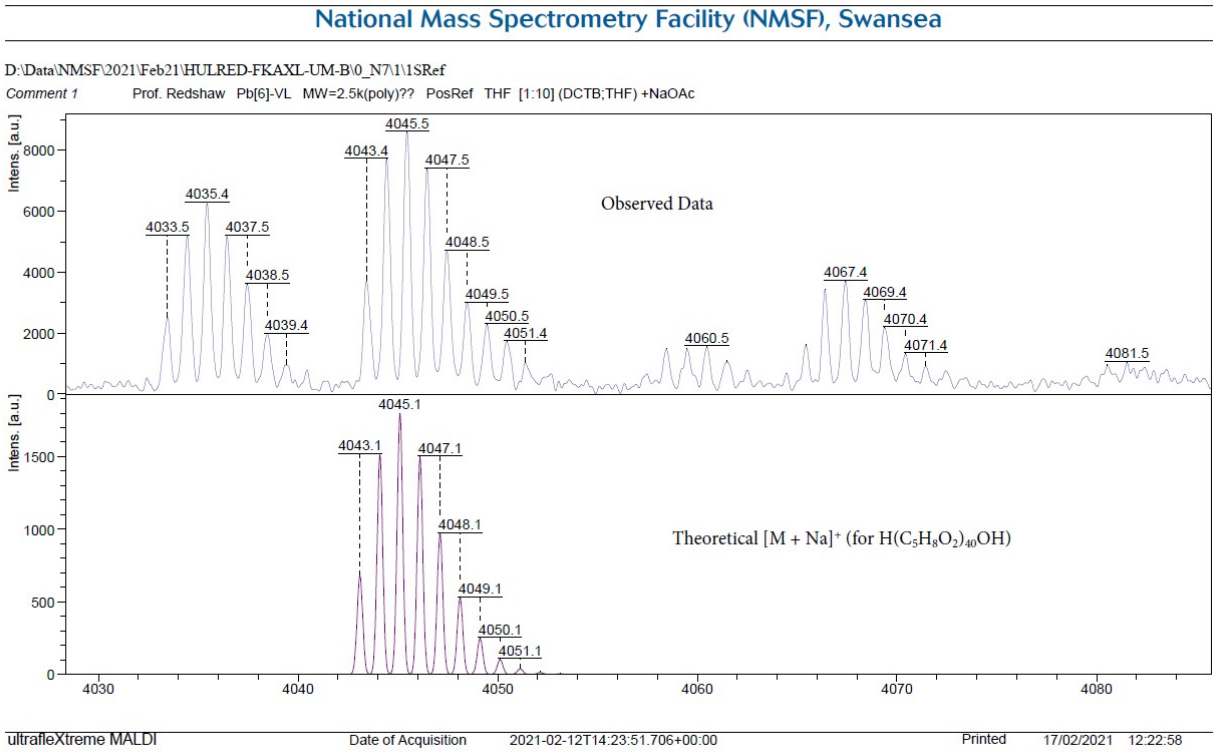


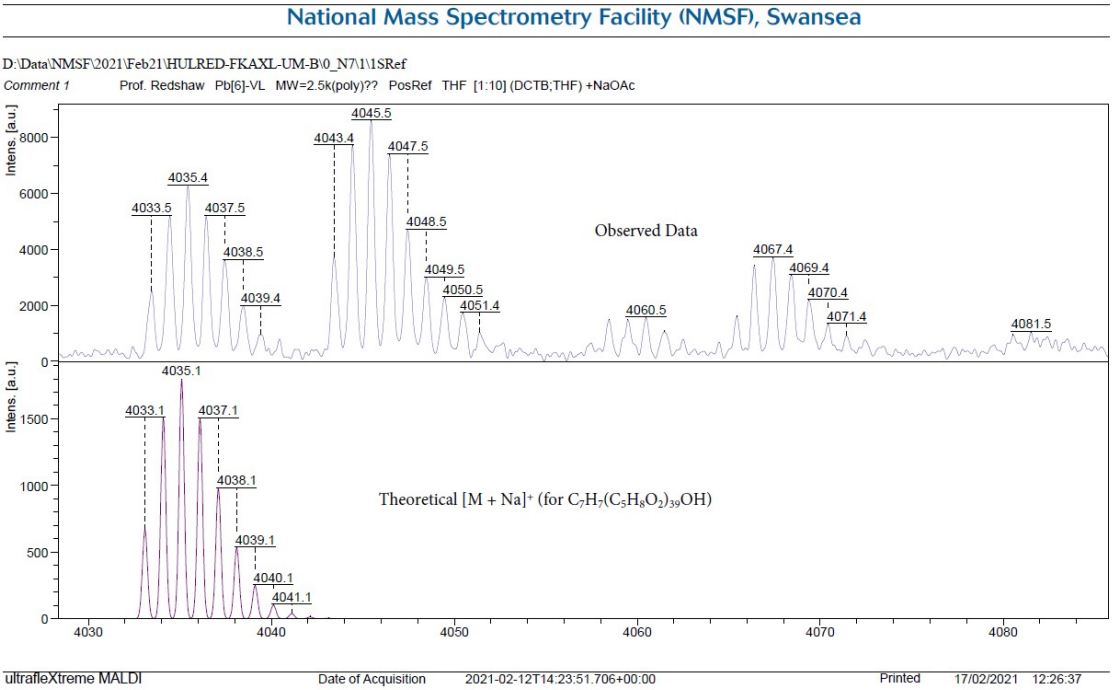


Figure S4. Mass spectrum of PVL synthesized with **2**/BnOH (run 8, Table 2).

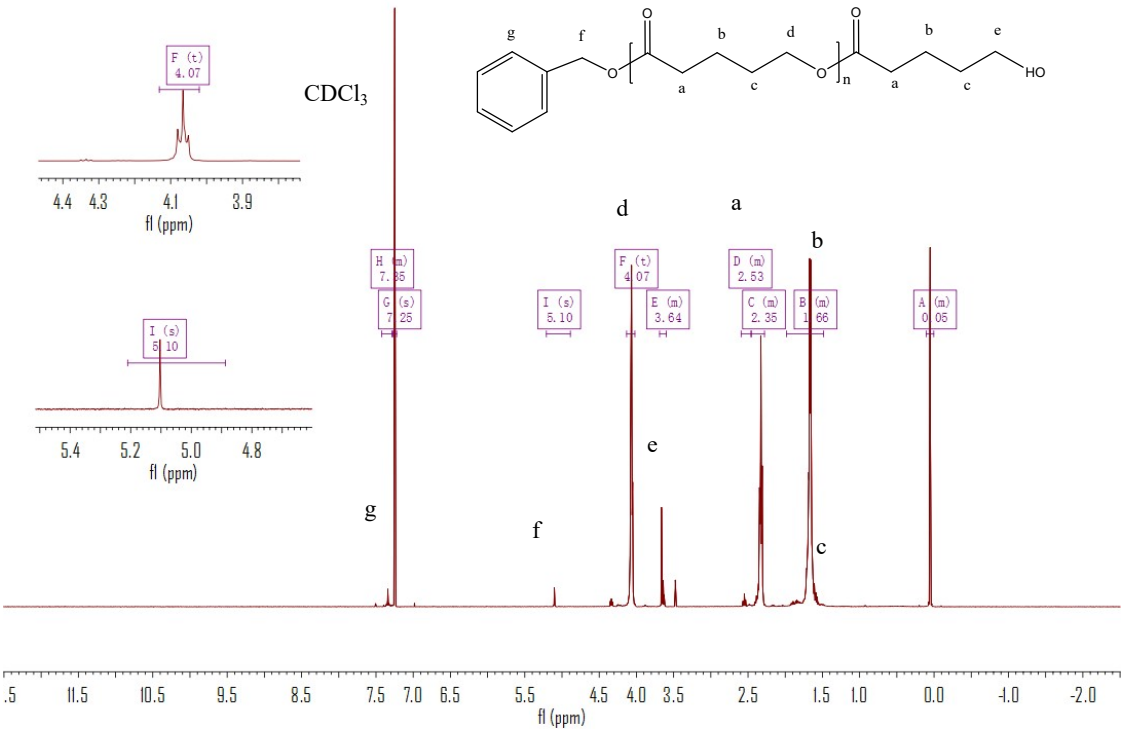


Figure S5. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PVL synthesized with **3**/BnOH (run 9, Table 2).

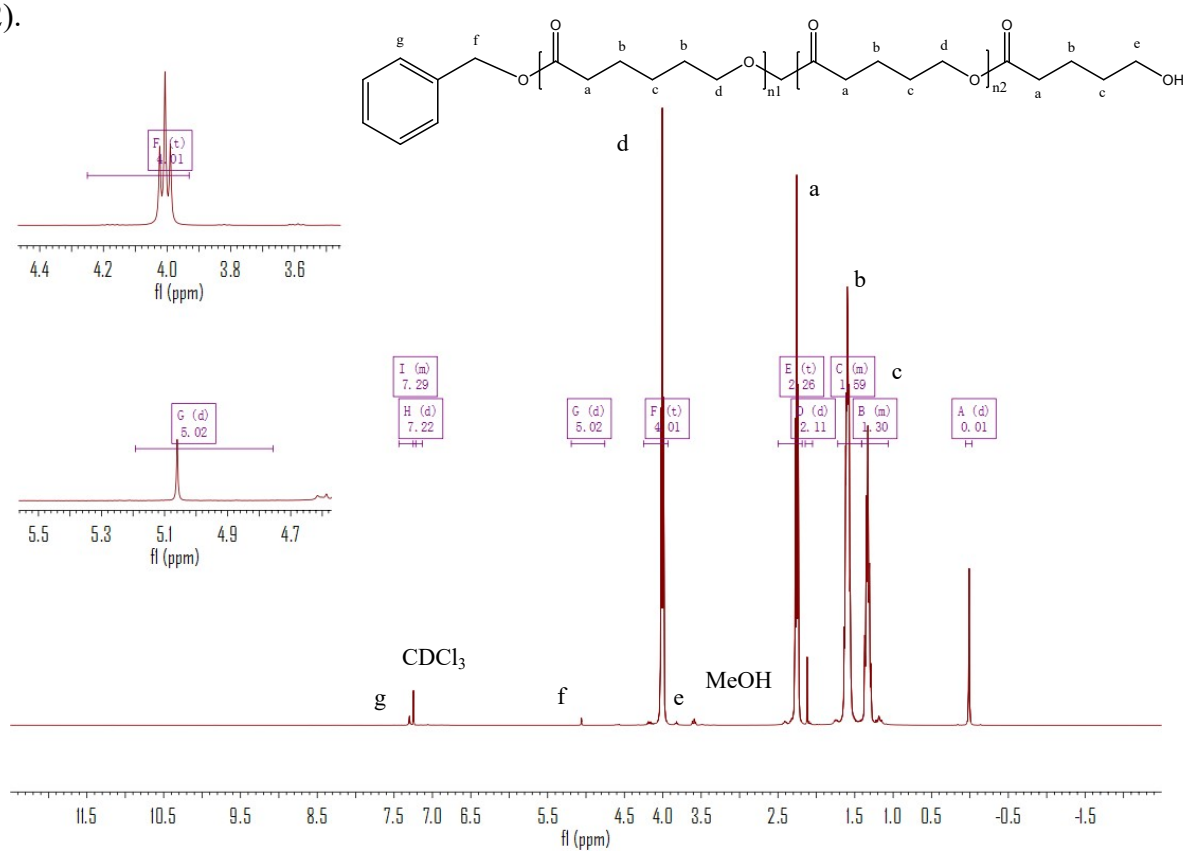


Figure S6. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PCL-PVL co-polymer synthesized with

3/BnOH (run 3, Table 3).

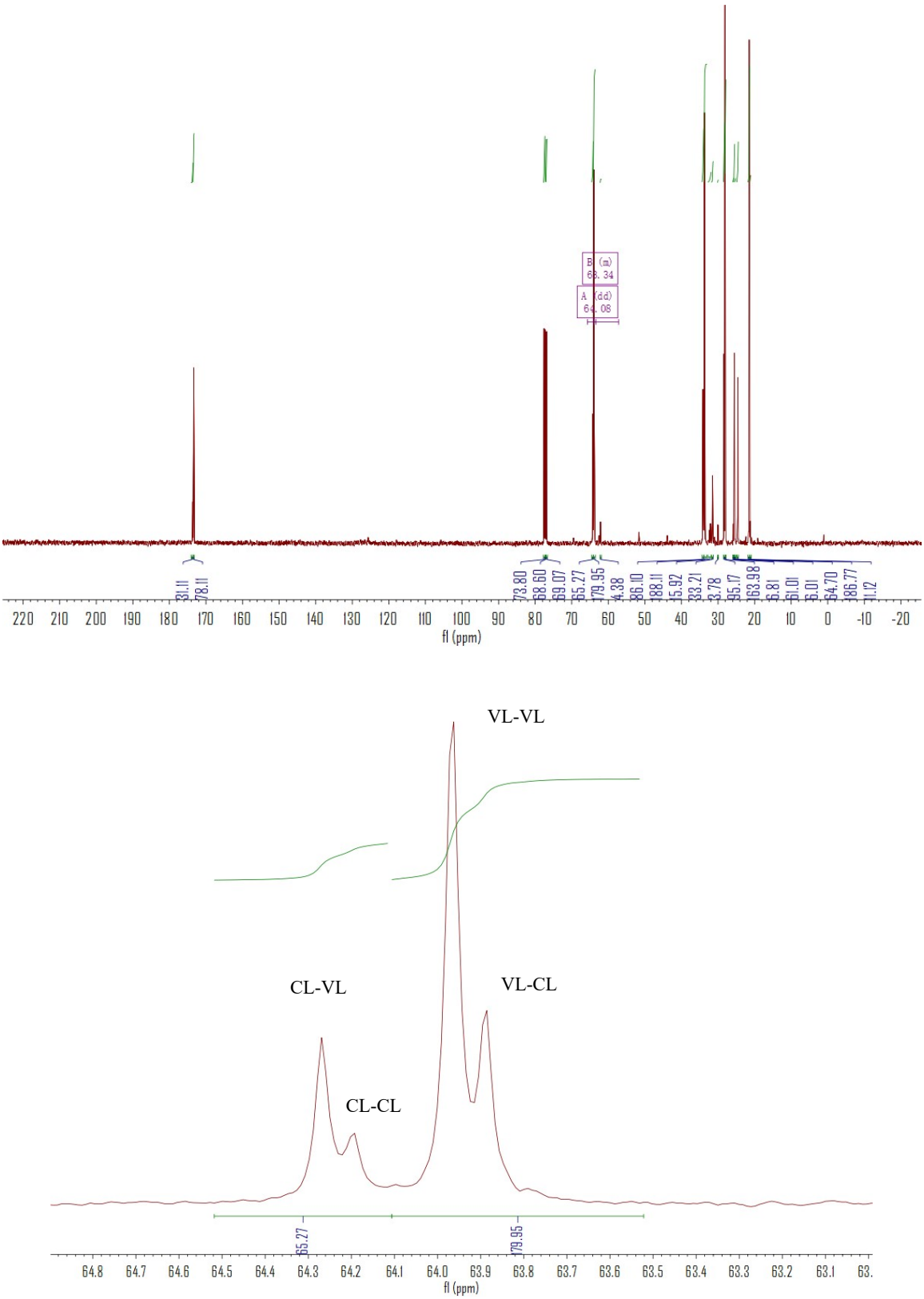


Figure S7. Carbonyl range of ^{13}C NMR spectrum ($CDCl_3$, 25 ºC) of PCL-PVL co-polymer synthesized with **3**/BnOH (run 3, Table 3).

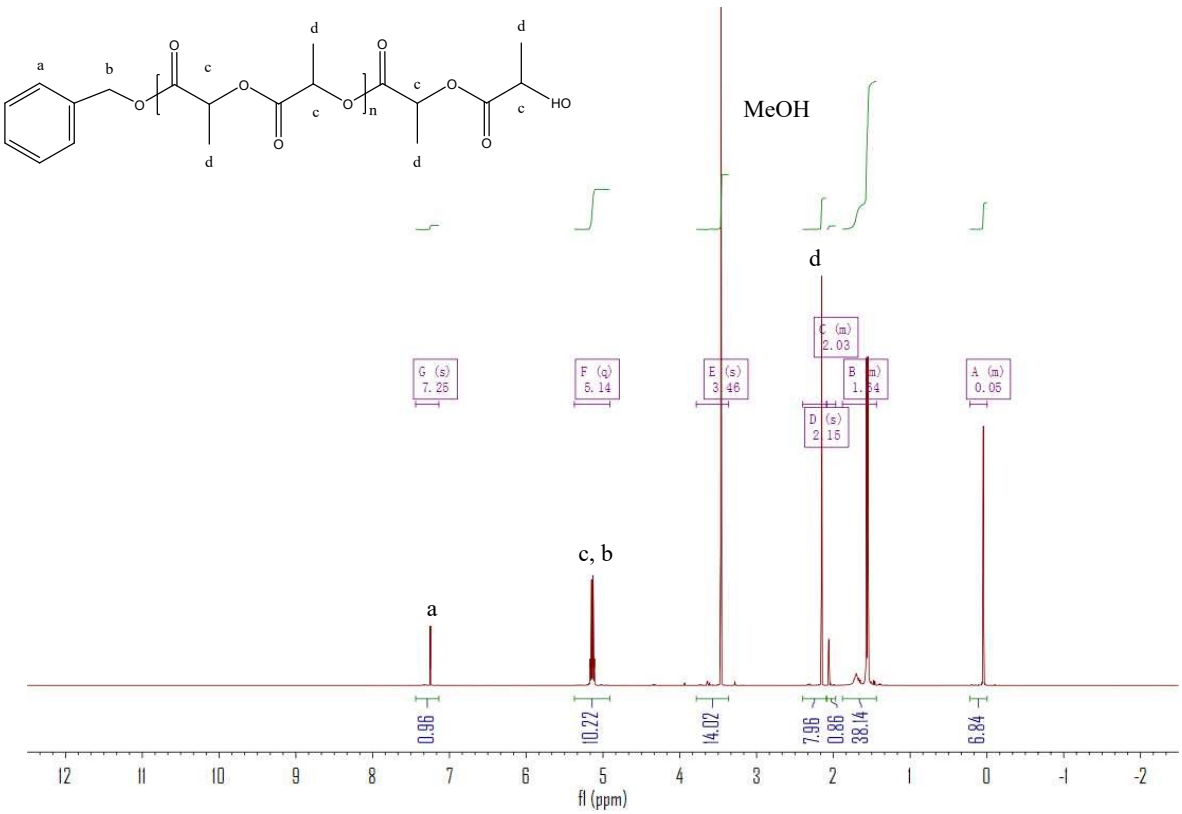
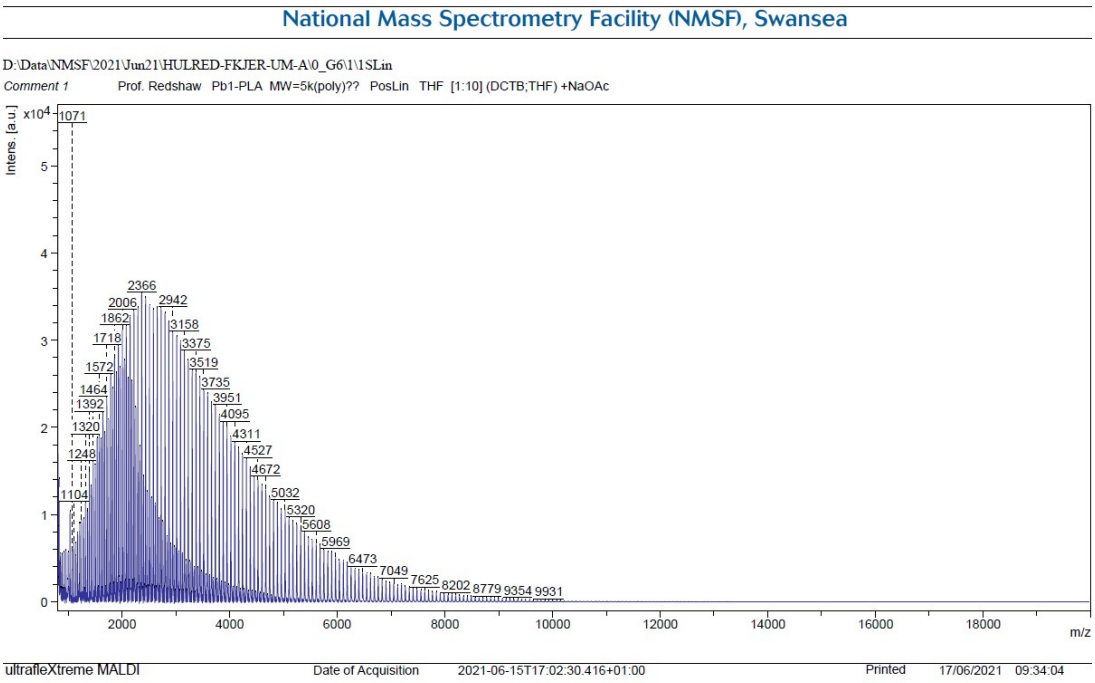


Figure S8. ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **1**/BnOH (run 1, Table 4).



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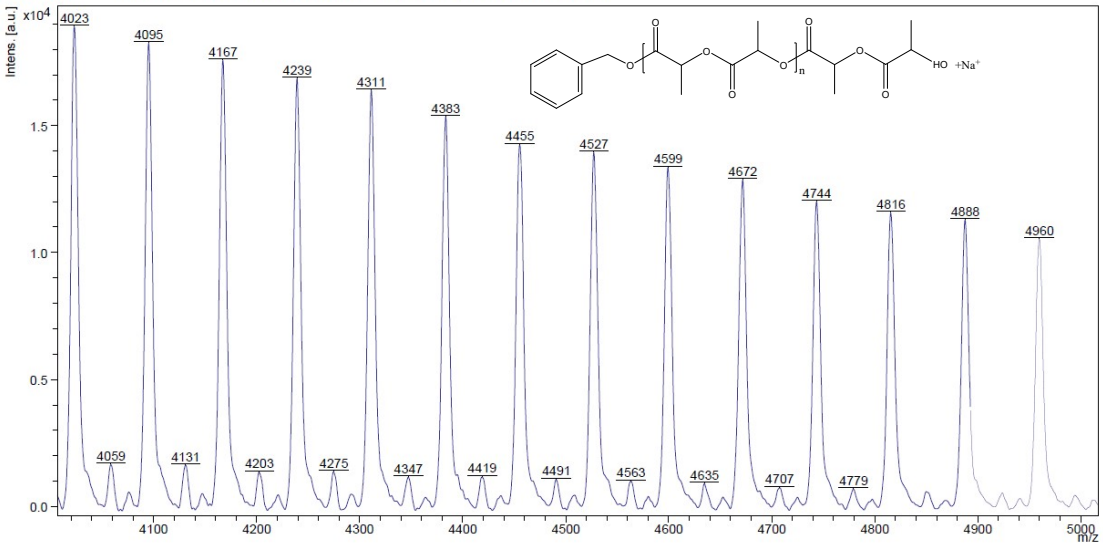

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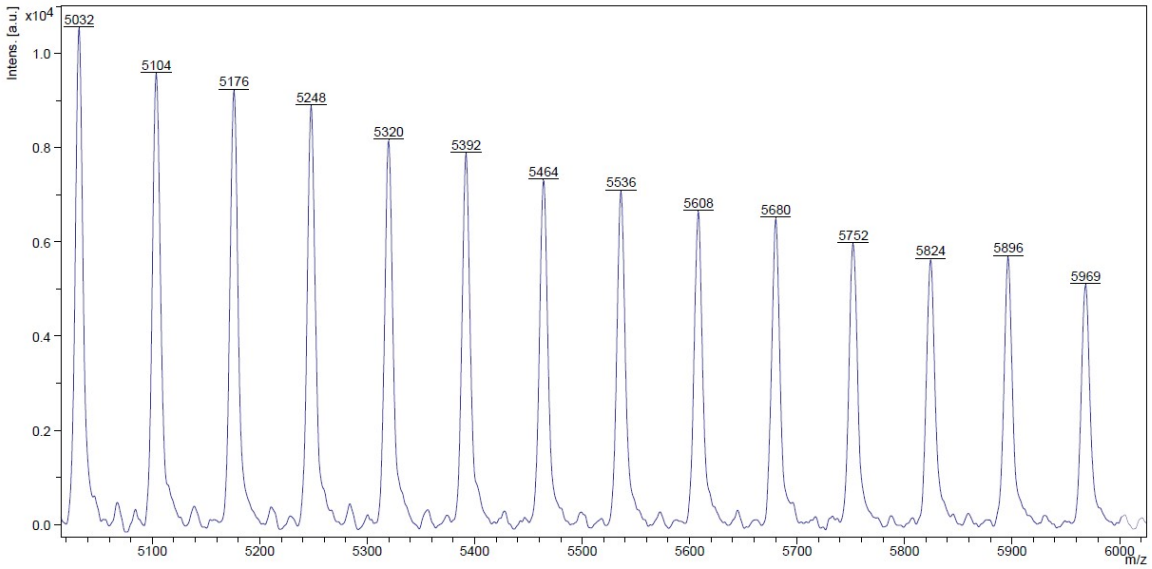

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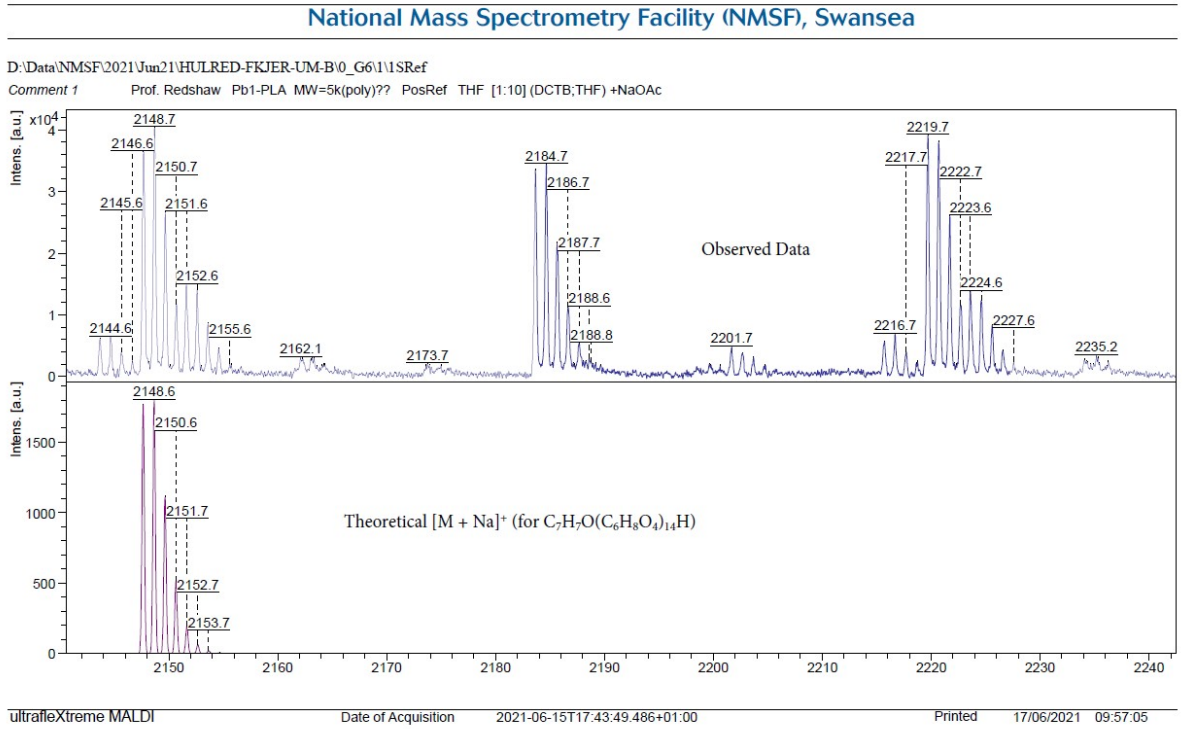
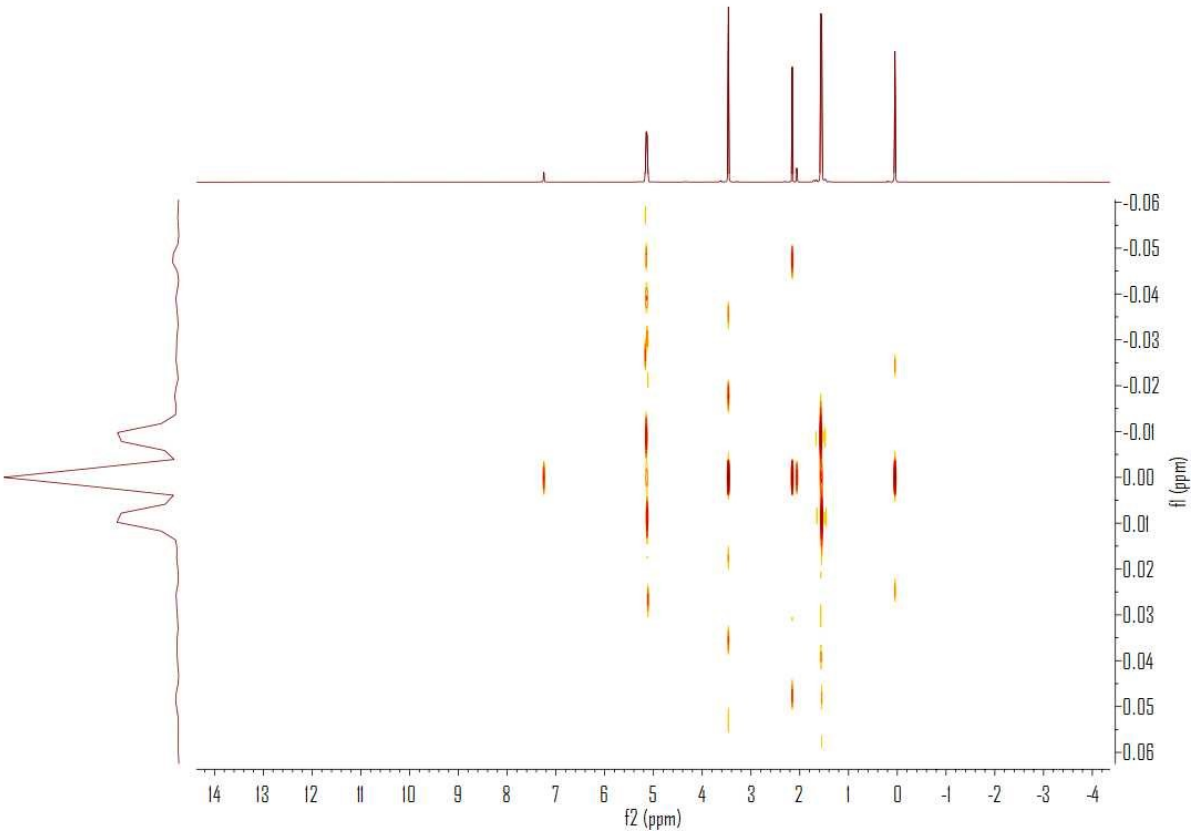


Figure S9. Mass spectrum of PLA synthesized with **2**/BnOH (run 2, Table 4).



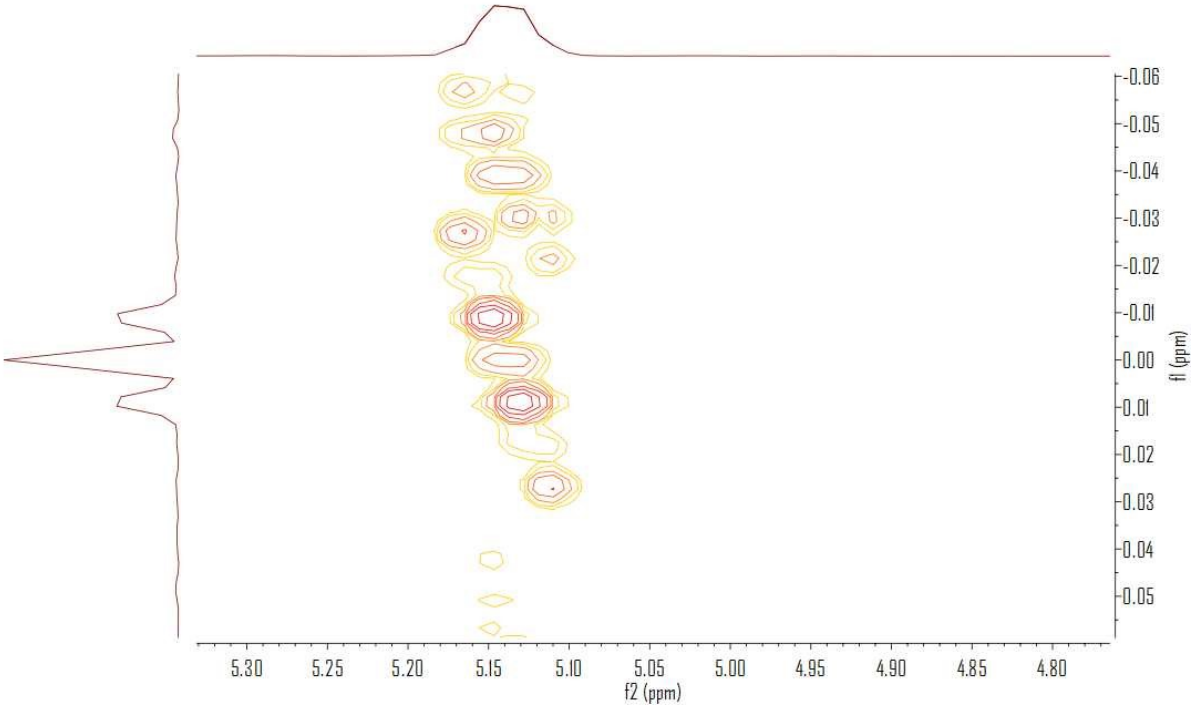


Figure S10. 2D J-resolved ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of the PLA synthesized with **1**/BnOH (run 1, Table 4).

Equation S1. Determination of number-average sequence length for CL[1]

$$L_{CL}=[(I_{CL\text{-}CL})/(I_{VL\text{-}CL})]+1$$

Where $I_{CL\text{-}CL}$ and $I_{VL\text{-}CL}$ is the area of the peak belonging to the CL-CL and VL-VL dyad, respectively.

Equation S2. Determination of number-average sequence length for VL. [1]

$$L_{VL}=[(I_{VL\text{-}VL})/(I_{CL\text{-}VL})]+1$$

Where $I_{VL\text{-}VL}$ and $I_{CL\text{-}VL}$ is the area of the peak belonging to the VL-VL and CL-VL dyad, respectively.

Equation S3. Determination of the Randomness Character (R). [1]

$$R=1/(L_{CL}) + 1/(L_{VL})$$

Completely block Copolymers: R = 0
Copolymers with a “blocking” tendency: R < 1
Completely random copolymers: R = 1
Copolymers with an alternating tendency: R >1

Completely alternating copolymers: R = 2

References

[1] (a) Q. Hu, S.-Y. Jie, P. Braunstein and B.-G. Lia, *Chinese J. Polym. Sci*. 2020, **38**, 240–247; (b) M. A. Woodruff and D. W. Hutmacher, *Prog. Polym. Sci.,* 2010, **35**, 1217−1256; (c) T. Wu, Z. Wei, Y. Ren, Y. Yu, X. Leng and Y. Li, *Polym. Degrad. Stab.,* 2018, **155**, 173−182; (d) M. T. Hunley, N. Sari, and K. L. Beers, *ACS Macro Lett*., 2013, **2**, 375−379. (e) Z. Sun, Y. Zhao, O. Santoro, M. R. J. Elsegood, E. V. Bedwell, K. Zahra, A. Walton, and C. Redshaw, *Catal. Sci. Technol.*, 2020, **10**, 1619−1639.