

Supplementary Material (ESI) for Polymer Chemistry
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Dual hydrophilic and salt responsive schizophrenic block copolymers – synthesis and study of self-assembly behaviour

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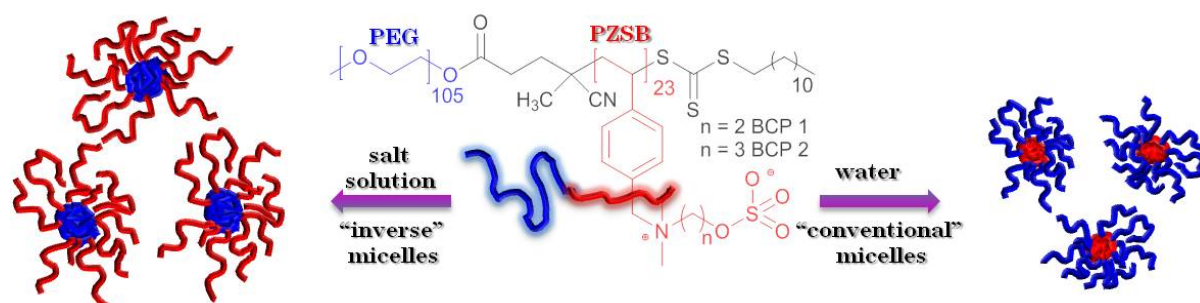
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Keywords: Dual hydrophilic block copolymer, zwitterionic polymer, polysulfobetaine, schizophrenic micelles, sulfobetaines, sulfobetaine, marine antifouling, salting in, salting out, salt responsive, stimuli responsive, conventional micelle, inverse micelle, salt resistance, halophilic, halo-tolerant, haloresponsive.

Graphical Abstract



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Supporting Information

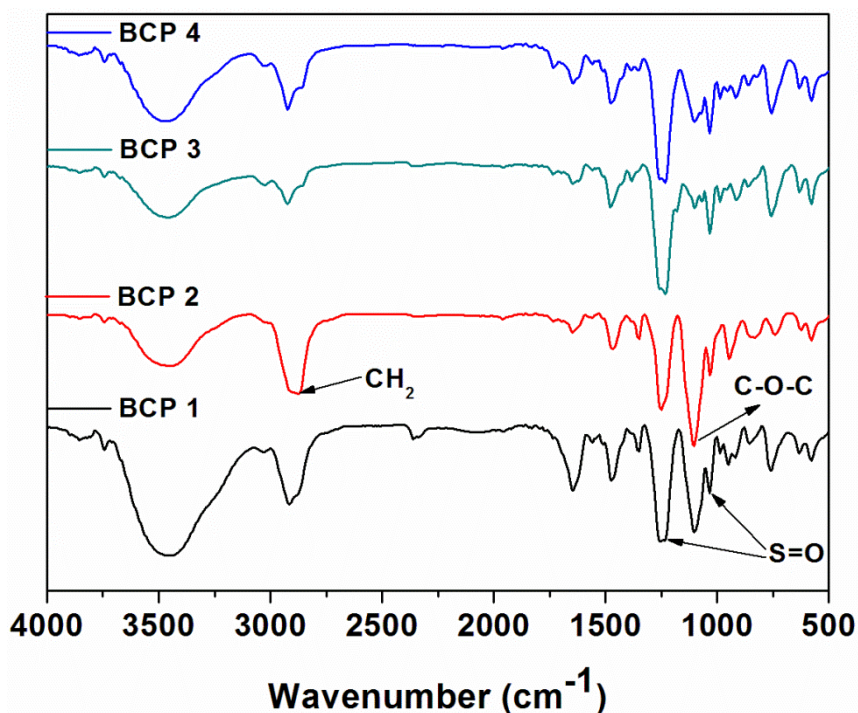


Fig. S1 FT-IR of polysulfobetaine block copolymers.

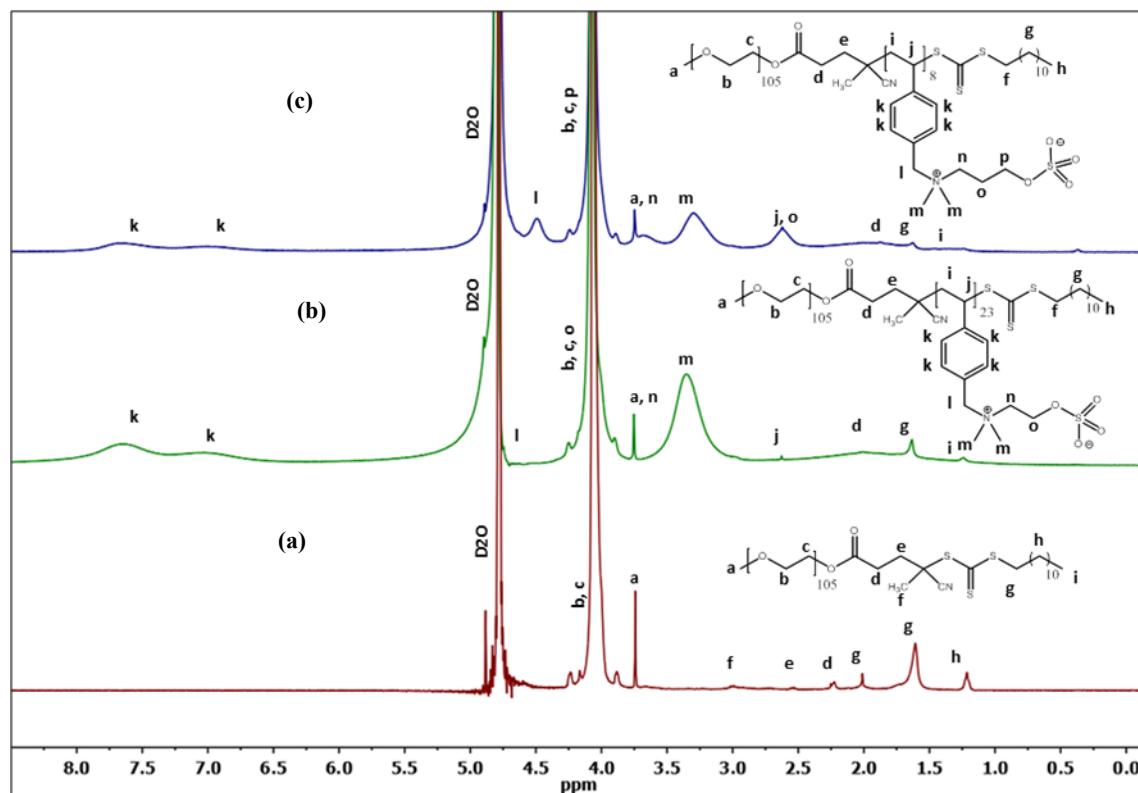


Fig. S2 ^1H NMR spectra of (a) PEG-RAFT 1, (b) BCP 1 and (c) BCP 2 in 5 % wt NaCl in D_2O .

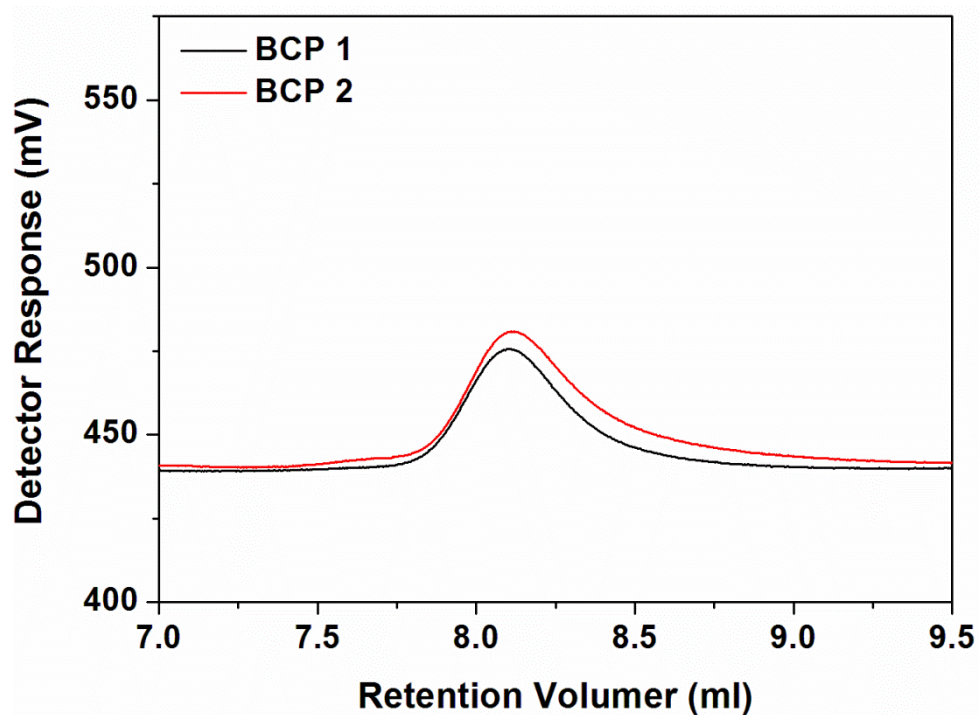


Fig. S3 GPC chromatograms of polysulfobetaine block copolymers.

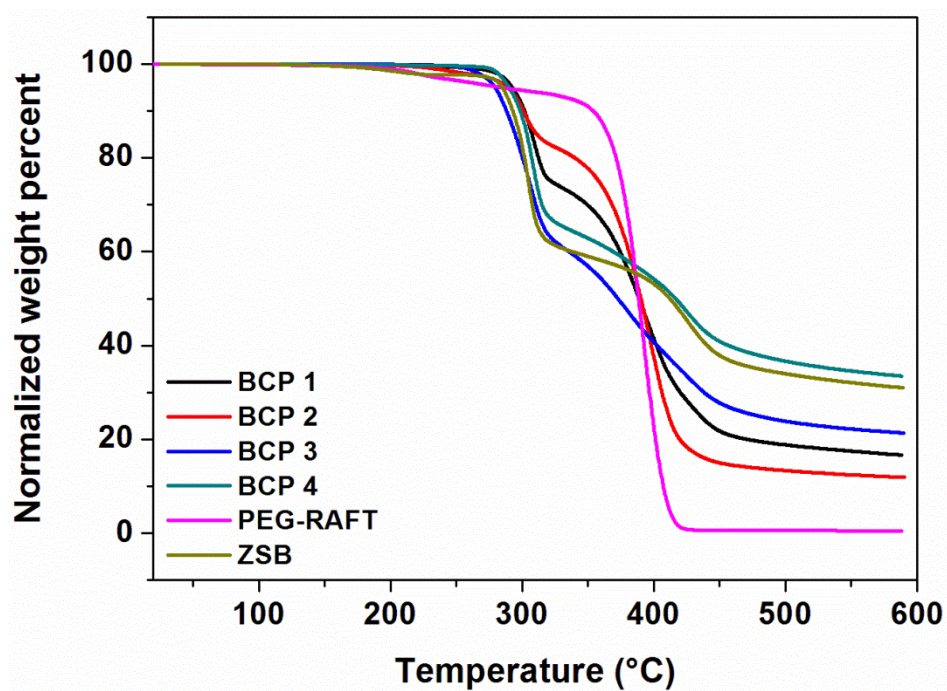


Fig. S4 Thermogravimetric analysis of BCP 1-4, PEG-RAFT 1 and ZSB.

Table S1. Melting temperature of PEG blocks in BCPs

Polymers	Composition from $^1\text{H NMR}^b$	$^c T_m$ (°C)
^a PEG-RAFT 1	(EG) ₁₀₅	59
BCP 1	(EG) ₁₀₅ - <i>b</i> -(ZSB 1) ₂₃	59
BCP 2	(EG) ₁₀₅ - <i>b</i> -(PZSB 2) ₈	62
BCP 3	(EG) ₁₉ - <i>b</i> -(ZSB 1) ₁₀	41
BCP 4	(EG) ₁₉ - <i>b</i> -(ZSB 1) ₂₄	43

^a PEG-RAFT 2 with (EG)₁₉ did not show any melting transition in the DSC analysis; ^b refer to experimental section for details on the molecular determination by $^1\text{H-NMR}$ analysis; ^c melting of PEG block as determined by DSC (heating rate 10 °C/min, N₂ atm.).

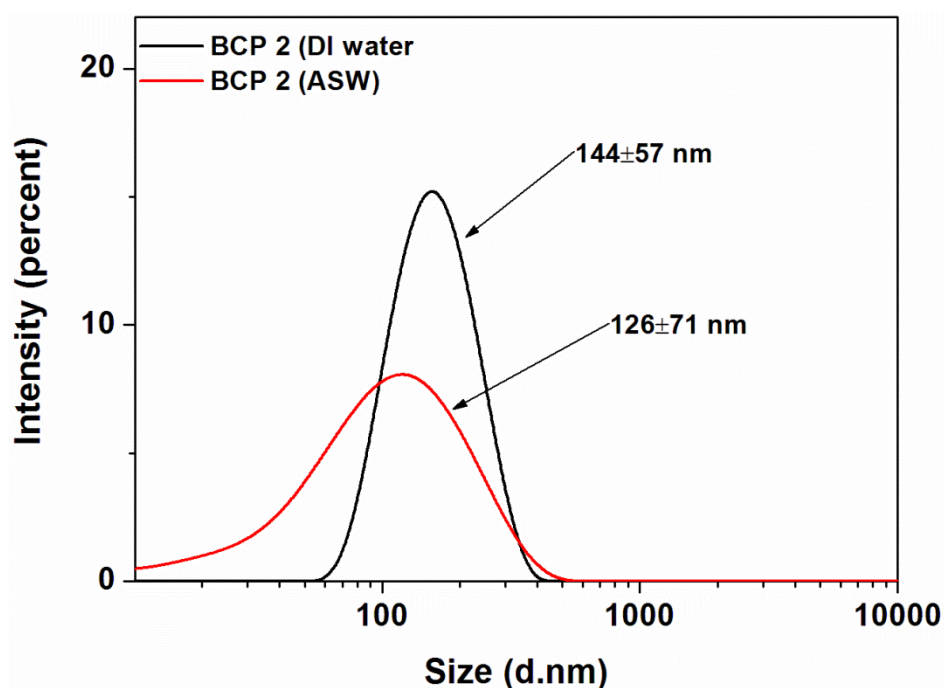


Fig S5 Size (Z-Average) distribution of micelles of BCP 2 in DI water and ASW.

Table S2 Summary of particle sizes for BCPs by DLS in water and ASW after two months

Polymer	Solvents	After two months			
		^a DLS (D_z , nm)	PDI (DLS)	^a DLS (D_z , nm)	PDI (DLS)
BCP 2	DI water	45	0.09	82	0.2
	ASW	149	0.1	126	0.5
BCP 2	DI water	144	0.13	97	0.4
	ASW	126	0.6	116	0.6

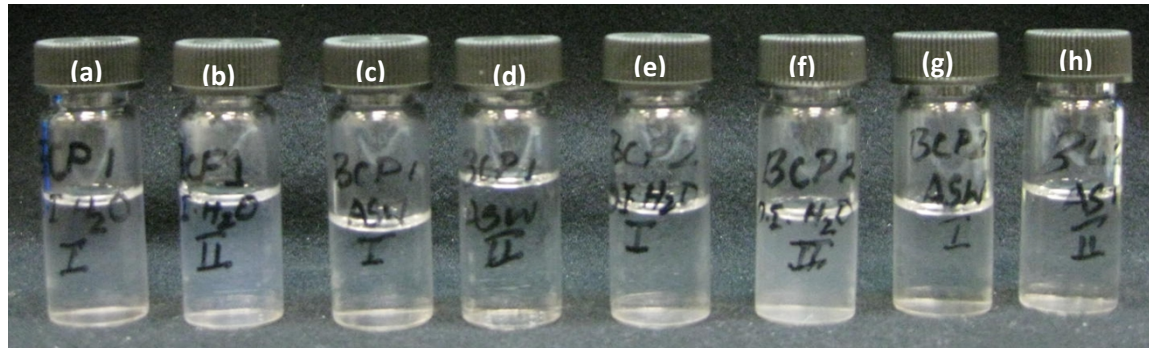


Fig S6. Photograph of zwitterionic “conventional” micelles in water BCP 1 (a and b) and BCP 2 (e and f) and “inverse micelles” in ASW (BCP 1 (c and d) and BCP 2 (g and h) (I) as prepared sample and (II) after storing for two months

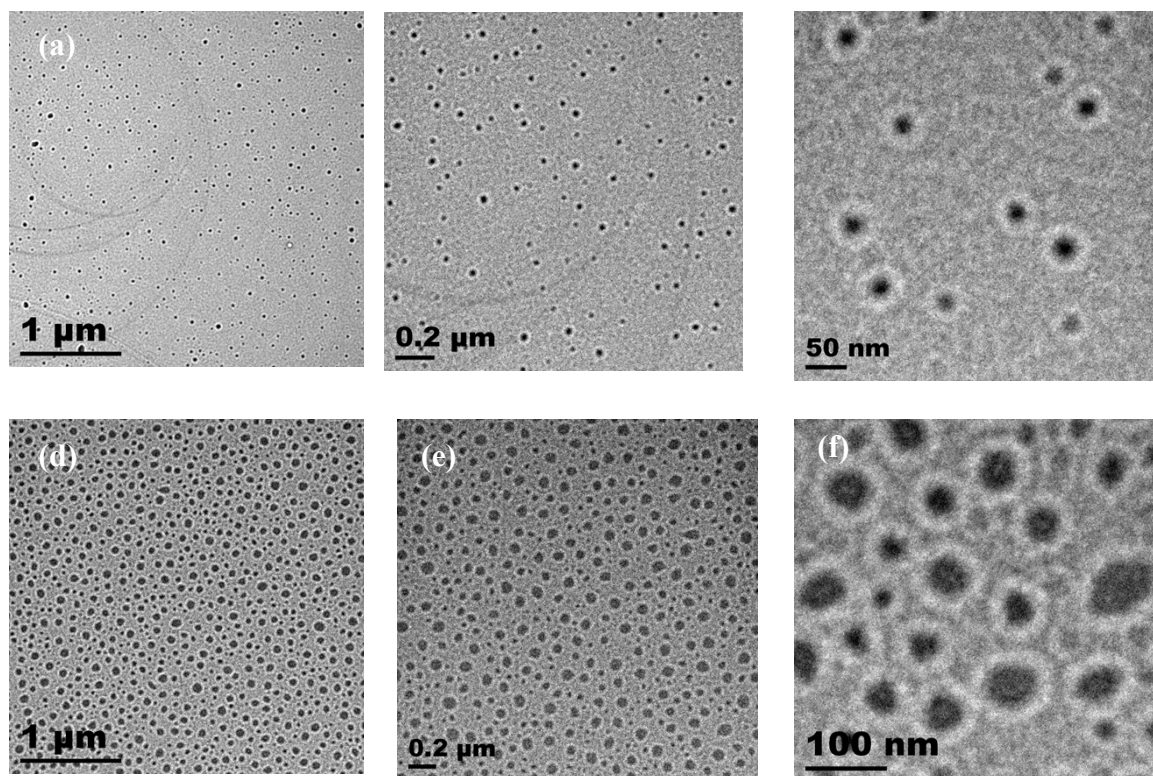


Fig. S7 TEM of BCP 1 (a, b and c) and BCP 2(c, d and e) in DI water (1mg/mL)

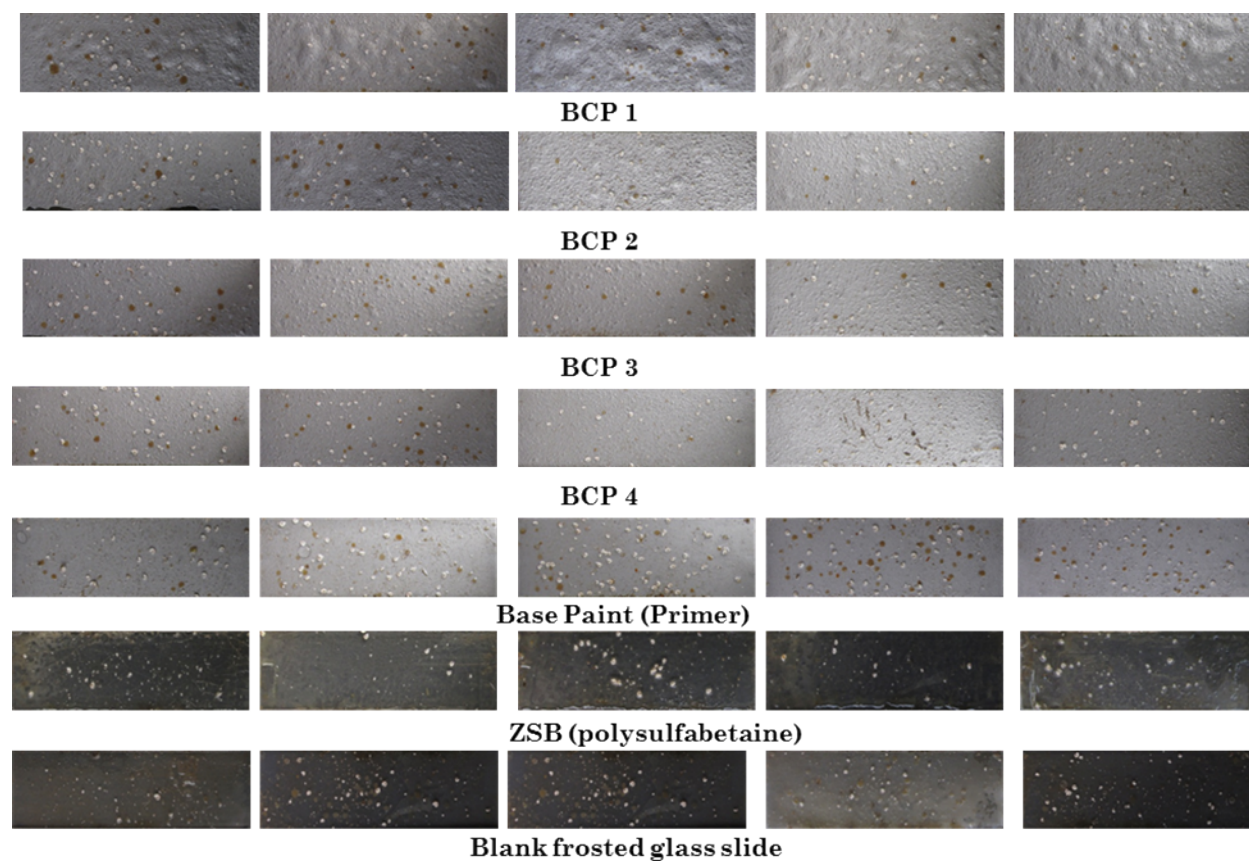


Fig. S8 Photographs of glass slides after two weeks of immersion in the sea.