Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supplementary Information

Monodisperse Oligo(δ-valerolactones) and Oligo(ε-caprolactones) with Docosyl (C_{22}) End-Groups

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ES1. *Synthesis of $C_{22}PVL_{5.2}$.* The procedure is similar to the synthesis of C_{22}-PVL (DP_{theo} = 6) described in the article. However, only the unreactive 1-docosanol ($C_{22}OH$) was isolated by flash column chromatography and obtaining the rest of oligomers in a single sample. NMR data at room temperature: ^{1}H NMR (500 MHz, C_7D_8, ppm). $PVL_{5.2}$ (Fig. S16): δ 3.99 (t, 2H, [e, –CH_2–O–], C_{22}), 3.91 (t, 2H, [i, –CH_2–O–], $PVL_{5.2}$), 3.40 (t, 2H, [a, –CH_2–OH], $PVL_{5.2}$), 2.06 (quintet, 2H, [d, –CH_2–CO–], $PVL_{5.2}$), 2.09 (quintet, solvent: toluene-d_8 (C_7D_8)), 1.60 (quintet, 2H, [f, –*CH_2*–CH_2–O–], C_{22}), 1.51 (quintet, 2H, [b, –*CH_2*–CH_2–O– or –*CH_2*–CH_2–OH], $PVL_{5.2}$), 1.42 (quintet, 2H, [b, –*CH_2*–CH_2–CO–], $PVL_{5.2}$), 1.32 (m, 2H, [g, –CH_2–], C_{22}), 0.90 (t, 3H, [h, –CH_3], C_{22}). ^{13}C NMR (125 MHz, C_7D_8, ppm). $PVL_{5.2}$ (Fig. S17): δ 173.37 [a´, *C*O(CH_2)$_4$OH, $PVL_{5.2}$], 172.95 [i´, *C*O(CH_2)$_4$O, $PVL_{5.2}$], 64.82 [e, –CH_2–O–, C_{22}], 64.22 and 64.09 [i, –CH_2–O–, $PVL_{5.2}$], 62.40 [a, –CH_2–OH, $PVL_{5.2}$]. DP_{NMR} = 5.2. SEC chromatograph is showed in Fig S10d. MALDI-TOF spectrum is visualized in Fig S13-S15. Thermal properties in Table S3.

ES2. *Synthesis of $C_{22}PCL_{6.8}$.* The procedure is similar to the synthesis of C_{22}-PCL described in the article, with a ε-caprolactone (CL)/1-docosanol ($C_{22}OH$) molar ratio equal to 6 (DP_{theo} = 6). However, only the unreactive 1-docosanol ($C_{22}OH$) was isolated by flash column chromatography and obtaining the rest of oligomers in a single sample. NMR data at room temperature: ^{1}H NMR (500 MHz, $CDCl_3$, ppm). $PCL_{6.8}$ (Fig. S21): δ 4.06 (t, 2H, [e, –CH_2–O–], C_{22} and t, 2H, [i, –CH_2–O–], $PCL_{6.8}$), 3.56 (t, 2H, [a, –CH_2–OH], $PCL_{6.8}$), 2.24 (quintet, 2H, [d, –CH_2–CO–], $PCL_{6.8}$), 1.59 (quintet, 2H, [b and d´, –*CH_2*–CH_2–O–, –*CH_2*–CH_2–OH, –*CH_2*–CH_2–CO], $PCL_{6.8}$), 1.51 (quintet, 2H, [f, –*CH_2*–CH_2–O–], C_{22}), 1.32 (quintet, 2H, [c, –*CH_2*–CH_2–CH_2–CO–], $PCL_{6.8}$), 1.19 (s, 2H, [g, –CH_2–], C_{22}), 0.81 (t, 3H, [h, –CH_3], C_{22}). ^{13}C NMR (125 MHz, C_7D_8, ppm). $PCL_{6.8}$ (Fig. S22): δ 173.56 [a´, *C*O(CH_2)$_4$OH, $PCL_{6.8}$], 173.34 [i´, *C*O(CH_2)$_4$O, $PCL_{6.8}$], 64.32 [e, –CH_2–O–, C_{22}], 63.95 and 63.90 [i, –CH_2–O–, $PCL_{6.8}$], 62.23 [a, –CH_2–OH, $PCL_{6.8}$]. DP_{NMR} = 6.8. SEC chromatograph is showed in Fig S10b. MALDI-TOF spectrum is visualized in Fig S18-S20. Thermal properties in Table S3.

Table S1. Monodisperse oligomeric species derived from δ-valerolactone (VL) and ε-caprolactone (CL) with docosyl [$CH_3(CH_2)_{21}$-] (C_{22}) terminal group, isolated by column chromatography, and detected by ^1H NMR.

No.	Sample	Precursor	Species	DP_{theo}	DP_{NMR}[a]	MW(theo)[b]	MW(NMR)[c]
1	$C_{22}VL_1$	VL	monomer	1.0	1.02	426.72	428.72
2	$C_{22}VL_2$	VL	dimer	2.0	2.23	526.84	549.86
3	$C_{22}VL_3$	VL	trimer	3.0	2.99	626.96	625.95
4	$C_{22}VL_4$	VL	tetramer	4.0	3.95	727.08	722.07
5	$C_{22}VL_5$	VL	pentamer	5.0	4.94	827.20	821.19
6	$C_{22}CL_1$	CL	monomer	1.0	0.98	440.74	438.45
7	$C_{22}CL_2$	CL	dimer	2.0	1.91	554.88	544.60
8	$C_{22}CL_3$	CL	trimer	3.0	2.77	669.02	642.76
9	$C_{22}CL_4$	CL	tetramer	4.0	3.66	783.16	744.35

[a] $DP_{NMR} = I_{oli}/\#H_{oli} \div I_{ter}/\#H_{ter}$. Case of VL: I_{oli} at 2.10 ppm (CH_2–CO–O, VL) and I_{ter} at 4.05 ppm (CH_2–O–CO, docosyl terminal group); $\#H_{oli}$ and $\#H_{ter}$ = 2. Case of CL: I_{oli} at 2.31 ppm (CH_2–CO–O, CL) and I_{ter} at 3.65 ppm (CH_2–OH, hydroxyl terminal group); $\#H_{oli}$ and $\#H_{ter}$ = 2.

[b] $MW(theo) = DP_{theo} \times MW_{lactone}$ (VL or CL) + $MW_{docosanol}$. MW_{VL} = 100.12 g/mol, MW_{CL} = 114.14 g/mol, and $MW_{docosanol}$ = 326.60 g/mol.

[c] $MW(NMR) = DP_{NMR} \times MW_{lactone}$ (VL or CL) + $MW_{docosanol}$. MW_{VL} = 100.12 g/mol, MW_{CL} = 114.14 g/mol, and $MW_{docosanol}$ = 326.60 g/mol.

Table S2. Comparison of measurements of MW and M_n obtained by NMR and SEC.

No.	Sample	Precursor	Species	DP_{NMR}[a]	DP_{SEC}[b]	M_n(NMR)[c]	M_n(SEC)[d]	$Đ_M$[d]	M_n(NMR)/M_n(SEC)[e]
2	$C_{22}VL_2$	VL	dimer	2.23	4.82	549.86	810	1.18	0.67
7	$C_{22}CL_2$	CL	dimer	1.91	6.77	544.60	1100	1.04	0.49
8	$C_{22}PVL_{5.2}$	VL	Oligomer	5.20	13.31	847.22	1660	1.11	0.51
9	$C_{22}PCL_{6.8}$	CL	Oligomer	6.80	16.41	1102.75	2200	1.09	0.50

[a] $DP_{NMR} = I_{oli}/\#H_{oli} \div I_{ter}/\#H_{ter}$. Case of $C_{22}VL_2$: I_{oli} at 2.10 ppm (CH_2–CO–O, VL, in C_6D_6) [case of $C_{22}PVL_{5.2}$: 3.91 ppm (CH_2–O, VL, in toluene-d_8)] and I_{ter} at 4.03 ppm (CH_2–O–CO, docosyl terminal group, in C_6D_6) [case of $C_{22}PVL_{5.2}$: 3.40 ppm (CH_2–OH, VL, in toluene-d_8)]; $\#H_{oli}$ and $\#H_{ter}$ = 2. Case of $C_{22}CL_2$: I_{oli} at 2.31 ppm (CH_2–CO–O, CL, in $CDCl_3$) [case of $C_{22}PCL_{6.8}$: 2.24 ppm (CH_2–CO–O, CL, in $CDCl_3$)] and I_{ter} at 3.65 ppm (CH_2–OH, hydroxyl terminal group of CL, in $CDCl_3$) [case of $C_{22}PCL_{6.8}$: 3.56 ppm (CH_2–OH, hydroxyl terminal group of CL, in $CDCl_3$)]; $\#H_{oli}$ and $\#H_{ter}$ = 2.

[b] DP_{SEC} = Mn(SEC) – MWdocosanol/MWVL or CL.

[c] MW(NMR) = DP_{NMR} x $MW_{lactone}$ (VL or CL) + $MW_{docosanol}$. MW_{VL} = 100.12 g/mol, MW_{CL} = 114.14 g/mol, and $MW_{docosanol}$ = 326.60 g/mol.

[d] Obtained by size-exclusion chromatography (SEC) using polystyrene standarts.

[e] Overestimation of M_n obtained by SEC for PCL is a common feature, since polystyrene standards are used in the construction of the calibration curve. MacLain and Drysdale found that M_n(calcd) / M_n(SEC) ratio is around 0.45 for PCL. [See reference: S.J., McLain, and N.E.,Drysdale, *Polym. Prepr. (Am. Chem. Soc., Polym. Div.)*, 1992, **33**, 174.]

Table S3. Thermal properties of oligomeric species derived from C_{22}-$PVL_{5.2}$ and C_{22}-$PCL_{6.8}$.

No.	Sample	Precursor	DP_{NMR}	C_{22} (wt. %)	Ester (wt. %)	T_m (°C)[a]	ΔH_m (J/g)[a]	ΔH_{mPVL} (J/g)[a,b]	ΔH_{mPCL} (J/g)[a,c]	x_i (%)[d]
1	$C_{22}PVL_{5.2}$	VL	5.2	35	65	52	155	100.7	–	–
2	$C_{22}PCL_{6.8}$	CL	6.8	30	70	44	152	–	106.4	78

[a] Obtained by differential scanning calorimetry (DSC).

[b] Calculated by the equation $\Delta H_{mPVL} = (\Delta H_m).(x_{PVL})$, where x_{PVL} represent the weight fraction of PVL in the oligomer.

[c] Calculated by the equation $\Delta H_{mPCL} = (\Delta H_m).(x_{PCL})$, where x_{PCL} represent the weight fraction of PCL in the oligomer.

[d] Analyzed according to the equation $x_i = \Delta H_{mPCL}/\Delta H_m^\circ$, where ΔH_m° is the enthalpy of fusion to the PCL 100 % crystalline with a value of 135.3 J/g [Reference].

Fig. S1 ^{1}H NMR spectrum of monodisperse monomer $C_{22}VL_1$ in C_6D_6 at 40 °C.

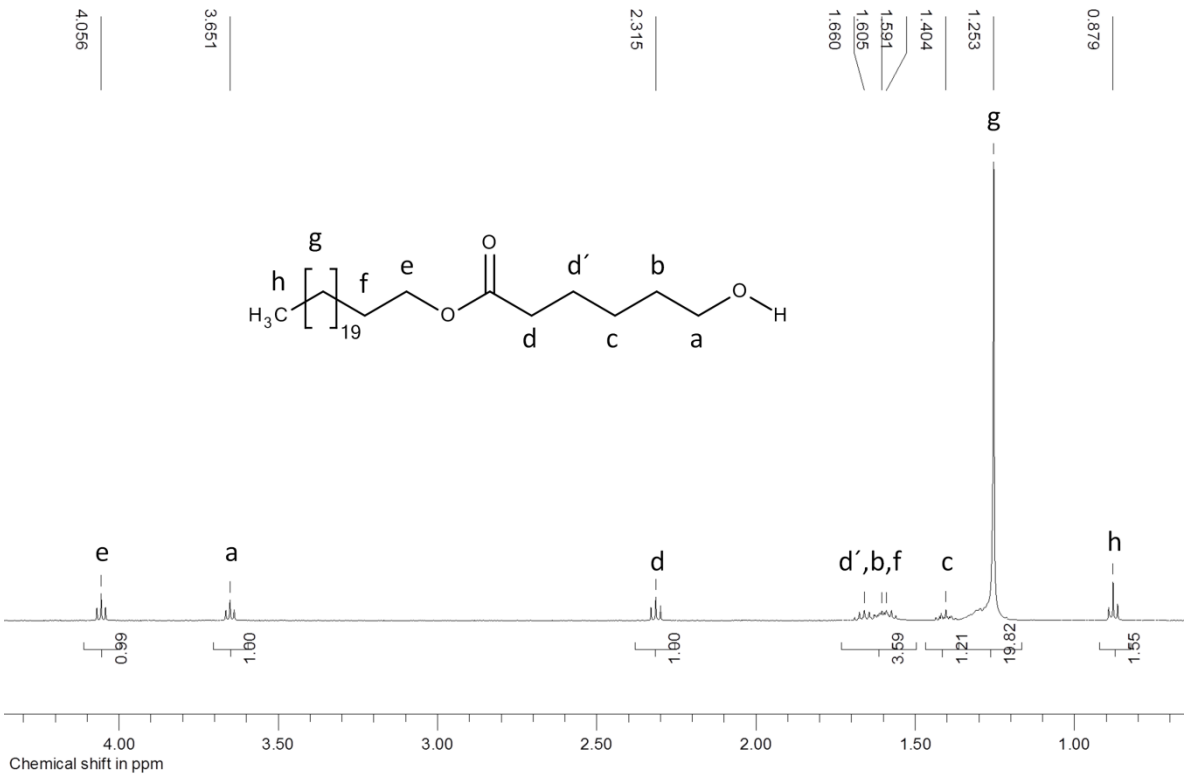
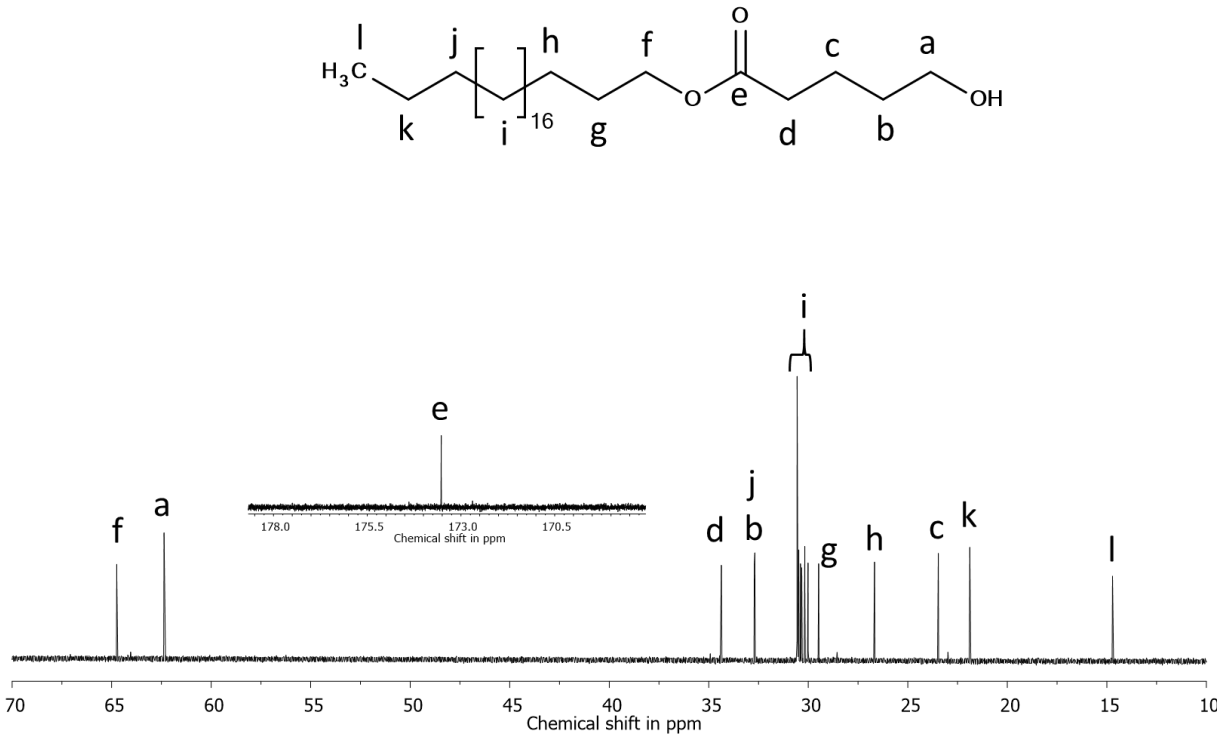
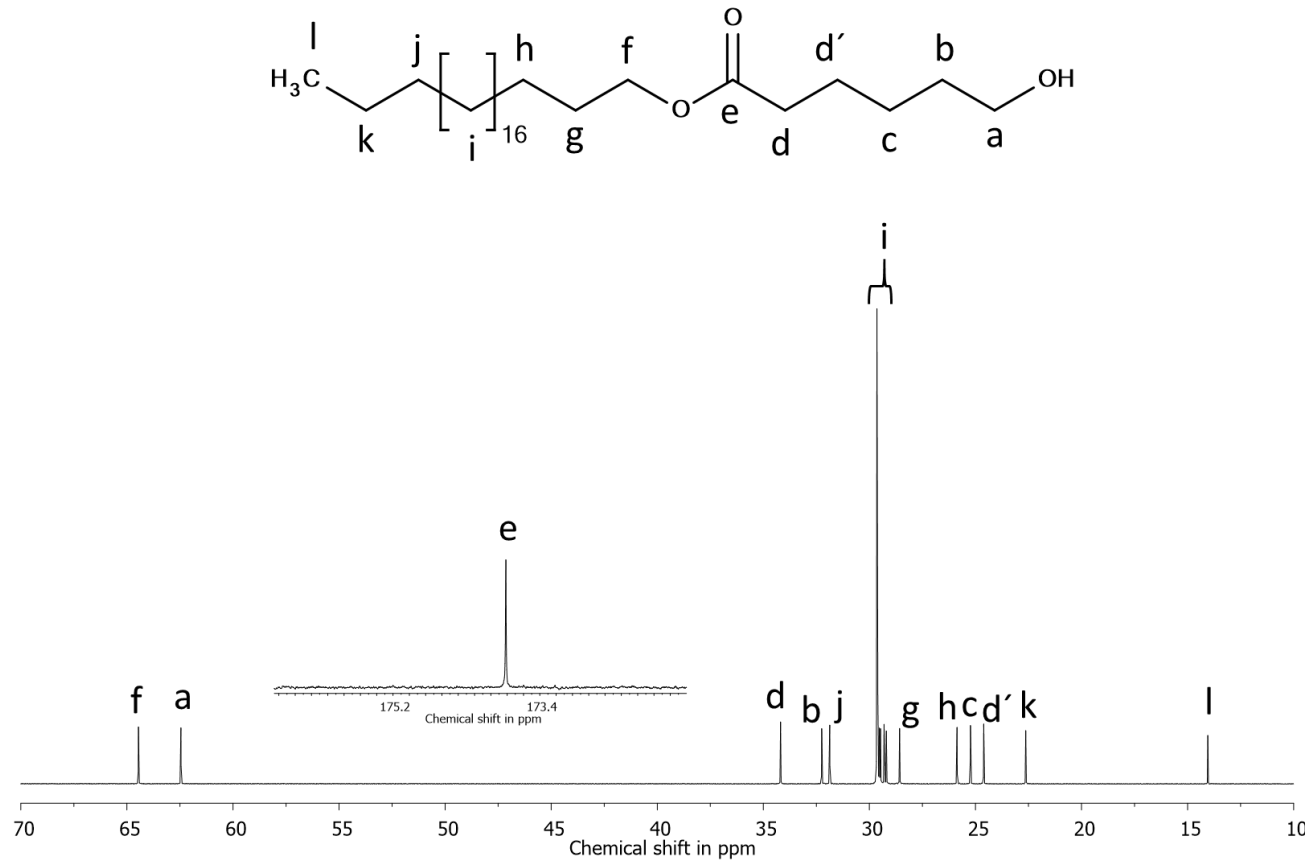


Fig. S2 ^{1}H NMR spectrum of monodisperse monomer $C_{22}CL_1$ in $CDCl_3$ at 40 °C.



carbon	δ	carbon	δ	carbon	δ
a	62.37	e	173.52	i	30.01 - 30.56
b	32.71	f	64.74	j	32.68
c	23.46	g	29.47	k	21.88
d	34.36	h	26.67	l	14.71

Fig. S3 ^{13}C NMR (125 MHz) spectrum (full view) in C_6D_6 at 40 °C and assignment of peaks from monodisperse monomer $C_{22}VL_1$.



carbon	δ	carbon	δ	carbon	δ
a	62.45	e	173.81	j	31.87
b	32.24	f	64.45	k	22.62
c	25.23	g	28.57	l	14.04
d´	24.61	h	25.86		
d	34.18	i	28.57 - 29.64		

Fig. S4 ^{13}C NMR (125 MHz) spectrum (full view) in $CDCl_3$ at 40 °C and assignment of peaks from monodisperse monomer $C_{22}CL_1$.

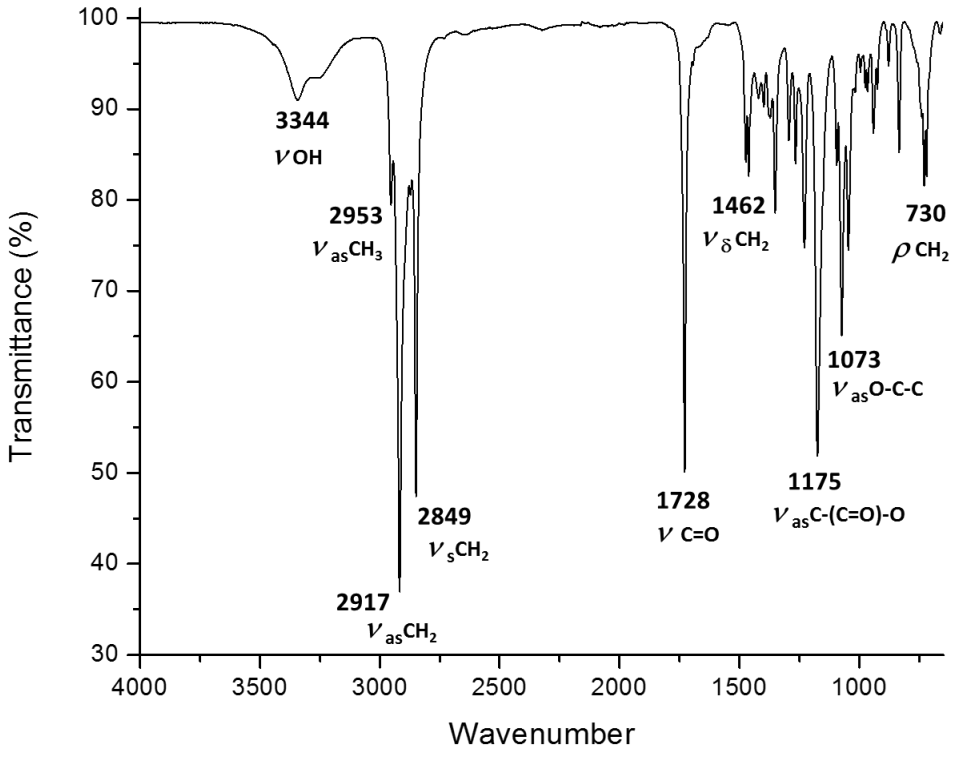


Fig. S5 FT-IR spectrum and assignment of bands from monodisperse monomer $C_{22}VL_1$ (Wavenumber in cm^{-1}).

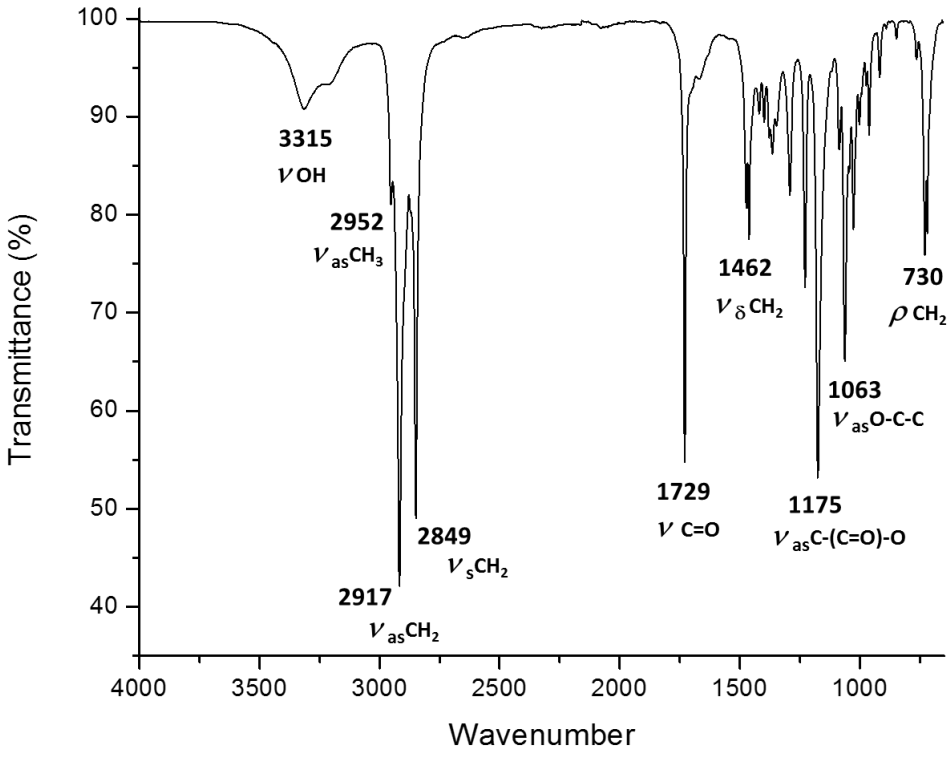


Fig. S6 FT-IR spectrum and assignment of bands from monodisperse monomer $C_{22}CL_1$ (Wavenumber in cm^{-1}).

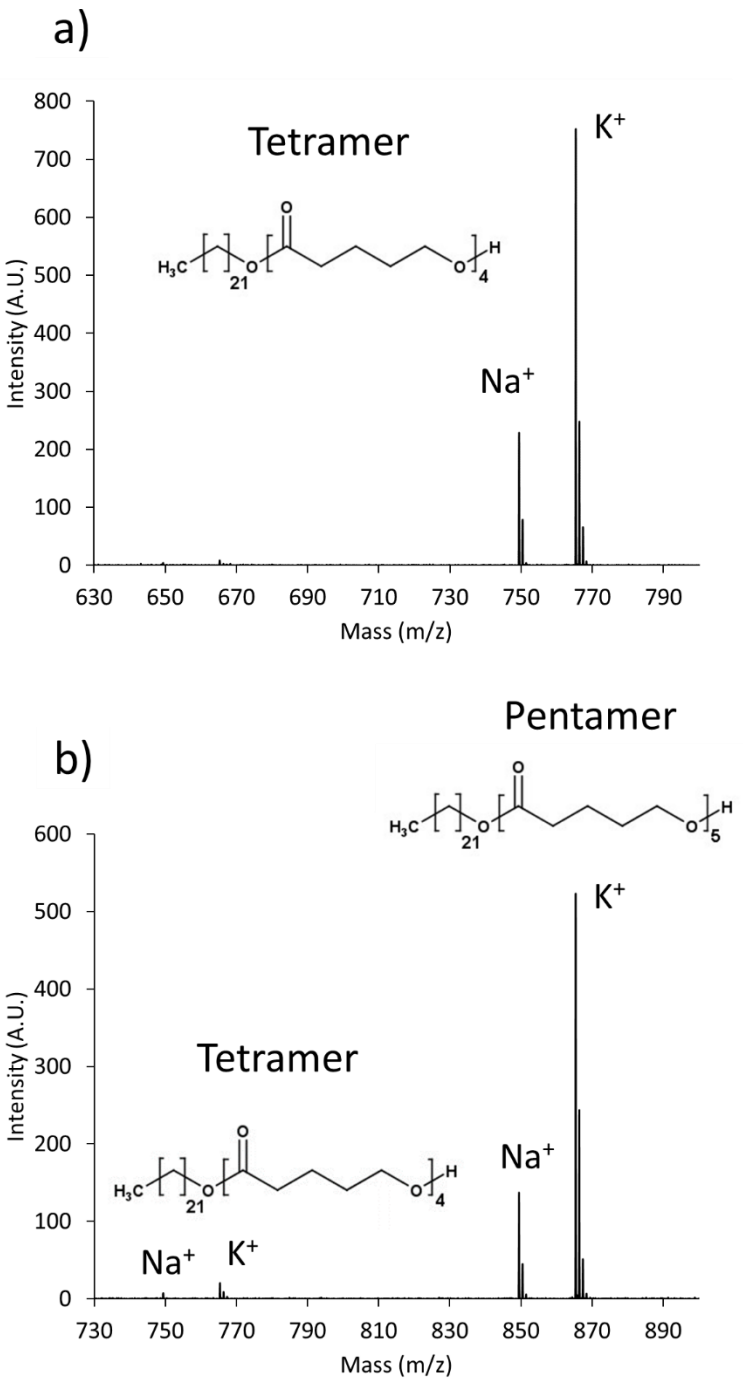


Fig. S7 MALDI-TOF spectra of a) $C_{22}VL_4$ and b) $C_{22}VL_5$.

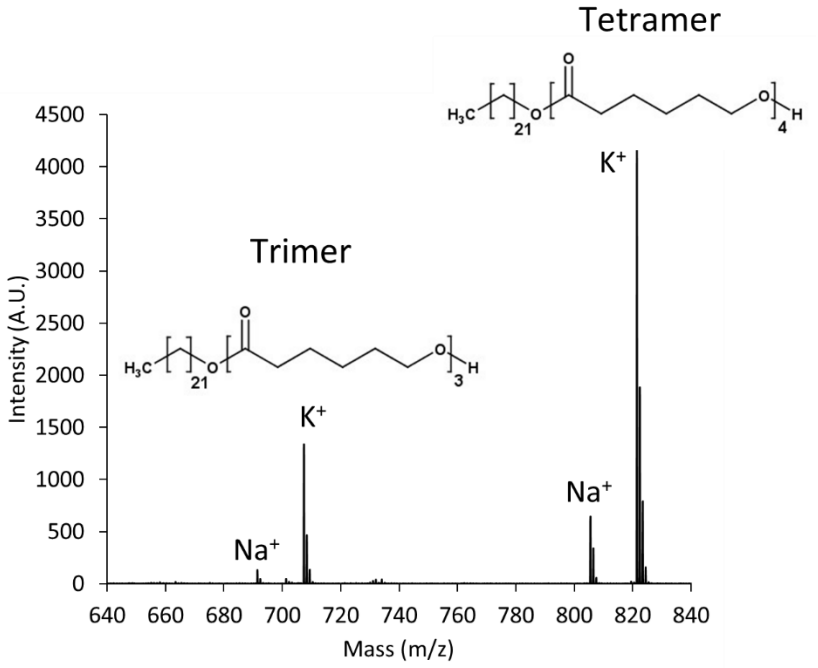


Fig. S8 MALDI-TOF spectrum of $C_{22}CL_4$.

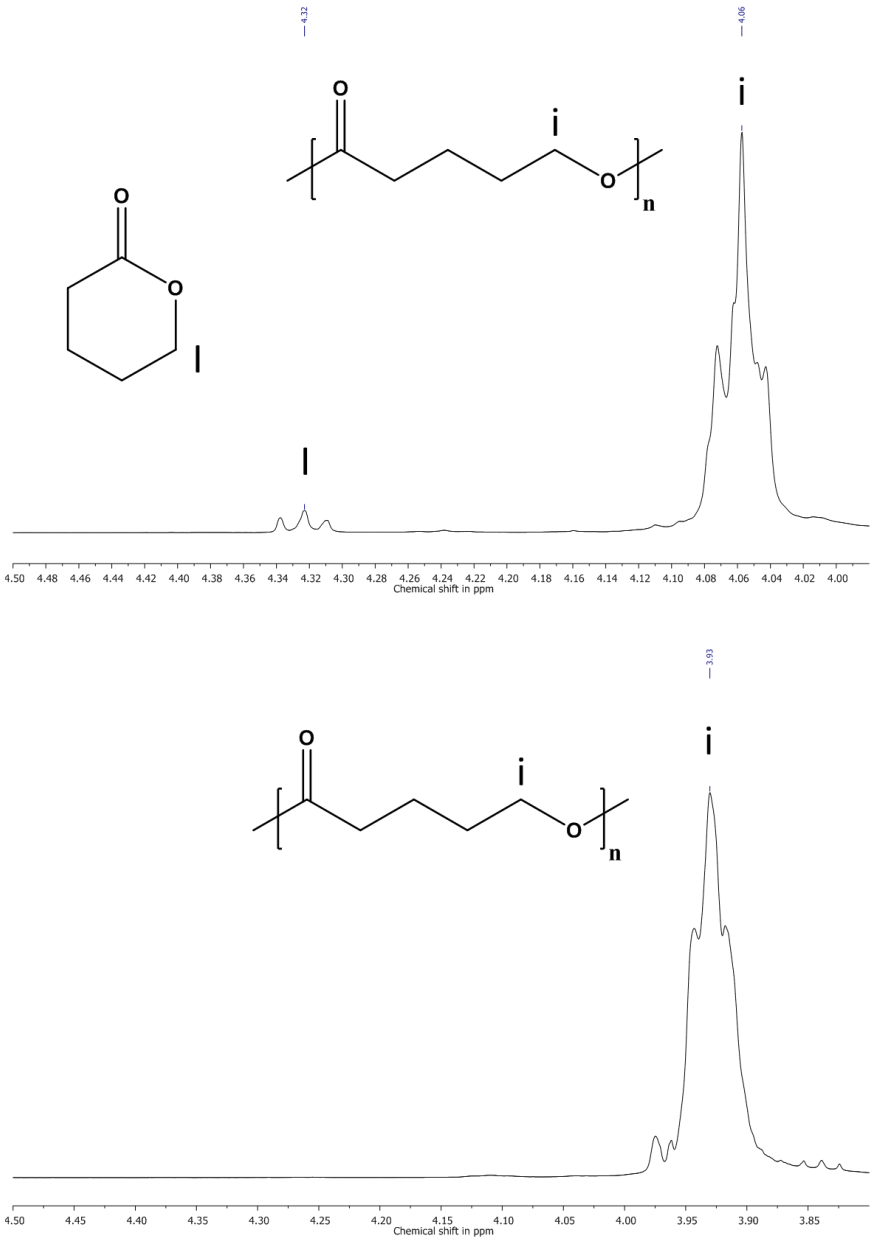


Fig. S9 ^{1}H NMR (400 MHz) spectra at room temperature for PVL using $CDCl_3$ (top) and toluene-d_8 (C_7D_8, bottom) as solvent.

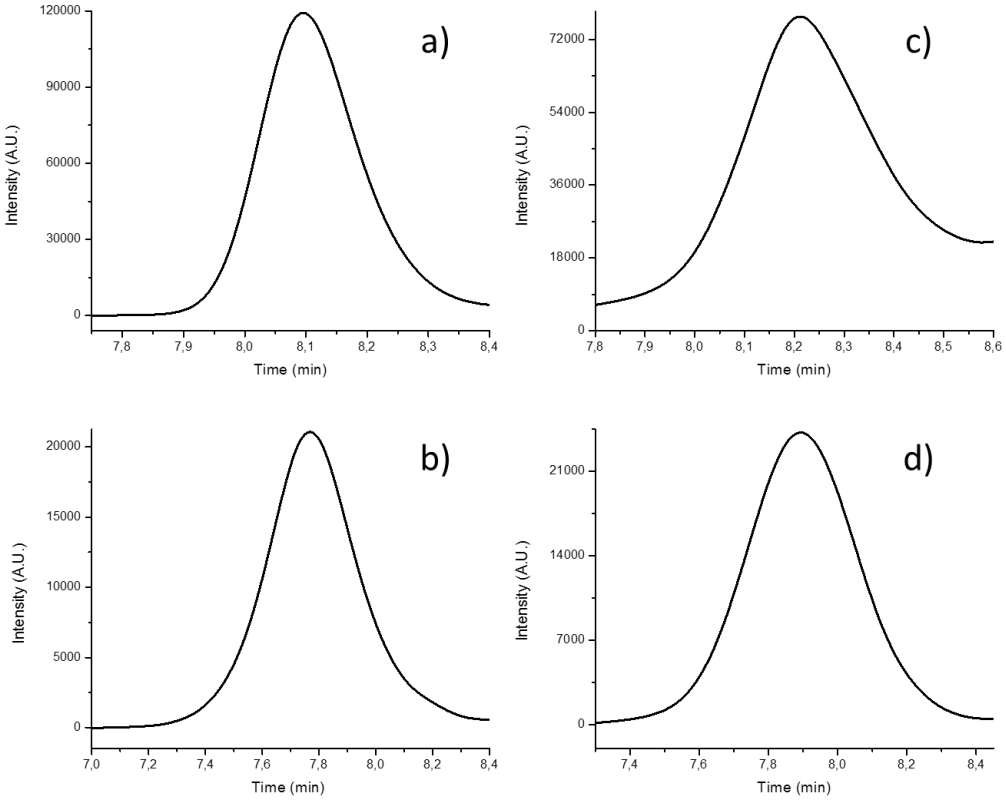


Fig. S10 SEC chromatograms profile for a) $C_{22}CL_2$, b) $C_{22}PCL_{6.8}$, c) $C_{22}VL_2$, d) $C_{22}PVL_{5.2}$ (See Table S2).

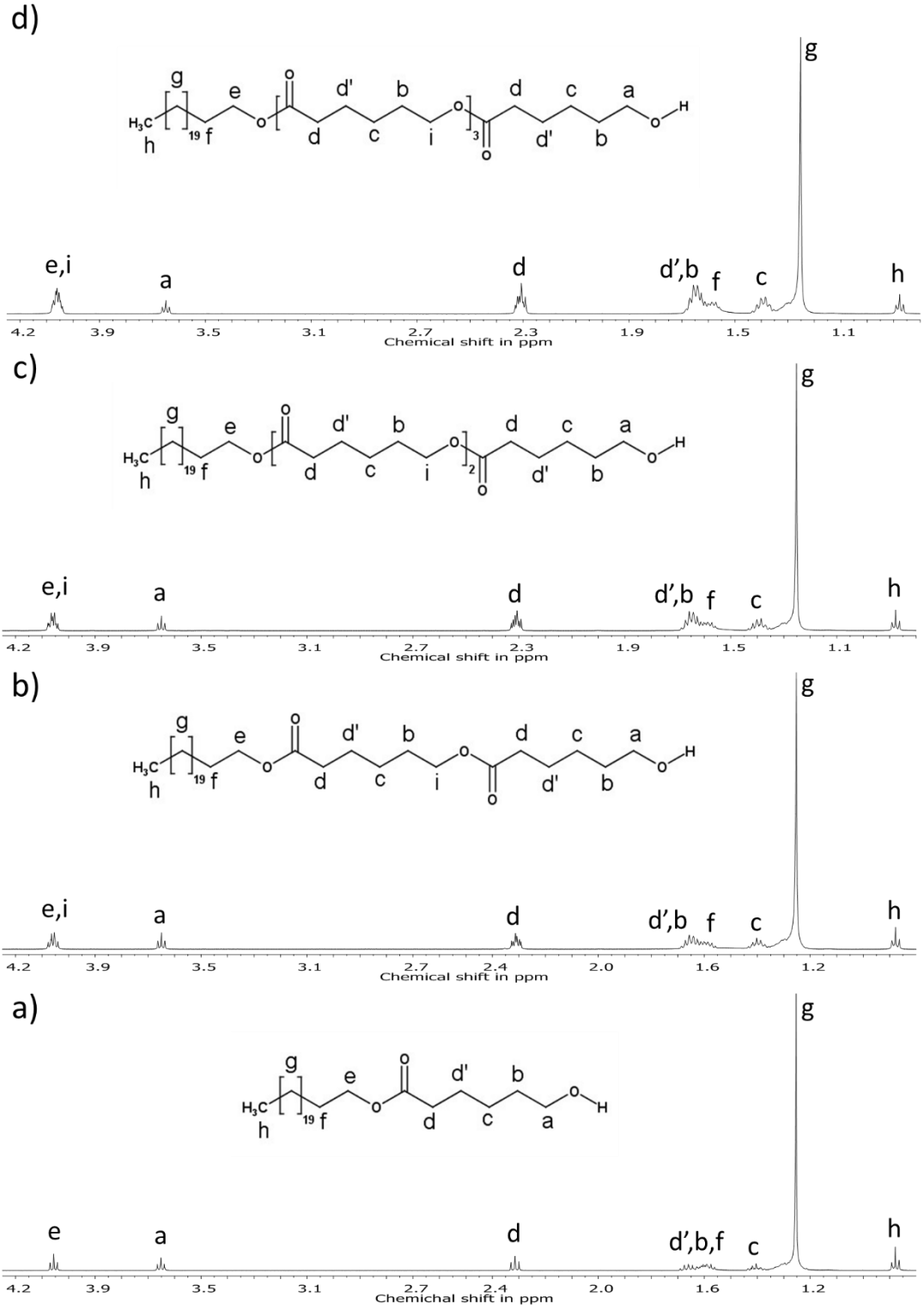


Fig. S11 ^{1}H NMR (500 MHz) spectra (full view) in $CDCl_3$ at 40 °C of different monodisperse oligomers derived from ε-caprolactone (CL) with docosyl (C_{22}) terminal group and isolated by column chromatography, a) monomer $C_{22}CL_1$, b) dimer $C_{22}CL_2$, c) trimer $C_{22}CL_3$, and d) tetramer $C_{22}CL_4$.

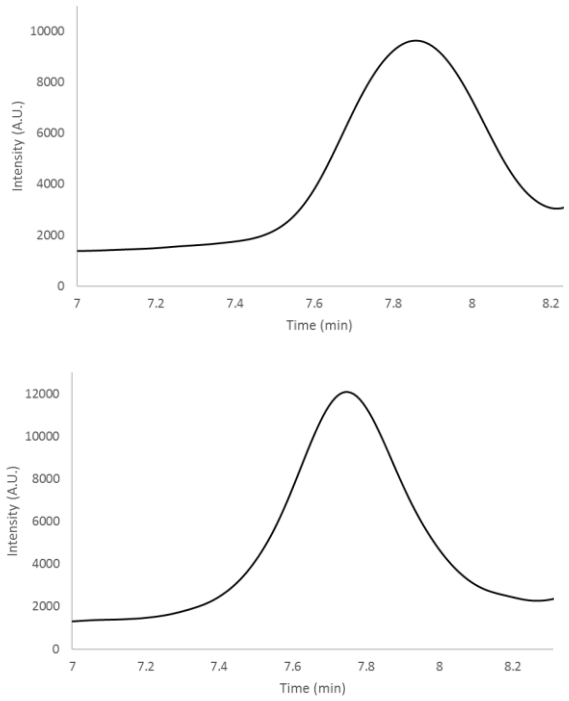


Fig. S12 SEC chromatograms profile (crude of the reaction) of samples C_{22}PVL (top, DP_{theo} = 6) and C_{22}PCL (bottom, DP_{theo} = 6).

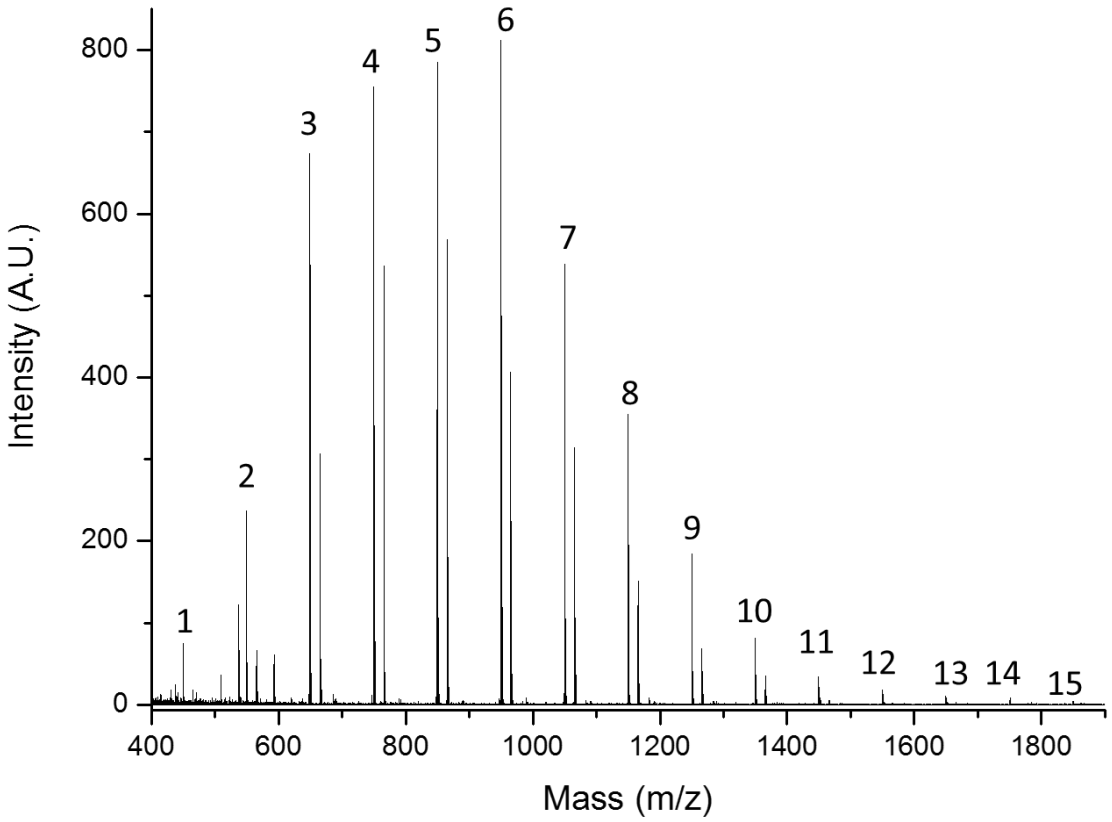


Fig. S13 MALDI-TOF spectrum of $C_{22}PVL_{5.2}$, the number indicates the degree of polymerization (DP) of each peak.

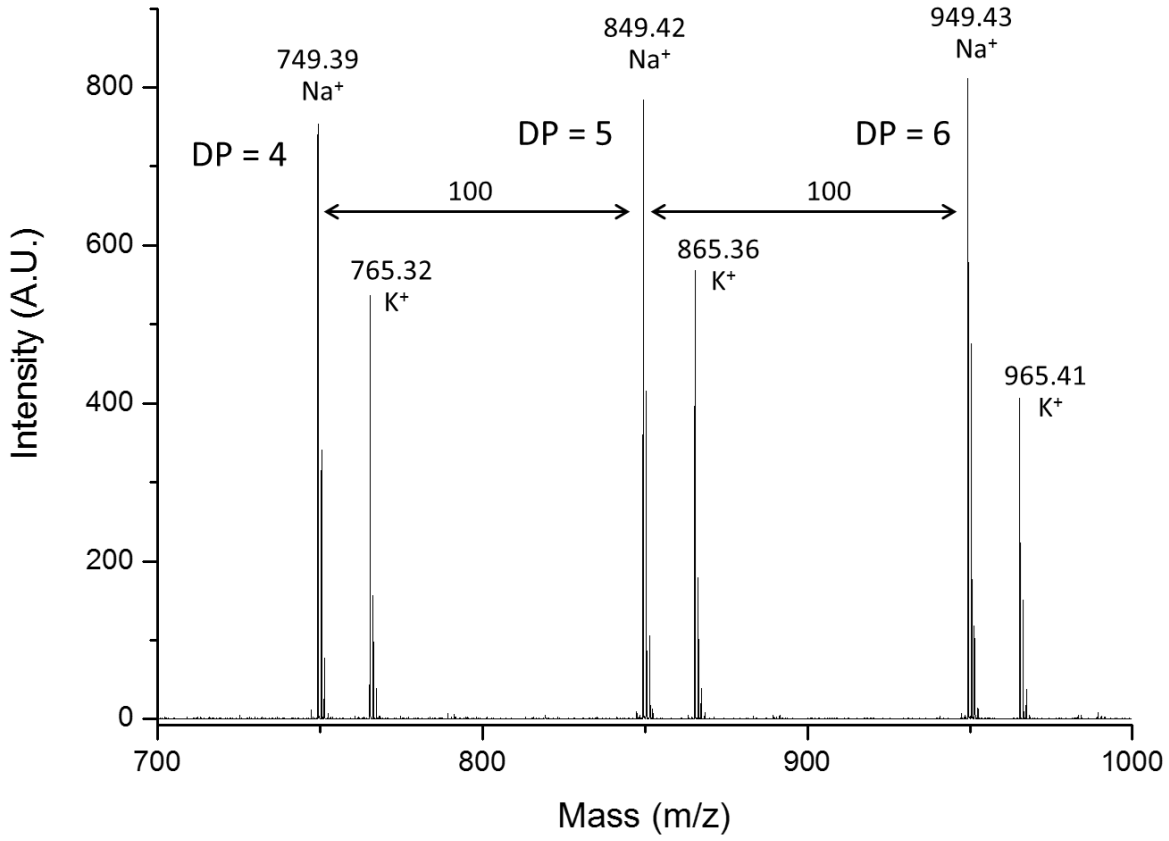


Fig. S14 MALDI-TOF spectrum of $C_{22}PVL_{5.2}$, expansion view (700-1000 m/z) of Fig. S13.

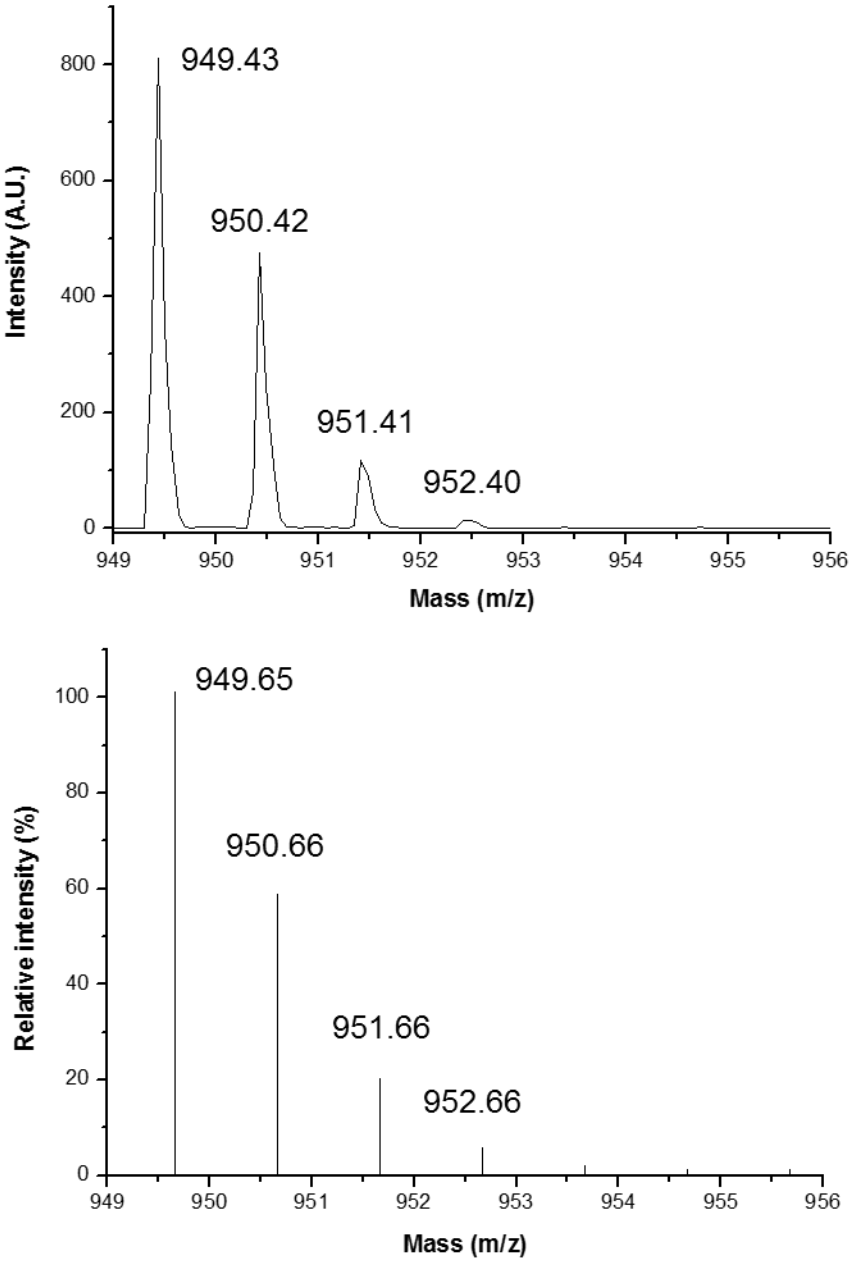


Fig. S15 Experimental MALDI-TOF mass spectrum of the hexamer species (Fig. S14) of VL with C_{22} end-group [$C_{22}VL_6Na^+$, top] and isotopic distribution calculated for DP = 6 [$C_{52}H_{94}O_{13}Na^+$ ($C_{22}VL_6Na^+$, bottom)] in http://www.chemcalc.org.

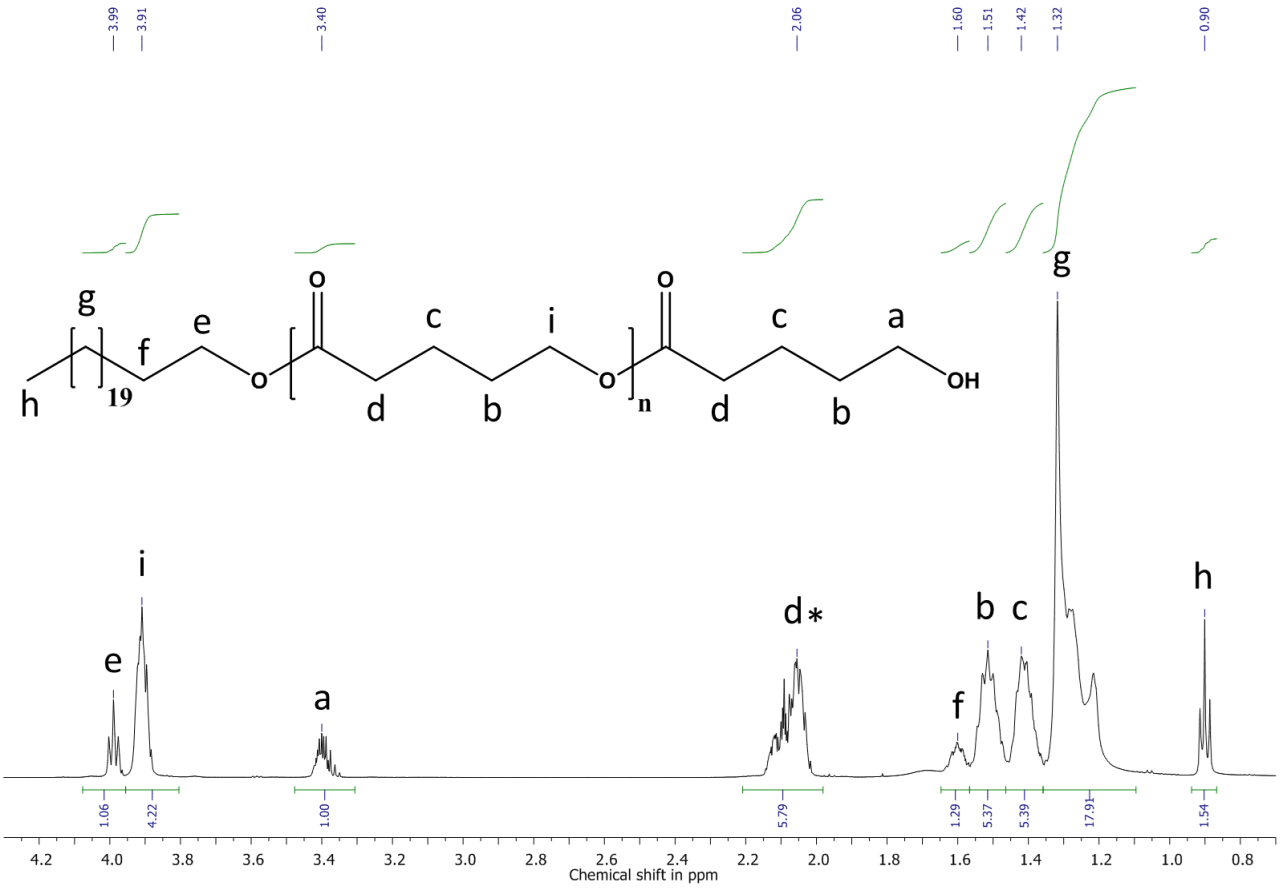


Fig. S16 ^{1}H NMR spectrum of $C_{22}PVL_{5.2}$ in C_7D_8 at 40 °C. The asterisk indicates the C_7D_8 solvent.

Fig. S17 ^{13}C NMR spectrum of $C_{22}PVL_{5.2}$ in C_7D_8 at 40 °C.

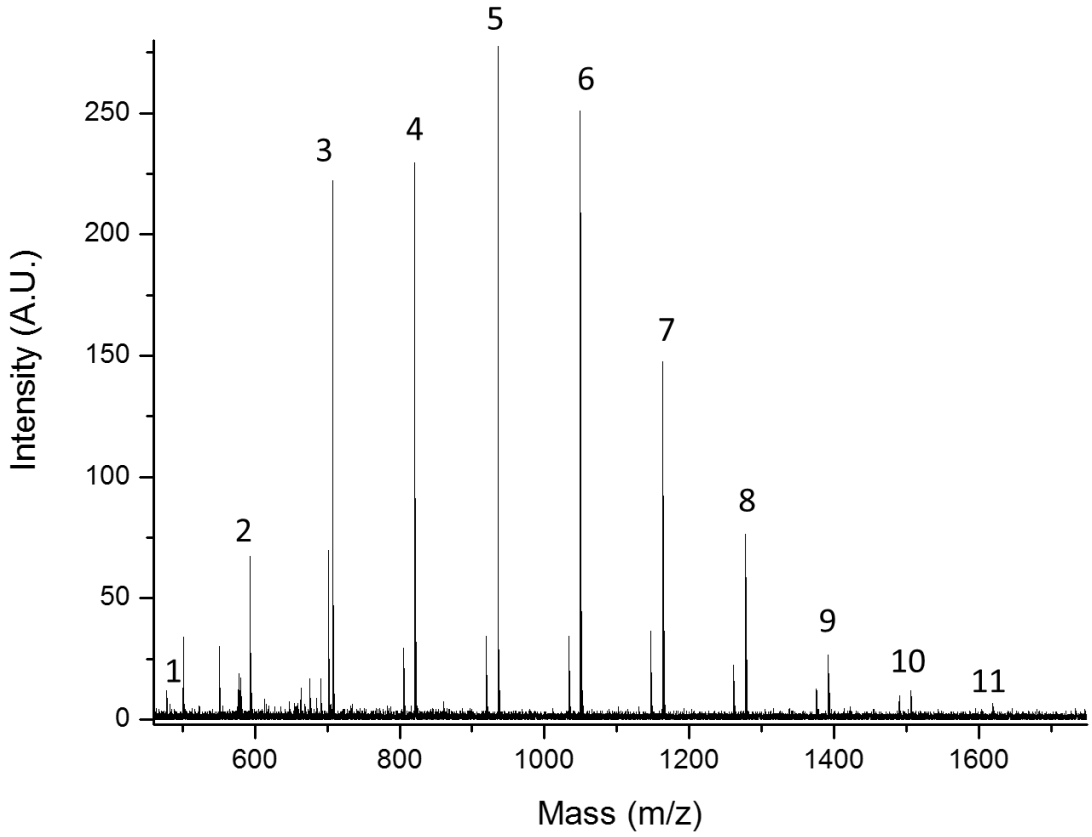


Fig. S18 MALDI-TOF spectrum of $C_{22}PCL_{6.8}$, the number indicates the degree of polymerization (DP) of each peak.

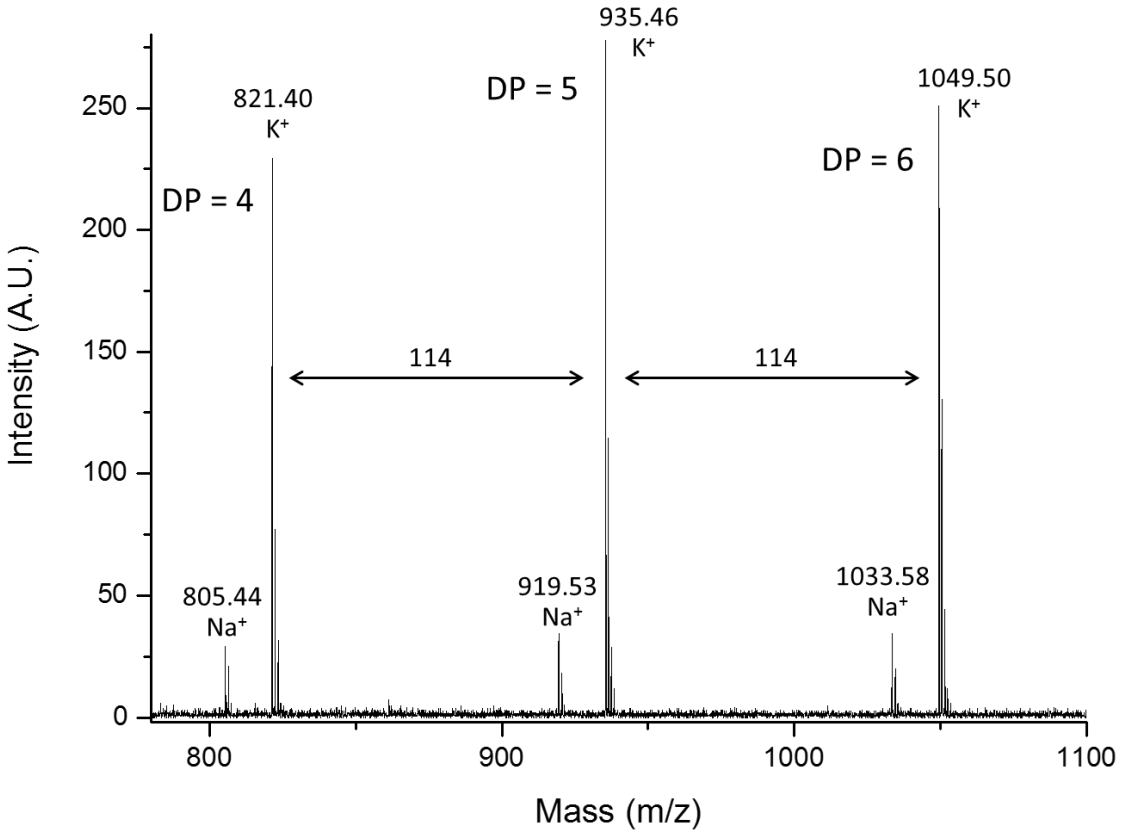


Fig. S19 MALDI-TOF spectrum of $C_{22}PCL_{6.8}$, expansion view (800-1100 m/z) of Fig. S18.

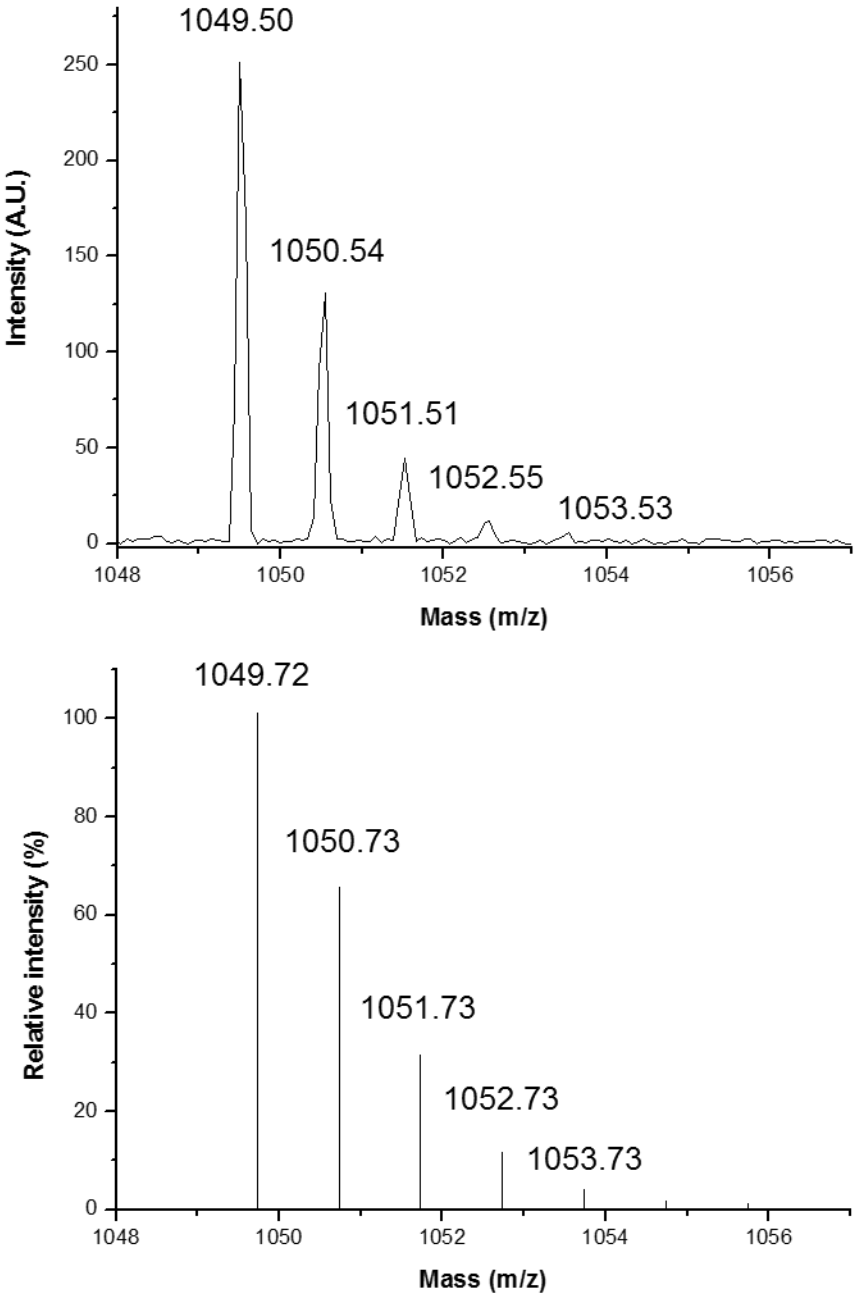


Fig. S20 Experimental MALDI-TOF mass spectrum of the hexamer species (Fig. S19) of CL with C_{22} end-group [$C_{22}CL_6K^+$, top] and isotopic distribution calculated for DP = 6 [$C_{58}H_{106}O_{13}K^+$ ($C_{22}CL_6K^+$, bottom)] in http://www.chemcalc.org.

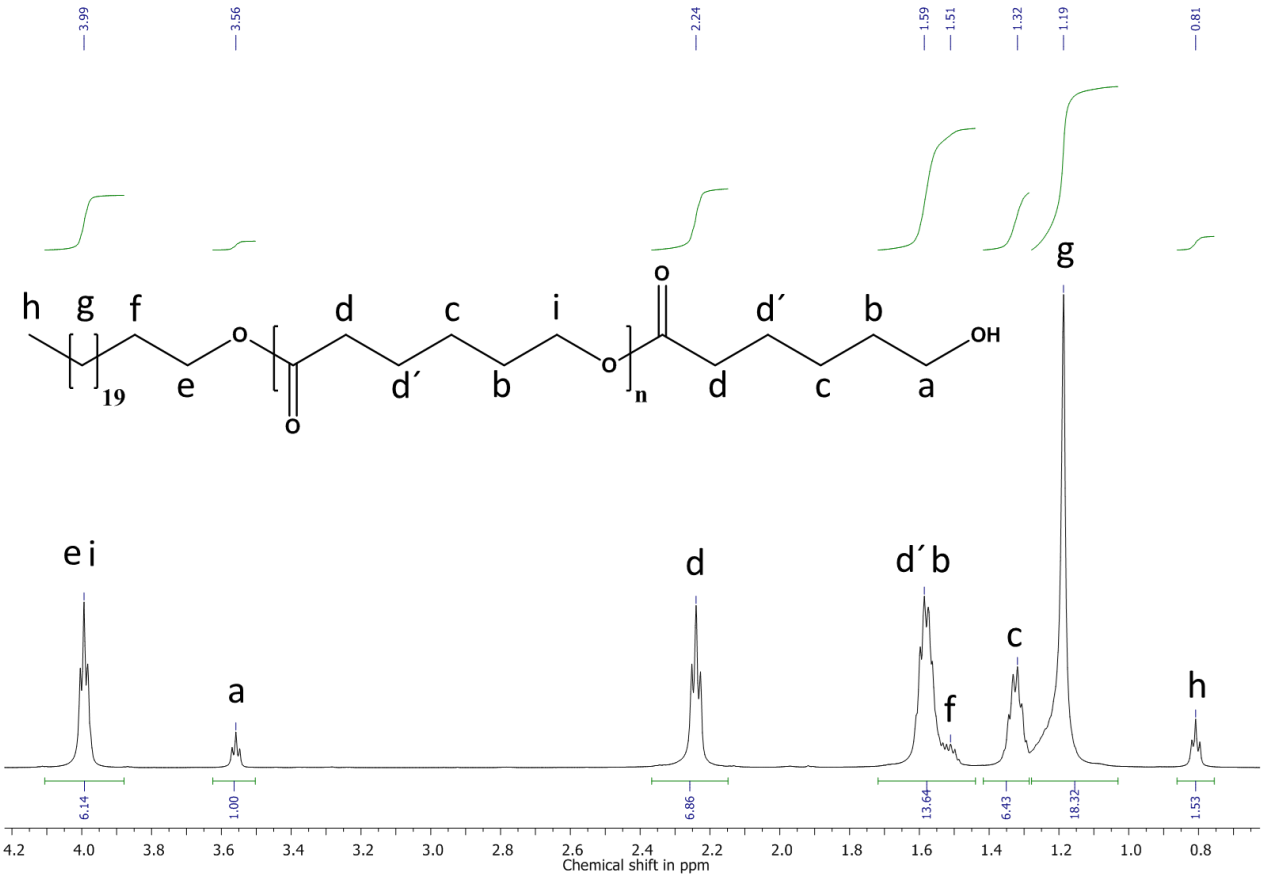


Fig. S21 ^{1}H NMR spectrum of $C_{22}PCL_{6.8}$ in $CDCl_3$ at 40 °C.

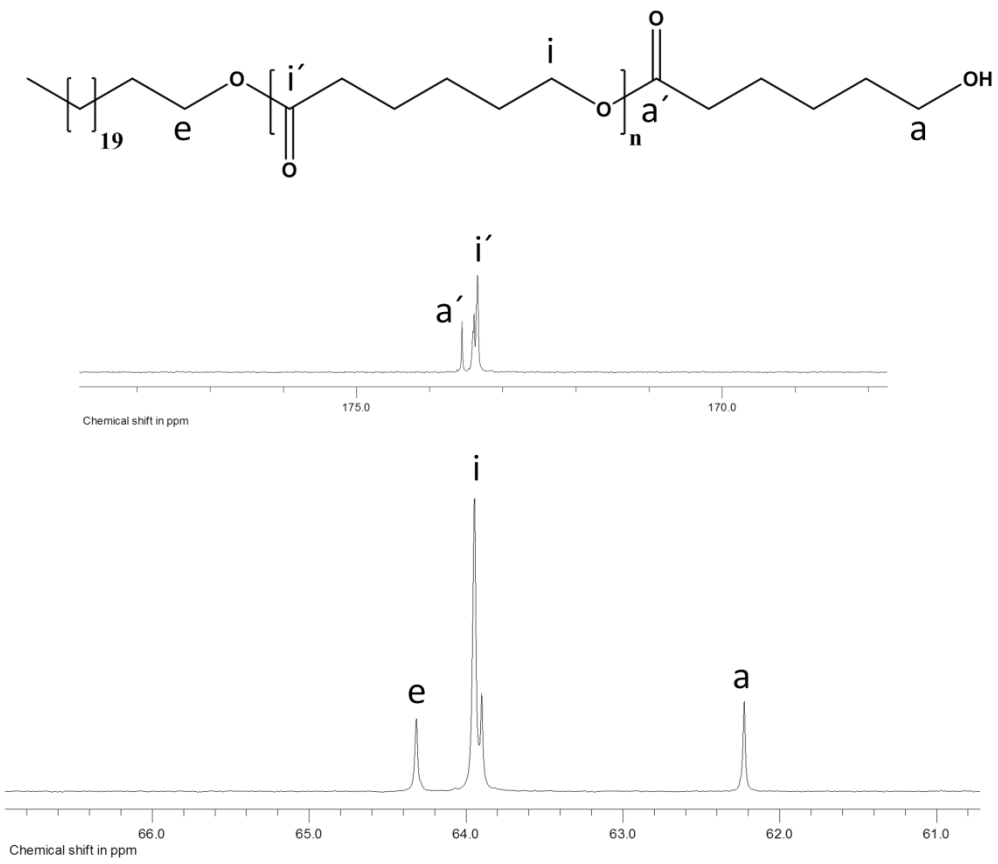


Fig. S22 ^{13}C NMR spectrum of $C_{22}PCL_{6.8}$ in $CDCl_3$ at 40 °C.