## Supporting Information

## Double Hydrophilic Polyphosphoester Containing Copolymers as Efficient Templating Agents for Calcium Carbonate Microparticles

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**Figure S1.** SEC overlay of PEO-OH macroinitiator (full line) and the corresponding block copolymer (dotted line) after chain extension by ROP of BYP. Conditions :  $[BYP]_0/[PEO-OH]_0/[DBU]_0/[TU]_0 = 34/2/3/1.5$ ,  $CH_2Cl_2$ , 0 °C.



**Figure S2.** MALDI-TOF spectrum of the starting PEO-OH macroinitiator. On the right, the zoom of the 4660-4700 range shows peaks at 4680.8 and 4696.8 corresponding to the expected  $CH_3$ -O-PEO-OH cationized with sodium and potassium, respectively. The peak at 4666.8 (i.e. 14 mass units below the main peak) corresponds to some contaminating HO-PEO-OH.



Figure S3. Overlay of the infrared spectra of PEO-*b*-PBYP 2 and PEO-*b*-PBYPCOOH 3.



**Figure S4.** SEC overlay of PEO-OH macroinitiators (full line) and the corresponding block copolymers (bold line) after chain extension by ROP of AllP 4. Conditions :  $([4]_0/[PEO-OH]_0/[DBU]_0/[TU]_0 = 30/1/5/5)$ , toluene 0 °C.



**Figure S5** Size distribution in number measured by light scattering for CaCO<sub>3</sub> particles obtained by scCO<sub>2</sub>

-		SEM	LS		Zeta
	Samples	Diameter	Diameter	PDI*	potential
		(μm)	(μm)		(mV)
	НА	8.5	8.0	0.8	-20 ± 2.4
	PEO-b-	1.5	2.1	1.1	-7.3 ± 1.5
	PBYPCOO <sup>-</sup>				
	PEO- <i>b</i> -PPDO <sup>-</sup>	6.7	6.4	1.2	-13.6 ± 2.1

Table S1 Characteristics of  $CaCO_3$  particles obtained in  $scCO_2$ 

\* Polydispersity index of the particles size from light scattering (LS)