Electronic Supplementary Information

Enzymatic recycling of polymacrolactones

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Table S1 Populations of different Gl isomeric MCOs (monomers and dimers) used for simulation studies.

MCO	11E[1] (wt%)	11Z[1] (wt%)	12E[1] (wt%)	12Z[1] (wt%)
Gl	47	13	31	9

	11E 11E[2] (wt%)	11E 11Z[2] (wt%)	11E 12E[2] (wt%)	11E 12Z[2] (wt%)	11Z 11Z[2] (wt%)	11Z 12E[2] (wt%)	11Z 12Z[2] (wt%)	12E 12E[2] (wt%)	12E 12Z[2] (wt%)	12Z 12Z[2] (wt%)
$c(Gl)_2$	22	12	29	8	2	8	2	10	5	1

[1] Content of different isomers determined by NMR. [2] Population estimated from statistical addition of two isomeric monomers.

Table S2 Thermal properties of synthesized PMLs

PML	TGA[a]			DSC[b]				
	$^{o}T_{d\ 10\%}$ (°C)	$^{max}T_d$ (°C)	R_w (%)	T_g (°C)	T_c (°C)	ΔH_c (J/g)	T_m (°C)	ΔH_m (J/g)
PPDL	399.1	425.1	3.0	n.d.	80.1	112.9	94.1	117.1
PGl	384.9	420.7	1.1	n.d.	32.2	54.8	47.1	56.2
P6HDL	388.3	426.3	1.4	n.d.	33.4	76.9	46.6	73.2

[a] Onset for 10 % ($^{o}T_{d\ 10\%}$) and maximum rate ($^{max}T_d$) thermal decomposition temperatures measured by TGA under inert atmosphere. R_w: remaining weight at 600 °C. [b] Melting (T_m), crystallization (T_c), and glass transition (T_g) temperatures and melting (ΔH_m) and crystallization (ΔH_c) enthalpies measured by DSC.

Table S3 Metanolytic activity of N435 before and after enzymatic polymerizations and cyclodepolymerizations

Sample	Metanolitic activity (a) (μmol·min^{-1}·mg^{-1})	Relative activity (%)
Fresh N435	179	100
N435 cyclodepolymerization PPDL, 0.5% w/v, 300% w/w, 70 °C	175	97.8
N435 cyclodepolymerization PPDL, 2.0% w/v, 300% w/w, 70 °C	178	99.7
N435 cyclodepolymerization PPDL, 5.0% w/v, 300% w/w, 70 °C	178	99.7
N435 polymerization PGl, bulk, 5.0% w/w, 80 °C	166	92.7
N435 polymerization PPDL, bulk, 5.0% w/w, 100 °C	145	81.0

Table S4 Thermogravimetric properties of macrolactones, PMLs and MCOs recovered after enzymatic depolymerization

Sample	$^{o}T_d^{5\%}$ [1] (°C)	$^{max}T_{d,1}$ [2] (°C)	$^{max}T_{d,2}$ [2] (°C)	$^{max}T_{d,3}$ [2] (°C)	R_w [3] (%)
PDL	144.9	221.3	-	-	0.2
c(PDL)$_n$	215.7	219.0	350.4	418.6	1.7
PPDL	387.1	426.2	-	-	0.9
Gl	177.1	252.4	-	-	0.2
c(PGl)$_n$	186.4	217.6	346.5	417.7	0.1
PGl	363.4	421.7	-	-	0.1
6HDL	182.4	269.6	-	-	0.2
c(P6HDL)$_n$	197.9	231.5	363.0	422.9	0.3
P6HDL	359.3	426.3	-	-	0.2

[1] Onset for 5% ($^{o}T_d^{5\%}$). [2] Maximum rate ($^{max}T_d$) thermal decomposition temperatures measured by TGA under inert atmosphere. [3] R_w: Remaining weight at 600 °C.

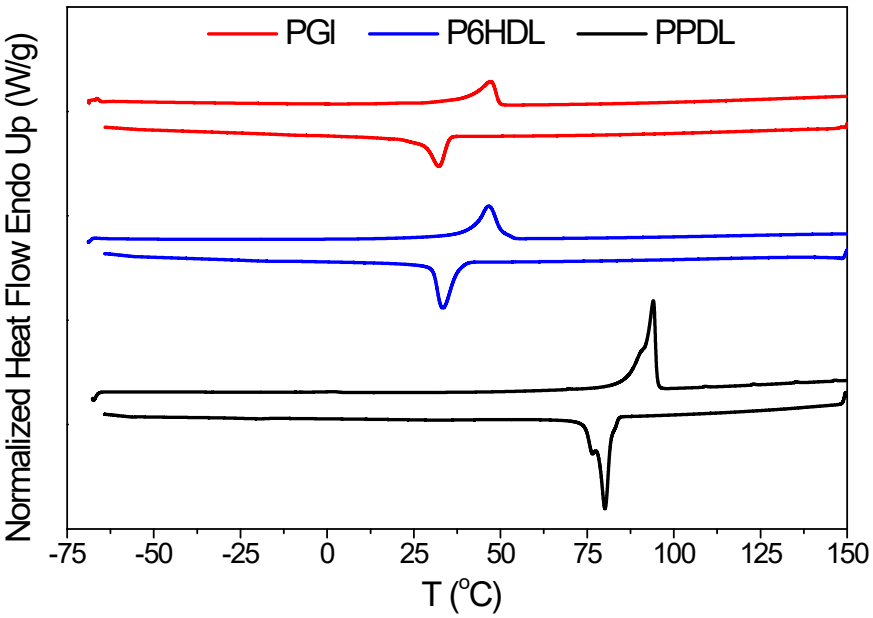

Fig. S1 DSC thermograms of the second heating (top) and first cooling (bottom) of the PMLs synthesised by e-ROP from their corresponding ML.

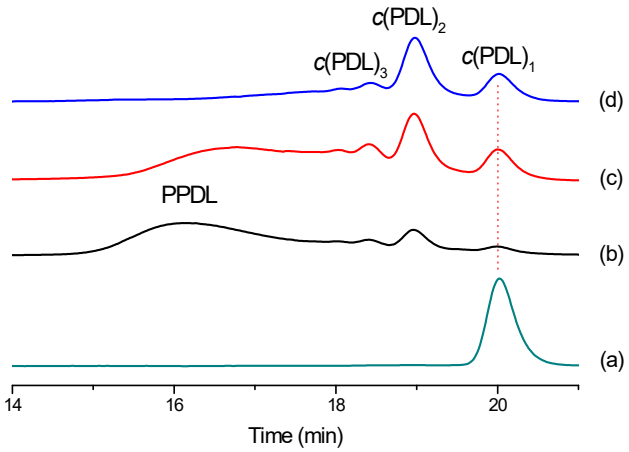

Fig. S2 GPC chromatograms of (a) PDL and samples collected after 24 hours of enzymatic recycling of PPDL carried out at 70 °C, 300% w/w CALB and at different polymer concentrations (b) 5% w/v, (c) 2% w/v and (d) 0.5% w/v.

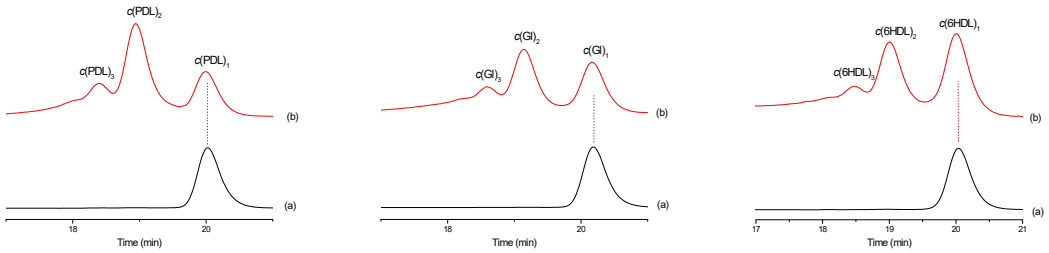

Fig. S3 Comparison of GPC chromatograms of (a) initial MLs (PDL, Gl, 6HDL) and (b) MCOs recovered after enzymatic cyclodepolymerizations.

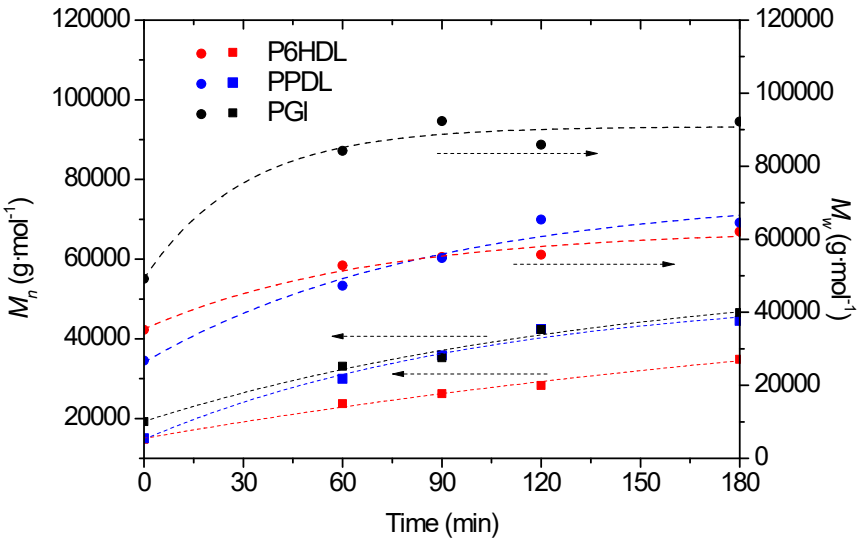

Fig. S4 Evolution of M_n and M_w of remaining PMLs along cyclodepolymerization reactions

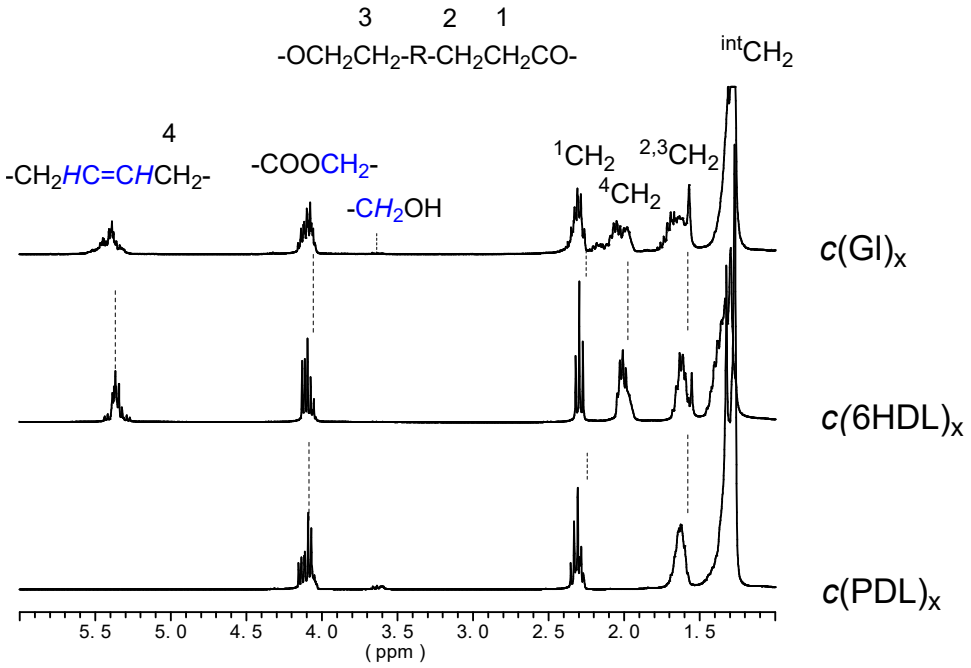

Fig. S5 ^{1}H NMR spectra of MCOs recovered after 48 h of enzymatic recycling of PPDL, P6HDL and PGl.

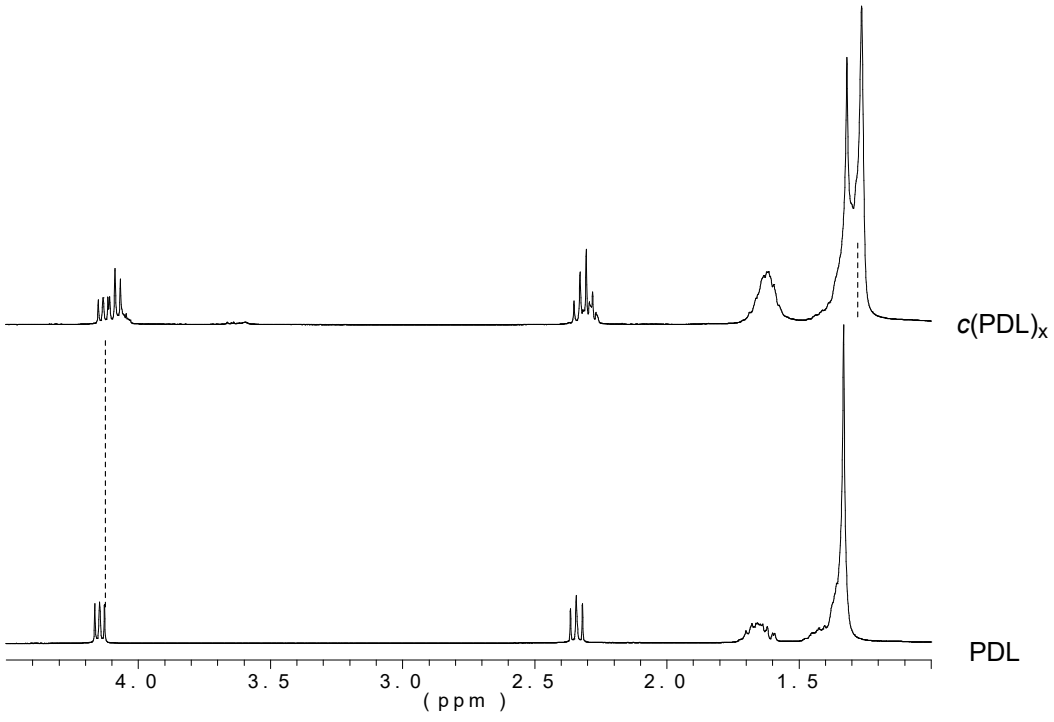

Fig. S6 ^{1}H NMR spectra of PDL and MCOs (c(PDL)$_x$) recovered after 48 h of enzymatic recycling of PPDL.

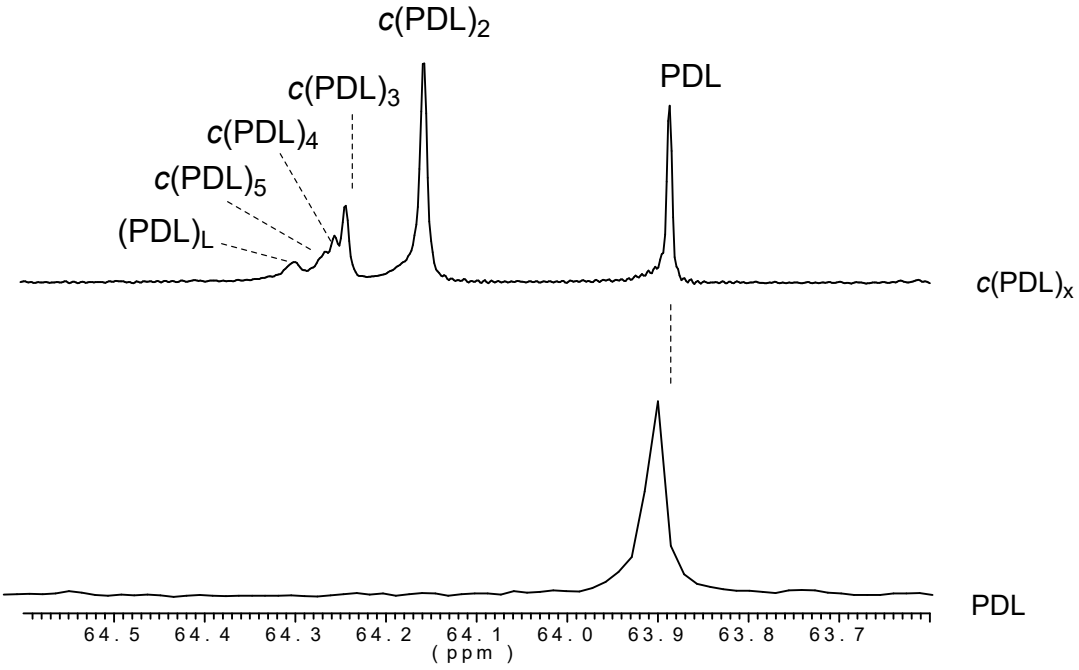

Fig. S7 ^{13}C NMR spectra of PDL and MCOs ($c(PDL)_x$) recovered after 48 h of enzymatic recycling of PPDL in the region of OCH_2.

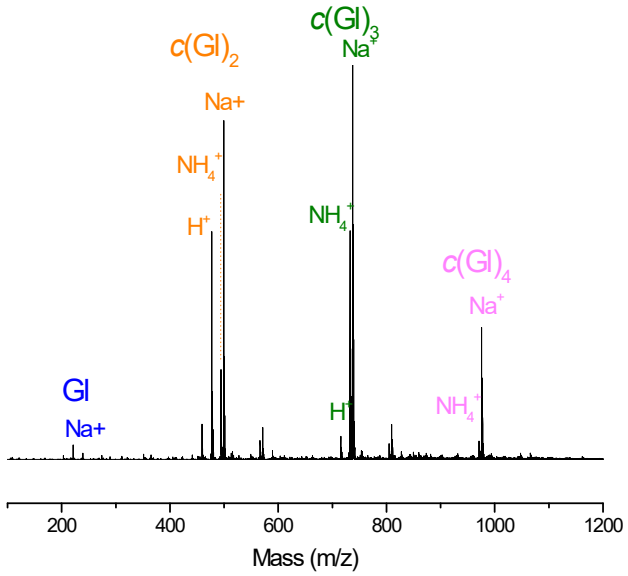

Fig. S8 ESI Mass spectrum of PGl after 48 h of enzymatic recycling.

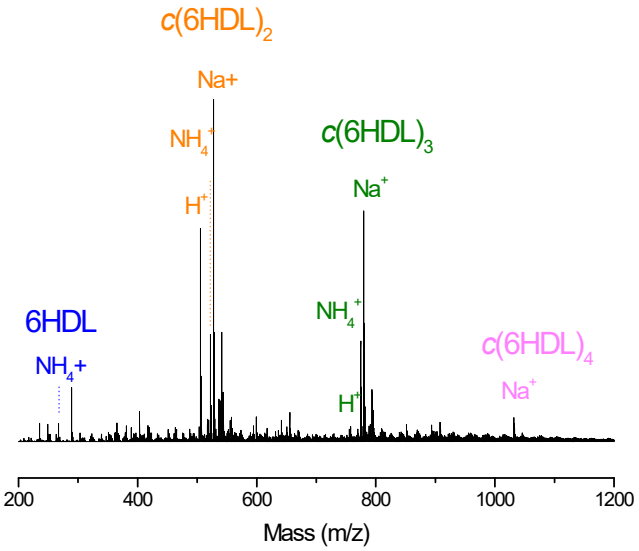

Fig. S9 ESI Mass spectrum of P6HDL after 48 h of enzymatic recycling.

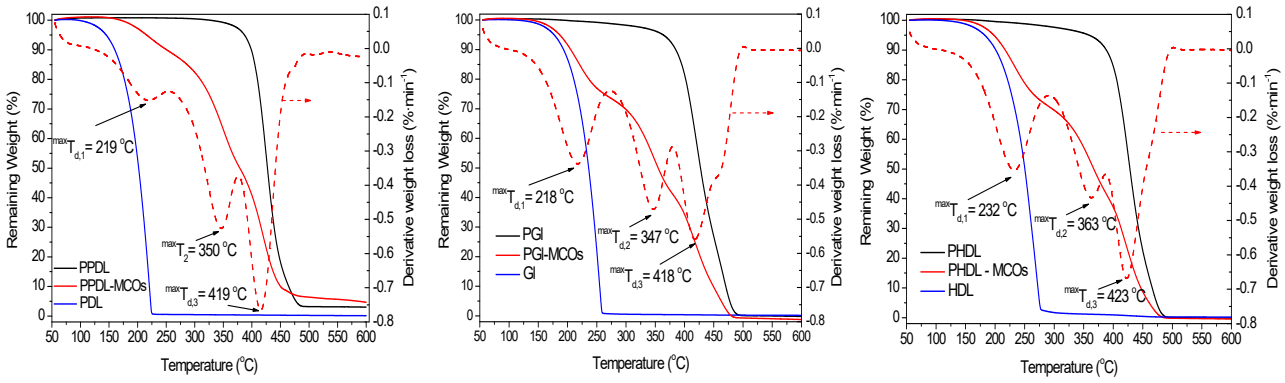

Fig. S10 Thermogravimetric analysis of MLs, PMLs and MCOs recovered after 48 h of PMLs enzymatic cyclodepolymerization

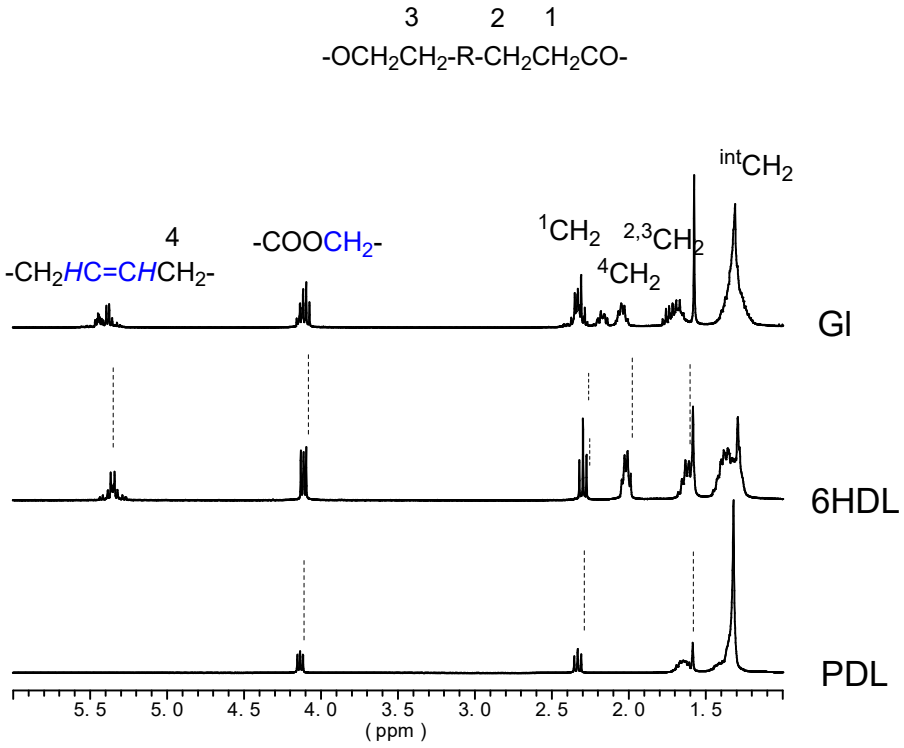

Fig. S11 ^{1}H NMR spectra of volatiles recovered after treating the different MCOs at high temperatures under nitrogen circulation (PDL, 6HDL and GI).

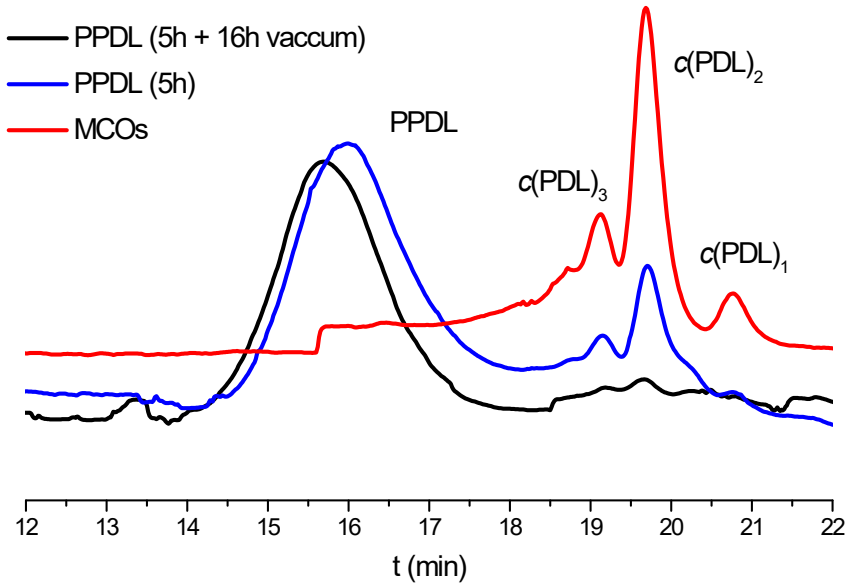

Fig. S12 GPC chromatograms of a) $c(PDL)_x$ and b) PPDL obtained by enzymatic polymerization in bulk of these MCOs ($c(PDL)_x$) without and with vacuum applied to the system.