Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Synthesis and self-assembly of polystyrene-based diblock and triblock coil-brush copolymers

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1. Calculation of composition and theoretical molecular weight of the polymers

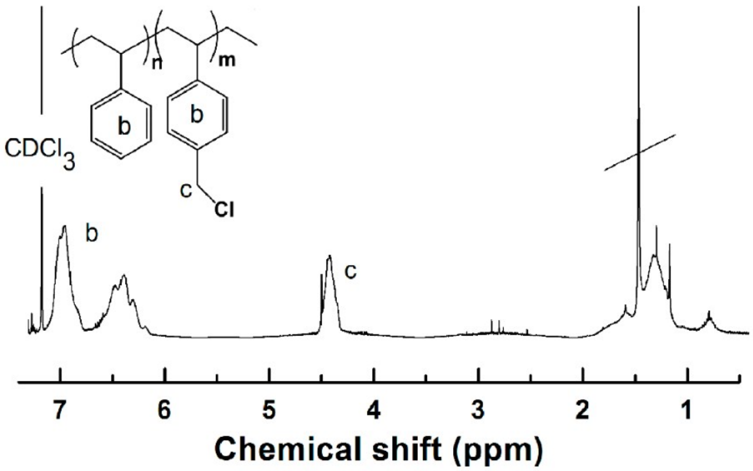

Fig. S1. ^{1}H NMR spectrum of the random copolymer P(St-*co*-VBC).

Molar ratio of the monomeric units F = [St]/[VBC] in random copolymers P(St-*co*-VBC) was calculated from ^{1}H NMR spectra according to the following equation[1]:

$$F = \frac{(I_b - 2 \times I_c)/5}{I_c/2} \qquad (S1)$$

where I_b is the integral value of the signals at 6.3–7.45 ppm attributed to the aromatic protons, and I_c is the integral value of the signal at 4.6 ppm attributed to the protons of chloromethyl group (–CH_2Cl) in VBC unit.

Molar composition of the random copolymers was calculated by solving the system of equations:

$$\begin{cases} \dfrac{[St]}{[VBC]} = F \\ [St] + [VBC] = 1 \end{cases} \qquad (S2)$$

where [St] and [VBC] are molar parts of St and VBC units in a copolymer, respectively.

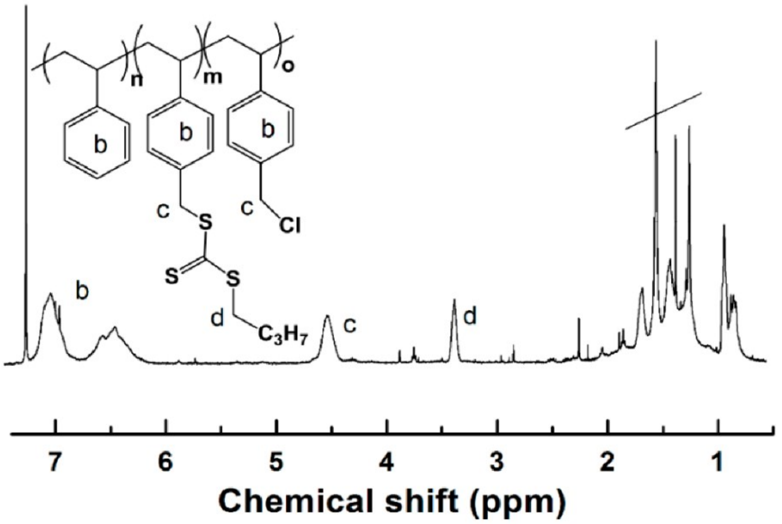

Fig. S2. ^{1}H NMR spectrum of the functionalized copolymer P(St-*co*-VBC-*co*-VBTC).

Degree of functionalization (DF, mol%) of the copolymers P(St-*st*-VBC) and PS-*b*-PVBC by butyl-trithiocarbonate (TTC) groups was calculated from ^{1}H NMR spectra by the following equation[2]:

$$DF = \frac{I_d}{I_c} \times 100\% \qquad (S3)$$

where I_d is the integral value of the signal at 3.4 ppm assigned to the methylene protons of butyl group adjacent to thiocarbonyl group, and I_c is the integral value of the signal at 4.6 ppm assigned to the methylene protons of benzyl group.

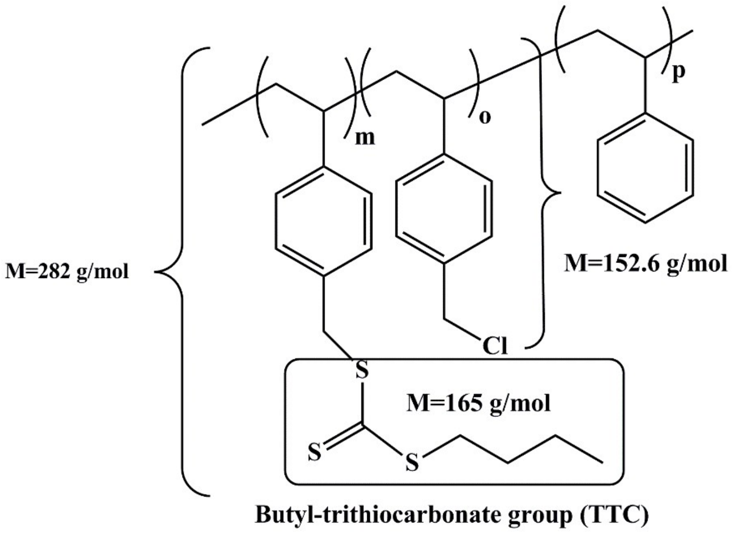

Fig. S3. Schematic representation of the composition of the functionalized copolymer P(St-*co*-VBC-*co*-VBTC).

Number of VBC units per backbone functionalized by TTC groups (n) (VBTC) was calculated according to the equation:

$$n = \frac{\left(M_{n,SEC} - M_{PS,SEC}\right) \times DF}{282} \qquad (S4)$$

where $M_{n,SEC}$ and $M_{PS,SEC}$ are the molecular weights of P(St-*co*-VBC-*co*-VBTC) and PS respectively, determined by SEC; DF is the degree of functionalization of the copolymers P(St-*co*-VBC), and 282 is the molecular weight of VBTC unit.

The following formulas were used to calculate theoretical molecular weight of diblock and triblock polystyrene-based copolymers:

$$M_n^{th} = \frac{[M]}{[CTA]} \times M_{Mon} \times q + M_{CTA} \qquad (S5)$$

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where [M] and [CTA] are initial concentrations of a monomer and chain transfer agent; M_{Mon}, M_{CTA} are molecular weights of a monomer and chain transfer agent; q is conversion of monomer.

theoretical molecular weight of functionalized with TTC groups copolymers:

$$M_n^{th} = M_{n,SEC} + DF \times DP(VBC) \times 165 - DF \times DP(VBC) \times 35.5 \quad (S6)$$

where $M_{n,SEC}$ is molecular weights of diblock and triblock polystyrene-based copolymers; DF is the degree of functionalization of the copolymers by TTC groups; DP(VBC) is the degree of polymerization of pVBC; 165 and 35.5 are the molecular weights of butyltrithiocarbonate group and chlorine atom, respectively (see Fig. S3).

theoretical molecular weight of anionic molecular brushes:

$$M_n^{th} = \left(\frac{[AA]}{[VBTC]} \times M_{AA} \times q + M_{VBTC}\right) \times n + M_{n,P(St-co-VBC)} \qquad (S7)$$

where [AA] and [VBTC] are initial concentrations of acrylic acid and repeating butyltritiocarbonate moieties in P(St-*co*-VBC-*co*-VBTC); M_{AA}, M_{VBTC} and $M_{n,P(St\text{-}co\text{-}VBC)}$ are the molecular weights of acrylic acid, one butyltritiocarbonate moiety (288 g/mol, see Fig. S3) and non-modified units of P(St-*co*-VBC) in the backbone, respectively; n is an average number of butyltritiocarbonate moieties per polymeric backbone, and q is conversion of a acrylic acid.

Degree of polymerization (DP) of PAA:

$$DP(PAA) = \frac{\left(M_n - M_{n,\ P(St-co-VBC-co-VBTC)}\right)}{72.06 \cdot n} \qquad (S8)$$

where M_n and $M_{n,P(St\text{-}co\text{-}VBC\text{-}co\text{-}VBTC)}$ are molecular weight of polystyrene-based anionic molecular brush and diblock/triblock or random polystyrene-based copolymer decorated with multiple TTC groups, respectively; n is an average number of butyltritiocarbonate moieties per polymeric backbone, 72.06 – is molecular weight of AA.

2. MWD and SEC curves of various copolymers

The completely consumption of macroCTA (PS) was confirmed by SEC (Fig. S4). The purity of polystyrene-based anionic molecular brush (CB1 as an example) is shown in Fig. 5.

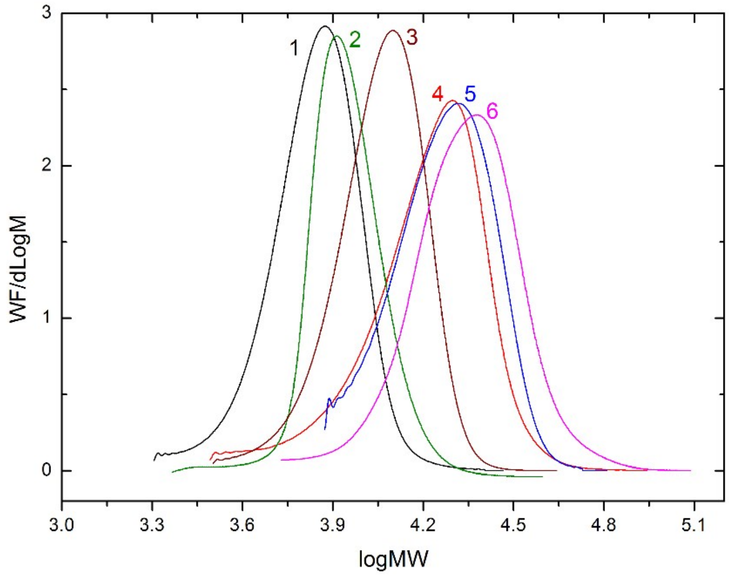

Fig. S4. MWD curves of PS1 (2), PS2 (1), PS3 (3) and their copolymers PS1-b-PVBC (5), PVBC-b-PS2-b-PVBC (4) and PVBC-b-PS3-b-PVBC (6) (see entries in Table 1)

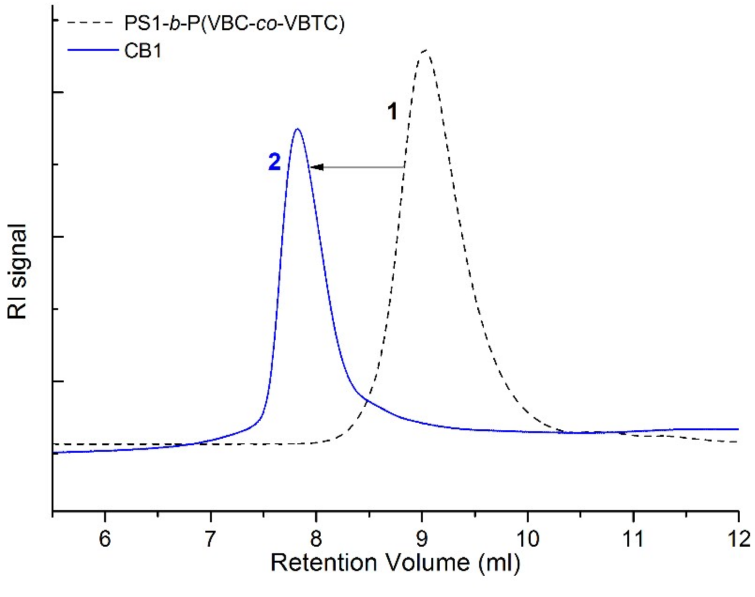

Fig S5. SEC curves of PS1-b-P(VBC-co-VBTC) (1) and CB1 (2)

Table S1. Results of functionalization of diblock, triblock and random copolymers of St and VBC with sodium butyl trithiocarbonate

Run	Target copolymer	DF (%)[1]	n(VBTC)[2]	$M_{n, th}$[3]	$M_{n, SEC}$	Đ
1	PS1-*b*-P(VBC-*co*-VBTC)	63	34	23600	25800	1.20
2	P(VBC-*co*-VBTC)-*b*-PS2-*b*-P(VBC-*co*-VBTC)	70	57	23000	29400	1.37
3	P(VBC-*co*-VBTC)-*b*-PS3-*b*-P(VBC-*co*-VBTC)	60	39	24000	29600	1.33
4	PS4-*b*-P(VBC-*co*-VBTC)-*b*-PS4	49	12	14700	19600	1.20
5	P(St-*co*-VBC-*co*-VBTC)	65	54	21300	22800	1.41

3. FT-IR spectra of various polystyrene-based polymers

Typical spectra of the polymers are presented in Fig. S6. In the spectrum of the copolymer PVBC-*b*-PS2-*b*-PVBC, new absorption bands at 1265 cm^{-1}, 822 cm^{-1} and 671 cm^{-1} attributed to the chloromethyl group in VBC units were recorded. The spectrum of the copolymer functionalized with butyltrithiocarbonate groups (TTC) contains absorption bands at 1049 cm^{-1} and 810 cm^{-1} characteristic for C=S and C-S vibrations, respectively. The spectrum of the brush copolymer additionally contains absorption bands at 3400-2400 cm^{-1}, 1700 cm^{-1} and 1250-1165 cm^{-1} attributed to -OH, C=O and C-O vibrations, respectively, of the carboxyl group from pAA.

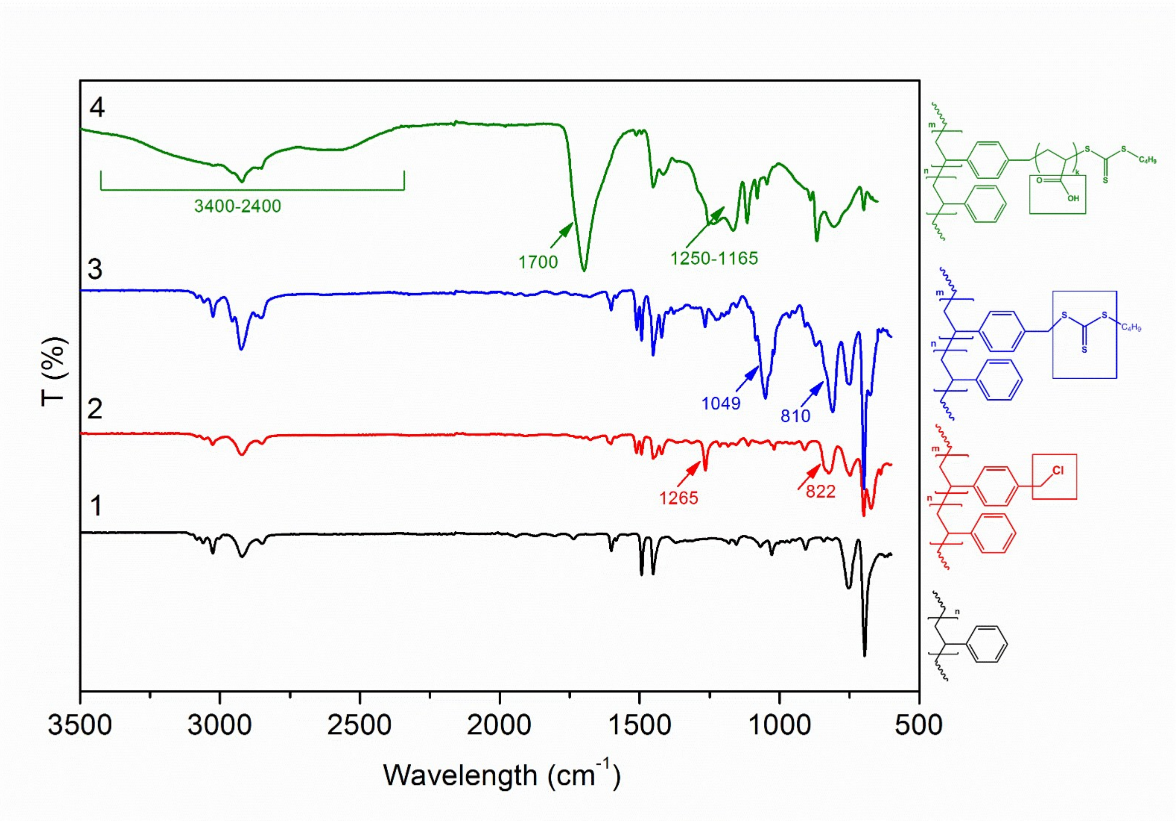

Fig. S6. FT-IR spectra of PS2 (**1**), PVBC-*b*-PS2-*b*-PVBC (2), P(VBC-*co*-VBTC)-PS2-*b*-P(VBC-*co*-VBTC) (**3**) and P(VBC-*co*-VB-*g*-PAA1)-*b*-PS2-*b*-P(VBC-*co*-VB-*g*-PAA1) (**4**).

4. Wettability of polystyrene-based copolymers

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[1] Degree of functionalization calculated according to equation S3.

[2] Number of VBTC units calculated according to equation S4.

[3] Theoretical molecular weight calculated according to equation S6.

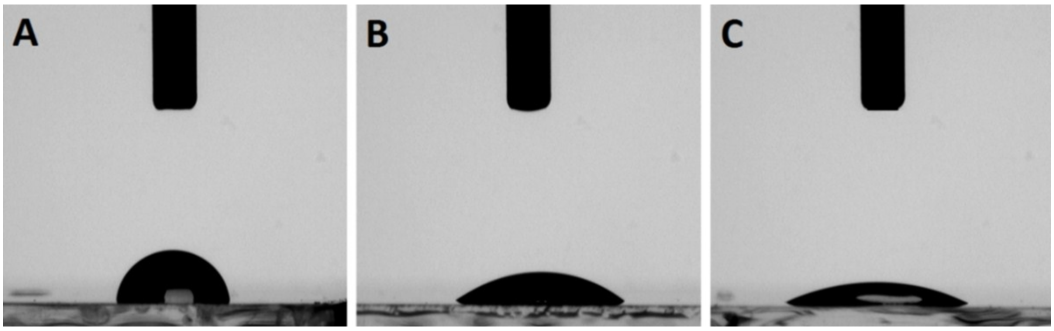

Fig. S7. WCA of the copolymers P(VBC-*co*-VBTC)-*b*-PS3-*b*-P(VBC-*co*-VBTC) (**A**), P(VBC-*co*-VB-*g*-PAA3)-*b*-PS3-*b*-P(VBC-*co*-VB-*g*-PAA3) (**B**) and P(VBC-*co*-VB-*g*-PAA4)-*b*-PS3-b-P(VBC-*co*-VB-*g*-PAA4) (**C**).

Wettability of the functionalised copolymer and two brush copolymers are visualised in Fig. S7. WCA value of the functionalized copolymer P(VBC-*co*-VBTC)-*b*-PS3-*b*-P(VBC-*co*-VBTC) is rather high (about 90°), while for the brush copolymers with short and relatively long PAA side chains only 45° and 31°, respectively.

5. DLS study of anionic polystyrene-based brush copolymers

Hydrodynamic diameters D_h of the brush copolymers in DO and their aggregates in DO/water mixture at several temperatures are presented in Table S2. Usually, the size of particles and aggregates is the largest at 30 °C while it decreases at 40 °C (Fig. S8).

Table S2. D_h of polystyrene-based brush copolymers and their aggregates in DO and in DO/H_2O mixture (50:50) at several temperatures

Polymer	D_h, in DO, nm			D_h, in DO/H_2O (50/50), nm		
	25 °C	30 °C	40 °C	25 °C	30 °C	40 °C
PS1-*b*-P(VBC-*co*-VB-*g*-PAA)	16.1	16.3	10.3 ↓	1070	830	440 ↓
P(VBC-*co*-VB-*g*-PAA1)-*b*-PS2-*b*-P(VBC-*co*-VB-*g*-PAA1)	14.2	14.1	13.2 ↓	870	910	750 ↓
P(VBC-*co*-VB-*g*-PAA2)-*b*-PS2-*b*-P(VBC-*co*-VB-*g*-PAA2)	11.4	14.6	13.8 ↓	880	1010	770 ↓
P(VBC-*co*-VB-*g*-PAA3)-*b*-PS3-*b*-P(VBC-*co*-VB-*g*-PAA3)	16.3	18.8	14.8 ↓	980	1060	790 ↓
P(VBC-*co*-VB-*g*-PAA4)-*b*-PS3-*b*-P(VBC-*co*-VB-*g*-PAA4)	16.3	19.2	19.8 ↑	210	330	385 ↑
PS4-*b*-P(VBC-*co*-VB-*g*-PAA)-*b*-PS4	7.9	10.2	8.3 ↓	670	780	505 ↓
P(St-*co*-VBC-*co*-VB)1-*g*-PAA1	15.5	15.6	20.0 ↑	-	715	475 ↓
P(St-*co*-VBC-*co*-VB)1-*g*-PAA2	13.9	24.8	21.6 ↓	495	620	610 ↓

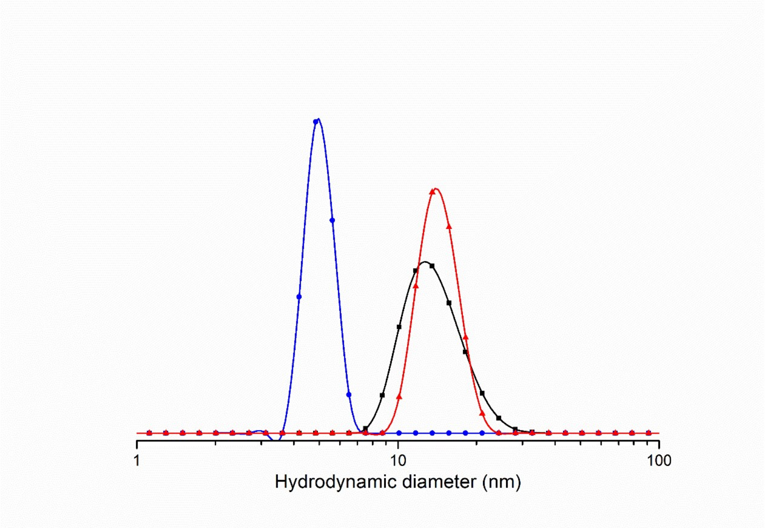

Fig. S8. Volume-based hydrodynamic diameter of PS1-*b*-P(VBC-*co*-VB-*g*-PAA) in dry DO at different temperatures: 25 °C (-■-), 30 °C (-▲-) and 40 °C (-●-).

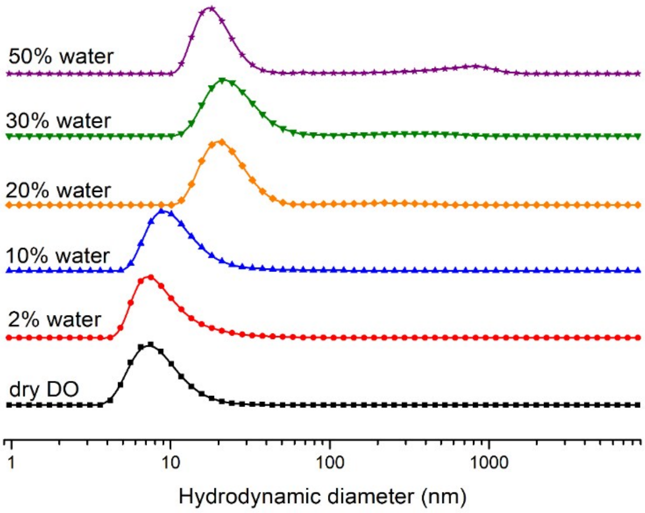

Fig. S9. Volume-based hydrodynamic diameter of the copolymer coil-brush-coil PS1-*b*-P(VBC-*co*-VB-*g*-PAA) in DO and its mixtures with water at 30 °C.

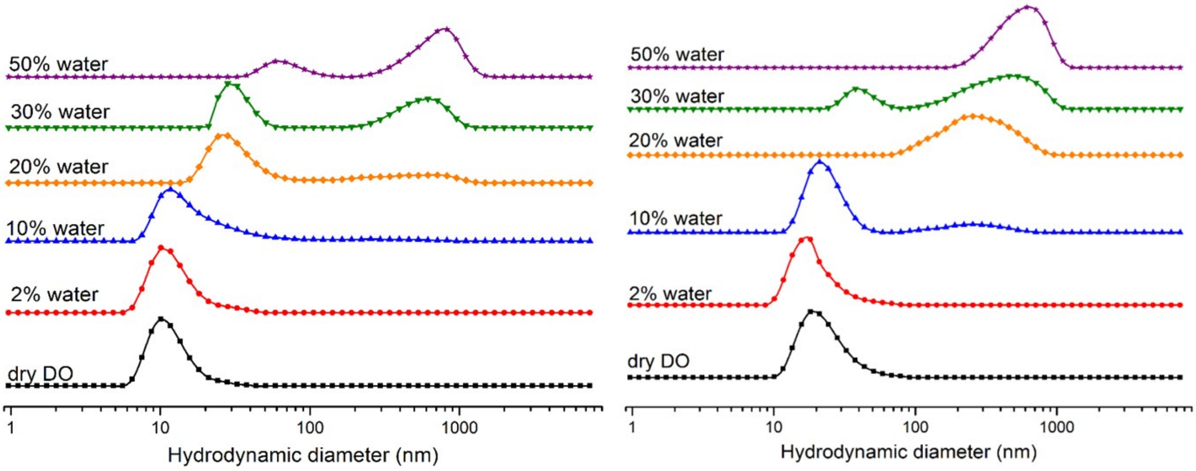

Fig. S10. Volume-based hydrodynamic diameter of polystyrene-based random brush copolymers P(St-*co*-VBC-*co*-VB)1-*g*-PAA1 (left) and P(St-*co*-VBC-*co*-VB)1-*g*-PAA2 (right) in DO and its mixtures with water at 30 °C.

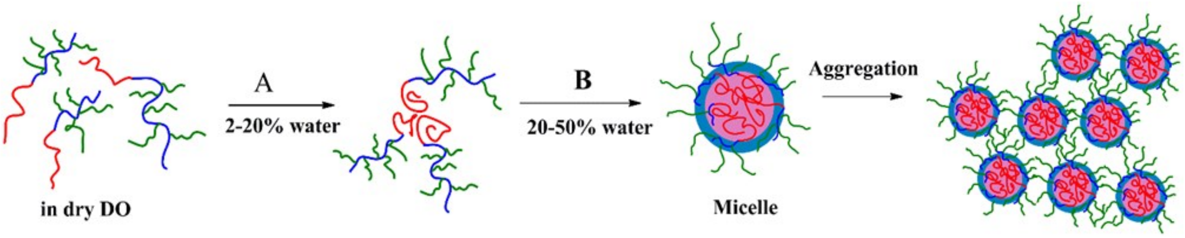

Fig. S11. Possible mechanism of self-assembly of anionic polystyrene-based coil-brush copolymers.

6. Study of polystyrene-based brush copolymer solutions by ^{1}H NMR spectroscopy

Fragments of ^{1}H NMR spectra of the brush copolymer P(VBC-*co*-VB-*g*-PAA2)-*b*-PS2-*b*-P(VBC-*co*-VB-*g*-PAA2) in DMSO-d$_6$ at several temperatures are given in Figs. S12 and S13. With increasing the temperature from 25 ºC to 40 ºC, the signal of the acidic proton of the carboxyl group from grafted PAA was shifted upfield from 12.30 ppm to 12.16 ppm (TMS), while its integral area was decreased (Fig. S12). Almost identical shift was observed for the brush copolymer P(VBC-*co*-VB-*g*-PAA1)-*b*-PS2-*b*-P(VBC-*co*-VB-*g*-PAA1) with shorter PAA side chains. "Movement" of the chemical shift attributed to the acidic proton could be explained by a decreased H-bonding between carboxyl groups present at different chains or molecules (intermolecular hydrogen bonding), while a decreased integral area could be related to the formation of hydrogen bonding between adjacent carboxyl groups (intramolecular hydrogen bonding is less affected by temperature).

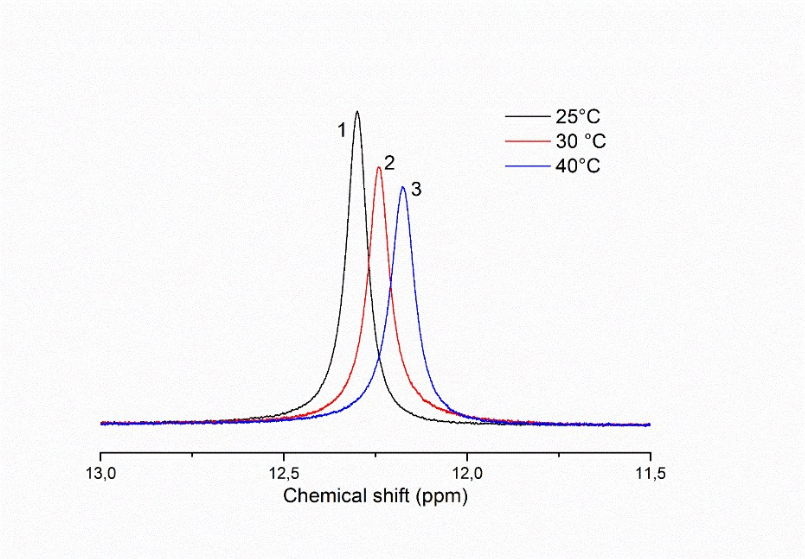

Fig. S12. ^{1}H NMR spectra (fragment, chemical shift of the proton from carboxyl group) of the copolymer P(VBC-*co*-VB-*g*-PAA2)-*b*-PS2-*b*-P(VBC-*co*-VB-*g*-PAA2) in DMSO-d$_6$ at various temperatures: 25 °C (**1**), 30 °C (**2**), and 40 °C (**3**).

1 S. Wang, Z. Cheng, J. Zhu, Z. Zhang and X. Zhu, *J. Polym. Sci. Part A Polym. Chem.*, 2007, **45**, 5318–5328.
2 Z. Zheng, J. Ling and A. H. E. Müller, *Macromol. Rapid Commun.*, 2014, **35**, 234–41.