Supporting Information for

One-pot Two-Step Efficient Metal-Free Process for the Generation of PEO-*b*-PCL-*b*-PLA Amphiphilic Triblock Copolymers

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A – MALDI-ToF spectra

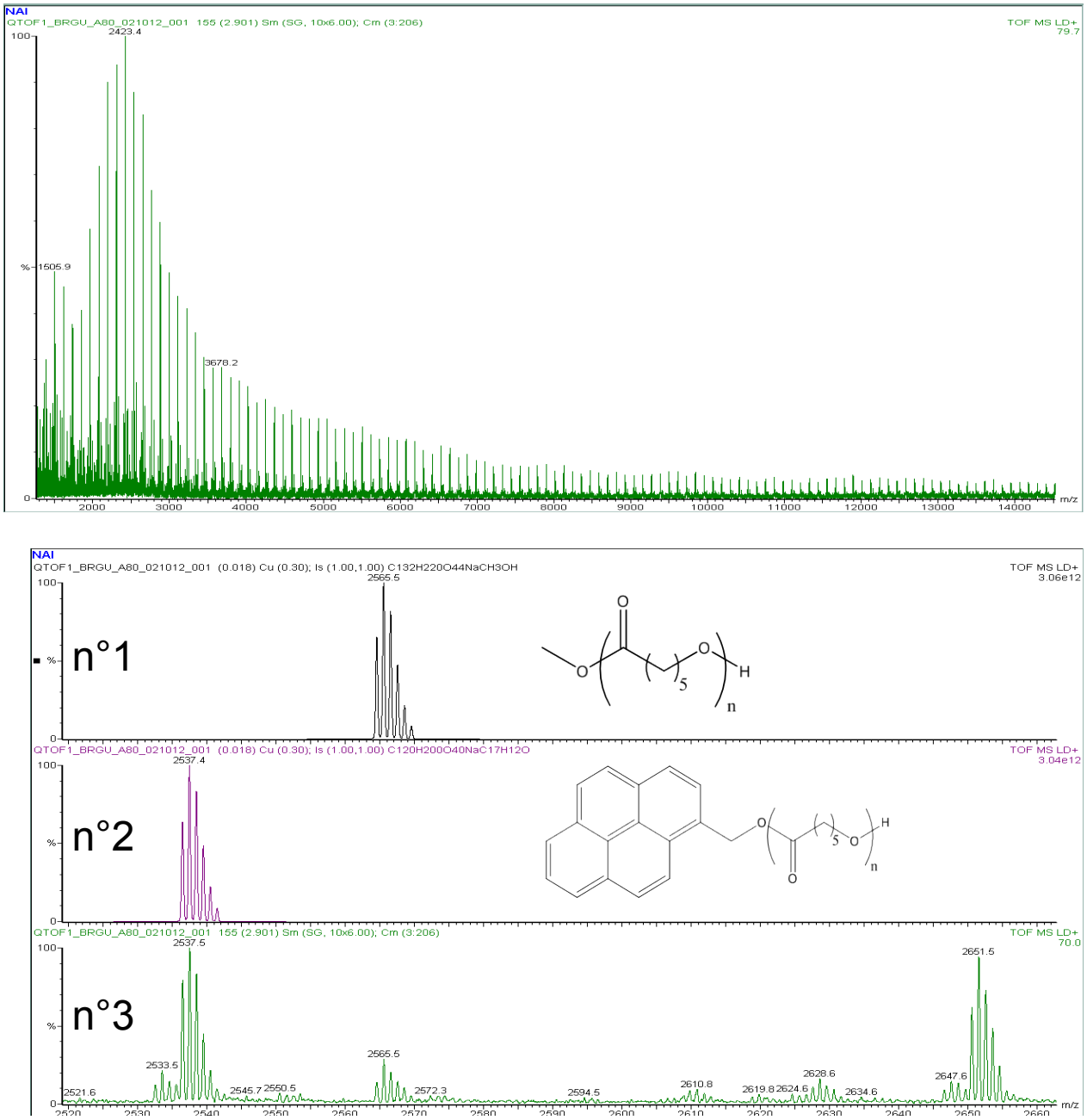


Figure S1. MALDI-ToF spectrum of PCL (top) initiated by 1-pyrenemethanol, catalyzed by TBD and precipitated in heptane. Theoretical model (n°1 and 2) and zoom of the MALDI-ToF spectrum of PCL (n°3) (bottom).

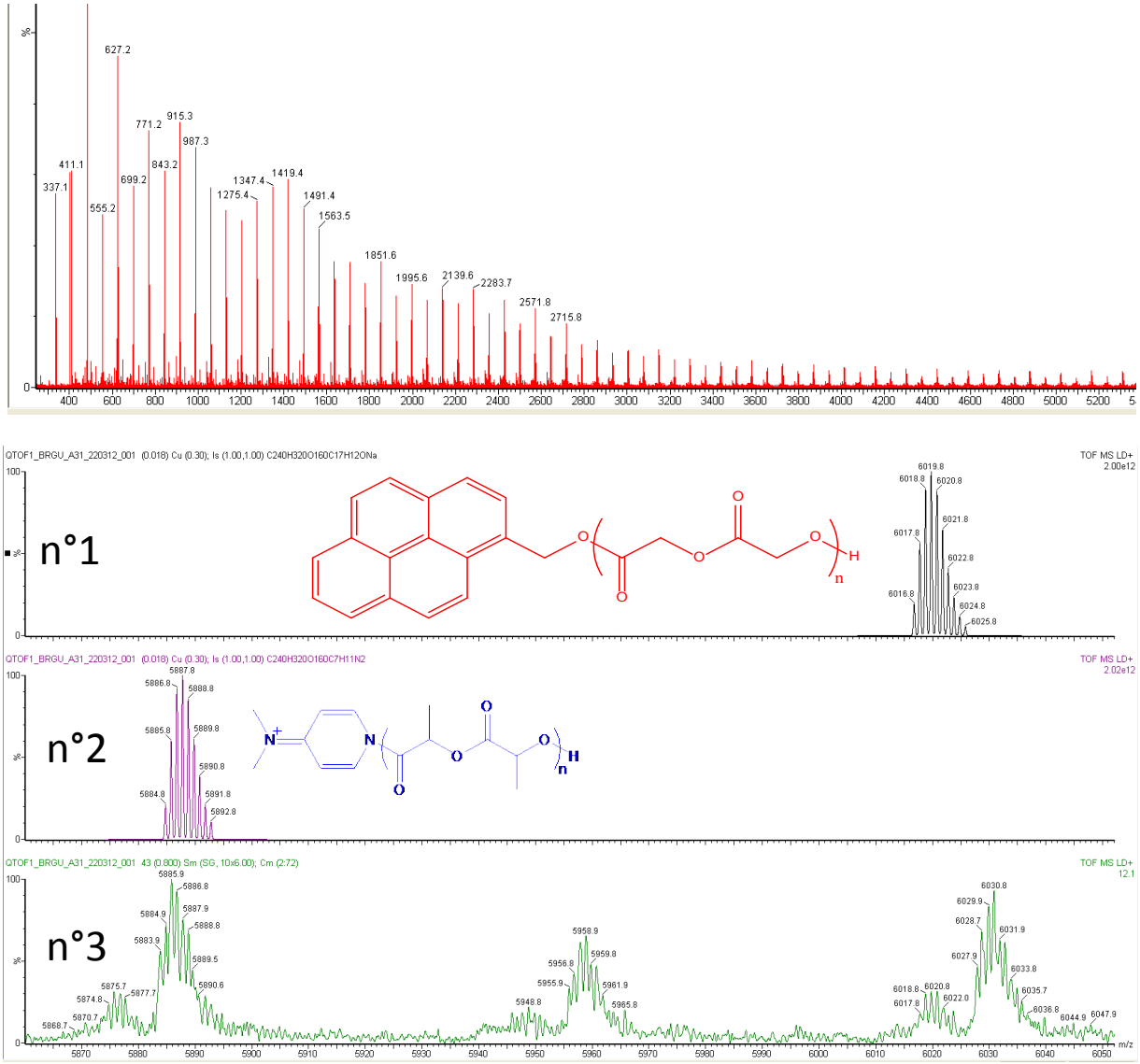


Figure S2. MALDI-ToF spectrum of P(L-LA) (top) initiated by 1-pyrenemethanol, catalyzed by DMAP and precipitated in heptane. Theoretical model (n°1 and 2) and zoom of the MALDI-ToF spectrum of P(L-LA) (n°3) (bottom).

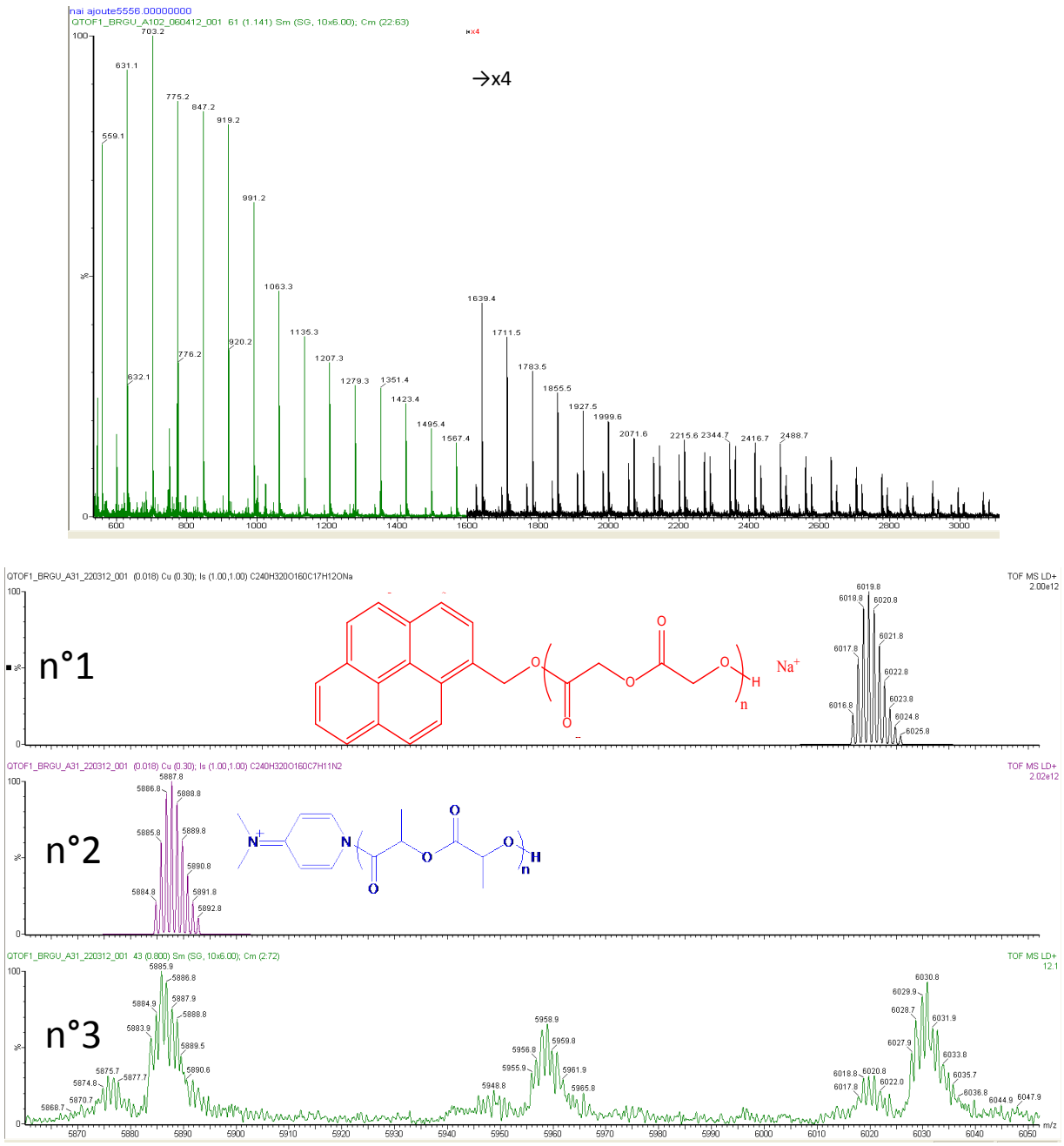


Figure S3. MALDI-ToF spectrum of P(L-LA) (top) initiated by 1-pyrenemethanol, catalyzed by DMAP/DCC and precipitated in methanol. Theoretical model (n°1 and 2) and zoom of the MALDI-ToF spectrum of P(L-LA) (n°3) (bottom).

B – Synthesis of PEO-*b*-P(CL-*co*-(L or D,L)LA) amphiphilic statistical copolymers[1]

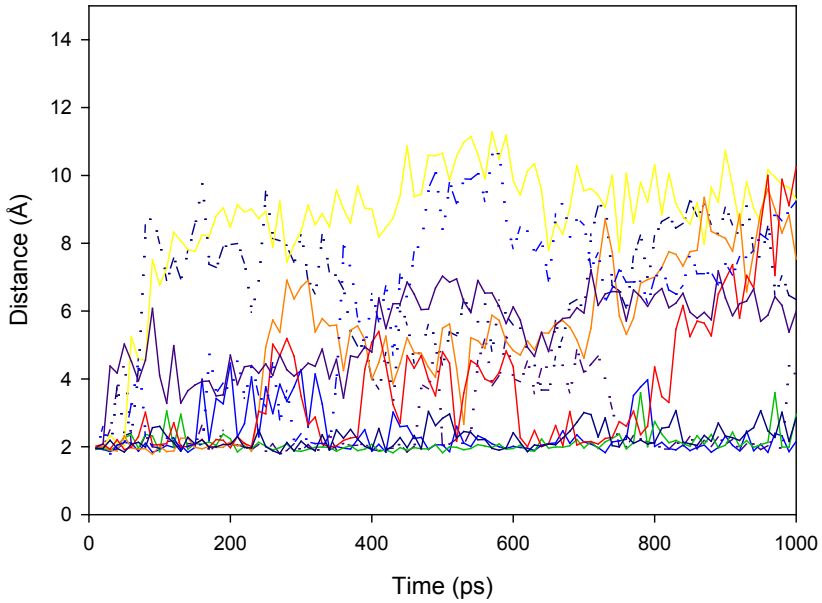
Statistical copolymers were synthesized by using 100 equivalents of ε-CL, 100 equivalents of (L or D,L)LA and 0.01 equivalent of $Sn(Oct)_2$ relative to the initiator PEO-OH (5,000 $g.mol^{-1}$). Copolymerizations were conducted at 160°C in bulk during 18 hours.

Table S1. Characterization data of amphiphilic statistical copolymers PEO-*b*-P(CL-*co*-(L or D,L)LA).

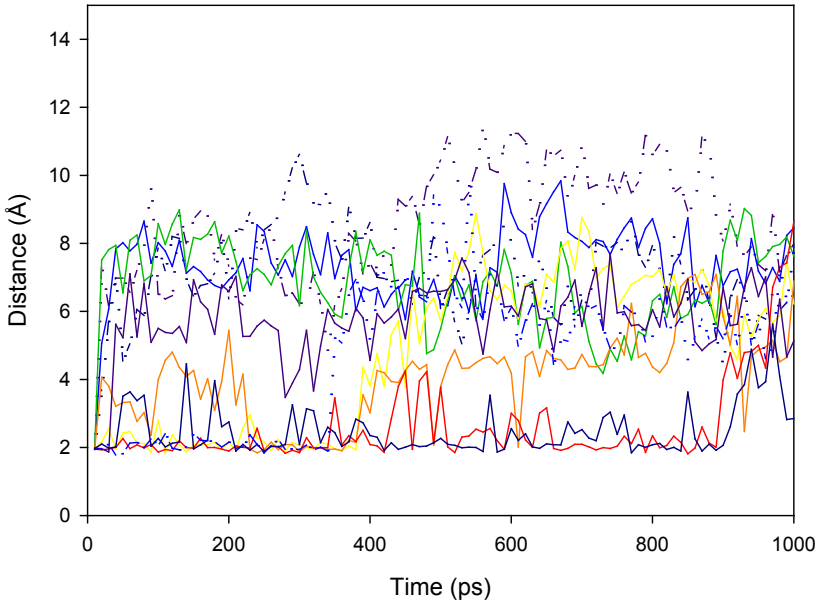
polymer	$[Sn(Oct)_2]_0/[PEO]_0$	$M_{n,th}$ ($g.mol^{-1}$)	$M_{n,NMR}$ ($g.mol^{-1}$)	$M_{n,exp}$[a] ($g.mol^{-1}$)	$Đ$[a]	Yield (%)
PEO-*b*-P(CL-*co*-L-LA)	0.01/1	13,800	14,800	22,500	1.62	77
PEO-*b*-P(CL-*co*-D,L-LA)	0.01/1	14,100	15,900	20,000	1.65	79

a: SEC in THF (+2% TEA), PS standards, 1 $mL.min^{-1}$, T = 35°C.

C – Molecular modeling



(a)



(b)

Figure S4. Evolution of the distance between the nitrogen atom #4 (see Table 4) of TBD and the hydrogen atom of the hydroxyl group of the initiator ($d_{N\text{-}H}$) as a function of the time in the first ns of

the MD runs for system 1 (a) (1-pyrenemethanol initiator, top) and system 2 (b) (PEO initiator, bottom).

D – Physico-chemical characterization of amphiphilic copolymers

Table S2. Characterization of amphiphilic copolymers in water by DLS experiments.

Copolymer	CONTIN	Cumulant		Angle (°)
	$R_{H,app}$	$R_{H,app}$	PDI	
	31	31	0.04	60
PEO-*b*-P(CL-*co*-L-LA)	31.5	31.5	0.04	90
	32	31.5	0.07	120
	35.5	36	0.12	60
PEO-*b*-P(CL-*co*-D,L-LA)	35.5	35	0.10	90
	35.5	34.5	0.11	135
	32.5	32	0.07	60
PEO-*b*-PCL-*b*-P(L-LA)	32	32	0.07	90
	32.5	32	0.07	135
	27	27.5	0.02	60
PEO-*b*-PCL-*b*-P(D,L-LA)	27.5	27.5	0.04	90
	28	27.5	0.04	135

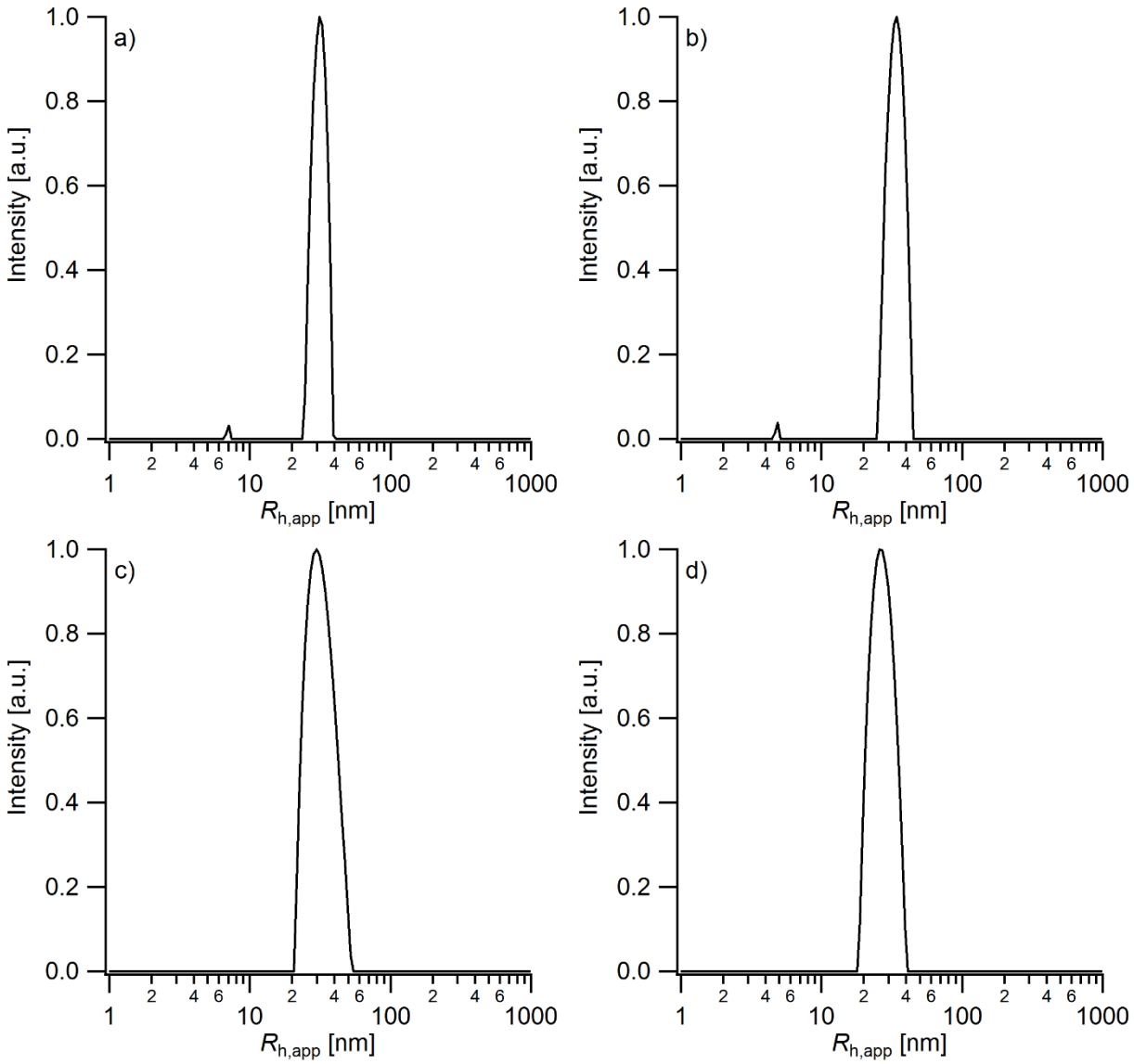


Figure S5. Distribution of the hydrodynamic radius calculated by CONTIN algorithm for 0.1% wt measured by DLS at scattering angle equal to θ = 90° and at 25 °C ((a) PEO-*b*-P(CL-*co*-L-LA), (b) PEO-*b*-P(CL-*co*-D,L-LA), (c) PEO-*b*-PCL-*b*-P(L-LA) and (d) PEO-*b*-PCL-*b*-P(D,L-LA)).

References

(1) Odent, J.; Leclère, P.; Raquez, J.-M.; Dubois, P. *European Polymer Journal* **2013**, *49*, 914.