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ARTICLE

Thermo-sensitive zwitterionic block copolymers via ATRP

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Novel thermo-sensitive zwitterionic ABC-type triblock copolymers poly(ethylene glycol)-block-[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)-ammonium hydroxide-block-poly[2-(dimethylamino)ethyl methacrylate] (MPEG-*b*-PSBMA-*b*-PDMAEMA) were synthesized by atom transfer radical polymerization (ATRP). The bromide-terminated diblock copolymers poly(ethylene oxide)-block-[2-(methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)-ammonium hydroxide (MPEG-*b*-PSBMA-Br) were prepared by the ATRP of 10 methacryloxyethyl sulfobetaine initiated by the macroinitiator MPEG-Br, which was obtained by the esterification of poly(ethylene glycol) monomethyl ether (MPEG) with 2-bromoisobutyryl bromide. Poly(2-(diethylamino)ethyl methacrylate) (PDMAEMA) was then introduced by a sequential ATRP process to obtain the triblock copolymers. These copolymers with varied compositions, molecular weights and polydispersities were characterized by ^{1}H NMR and GPC. Variable temperature ultraviolet analysis was employed to test their stimuli-sensitive properties. These block copolymers exhibited distinct thermo-sensitivity under different molecular compositions or 15 solution conditions. The resistance to non-specific protein adsorption of the triblock copolymers was evaluated, and excellent antifouling property occured. This can be attributed to the surface hydration via hydrogen bonds between PEG and water molecules and the surface hydration via ionic-induction between PSBMA and water molecules, and the synergistic effect resulted in an effective reduction of protein adsorption. These copolymers have potential applications in antifouling and antibacterial areas.

Introduction

Stimuli-responsive or "smart" materials capable of conformational and chemical changes upon in respond to external signals have attracting great attention due to their potential applications in various areas such as biotechnology, 25 pharmacology, and material science.[1] Materials capable of resisting long-term biofilm formation in complex media while maintaining nonfouling properties are highly desirable for many applications, and nonfouling coatings can be the most commonly used approaches to prevent the attachment and spreading of 30 microorganisms onto surfaces.[2] It can be anticipated that the integration of stimuli-responsiveness and noufouling may endue materials with more features, such as separation, purification, encapsulation, controlled release, etc. Especially, the design and fabrication of such materials is promising in biomedical area.

35 There have been considerable studies on designing and fabricating antifouling materials.[3] The copolymers containing non-fouling poly(ethylene glycol) (PEG) or low-fouling poly(hydroxyethyl methacrylate) (PHEMA) segments have been prepared for controlling cell and tissue responses. PEG-based 40 polymers as one of the most common nonfouling materials can suppress the accumulation of microorganisms onto surfaces.[4] It has been shown that PEG-coated surfaces can delay biofilm formation for 24 h.[5] Over the past few years, zwitterionic polymers have received growing attention in the new generation 45 of nonfouling materials due to their excellent protein

resistance.[6–24] Recent studies demonstrated that sulfobetaine-containing copolymers can effectively reduce platelet adhesion and protein adsorption.[9]

Poly(sulfobetaine methacrylate) (PSBMA) with a 50 poly(methacrylate) main chain and an analogue of the taurine betaine pendant group ($CH_2CH_2N^+(CH_3)_2CH_2CH_2CH_2SO_3^-$) has become the most widely studied zwitterionic polymer due to its ease of preparation.[19] Sulfobetaines are special classes of zwitterions with ammonium cation and sulfonic anion isolated 55 with alkyl, usually propyl or butyl group. One of the characteristic features of these complexes is that they are soluble in water and exhibit an upper critical solution temperature (UCST) that is sensitive to changes in the molecular weight and concentration of the polymer, the ionic strength, and the species 60 of added salts.[25-30] It is expected that zwitterions are capable of binding significant quantities of water and are therefore potentially excellent candidates for nonfouling materials, which is attributed to the strong capacity to form a hydration layer via electrostatic interaction between zwitterions and water molecules. 65 To further develop the zwitterionic-based materials for biomedical applications, smart polymer systems carrying both controllable biocompatibility and stimuli-responsive functions have been inspired to research. Recently, the physical micellization of synthesized sulfobetaine-containing diblock 70 copolymers with thermo-responsive and zwitterionic properties has been reported,[31-34] in which the thermo-responsive poly(*N*-isopropylacryl amide) (PNIPAM) or poly(*N,N*-diethylacryl amide)

(PDEA) with a lower critical solution temperature (LCST) was introduced, and these block copolymers have been found to exhibit double thermosensitive phase transition of LCST and UCST behaviors in water. It is worthy of note that most of the dual-thermoresponsive phase behaviors derive from nonionic/zwitterionic block self-assembly in aqueous solution. Recent study on the complex formation of the zwitterionic PSBMA with other polyelectrolytes have shown to cause a dramatic increase in viscosity as a result of the formation of a network structure through electrostatic interaction, thereby deceasing the UCST of PSBMA.[33a]

Poly(2-dimethylaminoethyl methacrylate) (PDMAEMA) is a pH- and temperature-sensitive polymer. It is a weak base with pKa about 7.0 and is water-soluble within wide pH range.[35] PDMAEMA exhibits a phase transfer between hydrophilic and hydrophobic characteristics below and above its pKa.[36-38] The chains of PDMAEMA are expanded in aqueous solution with tertiary amine groups of PDMAEMA are protonated and hydrated below the pKa. In contrast, the polymeric chains are collapsed by deprotonation and dehydration of the amine group above the pKa. PDMAEMA is also a thermoresponsive polymer with an LCST that is dependent on pH, ionic strength and molecular weight. There are also conformational changes in PDMAEMA below and above its LCST.[39-41] PDMAEMA was selected as a candidate polymer for electrografting because it can be modified to the polymers with zwitterionic character.[42] It has been introduced into biocompatible block copolymers and used as antifouling coatings.[43-45] Most recently, Hoogenboom and coworkes reported a triple thermoresponsive schizophrenic diblock copolymer based on PDMAEMA and poly(methoxy oligo-ethyleneglycol methacrylate) (PmOEGMA), which undergoes transitions from conventional micelles via unimers to reverse micelles and finally to a precipitated state upon heating.[46]

The combination of the LCST of the PDMAEMA with the UCST of the zwitterionic polymers displays intriguing temperature-induced self-assembly behavior of different types of polymeric aggregates in aqueous solution.[47] The objective of this work is to develop novel thermo-sensitive zwitterionic ABC-type triblock copolymers, where A represents a MPEG block, B a PSBMA block, and C a PDMAEMA block, schematically shown in Scheme 1. To the best of our knowledge, this is the first example of block copolymers containing zwitterionic PSBMA and nonionic/cationic PDMAEMA polyelectrolyte, additionally, the presence of hydrophilic PEG may stabilize the polymer chains or the formed micelles in aqueous solution. These materials can be very promising for a wide range of applications in medical diagnostics, biomaterials/tissue engineering, and drug delivery.

(Scheme 1)

Experimental section

Materials

Poly(ethylene oxide) monomethyl ether (MPEG) with number-average molecular weight of 1900 g/mol, were purchased from Fluka. [2-(Methacryloyloxy)ethyl]dimethyl(3-sulfopropyl)ammonium hydroxide (SBMA, 99%), tris[2-(dimethylamino)ethyl]amine (Me$_6$TREN) and 1,2-bipyridine were purchased from Changzhou Yipintang Chemical Company of China. 2-Bromoisobutyryl bromide was purchased from Creator Chemicals of China. 2-(Dimethylamino)ethyl methacrylate (DMAEMA) and 3-chloropropyltriethoxysilane (IPTMOS) were purchased from Aladdin Reagents Co. Ltd. CuBr (99.99%) were purchased from Adrich and used as received. MPEG-based maroinitiator, denoted as MPEG$_{43}$-Br, was synthesized following the literature method.[48] ^{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, -Br(CH$_3$)$_2$).

Diblock copolymer MPEG-*b*-PSBMA

A typical process for the synthesis of MPEG$_{43}$-*b*-PSBMA$_{30}$-Br was described as follows. 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 thermostatted 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 3500 Da molecular weight cutoff (MWCO) for removing the remaining monomers and the other small molecules. This purification procedure was dialysed 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 80.6% yield.

Triblock copolymer MPEG-*b*-PSBMA-*b*-PDMAEMA

The following procedure took the synthesis of MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{45}$ as example. Me$_6$TREN (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, 0.3 g, 1.9 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 merging the tube in liquid nitrogen. The product was diluted with ultrapure water and dropped into a dialysis bag with 8000 to 14000 Da MWCO for removing the remaining monomer and the other small molecules. This purification procedure was dialysed 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 45.6% yield.

Characterization

^{1}H NMR spectra were recorded on a Bruker ARX 400M spectrometer (400 MHz) using D$_2$O as solvent and

tetramethylsilane as internal standard. Molecular weights and their polydispersities of the prepared copolymers were determined by aqueous gel permeation chromatography (GPC) using one column of Agilent Technologies 1260 Infinity (the molecular weight range from 500 Da to 800 kDa) connected to a Waters 2414 refractive index detector at a 1.0 mL/min flow rate and a column temperature of 30 ^{o}C and 70 ^{o}C. Poly(ethylene oxide) (PEO) standards were used for calibration.

Transmittance measurements

Stimuli-responsive behavior of the zwitterionic copolymers was determined by turbidity analysis on a Shimadzu UV-1700 spectrophotometer equipped with a thermo-regulator 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.

Preparation of polymeric coatings

The glass substrates were cut into the size of 1×2 cm, and cleaned with piranha solution (30 wt% hydrogen peroxide/98 wt % sulfuric acid, 3:7, v/v). After washed by water and ethanol, the glass was dried and heated to 80-100 ^{o}C for 1 h, then cooled at room temperature. The casting solution was prepared by dissolving the triblock copolymer MPEG$_{43}$-b-PSBMA$_{30}$-b-PDMAEMA$_{45}$ (1.2 g) and IPTMOS (2 mL) in absolute methanol (15 mL). Then the solution was heated at 50 ^{o}C for 24 h, and the obtained homogeneous solution was cast on a glass sheet by double-sided, and dried under reduced pressure for 24 h. The reactive IPTMOS was incorporated into the PDMAEMA chains through sequential quaternization of the tertiary amino groups in PDMAEMA with 3-chloropropyltriethoxysilane, schematically shown in Scheme 2.

(Scheme 2)

Protein adsorption measurment

Bovine serum albumin (BSA) was used as a model protein to evaluate the protein-resistant characteristics of the prepared polymeric coatings. The coatings with 2 cm^2 of external surface area were immersed in ethanol for 10 min, followed by phosphate buffer solution (PBS) to pre-wet the coating surface for 30 min. Each sample was put into a tube with 5 mL of BSA solution of 1 mg/mL in PBS. The mixture was incubated at 30 ^{o}C for 24 h with a shaking speed of 100 rpm to reach adsorption equilibrium. Scanning electron microscopy (SEM) images was taken on a Quanta 200 (Philips-FEI, Holland).

Results and discussion

Synthesis and characterization of the block copolymers

ATRP is one of the most powerful polymerization techniques to synthesize block copolymers.[49] The triblock copolymers were prepared by a successive ATRP process, as shown in Scheme 1. The macroinitiator MPEG$_{43}$-Br with narrow molecular weight distribution of 1.03 was prepared through the esterification of poly(ethylene oxide) monomethyl ether (MPEG) and 2-bromoisobutyryl bromide.[48] The macroinitiator was firstly used to initiate the ATRP of the monomer SBMA using CuBr/1,2-bipyridine as a catalyst system at room temperature, resulting in the diblock copolymer MPEG-PSBMA-Br. The polymerization degree of SBMA is in accordance to the feed molar ratio of SBMA/MPEG$_{43}$-Br, indicating the completeness of the ATRP of SBMA initiated by the macroinitiator. The yield of $\sim$80% can be attributed to the loss of several purification. Then the bromine-terminated diblock copolymer was used to initiate the ATRP of DMAEMA using Me$_6$TREN/CuBr as a catalyst system at 90 ^{o}C, and the triblock copolymers MPEG-PSBMA-PDMAEMA-Br were obtained with comparatively low yield of $\sim$40%, maybe due to the low initiator activity.

Typical ^{1}H NMR spectra, shown in Fig. 1, confirmed the successful preparation of the diblock and triblock copolymers. The number-average compositions of the copolymers were calculated by comparing the relative intensities of the signal for -OCH$_2$CH$_2$- protons of the PEG block (3.6 ppm), for -NCH$_3^+$- protons of the SBMA block (3.2 ppm) and for -OCH$_2$- protons of the DMAEMA block (4.1 ppm), respectively. Aqueous GPC curves of the typical diblock and triblock copolymers were displayed in Fig. 2. Molecular weight distributions of the synthesized copolymers from GPC were shown in Table 1. The polydispersities are relatively low (PDI<1.5), which indicates that these polymerizations were living and controllable.

(Fig. 1)

(Fig. 2)

(Table 1)

Temperature-sensitive properties of the diblock copolymers

The homopolymer PSBMA at a concentration of 0.5 mg/mL in aqueous solution water exhibited an UCST between 16 and 18 ^{o}C, which decreases with decreasing molecular weight of PSBMA.[34b,d] In the diblock copolymers, the hydrophilic PEG blocks endow the stability of the polymer chains or the formed micelles in aqueous solution, resulting in an increase of UCST. Above the UCST of PSBMA block, the diblock copolymers are soluble in water at room temperature due to the electrostatic repusion between the polymer intrachains and interchains. Below the UCST, however, the core-shell micelles form with a core of insoluble PSBMA association and a shell of soluble, consequently the precipitation occurs. This is attributed to the contribution of the interaction level of mutual electrostatic attraction by ion pairings between ammonium cation and sulfoanion of the zwitterionic sulfobetain groups.[34b]

In this case, the effect of the solution concentration and the polymerization degree of PSBMA was mainly focused. To take MPEG$_{43}$-b-PSBMA$_{50}$ for example. The copolymer was dissolved in ultrapure water with varied concentration. The phase transition temperatures were measured using a UV-vis spectrophotometer coupled with a tempearture controller set to heat or cool at 1

^{o}C/10 min from 10-50 ^{o}C. As shown in Fig. 2A, the transmittance of the polymer solution increased with the temperature increasing. The corresponding temperature at 50% transmittance was defined as the solution's upper critical solution temperature (UCST). The UCST increased with an increase of the polymer solution concentration, and exhibited as 22, 21, and 15 ^{o}C for various concentration of 5, 10, and 20 mg/mL, respectively. The diblock copolymers with varied polymerization degree of PSBMA (n = 30, 40, or 50) were dissolved in ultrapure water at an identical concentration of 5 mg/mL, respectively. The transmittance of the polymer solution upon heating and cooling at varied temperatures between 10-36 ^{o}C was illustrated in Fig. 2B. The UCST increased with the polymerization degree of PSBMA increasing, and exhibited at 11, 17, and 21 ^{o}C for n = 30, 40, and 50, respectively.

A possible explanation can be proposed as follows. In aqueous solution, the higher polymer concentration or polymerization degree of PSBMA exists, the higher charge density generates, which gives rise to the enhancement of electrostatic repulsion and attraction. The micelle formation and aggregation can be easily realized, resulting in a higher USCT.

(Fig. 3)

Temperature-sensitive properties of the triblock copolymers

Chang et al. reported doubly thermo-responsive copolymers comprising of PSBMA and PNIPAM blocks. These copolymers exhibited an individual UCST and LCST.[34] In our case, the coexistence of PSBMA and PDMAEMA blocks via ATRP can be expected to display intriguing temperature-induced behavior in aqueous solution. Nonionic PDMAEMA exhibited an LCST in water between 64 and 68 ^{o}C. Above the LCST, PDMAEMA chains become hydrophobic and the hydrogen bond with water molecules weakens. The precipitation of PDMAEMA derives from nonionic DMAEMA segment associations in water. The origin of the phase behavior of PDMAEMA arises from the release of ordering water molecules and the formation of intrachain hydrophobic interactions associated with the side chain isopropyl moieties as the temperature increases above a critical point. Below the UCST, PSBMA exists as a collapsed coil and precipitates with the zwitterionic associations in aqueous solution. MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{45}$ and MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{90}$ were dissolved in ultrapure water at a concentration of 5 mg/mL and 10 mg/mL, respectively. Temperature dependence of transmittance between 28-68 ^{o}C was shown in Fig. 3. For MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{45}$, the UCST decreased from 62 to 52 ^{o}C with an increase of the polymer concentration from 5 to 10 mg/mL. Similar tendency ocuured for MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{90}$. At a concentration of 5 mg/mL, the UCST of MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{45}$ was higher than that of MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{90}$ (50 ^{o}C), and a similar result was obtained at a concentration of 10 mg/mL. It is worthy of note that the LCST did not occur due to the restriction of the aqueous media and the thermo-regulator.

(Fig. 4)

The effect of pH value on the UCSTs and LCSTs of the triblock copolymer solutions were further evaluated to investigate the solubility characteristics at a fixed polymer concentration of 10 mg/mL. The pH value of the aqueous medium was adjusted by phosphate buffer solution (PBS) at 4.0, 6.8, and 9.2, respectively. Temperature dependence of transmittance was shown in Fig. 4. The transmittance of the polymer solution increased with the temperature increasing at pH values of 4.0 and 6.8. For MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{45}$ （Fig. 4A）, the UCST at pH 4.0 (52 ^{o}C) was much higher than at pH 6.8 (35 ^{o}C). However, at pH 9.2, a sharp change of transmittance at 40 ^{o}C demonstrated that both PSBMA and PDMAEMA blocks were soluble, exhibiting an individual UCST (34 ^{o}C) and LCST (42 ^{o}C). For MPEG$_{43}$-*b*-PSBMA$_{30}$-*b*-PDMAEMA$_{90}$ （Fig. 4B）, the UCST at pH 4.0 (46 ^{o}C) was also higher than at pH 6.8 (38 ^{o}C). However, at pH 9.2, a sharp change of transmittance occured at 38 ^{o}C.

PDMAEMA shows pH-responsive behavior due to the protonation of the tertiary amine group. The higher protonization degree of PDMAEMA units, the better solubility of PDMAEMA chains in water at low pH value since pKa of PDMAEMA is 7.0. Thus, the steric hindrance of stretching PDMAEMA chains would prevent PEG-*b*-PSBMA-*b*-DMAEMA molecules from inter-molecular aggregation to large micelles. In this case, PEG-*b*-PSBMA-*b*-DMAEMA molecules tend to form unimer micelles by the intramolecular collapse of PSBMA chains. When pH increases to 7.0, PDMAEMA becomes partially deprotonated and less hydrophilic. At pH 9.2, PDMAEMA chains turn highly deprotonated. Thus, the increase of block lengths of PSBMA or PDMAEMA contributes to the formation of copolymers in soluble unimer states, resulting in the expansion of the intermediate temperature range (i.e., above the UCST and below the LCST). In the intermediate temperature range, copolymers were observed to exist as soluble unimers in water. However, in the solution temperature range below UCST or above LCST, morphological changes of PSBMA-*b*-PDMAEMA copolymers might preferentially expose one polymer block extended in the solution phase while the other one is buried inside micelle cores, resulting in the precipitation as collapsed associations in water. The doubly thermoresponsive transition behavior of the prepared copolymer MPEG-*b*-PSBMA-*b*-PDMAEMA results from the switchable nonionic/zwitterionic block self-assembly driven by the formation of inter and intramolecular electrostatic interactions by SBMA segments of zwitterionic sulfobetaine groups and intramolecular hydrophobic interactions by DMAEMA segments of nonionic isopropyl groups, as illustrated in Scheme 3.

(Fig. 5)

(Scheme 3)

Resistance to protein adsorption of the triblock copolymers

The extent of protein adsorption is mainly determined by the delicate balance of the interaction between the protein molecules and the membrane surface. The factors that affect the protein adsorption include hydrophilicity/hydrophobicity balance, surface

change, and surface roughness. It is believed that PEG uses a "steric repulsion" and a hydration layer via hydrogen bonding around molecular chain to prevent nonspecific protein adsorption.[50] PEG is usually used as the hydrophilic components

5 in the polymers, since it has been recognized as a materials uniquely suited for preventing the protein adsorption. It is generally accepted that the repulsive force between PEG and protein are created by favorable H_2O-PEG interaction and the mobility of the PEG chains in aqueous solution. The

10 hydrophilicity and unique coordination with the surrounding water molecules of PEG facilitate the resistance to protein adsorption.[51] PSBMA can bind water molecules even more strongly via electrostatically induce hydration, such sulfobetaine-based polymers or surfaces have been shown to greatly reduce

15 nonspecific protein adsorption,[52] and the quaterized PMDAEMA has antibacterial activity.[53]

    Fig. 5 shows the results of BSA adsorption on the surface of a sheet glass and the polymeric coating of the quaterized $MPEG_{43}$-b-$PSBMA_{30}$-b-$PDMAEMA_{45}$. In contrast with the sheet glass

20 surface, the polymeric coating of the quaterized $MPEG_{43}$-b-$PSBMA_{30}$-b-$PDMAEMA_{45}$ has a relatively low amount of BSA adsorption. The effective reduction in protein adsorption can be attributed to the SBMA segments that exhibit antifouling character and the PEG segments that stretch out from the coating

25 surface into the surrounding aqueous environment.

(Fig. 6)

Conclusions

In summary, temperature-sensitive zwitterionic triblock

30 copolymers have been successfully synthesized via atom transfer radical polymerization, following the idea that the conformation of MPEG-b-PSBMA and MPEG-b-PSBMA-b-PDMAEMA block copolymers in aqueous solution could change in response to temperature. A thermo-responsive morphological transition

35 occurs from zwitterionic PSBMA-core micelle to unimer to nonionic PDMAEMA-core micelle when the solution temperature increased, and the process is reversible when the solution temperature decreased. The coverage of PEG on the polymeric coating effectively prohibits the protein adsorption and

40 cell adhesion. This dual thermoresponsive behavior provides the core-shell micelles promising potential in addressing related theoretical and practical problems such as drug delivery. This study also suggests that the quaterized zwitterionic MPEG-b-PSBMA-b-PDMAEMA copolymer is a novel candidate for the

45 preparation of antifouling coatings and antifouling membranes with antibacterial activity.

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Notes and references

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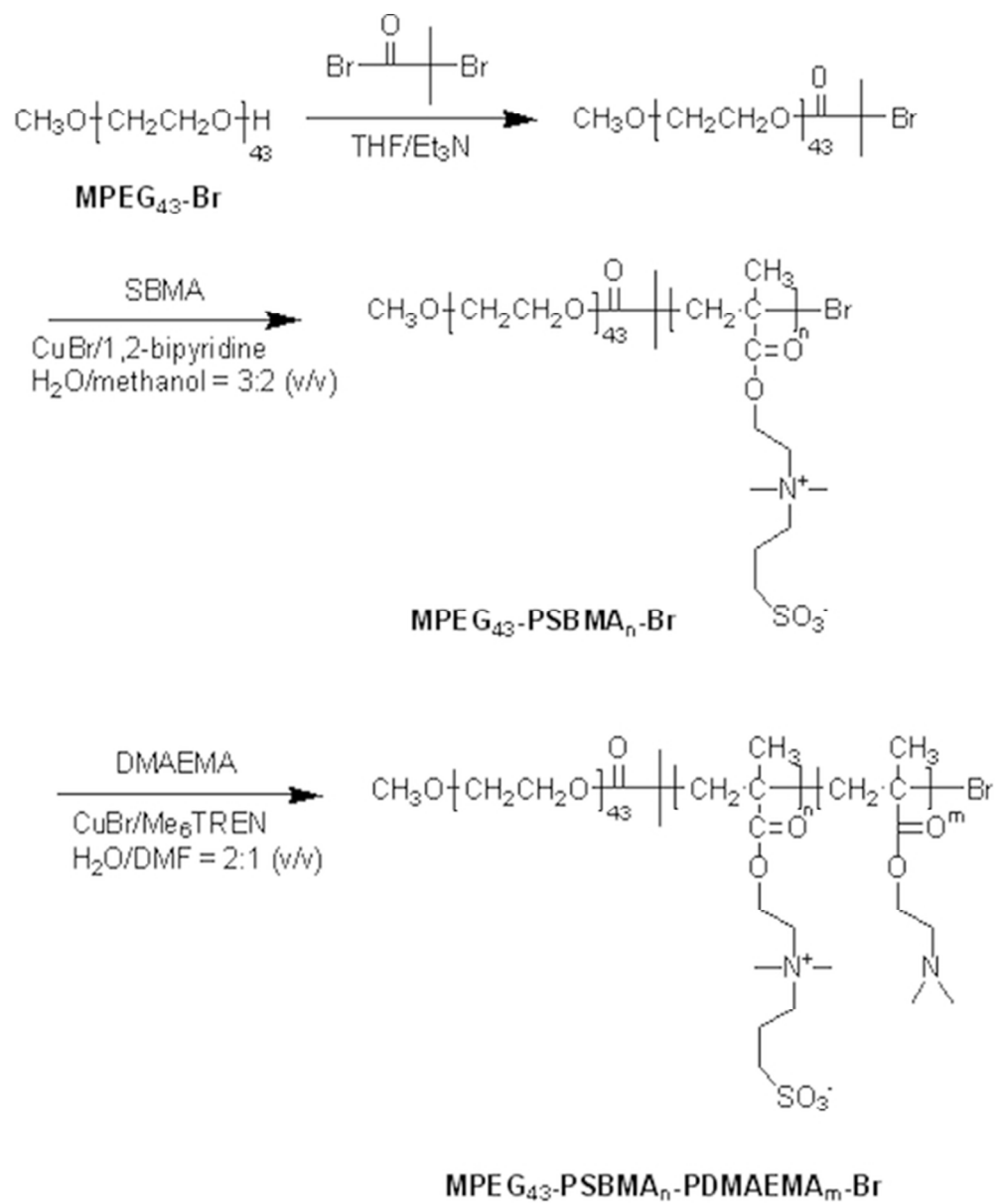
Scheme 1 Synthesis of the thermo-sensitive zwitterionic block copolymers by ATRP.
51x62mm (300 x 300 DPI)
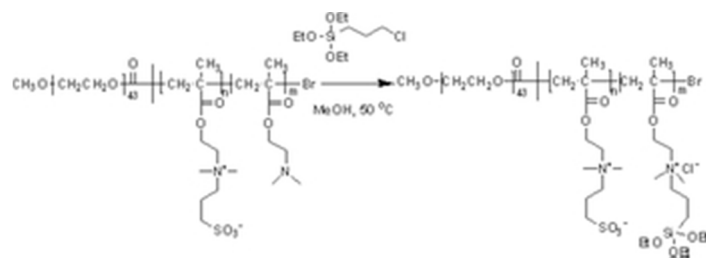
Scheme 2   Incorporation of triethoxysilyl groups into PDMAEMA.
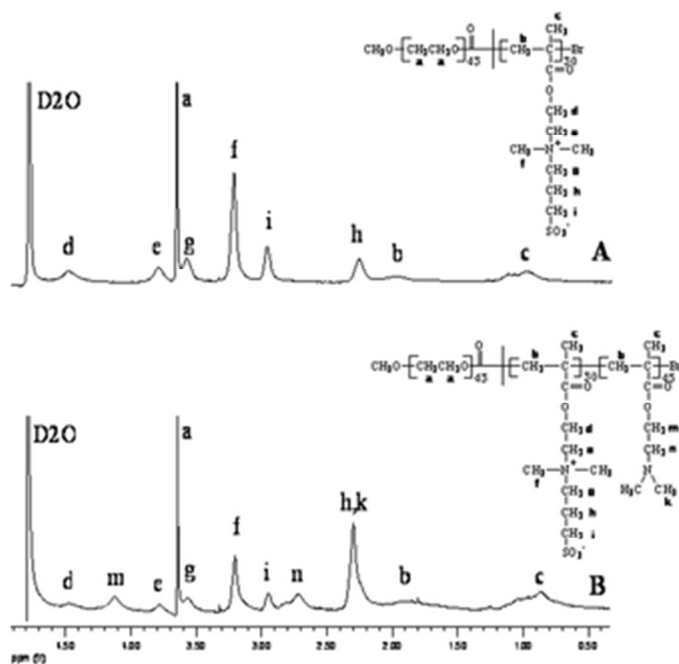29x10mm (300 x 300 DPI)

Fig. 1　1H NMR spectra of the diblock copolymer MPEG43-b-PSBMA30 (A) and the triblock copolymer
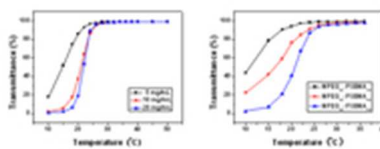MPEG43-b-PSBMA30-b-PDMAEMA45 (B).
28x28mm (300 x 300 DPI)

Fig. 3   Temperature dependence of transmittance for MPEG43-b-PSBMA50 with different concentration in aqueous solutions (A) and for MPEG43-b-PSBMAn (n = 30, 40, or 50) at a concentration of 5 mg/mL in aqueous solutions (B).
16x6mm (300 x 300 DPI)

Table

Table 1   Characteristics of the macroinitiator and the block copolymers.

Sample[a]	Yield (%)	$M_{n,NMR}$[b]	$M_{n,GPC}$[c]	M_w/M_n[d]
MPEG$_{43}$-Br	90.5	2050	2450	1.03
MPEG$_{43}$-PSBMA$_{30}$	80.6	10900	11100	1.37
MPEG$_{43}$-PSBMA$_{40}$	82.0	13900	12030	1.41
MPEG$_{43}$-PSBMA$_{50}$	70.5	16900	15250	1.28
MPEG$_{43}$-PSBMA$_{30}$-PDMAE MA$_{45}$	46.5	18000	20150	1.23
MPEG$_{43}$-PSBMA$_{30}$-PDMAE MA$_{90}$	41.1	25100	26700	1.08

[a] Molecular structure determined by NMR.

[b] Number-average molecular weight derived from ^{1}H NMR.

[c] Number-average molecular weight measured by GPC.

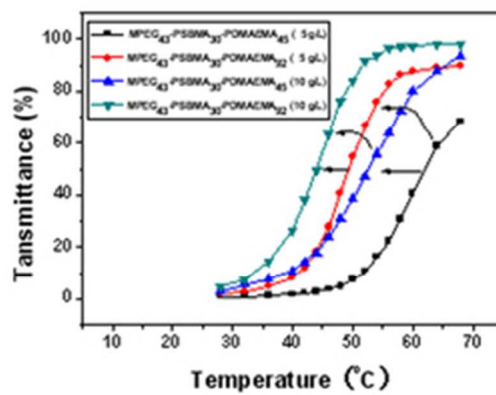[d] Molecular weight distribution measured by GPC.

Fig. 4 Temperature dependence of transmittance for MPEG43-b-PSBMA30-b-PDMAEMA45 and MPEG43-b-PSBMA30-b-PDMAEMA90 with different concentration in aqueous solutions.
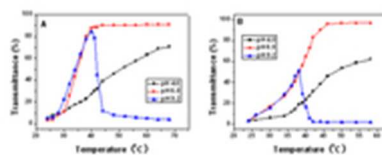23x18mm (300 x 300 DPI)

Fig. 5 Temperature dependence of transmittance of MPEG43-b-PSBMA30-b-PDMAEMA45 (A) and MPEG43-b-PSBMA30-b-PDMAEMA90 (B) at a concentration of 10 mg/mL in aqueous solutions under different pH values.
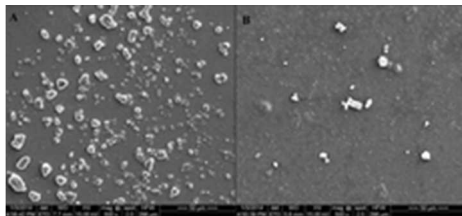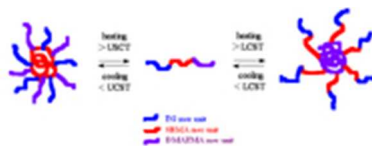17x7mm (300 x 300 DPI)

Fig. 6 SEM images of BSA adsorption on the surface of a sheet glass (A) and on the polymeric coating of
MPEG43-PSBMA30-PDMAEMA45 (B).
19x8mm (300 x 300 DPI)

Scheme 3 Simplified model of the temperature dependence of the polymer conformation in aqueous solution.
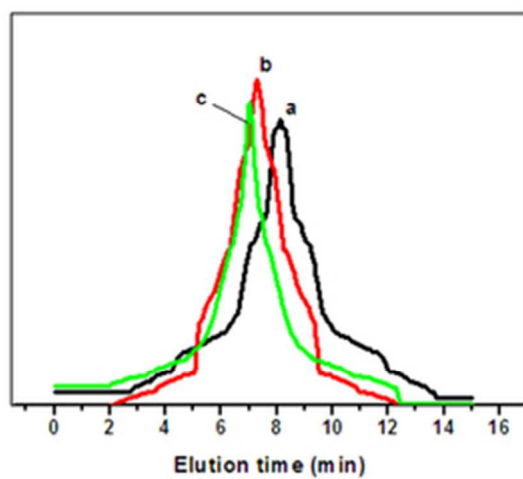16x6mm (300 x 300 DPI)

Fig. 2 GPC curves of MPEG43-PSBMA30 (a), MPEG43-PSBMA30-PDMAEMA45 (b), and MPEG43-PSBMA30-PDMAEMA90 (c).
25x22mm (300 x 300 DPI)