

Electronic Supplementary Information

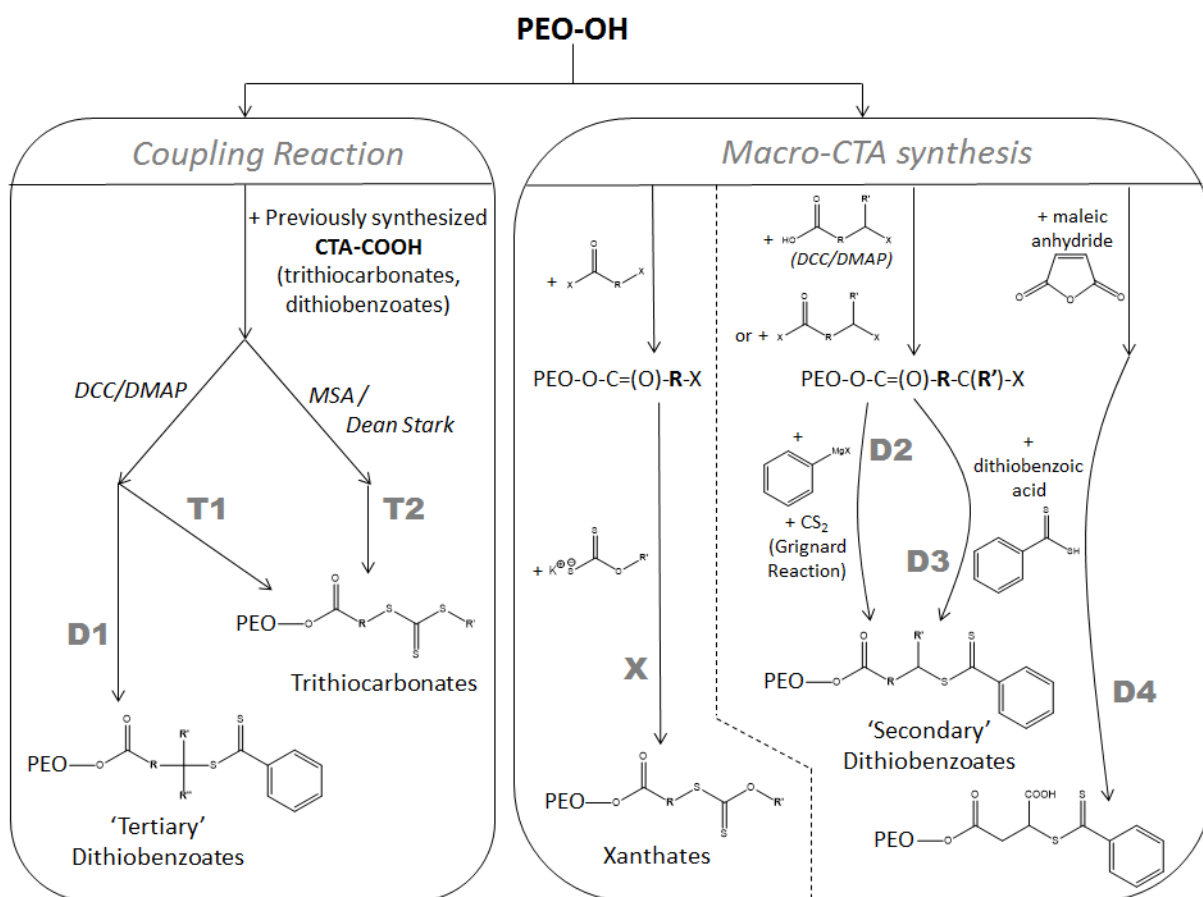
Asymmetric neutral, cationic and anionic PEO-based double-hydrophilic block copolymers (DHBCs): Synthesis and reversible micellization triggered by temperature or pH

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Scheme S1: Synthesis routes described in the literature¹ to access to PEO-based macromolecular chain transfer agent (PEO-CTA) from hydroxylated PEO chains (PEO-OH). See **Table S1** below for comments and references.

[DCC: *N,N'*-dicyclohexylcarbodiimide; DMAP: 4-dimethyl-aminopyridine; MSA: methanesulfonic acid; R' and R'' ≠ H].

Table S1: Reported efficiency of synthesis routes depicted in **Scheme S1**.

	Synthesis Route	Starting from PEO < 3000 g.mol ⁻¹	Starting from PEO ~ 5000 g.mol ⁻¹
Coupling reaction	D1	ref. 2,3 : Capping efficiency ~100%	ref. 4: Low capping efficiency ref. 5,6: No dertermination of capping efficiency
	T1	ref. 7,8: Capping efficiency ~100%	ref. 9,10,present study: Capping efficiency ~100%
	T2	ref. 11: Capping efficiency ~100%	ref. present study: Capping efficiency ~45%
Macro-CTA synthesis	X	ref. 12: Conversion of the halogenated end-group ~100%	-
	D2	ref. 13: (refluxing THF overnight) PEO homopolymer detected after polymerization. ref. 14: (ambient T°, 3h) degree of functionalization of PEO chains ~100%	ref. 15: (refluxing THF overnight) No dertermination of capping efficiency ref. 16: (refluxing THF overnight) PEO homopolymer detected after polymerization. ref. 14,present study: (ambient T°, 3h) degree of functionalization of PEO chains ~100%
	D3	ref. 17: degree of functionalization of PEO chains ~100%	ref. 18: degree of functionalization of PEO chains ~90%
	D4	-	ref. 4: degree of functionalization of PEO chains ~100%

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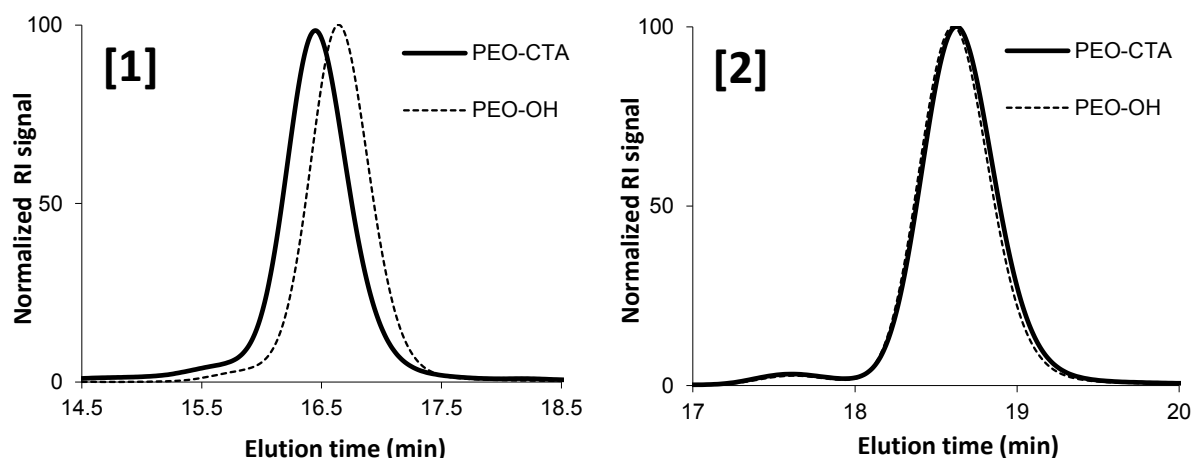


Figure S1: SEC chromatograms (in DMF, columns from Polymer Laboratories, arbitrarily normalized RI signal) of the initial PEO-OH and of the PEO-based macro-CTA (PEO-CTA): column = PolarGel L [1], column = PLgel MixD [2].

Table S2: Results of analyses of PEO-OH and PEO-CTA using different characterization techniques: NMR ^1H , MALDI-ToF mass spectrometry, Size Exclusion Chromatography (SEC) in DMF with polar columns PolarGel L or with columns PLgel Mixed D (columns from Polymer Laboratories).

	PEO-OH				PEO-CTA		
	MALDI-ToF MS	SEC PolarGel L	SEC PLgel Mixed D	NMR ^1H	SEC PolarGel L	SEC PLgel Mixed D	NMR ^1H
M_n (g.mol $^{-1}$)	4640	4630	4520	-	4800	4490	-
M_w (g.mol $^{-1}$)	4690	4830	4650	-	5010	4640	-
\bar{D}	1.01	1.04	1.03	-	1.04	1.03	-
n^*	105	105	103	123**	-	-	123**

*Polymerization degree $n = M_n / 44$, where 44 g.mol $^{-1}$ is the molecular weight of EO unit.

** determined by $n = (I_{4,0-3,4}/4)/(I_{3,4-3,3}/3)$ where I_{x-y} means integration value between x and y ppm.

MALDI-ToF MS

Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-ToF MS) measurements were performed with a Voyager-DE STR equipped with a nitrogen laser (wavelength 337 nm). The accelerating voltage was 20 kV. The positive ions were detected in all cases. Samples were prepared by dissolving the polymer in CHCl_3 at a concentration of 10 g.L $^{-1}$. The matrix was 1,8,9-trihydroxyanthracene (dithranol, Sigma-Aldrich) dissolved in CHCl_3 (10 g.L $^{-1}$). NaI solution in CHCl_3 (10 g.L $^{-1}$) is also prepared. Matrix, polymer and NaI solutions were mixed at a volume ratio of 1:1:0.2 and 1 μL of the resulting mixture was deposited onto a stainless steel target and dried before insertion into the ion source chamber.

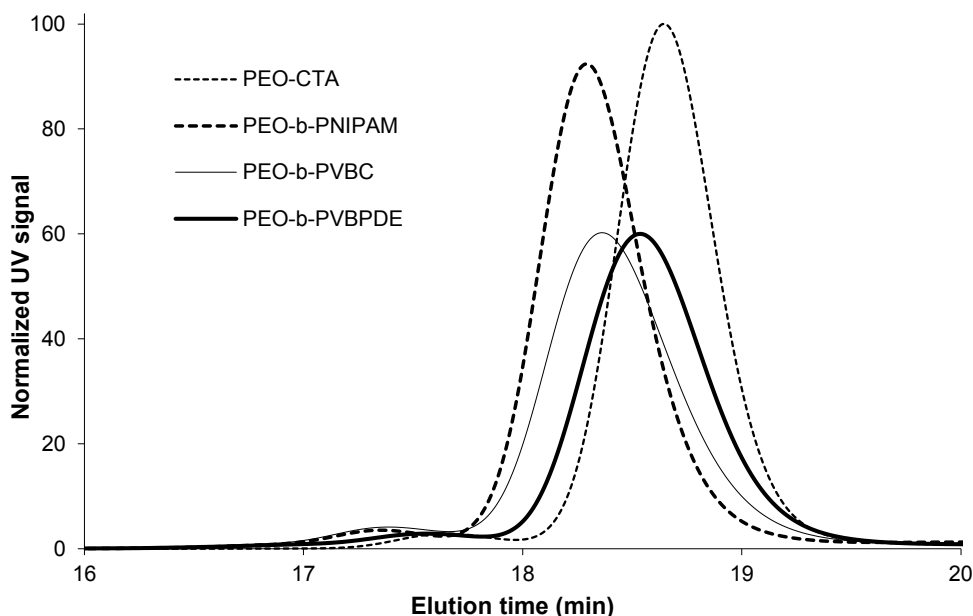


Figure S2: Size exclusion chromatograms (in DMF, column = PLgel Mixed D; **Normalized UV signal**) of the macro-CTA and of the different PEO-based block copolymers synthesized: macro-CTA (dashed line), PEO-*b*-PNIPAM (bold dashed line), PEO-*b*-PVBC (normal line), PEO-*b*-PVBPDE (bold line).

Normalization of the UV signal (309 nm) (SEC data)

The UV signal at 309 nm (maximum of absorption of dithiobenzoate moieties) is proportional to the number of moles of dormant chains. Considering the conservation of these dormant chains during the polymerization process, the UV signal in Figure S2 is normalized in such a way that the value of the area under the graph of the copolymer is equal to the one of the initial macro-CTA. The UV signal in Figure S4 and Figure S8 is normalized in such a way that the value of the area under the graph of the copolymer *before* purification (analysis of raw samples from polymerization medium) is equal to the one of the initial macro-CTA. Then, the normalization factor thus determined is applied to the graph of the copolymer *after* purification. The molar proportion of eliminated chains after purification is respectively 20% and 25% for PEO-*b*-PVBC and PEO-*b*-PVBPDE blocks copolymers. These values correspond almost exactly to the maximum proportion of AIBN-initiated chains possibly created during the polymerization process in regard to the initial [macro-CTA]/[AIBN] ratios used (respectively 4.2 and 2.8).

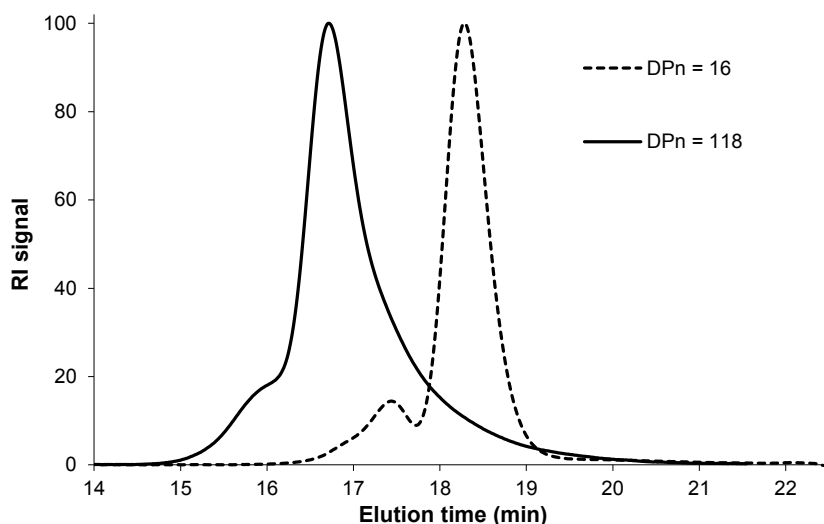


Figure S3: Size exclusion chromatograms (in DMF, column = PLgel Mixed D; **RI signal, arbitrary unit**) of copolymers PEO-*b*-PNIPAM of different PNIPAM block lengths: DP_n = 16 (dashed line, copolymer **1a**), DP_n = 118 (normal line, copolymer **1b**).

Characterization by ¹H NMR of copolymer PEO-*b*-PNIPAM

The average polymerization degree of PNIPAM block was calculated from the ¹H NMR spectrum in CDCl₃ of the PEO-*b*-PNIPAM copolymer (cf. Figure 3A in main manuscript) through the following relation: $DP_{\text{PNIPAM}}(\text{NMR}) = [(I_1 + I_2 + I_3 / 9) / 3] / (I_4 / 3)$. I₁, I₂ and I₃ correspond to the protons of the PNIPAM block (I₁: integration of the broad -NH peak at 5.4-7.1 ppm; I₂: integration of the -CH peak at 3.8-4.3 ppm; I₃: integration of the peaks included on the δ range 0.2-2.7 ppm), and I₄ corresponds to the protons of the methyl ether chain-end of the PEO block (3.35 ppm).

Characterization by ¹H NMR of copolymer PEO-*b*-PVBC⁺

The average polymerization degree of PVBC block was calculated from the ¹H NMR spectrum in *d*-acetone of the PEO-*b*-PVBC copolymer (cf. Figure S5) through the following relation: $DP_{\text{VBC}}(\text{NMR}) = (I_1 / 2) / (I_2 / 3)$. I₁ corresponds to 2 protons of the VBC block (integration of the broad -CH₂-Cl peak at 4.5 ppm), and I₂ corresponds to the protons of the methyl ether chain-end of the PEO block (3.29 ppm).

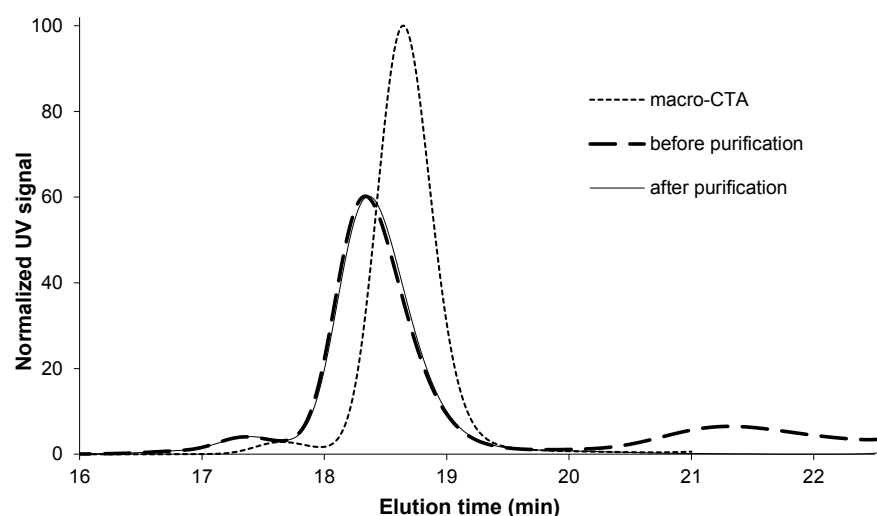


Figure S4: Size exclusion chromatograms (in DMF, column = PLgel Mixed D; normalized UV signal) of the macro-CTA and of PEO-*b*-PVBC block copolymers: macro-CTA (dashed line), PEO-*b*-PVBC **before purification** (bold dashed line), PEO-*b*-PVBC **after purification** (normal line).

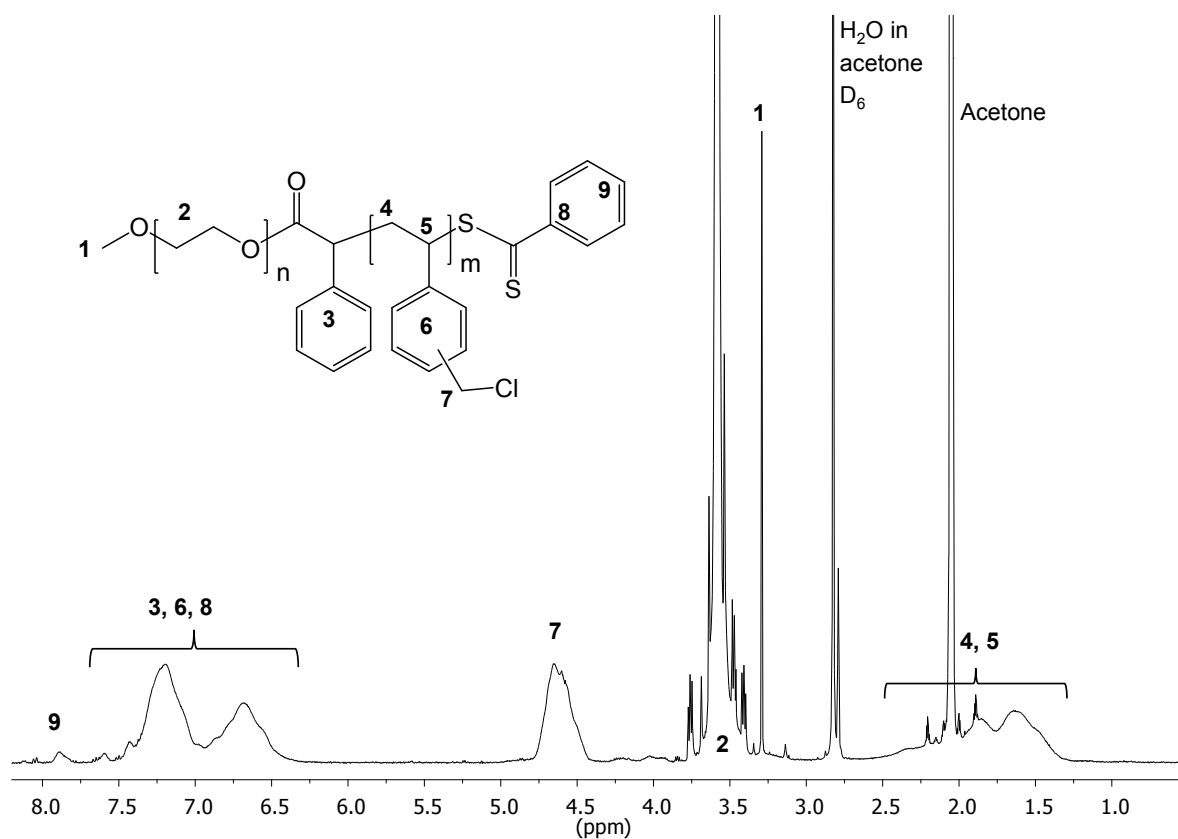


Figure S5: ^1H NMR spectrum (400MHz, Acetone D_6) of PEO-*b*-PVBC block copolymer.

Synthesis of VBPDE monomer

NaH (60% in grease, $M=24.00 \text{ g mol}^{-1}$, 6.88 g, 0.287 mol) was suspended in anhydrous THF (dried on molecular sieve, 140 mL) at 0°C . Diethylphosphite ($M=138.10 \text{ g mol}^{-1}$, 41.7 g, 0.302 mol) was added dropwise. The mixture was allowed to come to RT, then a solution of 1-chloromethyl-vinylbenzene (mixture of meta and para isomers 53/47, 96%, $M=152.62 \text{ g mol}^{-1}$, 41.5 g, 0.288 mol) and NaI ($M=149.89 \text{ g mol}^{-1}$, 4.08 g, 27 mmol) in anhydrous THF (70 mL) was transferred to the first solution by cannula at 0°C . The solution turned from pale yellow to orange. The mixture was stirred overnight. Salts were precipitated by the addition of AcOEt, and the mixture was filtered through celite. Volatiles were removed and the residue was purified by column chromatography (eluent: AcOEt, Rf (ethyl acetate) = 0.4). The product VBPDE was isolated as a pale yellow oil (45 g, 66%). ^1H NMR and ^{31}P NMR spectra are shown in Figure S6 and Figure S7 respectively. 4 % of diethylphosphite remained in the monomer.

^1H NMR 400MHz (CDCl_3 , RT, ppm) (Figure S6): 1.23 (t, $\text{CH}_3\text{-CH}_2\text{-O-P-}$); 3.13 (m, $\text{-Ph-CH}_2\text{-P-}$); 4.00 (m, $\text{-CH}_2\text{-O-P-}$); 5.23 and 5.73 (dd, $\text{CH}_2=\text{CH-}$); 6.68 (dd, $\text{CH}_2=\text{CH-}$); 7.17-7.35 (m, benzenic protons).

^{31}P NMR 100MHz (CDCl_3 , RT, ppm) (Figure S7) : 26.48 (s, P in para position) ; 26.36 (s, P in meta position) ; 7.47 (s, residual diethylphosphite).

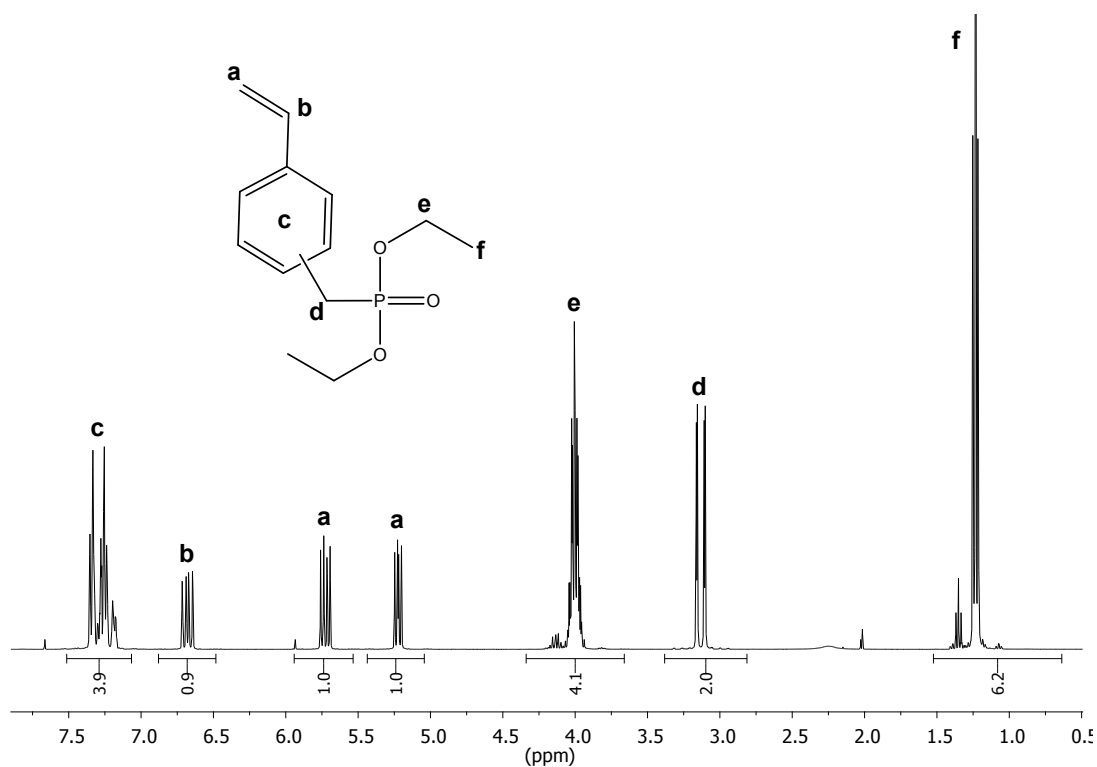


Figure S6: ^1H NMR (400MHz, CDCl_3) of vinylbenzyl phosphonyl diethyl ester monomer after purification.

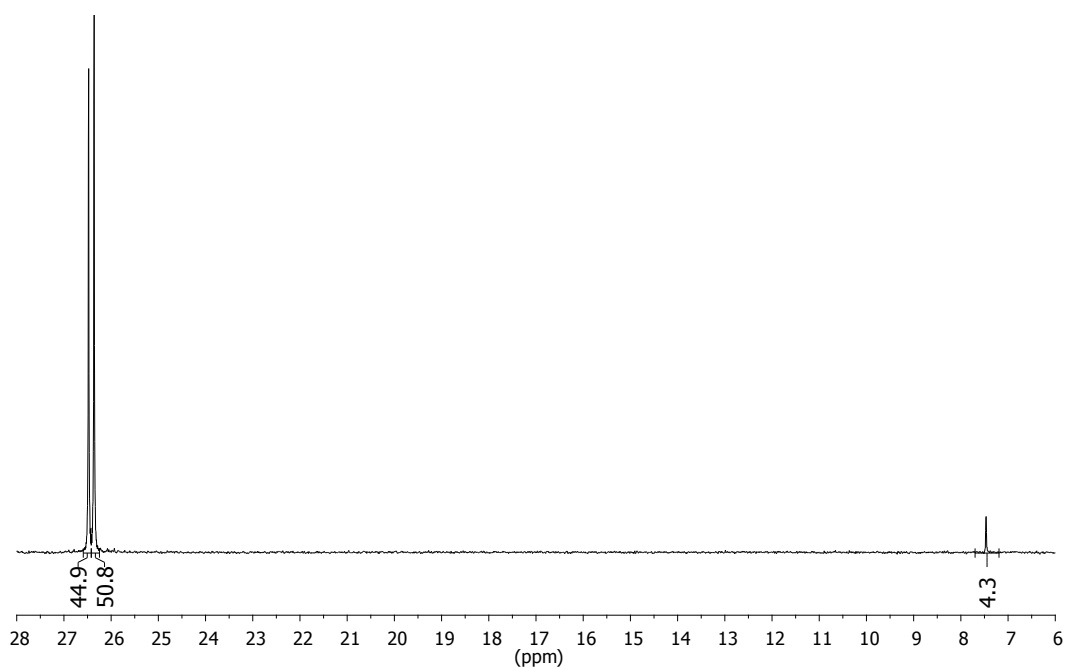


Figure S7: ^{31}P NMR (100MHz, CDCl_3) of vinylbenzyl phosphonyl diethyl ester monomer after purification.

Characterization by ^1H NMR of copolymer PEO-*b*-PVBPE

The average polymerization degree of PVBPE block was calculated from the ^1H NMR spectrum in *d*-acetone of the PEO-*b*-PVBPE copolymer (cf. Figure S9) through the following relations: $\text{DP}_{\text{VBPE}}(\text{NMR}) = [(I_1/2 + I_2/4)/2]/(I_3/3)$, I_1 corresponds to 2 protons $-\text{CH}_2\text{-P-}$ (3.13 ppm), and I_2 corresponds to 4 protons $\text{CH}_3\text{-CH}_2\text{-O-P-}$ (3.97 ppm), and I_3 corresponds to the protons of the methyl ether chain-end of the PEO block (3.29 ppm).

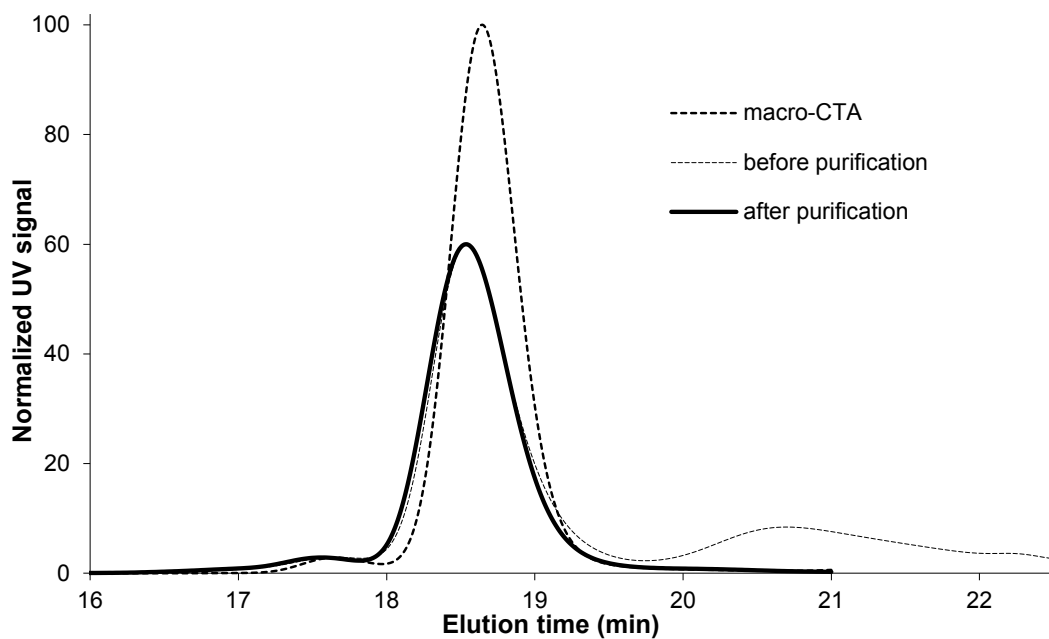


Figure S8: Size exclusion chromatograms (in DMF, column = PLgel Mixed D; normalized UV signal) of the macro-CTA and of PEO-*b*-PVBPDE block copolymers: macro-CTA (dashed line), PEO-*b*-PVBPDE *before purification* (dashed line), PEO-*b*-PVBPDE *after purification* (bold line).

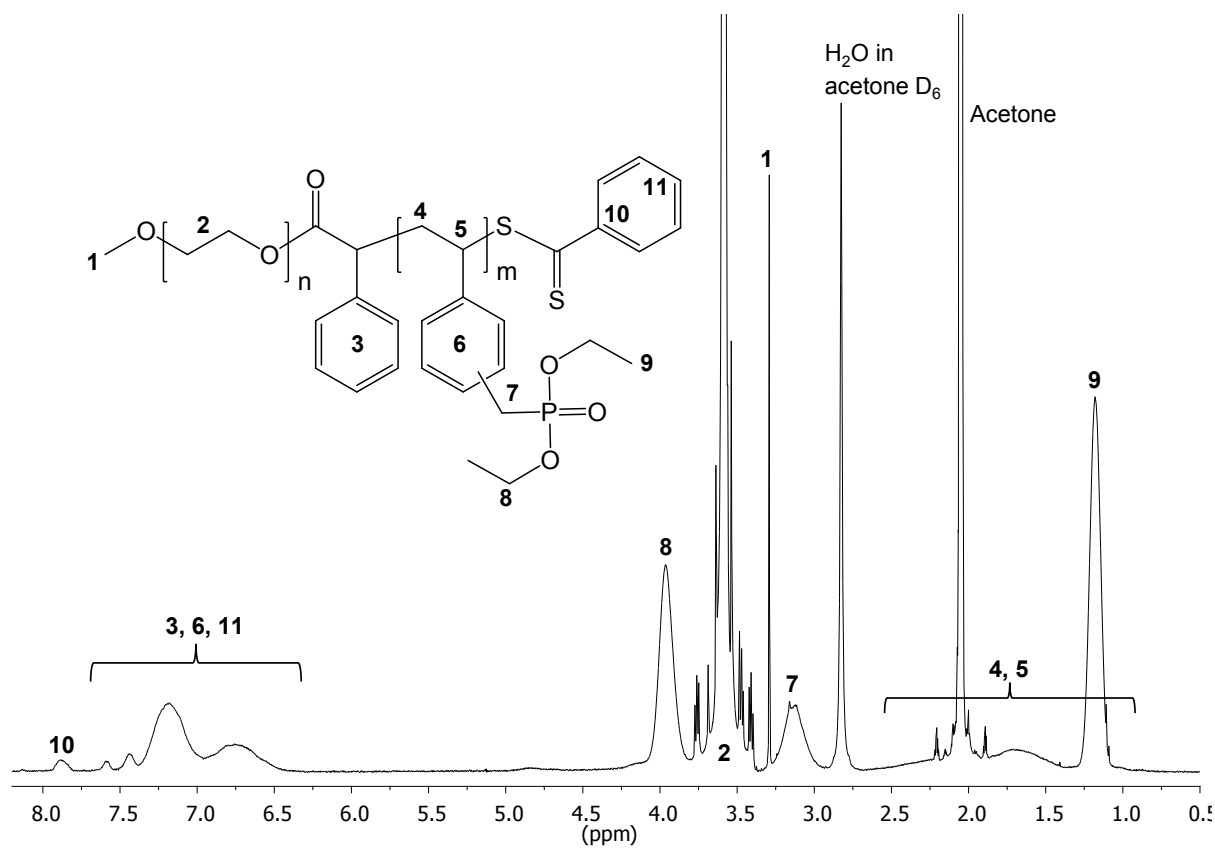


Figure S9: ^1H NMR spectrum (400MHz, Acetone D_6) of PEO-*b*-PVBPDE block copolymer.

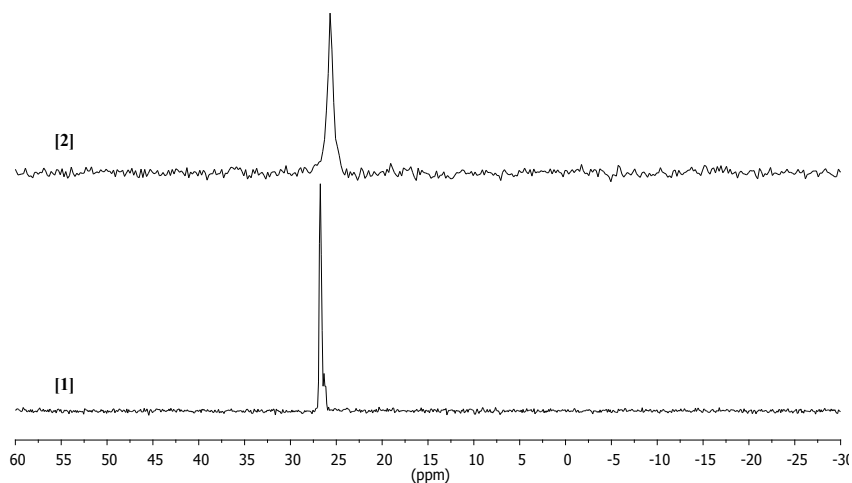


Figure S10: ^{31}P NMR (100MHz, CDCl_3) spectrum of PEO-*b*-PVBPDE block copolymer [1] and ^{31}P NMR (100MHz, D_2O) spectrum of PEO-*b*-PVBPDA block copolymer [2].

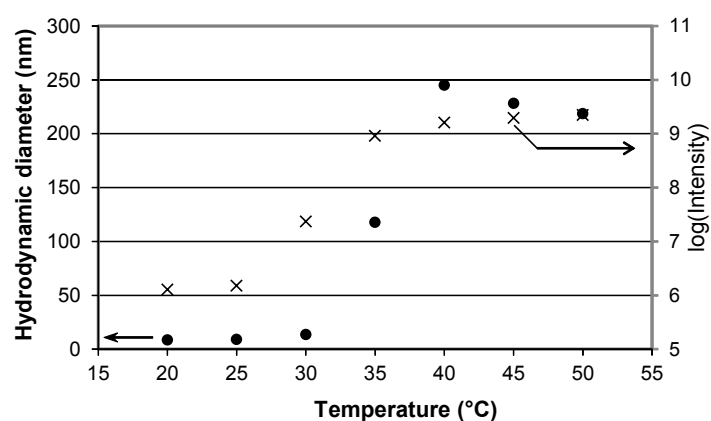


Figure S11: Hydrodynamic diameter of scattering objects obtained with copolymer PEO-*b*-PNIPAM **1b** in aqueous solutions at 1 wt% as a function of temperature.

N_2 adsorption/desorption experiments were performed on a Micromeritics TriStar instrument, for analysis of the specific surface area and porosity. Before adsorption measurements, the samples were outgassed under vacuum for 6 h at 250 °C.

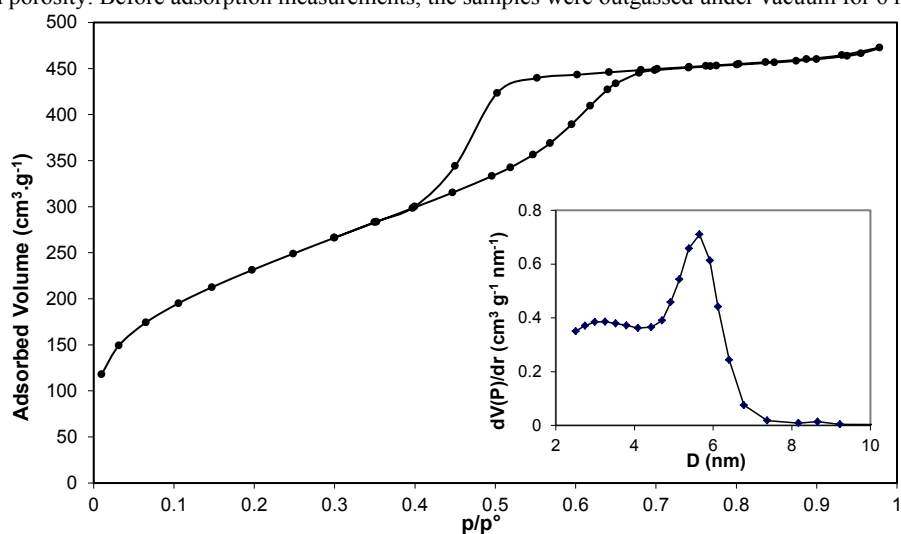


Figure S12: N_2 adsorption/desorption isotherms of the mesoporous silica material (after calcination) synthesized using aggregates of copolymer PEO-*b*-PNIPAM **1a** as SDA. Inset: mesopore size distribution (adsorption branch).