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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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The syntheses of three poly(ethylene oxide)-based (PEO) double hydrophilic block copolymers (DHBCs) of different second block nature (thermosensitive poly(*N*-isopropylacrylamide) (PNIPAM) block, anionic poly(vinylbenzyl phosphonic di-acid) block, and cationic poly(vinylbenzyl triethyl ammonium chloride) block) are described. The synthesis strategy holds on the synthesis of a single 5kD-PEO-based macro-chain transfer agent being able to control the RAFT polymerizations of various functional monomers. Low molecular weights of the second block were targeted to obtain asymmetric structures for the DHBCs. Their ability to form micelles under appropriate conditions (specified temperature, pH and nature of the auxiliary of micellization) and the reversibility of the micellization process were checked. Finally, a nanostructured hybrid silica material was obtained using the PNIPAM-based copolymer as a structure directing agent (SDA), which yielded well-organized mesoporous silica after template removal.

A Introduction

Double hydrophilic block copolymers (DHBCs) contain two chemically connected hydrophilic segments. In aqueous solution and under appropriate conditions, they are able to form aggregates or micelles,^{1, 2} which can be exploited in many applications ranging from separation technology to controlled drug delivery. Recently, in the frame of an ‘ecodesign of ordered mesoporous silica materials’,³ poly(ethylene oxide)-based (PEO) ionizable DHBCs complexed with a counter-polyion (called the auxiliary of micellization) have been successfully used as structure directing agents (SDA) for the formation of mesoporous silica.^{4–6} PEO block (linear or comb structure) ensures both the stabilization of the complex micelles and a cooperative assembly with silica precursors during the hybrid material synthesis, leading to various long-range ordered nanostructures. Moreover, it was shown that the hydrosoluble auxiliary of micellization and the PEO-*b*-poly((meth)acrylic acid) (PEO-*b*-P(M)AA), could be removed from silica material by simple water washing yielding mesoporous materials under soft conditions. If the DHBC could be left on purpose in the material (PEO in silica walls and P(M)AA blocks in the mesopores) while the auxiliary of micellization would be completely removed, then polymer-functionalized mesopores could be obtained.⁴ Following this strategy, the use of various PEO-based DHBCs containing a functional block would be valuable to produce polymer-functionalized nanostructured materials. These DHBCs should ideally fulfill the following requirements: (a) nature of the non-PEO block (polyacid/polybase/thermosensitive) chosen according to the desired functionality to be finally introduced in the material mesopores, (b) well-defined structure (low dispersity *D*) to ensure the formation of monodisperse micelles, (c) asymmetric structure

(degree of polymerization of the functional block lower than that of the PEO block) in order to, firstly, form micellar structures in water, and secondly, provide anchorage in silica walls of mesopores by interaction of PEO units with silica precursor (*d*) easy synthesis from a single PEO-based precursor. All these requirements obviously need the use of a controlled polymerization technique such as RAFT (reversible addition-fragmentation chain transfer) process which is one of the most versatile methods. An overview about the synthesis of PEO-based macro-chain transfer agents (macro-CTA) and the subsequent block copolymers obtained *via* RAFT polymerization was recently published by Gregory *et al.*⁷ It is noteworthy that among all the previously synthesized PEO-based DHBCs, only few of them satisfy requirement (c).

Choice of synthetic access toward PEO-based macro CTA.

Three families of RAFT chain transfer agents (of general formula **R**-S-C(=S)-**Z**) and two main synthetic accesses are reported in the literature about PEO-based macro-CTAs (**R** = PEO-R’-):⁷ PEO-based trithiocarbonates (**Z** = -S-R’’) are exclusively synthesized by a coupling reaction (esterification,^{8, 9} amidation,^{10, ...}) of a previously synthesized CTA with a PEO chain (see Scheme S1). On the other hand, PEO-based xanthates (**Z** = -O-R’’) are, usually, directly synthesized from hydroxyl-terminated PEO chains using potassium xanthogenate.¹¹ Concerning the PEO-based dithiobenzoates (**Z** = phenyl), the two approaches are reported: coupling reaction to get ‘tertiary’ CTAs,^{12, 13} or direct synthesis using Grignard reaction to obtain ‘secondary’ CTAs^{14, 15} (where ‘tertiary’ and ‘secondary’ refer to the nature of the fragment radical **R**• produced by the fragmentation of the CTA during the RAFT process, see Scheme S1). Around 60% of the reported works deal with PEO chains smaller than 3000 g.mol⁻¹ (mostly ~2000 g.mol⁻¹); the other works mainly use PEO chains of about 5000 g.mol⁻¹.

In order to get different final block copolymers presenting low $\bar{D}$ (as low as possible, as the very low $\bar{D}$ of the starting PEO-OH), dithiobenzoates family was chosen because it offers better control over molecular weight distribution and end-group fidelity in the RAFT polymerization of a wide range of monomers (styrenic, acrylamide, (meth)acrylate,...).^{16, 17} The only major drawback of dithiobenzoates is a strong retardation in the polymerization kinetics.^{17, 18}

Moreover, the targeted asymmetric structure of the final block copolymers (degree of polymerization of the functional block much lower than the one of the PEO block) implies two constraints: first, high molecular-weight ($\sim 5000 \text{ g.mol}^{-1}$) PEO chains should be used; secondly, the synthetic access to PEO-based CTA must be fully quantitative as residual non-functionalized PEO chains could not be easily eliminated (indeed, the polymerization of a small second block will not change considerably the solubility of the copolymer chains compared to that of initial PEO chains and, for example, selective precipitation of block-copolymer will not be possible). It is well known that the yield of chemical modification of a polymer chain-end decreases with the increase in the polymer chain length. So, successful synthetic access to macro-CTA of low molecular weight cannot be automatically applied for the synthesis of macro-CTA of greater M_n (see Table S1). For example, Chong *et al.* firstly described the capping of a dithiobenzoate group on small hydroxylated PEO chains (750 g.mol^{-1}) via esterification reaction with the aid of *N,N'*-dicyclohexylcarbodiimide (DCC) and 4-dimethylaminopyridine (DMAP).¹² The same procedure was successfully used with PEO chains of 2000 g.mol^{-1} ,¹³ but Hong *et al.* reported low capping efficiency for higher molecular-weight PEO.¹⁹ Luo *et al.* and Achillos *et al.* also described the use of 5kD-PEO-OH with the same dithiobenzoate-carboxylic acid but no reliable determination of the capping efficiency is given in the respective articles.^{20, 21} Actually, in a preliminary work, we confirmed that this esterification route is a very slow reaction but can be efficient even for high molecular-weight: the yield of capping reaction (in dichloromethane, room temperature, 6 days) of a trithiocarbonate-carboxylic acid on 5kD-PEO-OH using DCC/DMAP (respective molar ratio TTC-COOH/PEO-OH/DCC/DMAP 20:1:20:0.2) is near 100%; this is in agreement with similar studies using 5kD-PEO.^{22, 23} On the contrary, previously reported esterification route of 2kD-PEO using methanesulfonic acid (MSA) as catalyst (and using a Dean–Stark device to remove water, shifting the equilibrium of the reaction toward the ester product)²⁴ is not efficient with 5kD-PEO: using a catalytic quantity of MSA, the capping yield is only $\sim 45\%$ after 4 days. In addition, by increasing MSA amount, cleavage of PEO chains (leading to methylsulfone chain-end) was observed.

It is important to notice that the determination of capping yield by ^1H NMR is reliable only if integration values of the CTA moiety are compared to the one of the methoxy chain-end ($\text{CH}_3\text{O}-$) of PEO (singlet at 3.35ppm). But to be able to do that, NMR analyses have to be performed on a 400MHz (or higher field) spectrometer: 200MHz or 300MHz spectrometers do not offer enough resolution to separate this crucial peak at 3.35ppm from the huge peak of PEO units at 3.6ppm. Moreover, using the latter to calculate the capping yield is really reliable only if the average degree of polymerization of the initial PEO is accurately known (regrettably, that is not

always guaranteed by data from suppliers). For example, in the present study, the M_n of our 5kD-PEO is actually 4630 g.mol^{-1} (average polymerization degree $DP_n = 105$) as determined by SEC and MALDI-ToF analyses, but the DP_n value determined by ^1H NMR (400MHz) analysis is 123 (cf. Table S2, this discrepancy can be interpreted by the presence of a small proportion of di-hydroxylated PEO chains).

The chain-end modification route needs the prior synthesis of a CTA bearing carboxylic acid moiety, which can be difficult and/or time-consuming to purify (column chromatography). On the other hand, direct syntheses of PEO-CTAs from hydroxylated PEO reduce the number of synthesis steps and can offer easy purification procedures (precipitation in diethylether or in hexane). Perrier *et al.* firstly described in 2004 such a synthesis (see Scheme 1) where the Grignard reaction was performed in refluxing THF overnight.¹⁴ Degree of functionalization for the obtained PEO-CTA was not examined in this study. In 2006, two other works used the same synthesis procedure: noticeably, after polymerization of a ‘long’ hydrophobic second block, PEO homopolymer chains were detected (and, in this case, they could be eliminated by selective precipitation of the block copolymers).^{25, 26} In 2008, Walther *et al.* reported the occurrence of cleavage of the initially formed ester function (regenerating initial PEO-OH) during the Grignard reaction step.¹⁵ We can confirm that, in the experimental condition firstly described by Perrier *et al.*, the final product could be a mixture of PEO-CTA and PEO-OH in a 50:50 molar ratio. Walther *et al.* preconize to reduce the reaction time and temperature to 3h at room temperature for avoiding ester cleavage. Full characterization (^1H NMR, 2D-NMR, MS-ESI, LACCC) of a 2kD-PEO-CTA strongly supports this claim. For a 5kD-PEO-CTA, only LACCC (liquid adsorption chromatography at critical conditions) chromatogram is provided showing a tiny peak at the elution volume of PEO-OH. It is reported that estimation of the extent of end-group functionalization based on ^1H NMR analysis loses reliability for higher DP_n of PEO, i.e., for the 5kD-PEO-CTA having a presumed DP_n of 114.¹⁵ As a 250MHz spectrometer was used in this study, we think that this loss of reliability is only the consequence of using the peak of PEO units at 3.6ppm without being confident in the real DP_n of the initial PEO-OH (see above).

Alternatively, the same structure of PEO-based dithiobenzoate can be obtained via the procedure firstly described by Ten Cate *et al.*²⁷ and then used by Chen *et al.* with a 5kD-PEO: the Grignard reaction is substituted by reaction of dithiobenzoic acid on the halogenated chain-end (product of the first step). A degree of functionalization for PEO-CTA of about 90% is reported.²⁸ Another alternative to get ‘secondary’ PEO-based dithiobenzoate was reported by Hong *et al.*: esterification reaction between a 5kD-PEO-OH and maleic anhydride, then, addition of dithiobenzoic acid on the available double bond. The integration ratios of the proper peaks in the ^1H NMR spectrum of the final product indicates a degree of functionalization of about 100%.¹⁹

Scheme 1: Synthetic access to various PEO-based block copolymers via a PEO-based macro-Chain Transfer Agent (PEO-CTA, $n = 105$).

See Figure 3 for the structure of the different final block copolymers.

Exp. Cond.: (1) DCC/DMAP in CH_2Cl_2 , 24h, RT; (2) THF, 1h, $0^\circ\text{C} \rightarrow \text{RT}$; (2') THF, 3h, RT; (3) AIBN in dioxane, 4h, 90°C ; (3') AIBN in TFT, 16h, 80°C ; (3'') AIBN in TFT, 15h, 80°C ; (4') CH_2Cl_2 , 4 days, RT; (4'') CH_2Cl_2 , 15h, RT.

In the present paper, the chosen synthetic access toward a single PEO-based CTA is outlined in Scheme 1 and was largely inspired from Walther *et al.*¹⁵ Then, this macro-CTA is used in the RAFT polymerizations of N-isopropylacrylamide (NIPAM), of vinylbenzyl chloride (VBC) and of vinylbenzylphosphonic diethyl ester (VBPDE) leading (after backbone modification) to well-defined block copolymers of different nature (respectively, thermosensitive, cationic and anionic) (see Scheme 1). The ability of these different block copolymers to form micelles in appropriate conditions was checked: PEO-*b*-PNIPAM is expected to spontaneously form micellar aggregates above a specified temperature, while PEO-*b*-PQVBC⁺ and PEO-*b*-PVBPDA⁻ need an auxiliary of micellization in a determined pH range to create polyion electrostatic complex (PIC) micelles. Finally, the use of PEO-*b*-PNIPAM block copolymer as structure directing agent (SDA) in the synthesis of nanostructured hybrid DHBC-silica materials is described.

B Experimental section

B.1 Materials

α -methoxy- ω -hydroxy poly(ethylene oxide) (PEO-5k-OH) was obtained from Fluka ($M_w \sim 5000 \text{ g.mol}^{-1}$) and used as received: $M_n = 4630 \text{ g.mol}^{-1}$ (average polymerization degree $n = 105$) and $M_w/M_n = 1.04$ as determined by SEC analysis (and confirmed by MALDI-ToF analysis, cf. Table S2). N-isopropylacrylamide (NIPAM, Aldrich, 97%) was purified by recrystallization from hexane. Dioxane (Acros organics, 99%), α, α, α -trifluorotoluene (TFT, Sigma-Aldrich, >99 %) and vinylbenzyl chloride (VBC, Aldrich, 97%, mixture of 3- and 4-isomers) were distilled under

vacuum. 2,2'-azobis(2-methylpropionitrile) (AIBN, Fluka, 98%) was purified by recrystallization twice from ethanol. All other reagents were purchased from Aldrich and were used as received.

B.2 Syntheses

B.2.1 Synthesis of PEO-based macro CTA

α -bromophenylacetate-terminated poly(ethylene oxide) (PEO-PhBr). Drying of PEO-OH by azeotropic distillation: 60 g of PEO-OH were introduced in a 1 L round-bottom flask and then dissolved in $\sim 300 \text{ mL}$ of anhydrous toluene. After evaporation of solvent ($\sim 20 \text{ mbar}$, 45°C), the flask was conditioned in argon atmosphere. Anhydrous dichloromethane (300 mL) was introduced in the flask and, after complete dissolution of PEO-OH, α -bromophenylacetic acid (9.01 g), N,N' -dicyclohexylcarbodiimide (DCC, 14.42 g) and 4-(dimethylamino)pyridine (DMAP, 0.34 g) were added dropwise. The solution was kept at room temperature ($\sim 20^\circ\text{C}$) for 24 h under magnetic stirring. After filtration, the solvent was partially removed by rotary evaporation. PEO-PhBr (62.8 g) was then recovered by two consecutive precipitations in cold diethylether and finally dried under vacuum at 40°C (gravimetric yield = 102%, it contains residual dicyclohexylurea).

^1H NMR 400MHz (CDCl_3 , RT, ppm) (Figure 1-1): 3.35 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.62 (s, $\text{-O-CH}_2\text{-CH}_2\text{-O-}$); 4.24-4.36 (m, $\text{-CH}_2\text{-O-C(=O)-}$); 5.41 (s, -C(=O)-CH(-Ph)-Br); 7.31-7.54 (m, all benzenic protons).

PEO-based macro-Chain-Transfer Agents (PEO-CTA). Drying of PEO-PhBr by azeotropic distillation: 62.8 g of PEO-PhBr were introduced in a 1 L round-bottom flask and then dissolved in $\sim 300 \text{ mL}$ of anhydrous toluene. After evaporation of solvent ($\sim 20 \text{ mbar}$, 45°C), the flask was conditioned in argon atmosphere. PEO-PhBr was dissolved again by addition of anhydrous THF (315 mL). In a second reaction flask, carbon disulfide (2 mL) was added with a syringe to a degassed THF solution of phenylmagnesium bromide (27.9 mL of 1 M solution) at 0°C . This flask was allowed to stand at room temperature for 1 hour. Afterward, the dark-red solution was transferred with a syringe to an addition funnel connected to the flask containing the PEO-PhBr solution in anhydrous THF. The solution was added drop wise at room temperature ($\sim 20^\circ\text{C}$), and the reaction was allowed to proceed for 3 h. The solvent was partially removed by rotary evaporation and the product was recovered by precipitation in cold diethylether. It was dissolved again in 200 mL of dichloromethane. The resulting solution was washed with a saturated sodium bicarbonate aqueous solution and the organic phase was dried over anhydrous magnesium sulfate and filtered. The solution was concentrated by rotary evaporation and the PEO-CTA (57.7 g) was recovered by precipitation in cold diethylether and dried under vacuum at 40°C (yield = 89%).

SEC in DMF (calibration with PEO standards) (Figure S1 and Table S2): $M_n = 4800 \text{ g.mol}^{-1}$, $M_w/M_n = 1.04$.

^1H NMR 400MHz (CDCl_3 , RT, ppm) (Figure 1-2): 3.35 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.62 (s, $\text{-O-CH}_2\text{-CH}_2\text{-O-}$); 4.22-4.39 (m, $\text{-CH}_2\text{-O-C(=O)-}$); 5.70 (s, -C(=O)-CH(-Ph)-S-); 7.33-7.53 (m, benzenic protons); 7.96-7.98 (m, benzenic protons in β position from C=S).

B.2.2 Synthesis of block copolymer PEO-*b*-PNIPAM

RAFT Polymerization. NIPAM (5 g, 44.2 mmol), PEO-CTA (2.67 g, 0.55 mmol), AIBN (18 mg, 0.11 mmol), dioxane (26 mL), and trioxane (0.2 g, internal reference for ^1H NMR determination of monomer consumption) were introduced in a Schlenk tube

equipped with a magnetic stirrer. The mixture was degassed by four freeze-evacuate-thaw cycles and then heated for 4 hours at 90 °C under nitrogen in a thermostated oil bath. Final conversion = 19%. Monomer conversion was determined by ^1H NMR spectroscopy, using a Bruker DRX 400 spectrometer, by comparison of one vinylic proton (5.6 ppm) with trioxane (5.1 ppm) used as internal reference. 0.5 mL of *d*-chloroform was added to 0.3 mL of polymerization medium. The block polymer was precipitated in a large volume of cold diethyl ether, recovered by filtration, and finally dried under vacuum before analysis by size exclusion chromatography and ^1H NMR.

SEC in DMF (calibration with PEO standards) (Figure 2): $M_n = 5820 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.11$.

^1H NMR 400MHz (CDCl_3 , RT, ppm) (Figure 3A): 1.11 (s, $-\text{CH}_3$ of NIPAM unit); 0.9–2.4 (broad, ethylenic protons); 3.35 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.61 (s, $-\text{O-CH}_2\text{-CH}_2\text{-O-}$); 3.99 (s, $-\text{CH-}$ of NIPAM unit); 5.5–6.7 (broad, $-\text{NH-}$); 7.15–7.55 (m, benzenic protons); 7.93 (m, benzenic protons in β position from $\text{C}=\text{S}$). Average polymerization degree of PNIPAM block (determined by ^1H NMR, see ESI for calculation) = 16.1.

B.2.3 Synthesis of block copolymer PEO-*b*-PQVBC $^+$

RAFT Polymerization. VBC (4 g, 26.2 mmol), PEO-CTA (3.2 g, 0.67 mmol), AIBN (27 mg, 0.17 mmol), and TFT (6.7 mL) were introduced in a Schlenk tube equipped with a magnetic stirrer. The mixture was degassed by four freeze-evacuate-thaw cycles and then heated for 16 hours at 80 °C under nitrogen in a thermostated oil bath. Final conversion = 41%. Monomer conversion was determined by ^1H NMR spectroscopy, using a Bruker DRX 400 spectrometer, by comparison of one vinylic proton (5.25 ppm) with PEO block (3.62 ppm) used as internal reference. 0.5 mL of *d*-acetone was added to 0.1 mL of polymerization medium. The block polymer was precipitated in a large volume of cold diethyl ether ($\rightarrow$ elimination of homopolymer chains initiated by AIBN, see Figure S4), recovered by filtration, and finally dried under vacuum before analysis by size exclusion chromatography and ^1H NMR.

SEC in DMF (calibration with PEO standards) (Figure 2): $M_n = 5150 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.12$.

^1H NMR 400MHz (Acetone D_6 , RT, ppm) (Figure S5): 1.2–2.5 (broad, ethylenic protons); 3.29 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.59 (s, $-\text{O-CH}_2\text{-CH}_2\text{-O-}$); 4.65 (s, $-\text{Ph-CH}_2\text{-Cl}$); 6.35–7.7 (m, benzenic protons); 7.88 (m, benzenic protons in β position from $\text{C}=\text{S}$). Average polymerization degree of PVBC block (determined by ^1H NMR, see ESI for calculation) = 13.7.

Quaternisation of block copolymer. 4.3 g of PEO-*b*-PVBC block copolymer (8.85 mmol VBC units) is dissolved in 60 mL of dichloromethane and then 2.69 g (26.6 mmol) of triethylamine is added. The solution was kept at room temperature ($\sim 20^\circ\text{C}$) for 4 days under magnetic stirring. The product was recovered by precipitation in cold diethylether. Finally, the quarternized block copolymer PEO-*b*-PQVBC $^+$ was dialyzed against water (to remove the by-product formed by reaction of dichloromethane with triethylamine) and dried under vacuum at 40°C with a final yield of around 70%.

Elem. Anal. found: C, 57.72; H, 9.39; O, 23.12; N, 2.04; Cl, 5.50. Degree of quaternisation = $(\% \text{N}/M_n)/(\% \text{Cl}/M_{\text{Cl}}) \times 100 = 94.1 \%$. Average polymerization degree of PQVBC $^+$ block (determined from Elem. Anal. results) = 13.6.

^1H NMR 400MHz (D_2O , RT, ppm) (Figure 3B): 1.34 (t, $-\text{CH}_3$ of

TEA); 0.9–2.4 (broad, ethylenic protons); 3.13 (q, $-\text{CH}_2\text{-}$ of TEA); 3.41 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.73 (s, $-\text{O-CH}_2\text{-CH}_2\text{-O-}$); 4.31 (s, $-\text{Ph-CH}_2\text{-N}\equiv$); 6.3–7.7 (m, all benzenic protons).

B.2.4 Synthesis of block copolymer PEO-*b*-PVBPA

VBPDE Monomer synthesis. See ESI.

RAFT Polymerization. VBPDE (2.5 g, 9.8 mmol), PEO-CTA (4.0 g, 0.83 mmol), AIBN (45.6 mg, 0.28 mmol), and TFT (4.5 mL) were introduced in a Schlenk tube equipped with a magnetic stirrer. The mixture was degassed by four freeze-evacuate-thaw cycles and then heated for 15 hours at 80 °C under nitrogen in a thermostated oil bath. Final conversion = 68%. Monomer conversion was determined by ^1H NMR spectroscopy, using a Bruker DRX 400 spectrometer, by comparison of one vinylic proton (5.18 ppm) with PEO block (3.62 ppm) used as internal reference. 0.5 mL of *d*-acetone was added to 0.1 mL of polymerization medium. The block polymer was precipitated in a large volume of cold diethyl ether ($\rightarrow$ elimination of homopolymer chains initiated by AIBN, see Figure S8), recovered by filtration, and finally dried under vacuum before analysis by size exclusion chromatography and ^1H NMR.

SEC in DMF (calibration with PEO standards) (Figure 2): $M_n = 5000 \text{ g}\cdot\text{mol}^{-1}$, $M_w/M_n = 1.16$.

^1H NMR 400MHz (Acetone d_6 , RT, ppm) (Figure S9): 1.18 (s, $\text{CH}_3\text{-CH}_2\text{-O-P-}$); 1.0–2.6 (broad, ethylenic protons); 3.13 (s, $-\text{Ph-CH}_2\text{-P-}$); 3.29 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.59 (s, $-\text{O-CH}_2\text{-CH}_2\text{-O-}$); 3.97 (s, $\text{CH}_3\text{-CH}_2\text{-O-P-}$); 6.3–7.6 (m, benzenic protons); 7.88 (m, benzenic protons in β position from $\text{C}=\text{S}$).

^{31}P NMR 100MHz (CDCl_3 , RT, ppm) (Figure S10): 26.75 (s). Average polymerization degree of PVBPA block (determined by ^1H NMR, see ESI for calculation) = 8.4.

Deprotection. In an argon conditioned flask, 1.04 g of PEO-*b*-PVBPA block copolymer (1.2 mmol of VBPDE unit) was dissolved in 5.3 mL of anhydrous dichloromethane, and then 0.46 mL (3.6 mmol) of trimethylsilyl bromide was added. The solution was kept at room temperature ($\sim 20^\circ\text{C}$) for 15 h under magnetic stirring. 0.43 mL of methanol was added. After additional 4 hours of stirring, the solution was concentrated by rotary evaporation and the PEO-*b*-PVBPA block copolymer (0.9 g) was recovered by precipitation in cold diethylether and dried under vacuum at 40°C (yield = 97%).

^1H NMR 400MHz (Acetone D_6 , RT, ppm) (Figure 3C): 1.0–2.25 (broad, ethylenic protons); 2.88 (s, $-\text{Ph-CH}_2\text{-P-}$); 3.24 (s, $\text{CH}_3\text{-O-CH}_2\text{-}$); 3.50 (s, $-\text{O-CH}_2\text{-CH}_2\text{-O-}$); 4.90 (broad, $-\text{P-OH} \leftrightarrow \text{H}_2\text{O}$); 6.3–7.7 (m, benzenic protons); 7.83 (m, benzenic protons in β position from $\text{C}=\text{S}$).

^{31}P NMR 100MHz (D_2O , RT, ppm) (Figure S10): 25.65 (s).

B.3 Micelles formation

PEO-*b*-PNIPAM: 20 mg of PEO-*b*-PNIPAM block copolymer was dissolved in 2 mL of deionized water at room temperature (pH = 6.7) and filtered through a 1.2 μm Millipore filter. The solution was rapidly warmed to 75°C in the DLS instrument. DLS measurements were performed every 5°C during cooling process. DLS measurements performed every 5°C during a warming process from room temperature gave the same results.

PEO-*b*-PVBPA/pentaethylenehexamine: 240 mg of PEO-*b*-PVBPA block copolymer was dissolved in 17.88 mL of deionized water at room temperature. Separately 11.4 mg of pentaethylenehexamine (from Aldrich) was dissolved in 17.88 mL

of deionized water at room temperature. 1 mL of each solution was mixed together in 8 different flasks (pH = 3.43) and some drops of solutions of HNO₃ (1M) or NaOH (0.5, 1 or 2M) were added to adjust pH in the range [2.9–12.2]. DLS measurements were carried out after 4 hours of stirring at room temperature.

PEO-*b*-PQVBC⁺/PAANa: 364 mg of PEO-*b*-PQVBC⁺ block copolymer was dissolved in 21 mL of deionized water at room temperature (pH = 6.5). Separately 56 mg of poly(acrylic acid, sodium salt) (Aldrich; M_w = 5100 or 1200 g.mol⁻¹) was dissolved in 21 mL of deionized water at room temperature. 1 mL of each solution was mixed together in 8 different flasks (pH = 7.5) and some drops of solutions of HNO₃ (0.1 or 1M) or NaOH (0.1M) were added to adjust pH in the range [2.3–9.5]. DLS measurements were carried out after 48 hours of stirring at room temperature.

B.4 Silica/polymer hybrid material synthesis

200 mg of block copolymer **1** (PEO-*b*-PNIPAM) was first dissolved in 4 mL of deionized water at ~20°C. The pH of the solution was adjusted at 2 by addition of a small volume of HNO₃ (2M). Then, the solution was heated at 75°C, stirred for several minutes, and 0.72 mL of TEOS was added. Quantitative hydrolysis of TEOS was completed after 30 min and then condensation of the silicate species was induced by addition of NaOH (0.1M) until pH=5 was reached. Reaction mixture was kept under moderate magnetic stirring at 75°C for 20 h. After centrifugation and drying at 80°C overnight, a pink powder was recovered. The powder was then calcined in air at 550°C for 8 hours with a heating ramp of 2°C/min; the mesoporous silica material was then characterized by transmission electron microscopy and N₂ adsorption/desorption measurements.

B.5 Characterization

¹H NMR and ³¹P NMR spectra were recorded in deuterated solvent at room temperature with a Bruker DRX 400 spectrometer. Size exclusion chromatography (SEC) was performed in DMF : flow rate 0.8 mL.min⁻¹, pump Varian Prostar model 210 with two columns PLgel Mixed D from Polymer Laboratories thermostated at 70°C, a refractive index detector Shodex RI-101, and an UV detector Kontron Instruments model 430 adjusted at 309 nm (maximum absorption of dithiobenzoate moieties). PEO standards from Polymer Laboratories with M_n ranging from 620 to 42000 g.mol⁻¹ were used for calibration.

Dynamic light scattering (DLS) measurements were carried out with a Zetasizer Nano ZS instrument (Malvern, UK). Intensity-averaged hydrodynamic diameters were obtained from measured diffusion coefficients using the Stokes–Einstein equation.

Elemental analyses and MALDI-ToF mass spectrometry were carried out by the “Service Central d’Analyses du CNRS” (Solaize, France).

The mesoporous silica material was characterized by Transmission Electron Microscopy (TEM): TEM images were collected on a JEOL 1200 EX II (80–100 kV) microscope on microtomed samples.

C Results and discussion

C.1 Synthesis and characterization of the PEO-based macro-CTA

Synthetic access toward PEO-based CTA is outlined in Scheme

1 and was largely inspired from Walther *et al.*¹⁵ In this previous study, meticulous purifications of the bromo-terminated PEO (PEO-PhBr) and of the final PEO-CTA were performed using several cycles of redissolution/precipitation, centrifugation and even dialysis against benzene. Indeed, trace of residual dicyclohexylurea (DCU) could be seen by ¹H NMR analysis when performing only two precipitations in diethylether to purify PEO-PhBr (see Figure 1-1). But it was found that the presence of such an impurity did not disturb the subsequent Grignard reaction and it was totally eliminated when purifying the final PEO-CTA (see experimental part and Figure 1-2). Finally, the adapted synthesis procedure uses easy purification steps while ensuring the recovery of a pure product in a high yield (89%). The evidence of the complete PEO chain-end modification is provided by ¹H NMR analysis: perfect matching in integration values in Figure 1-2 (integration values calibrated on the methyl chain-end of PEO, peak **a**; the slight excess in values of CTA moiety supports the hypothesis of the presence of di-hydroxylated PEO chains in the initial PEO-OH). Note that if the actual DP_n value (105) and the integration value of PEO units (peak **b**) were used together to estimate the degree of functionalization, an erroneous (under-estimated) value of ~90% would be found.

In a general way, with size exclusion chromatography (SEC), no shifting in the elution volume can be expected when performing a chain-end modification of polymer chains of sufficiently high molecular weight (see Figure S1-2). But surprisingly, it was found that performing SEC in DMF using polar columns was suitable for supporting the complete PEO chain-end modification: whole peak shifting in Figure S1-1 with no change of dispersity value (see Table S2).

C.2 Synthesis and characterization of block copolymers

RAFT polymerizations mediated by PEO-CTA of three different monomers were performed to access the various targeted DHBCs. Thermo-sensitive block copolymer **1** is directly obtained by polymerization of *N*-isopropylacrylamide (NIPAM) while cationic block copolymer **2** and anionic block copolymer **3** need an additional chemical modification of the new polymerized block: polymerization of vinylbenzyl chloride (VBC) followed by quaternisation with triethylamine (TEA) leads to a poly(quaternized vinylbenzyl chloride) (PQVBC⁺) cationic block, and polymerization of vinylbenzylphosphonic diethyl ester (VBPDE) followed by deprotection reaction with trimethylsilyl bromide ((Me)₃SiBr) and methanol leads to a poly(vinylbenzylphosphonic di-acid) (PVBPA) polyacid block. Other phosphonated PEO-based DHBCs are also prepared in our laboratory using dimethyl(methacryloyloxy)methyl phosphonate as monomer;²⁹ and their synthesis which relies on a different synthetic pathway will be reported elsewhere.³⁰

Figure 1: ^1H NMR spectra (400MHz, CDCl_3) of the bromo-terminated precursor (PEO-PhBr) [1] and of PEO-CTA [2].

When polymerizing a second monomer using the RAFT process in order to obtain a block copolymer, the $[\text{macro-CTA}]/[\text{AIBN}]$ ratio should be maximized in order to reduce the proportion of AIBN-initiated chains, which will be homopolymer chains of the second monomer. However, a high $[\text{macro-CTA}]/[\text{AIBN}]$ ratio can lead to slow kinetics and low final conversion, in particular when using dithiobenzoates as CTA. Indeed, dithiobenzoates are well-known to induce an ‘induction period’ and/or a ‘retardation effect’ in the RAFT polymerization of some monomers.^{17, 18} In some preliminary experiments, we found that PEO-CTA induces a quite long induction period (>4hours) in the polymerization of NIPAM at 70°C. An increase of the polymerization temperature to 90°C reduces this induction period to ~30min. But with $[\text{macro-CTA}]/[\text{AIBN}] = 10$, the final conversion is very low (~10%). Finally, a $[\text{macro-CTA}]/[\text{AIBN}]$ ratio of 5 was used in the RAFT polymerizations of NIPAM: this value seemed to be a good compromise to slightly increase the final conversion without creating an important proportion of hydrophilic homopoly(NIPAM) chains (which should be very difficult to eliminate from the block copolymer; see also discussion below). No significant induction period was detected during the RAFT polymerizations of VBC or VBPDE at 80°C mediated by PEO-CTA. This could be the consequence of the similarity in the chemical structures of the fragment radical $\text{R}^\bullet$ (of the macro-CTA) and of the propagating radical of styrenic monomer. However, a ‘retardation effect’, slowing down kinetics, was still present with both monomers. But in polymerizations of VBC or of VBPDE, AIBN-initiated chains are hydrophobic polymeric chains, which are soluble in non-polar solvent: they can be easily eliminated after polymerization by precipitation in diethyl ether of the block copolymers. Consequently, lower $[\text{macro-CTA}]/[\text{AIBN}]$ ratio can

be used in order to get acceptable final conversion.

SEC analyses of the various samples (after purification but before modification) give evidence of the good control of the different RAFT polymerizations: whole peaks shifting in Figure 2 and very low dispersity ($\bar{D}$) were obtained (see Table 1). The RI signals of the chromatographs (Figure 2) seem to enhance the small proportion of chains of double-molecular weight which are already visible in the PEO-CTA and in the initial PEO-OH (see Figure S1-2). However, the normalized UV signals of the chromatographs (see Figure S2) provide other information: adjusted at 309 nm (maximum of absorption of dithiobenzoate

Figure 2: Size exclusion chromatograms (in DMF, column = PLgel Mixed D; RI signal, arbitrary unit) of the macro-CTA and of the different PEO-based block copolymers synthesized: PEO-CTA (dashed line), copolymer 1a (bold dashed line), copolymer 2 (normal line), copolymer 3 (bold line).

moieties), the signal intensity is directly proportional to the number of moles of the main population of dormant chains. In

Figure S2, it is clear that the molar proportion of dormant chains of double-molecular weight does not significantly change after the polymerizations were performed. Therefore, in Figure 2, the minor population at lower elution time could be mainly attributed to some dead-chains created by radical recombination (termination event). If neglecting this population, dispersity reduce to ~ 1.05 (or values about 1.09 if using UV signals), confirming the very efficient control of the polymerization usually provided by dithiobenzoate-based CTA.

As expected, a new distribution of chains of lower molecular mass appears in SEC analyses of raw samples from polymerization of VBC or VBPDE. The UV signal of the chromatographs was exploited (by calculating the area under each peak/population) to quantify the proportion of these new chains: its molar proportion is respectively 20% and 25% for PEO-*b*-PVBC and PEO-*b*-PVPDE block 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). SEC analyses performed after purification steps give evidence of the total elimination of these homopolymer chains (see Figure S4 and S8). In the polymerization of NIPAM using a [macro-CTA]/[AIBN] equal to 5, a molar proportion of $\sim 16\%$ of AIBN-initiated chains should be expected. However, no chain of low molecular mass was detected in SEC chromatogram (see Figure S3) suggesting that very few AIBN-initiated chains are present in the copolymer **1a**. Actually, during the ‘induction period’ of the polymerization, a lot of primary radicals are created but termination events are quite frequent that induce the formation of AIBN-initiated oligomeric dead-chains (which are eliminated during precipitation of the block copolymer). In the present case, at the end of the ‘induction period’, more than 75% of the initial amount of AIBN is already decomposed.

Because PEO calibration of the SEC is not appropriate for molecular weight determination of the block copolymers, average degrees of polymerization of the second blocks were determined by ^1H NMR analyses (see Figure 3A, Figure S5, Figure S9, and ESI for calculations) that lead to the values *m* in Table 1.

Table 1: Properties of the macro-CTA and of the different synthesized PEO-based block copolymers.

Sample ref.	Nature of 2 nd block	<i>m</i> [*]	<i>M_n</i> (g.mol ⁻¹) ^{**}	<i>D</i> ^{***}	Micellisation conditions
PEO-CTA	-	-	4800	1.04	-
1a	PNIPAM	16.1	6620	1.11	Temp. > 53°C
1b	PNIPAM	118	18100	1.36	Temp. > 32°C
2	PQVBC [†]	13.7	8270	1.12	PICm [‡]
3	PVBPA	8.4	6460	1.16	PICm [‡]

^{*} *m* = Average degree of polymerization of 2nd block determined by ^1H NMR.

^{**} *M_n* = 4800 + *m* × *M*(monomer unit of 2nd block).

^{***} Determined by SEC in DMF (before quaternisation for sample **2**; before deprotection for sample **3**).

[†] PICm = polyion complex micelles (see text for the nature of the counter-polyion, which define the pH range of micellization).

Figure 3: ^1H NMR (400MHz) spectra of copolymer **1a** (CDCl_3)[A], copolymer **2** (D_2O)[B], and copolymer **3** (*d*-DMSO)[C].

As targeted, the three block copolymers have an asymmetric structure: the degree of polymerization of the functional block is about 10-times smaller than the one of the PEO block. In addition, to be able to perform a comparative experiment in mesoporous silica synthesis, symmetrical block copolymer **1b** was synthesized: the *DP_n* of the PNIPAM block is 118, which is quite close to the one of the initial PEO block (105) (see Table 1 and Figure S3 for SEC analysis).

Successful chemical modification was checked by ^1H NMR analysis (see Figure 3B-C): in both spectra, disappearance and appearance of proper peaks reveal quantitative modification of the polymer backbone. Moreover, a degree of quaternisation of 94% was determined by elemental analysis of copolymer **2**, and the ^{31}P NMR spectrum of copolymer **3** (Figure S10) displays only one peak indicating complete deprotection of phosphonic moieties. In addition, while the dithiobenzoate moiety is still present in copolymers **1a** and **3**, it is converted into thiol moiety during the quaternisation step needed to obtain copolymer **2**. Note that the quaternized block copolymer **2** needed a purification step by dialysis in order to remove a by-product formed by reaction of solvent with triethylamine. We preconize to perform this kind of reaction in chloroform (instead of dichloromethane), which appears to be non-reactive with triethylamine.³¹

C.3 Aggregation of block copolymers in water

As polyNIPAM is a thermo-sensitive polymer exhibiting a LCST (low critical solubility temperature) in water, double-hydrophilic block copolymers **1a** and **1b** are expected to change into amphiphilic copolymers by increasing the temperature. This ability was confirmed by dynamic light scattering (DLS) measurements of copolymer solution in water at different temperatures (see Figure 4): below 50°C, copolymer **1a** is completely soluble as random coils with a hydrodynamic diameter (D_h) of about 6 nm, but above 55°C, the sizes of scattering objects sharply increase to ~22 nm, revealing the formation of micelles. The micellization process is obviously reversible as DLS measurements performed during warming or cooling process gave the same results. Thus, the micellization temperature of copolymer **1a** is around 53°C, which is much higher than the usual LCST of polyNIPAM (~32°C). However, this elevated LCST value is consistent with previous studies where polymer samples (or block copolymers) of low molecular weight and low dispersity were also synthesized and investigated.^{32–34} With a much higher DP_n of PNIPAM block, symmetrical copolymer **1b** exhibits a micellization temperature much closer to 32°C (~33°C, see Figure S11) as commonly reported in the literature.^{35–39} So, the high increase of micellization temperature for copolymer **1a** is mainly a result of the shortness of the PNIPAM block, and only in a minor extent, due to the PEO chain. Complete study about the influence of the (low) degree of polymerization of PNIPAM block on the micellization temperature of PEO-*b*-PNIPAM copolymers will be published in a forthcoming paper.

Figure 4: Hydrodynamic diameter (●) and scattered intensity (log scale; ×) of objects obtained with copolymer PEO-*b*-PNIPAM **1a** in aqueous solutions at 1 wt% as a function of temperature [dashed lines are only guides for the eyes].

Polyion complex (PIC) micelles resulting from the electrostatic complexation between charged DHBC and oppositely charged homopolymers could be obtained with copolymers **2** and **3**. By choosing adequate weak polyacid (for copolymer **2**) or weak polybase (for copolymer **3**), micellization process can be triggered by a pH change since the micellization domain is determined by the pK_a values of the polyacid and of the polybase.⁴⁰ Aqueous solutions were prepared according to a charge mixing ratio R equal to 1. R was defined as the number of anionic units against the number of cationic units added in the mixture ($R = n_{VBPDA} / n_{Amine}$ or $R = n_{AA} / n_{QVBC}$). Mixtures of PEO-*b*-PVBPDa copolymer **3** with a weak polybase such as pentaethylenhexamine show effectively a pH triggering: when pH is higher than 8, scattered intensity is low but when pH is smaller than the pK_a of the polyamine (~7), it sharply increases indicating that polymer aggregation occurs (see Figure 5). The sizes of the copolymer **3**/

pentaethylenhexamine aggregates (~40–60 nm) for $3 < \text{pH} < 7$ are of the same order of magnitude as those formed by the mixture of PEO-*b*-poly(acrylic acid)/oligochitosan previously studied (25–30 nm for $5 < \text{pH} < 6$).⁵ Reversibility of the micellization process was checked by increasing the pH from 4 to ~9 (scattered intensity strongly decreased) and then by decreasing it again below 6 (scattered intensity strongly increased).

Figure 5: Hydrodynamic diameter (●) and scattered intensity (log scale; ×) plotted as a function of pH for water mixture composed of copolymer PEO-*b*-PVBPDa **3** with pentaethylenhexamine (0.7 wt% polymer content) [dashed lines are only guides for the eyes].

Mixture of PEO-*b*-PQVBC⁺ copolymer **2** with a weak polyacid such as poly(acrylic acid) sodium salt (PAA_{Na}, $pK_a \sim 6$) induces PIC micelles only for pH above 6 (see Figure 6). Molecular weight of PAA_{Na} (1200 or 5100 g.mol⁻¹) does not seem to have significant influence on the size of the micellar structures (around 20 nm in both case). Reversibility of the micellization process was checked in the same manner as with the copolymer **3**/pentaethylenhexamine system.

Figure 6: Hydrodynamic diameter (●, ■) and scattered intensity (log scale; ×, +) plotted as a function of pH for water mixture composed of copolymer PEO-*b*-PQVBC⁺ **2** with poly(acrylic acid, sodium salt) (1 wt.% polymer content): $M_w(\text{PAA}_{Na}) = 1200 \text{ g.mol}^{-1}$ (●, ×); $M_w(\text{PAA}) = 5100 \text{ g.mol}^{-1}$ (■, +) [dashed lines are only guides for the eyes].

C.4 Silica/polymer hybrid material synthesis

Micellar aggregates of PEO-*b*-PNIPAM copolymer **1a** acted as efficient SDA in mesoporous silica synthesis. A hybrid copolymer-silica material was first prepared by hydrolysis and condensation of tetraethoxysilane in the presence of copolymer **1a** at 75°C (above the micellization temperature). Silica yield was 97%, and it was determined, by both thermo-gravimetric and elemental analyses that 54% of the block copolymer was incorporated in the mesoporous material. After calcination, the material was characterized by TEM and N₂ adsorption/desorption analysis. TEM image of the resulting silica shows a homogeneous nanostructured material with short-range ordered gyroidal domains (see Figure 7). The mean pore diameter (estimated by TEM) appears to be approximately 6 nm, being in agreement with

the value determined by N₂ adsorption/desorption experiment (5.6 nm; see Figure S12). It is important to note that the hydrodynamic diameter of the micellar aggregates does not depict the final pore diameter in the mesoporous silica material: firstly, because of the asymmetric structure of our DHBCs, the hydrodynamic diameter is much larger than the size of the micelle water-insoluble core (which is close to the pore size); secondly, interaction of silica precursors with DHBC leads to a cooperative self-assembly process in which the size of the subsequent porogenic nano-domains could be strongly modified depending on the extent of PEO trapping within silica walls.⁴¹ As a consequence of the nanostructuring process, this silica material offers a high specific surface area of 855 m².g⁻¹. As a 'control' experiment, silica structuring in the presence of symmetrical copolymer **1b** (symmetrical in terms of degrees of polymerization of blocks) was also performed (the EO unit /TEOS molar ratio was fixed at 1). Silica yield was only 30% and only 12% of the block copolymer was incorporated in the hybrid material. The N₂ adsorption/desorption isotherms of the material after calcination showed the absence of well-defined mesopores. These poor results with copolymer **1b** could be partly explained by the too high PNIPAM/PEO mass ratio inhibiting the formation of stabilized nanosized PNIPAM domains structuring the silica matrix. The detailed use of PEO-*b*-PNIPAM block copolymers (of various lengths) in the synthesis of mesoporous silica will be reported in a forthcoming paper while the elaboration of functional mesoporous silica with PEO-*b*-PQVBC⁺ or PEO-*b*-PVBPA is currently under investigation.

Figure 7: TEM image of mesoporous silica (after calcination) synthesized using aggregates of copolymer PEO-*b*-PNIPAM **1a** as structuring agent.

D Conclusions

The RAFT process was efficiently used to produce various functional DBHCs which satisfy all the requirements [(a) to (d), see above] defined for acting as effective structuring agents in mesoporous silica synthesis. In particular, depending on temperature (in the case of thermosensitive polymers) or the presence of an auxiliary of micellisation (in the case of ionizable DHBCs), DHBCs are able to organize themselves in micellar aggregates and their size is compatible with the production of mesoporous silica. In the case of PIC micelles, the hydrophilic nature of the homopolymer auxiliary of micellization should ensure its removal from the pores using only water washing, and is expected to lead to DHBC-functional nanostructured silica.

PNIPAM-functionalized pores could be useful, for example, in loading and controlled release of drugs,⁴² or in enzymes accommodation (for biocatalyst nano-reactor),⁴³ while polyionic-functionalized materials could be of great interest for trapping/releasing ions, molecules, contaminants or drugs of opposite charge,⁴⁴ or to act as proton-exchange membrane in high temperature fuel cells,⁴⁵⁻⁴⁷ or as anion-exchange membrane for alkaline fuel cells.^{48, 49} Moreover, expanding the pH range of PIC micelle formation (toward lower pH with PVBPA or higher pH with PQVBC compared to the reference PEO-*b*-P(M)AA DHBC), these DHBCs could be useful in the synthesis of various other metal oxide mesoporous materials.⁵⁰

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Notes and references

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† Electronic Supplementary Information (ESI) available: Scheme of synthesis routes described in the litterature to access to PEO-based macro-CTA; SEC chromatograms (RI signal) of PEO-CTA; SEC chromatograms (UV signal) of synthesized block copolymers; SEC chromatograms (RI signal) of PEO-*b*-PNIPAM block copolymers; Synthesis of VBPDE monomer; SEC chromatograms (UV signal) before and after purification and ¹H NMR spectra of PEO-*b*-PVBC and PEO-*b*-PVBPA block copolymers; ³¹P NMR spectra of PEO-*b*-PVBPA and PEO-*b*-PVBPA block copolymers; Hydrodynamic diameter of scattering objects obtained with copolymer **1b** in aqueous solutions as a function of temperature. N₂ adsorption/desorption isotherms of mesoporous silica. See DOI: 10.1039/b000000x/

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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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The syntheses of three different DHBCs (cationic, anionic, or thermosensitive) are described. To act as structure directing agents in mesoporous silica synthesis, their ability to undergo micellization under appropriate conditions was checked.