Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supporting Information

Temperature-/CO_2- dual-responsiveness of a zwitterionic "schizophrenic" block copolymer

Xinde Tang[a,*], Qun Zhang[b], Meishan Pei[b,*]

[a] *School of Material Science and Engineering, Shandong Jiaotong University, Jinan 250023, PR China*

[b] *School of Chemistry and Chemical Engineering, University of Jinan, Jinan 250022, PR China*

* Corresponding authors.

E-mail addresses: xdtang8033@163.com (X. Tang), chm_peims@ujn.edu.cn (M. Pei)

Materials

Poly(ethylene oxide) monomethyl ether (MPEG) with number-average molecular weight of 1900 g/mol, was purchased from Fluka. [2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)-ammonium hydroxide (SBMA, 99%) and tris[2-(dimethylamino)ethyl]amine (Me_6TREN) were purchased from Changzhou Yipintang Chemical Company of China. 1,2-Bipyridine, 2-bromoisobutyryl bromide, and 2-(*N,N*-dimethylamino)ethyl methacrylate (DMAEMA) was purchased from Aladdin. CuBr (99.99%) was purchased from Adrich and used as received. All the other reagents and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. MPEG-based maroinitiator, denoted as $MPEG_{43}$-Br was synthesized following the literature method [1]. ^{1}H NMR for $MPEG_{43}$-Br ($CDCl_3$, 400 MHz): δ = 4.32 (t, 2H, -$COOCH_2$), 3.65–3.58 (m, 158H, -CH_2-), 3.38 (s, 3H, -OCH_3), 1.94 (s, 6H, -$CBr(CH_3)_2$).

Synthesis

Synthesis of the target block copolymers has been reported elsewhere [2].

Diblock copolymer MPEG-b-PSBMA

The macroinitiator $MPEG_{43}$-Br (205 mg, 0.1 mmol), SBMA (0.84 g, 3 mmol), CuBr (17 mg, 0.12 mmol), 1,2-bipyridine (15.6 mg, 0.1 mmol), and deionized water–methanol mixture (3:2, v/v, 2.0 mL) as solvent were charged to a dry Schlenk tube. After three freeze–pump–thaw cycles to remove oxygen, the tube was sealed and placed in a thermostat oil bath at room temperature for 5 h. The polymerization was then quenched by merging the tube in liquid nitrogen. The product was diluted with ultrapure water and dropped into a dialysis bag with a 3500 D molecular weight cut off (MWCO) for removing the remaining monomers and other small molecules.

This purification procedure was continued for two days. Then, the water in the dialysis bag was evaporated under reduced pressure, and the collected sample was dried in a vacuum oven for 24 h at room temperature in a yield of 80.6%.

Triblock copolymer MPEG-b-PSBMA-b-PDMAEMA

Me_6TREN (28 μL, 0.1 mmol), CuBr (17 mg, 0.12 mmol), $MPEG_{43}$-b-$PSBMA_{30}$-Br (0.13 g, 0.012 mmol) as the macroinitiator, 2-(dimethyl-amino)ethyl methacrylate (DMAEMA, 0.7 g, 4.46 mmol) as the monomer, and deionized water–DMF mixture (2:1, v/v, 2.0 mL) as solvent were added to a dry Schlenk tube. After three freeze–

pump–thaw cycles to remove oxygen, the tube was sealed and placed in preheated oil bath at 90 ^{o}C for 6 h. The polymerization was then quenched by immersing the tube in liquid nitrogen. The product was diluted with ultrapure water and dropped into a dialysis bag with 8000 to 14 000 Da MWCO for removing the remaining monomer and other small molecules. This purification procedure was lasted for two days. Then, the water in the dialysis bag was evaporated under reduced pressure, and the collected samples were dried in a vacuum oven for 24 h at room temperature in a yield of 42.1%.

Characterization

Nuclear magnetic resonance (NMR) spectroscopy

^{1}H NMR measurements were conducted in a Bruker ARX 400M spectrometer (400 MHz) by using D_2O as the solvent and tetramethylsilane as the internal standard.

UV-vis spectroscopy

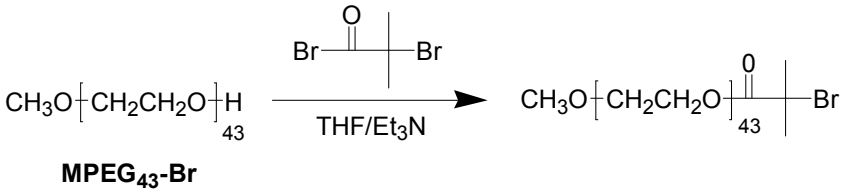
Transmittance measurements were carried out in a Shimadzu UV-1700 spectrophotometer equipped with a thermo-regulator. Samples were prepared with a copolymer concentration of 1.0 mg/mL. The transmittance was recorded with the heating/cooling rate at 1 ^{o}C/10 min, in which 500 nm wavelength was set for the polymer solution. The UCST or LCST values were determined at 50% transmittance.

Dynamic light scattering (DLS)

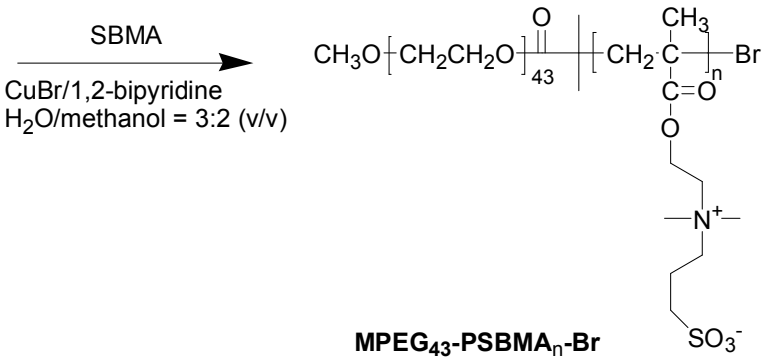
DLS measurements were performed in sealed cylindrical scattering cells (d ¼ 10 mm) at an angle of 90 on ALV DLS/SLS-SP 5022F equipment consisting of an ALV-SP 125 laser goniometer with an ALV 5000/E correlator and a He–Ne laser with the wavelength of 632.8 nm. Prior to the light scattering measurements the sample solutions were filtered using Millipore syringe filters with a pore size of 0.45 or 0.2 mm (polyethersulfone). The average diameter and dispersity index were determined by fitting the correlation function with the cumulant method. The CONTIN algorithm was applied to obtain the size distribution.

Scanning electron microscopy (SEM)

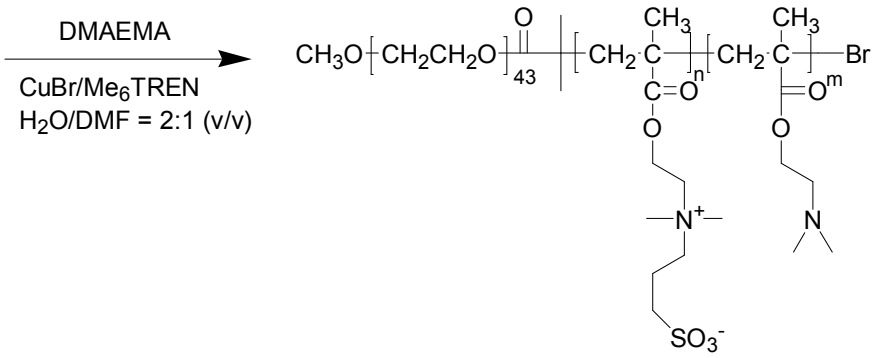
The surface morphology of aggregates was analyzed using a JSM-6510LV scanning electron microscope (SEM) for observation, and the samples were prepared by drop-coating the aqueous solution on a silicon wafer and then drying under vacuum overnight.



$MPEG_{43}$-Br



$MPEG_{43}$-$PSBMA_n$-Br



$MPEG_{43}$-$PSBMA_n$-$PDMAEMA_m$-Br

Scheme S1 Synthesis of the zwitterionic, schizophrenic triblock copolymer by ATRP.

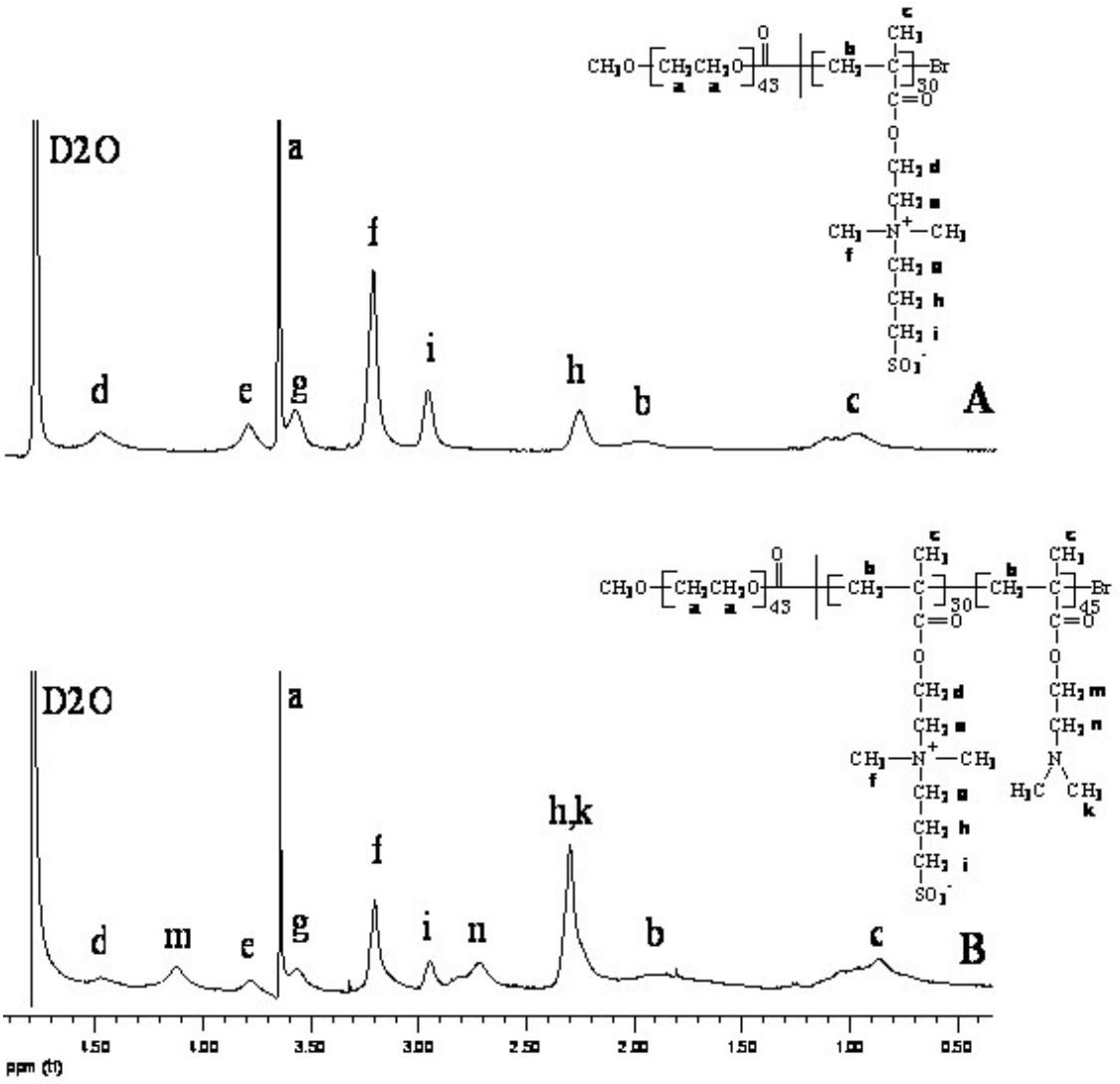


Fig. S1 ^{1}H NMR spectra of the diblock copolymer $MPEG_{43}$-*b*-$PSBMA_{30}$ (A) and the triblock copolymer $MPEG_{43}$-*b*-$PSBMA_{30}$-*b*-$PDMAEMA_{45}$ (B).

References

[1] K. Jankova, X. Chen, J. Kops and W. Batsberg, Macromolecules, 1998, 31, 538.

[2] Q. Zhang, X. Tang, T. Wang, F. Yu, W. Guo and M. Pei, RSC Adv., 2014, 4, 24240.