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Stimuli-induced core-corona inversion of micelles of water-soluble poly(sodium 2-(acrylamido)-2-methyl propanesulfonate-*b*-*N*-isopropylacrylamide)

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ABSTRACT

Micelles of poly(sodium 2-(acrylamido)-2-methylpropanesulfonate-*b*-*N*-isopropylacrylamide) (PAMPS-*b*-PNIPAM) have been investigated in aqueous solutions using various techniques including dynamic light scattering, scanning electron microscopy, transmission electron microscopy and ζ-potential measurements. It was found that PAMPS-*b*-PNIPAM produces two distinct types of micelle structures; one is a PAMPS-core/PNIPAM-corona structure and the other is a PNIPAM-core/PAMPS-corona structure. The PAMPS-core micelle with the PNIPAM-corona was obtained by insolubilizing the PAMPS block with ferric ion (Fe^{3+}) at room temperature, and the PNIPAM-core micelle with the PAMPS-corona was obtained by increasing the solution temperature above the lower critical solution temperature (LCST) of the PNIPAM block in the absence of the Fe^{3+} ion. We have also found that the inversion from one type to the other is reversible. The transformation from the PAMPS-core micelle to the PNIPAM-core micelle was induced by removing Fe^{3+} ion using ethylenediaminetetraacetic acid followed by elevating the temperature above the LCST of the PNIPAM block, while the reverse transformation was triggered by adding Fe^{3+} ion at a lower temperature.

1. Introduction

Since the pioneering work of Armes group [1] in 1998, much attention has been paid to novel water-soluble diblock copolymers that exhibit the so-called "schizophrenic" character. Here, the schizophrenic character means that some AB diblock copolymers can form two distinct micelle structures, i.e., the A-core/B-corona structure and B-core/A-corona structure, and the two structures can be reversibly converted to each other by stimuli such as pH, heat, ionic strength, etc. The original report by Armes and coworkers involved a tertiary amine methacrylate-based diblock copolymer, poly(2-(diethylamino)ethyl methacrylate-*b*-2-(*N*-morpholino)ethyl methacrylate) (PDEA-*b*-PMEMA), synthesized by group transfer polymerization [1]. This polymer is both pH and salt-responsive, allowing the formation of either PMEMA-core micelles or PDEA-core micelles in aqueous solution with diameters of 26 and 33 nm, respectively. The PDEA-*b*-PMEMA diblock copolymer molecularly dissolved in dilute hydrochloric acid at pH 4 to give a 1.0 w/v% copolymer solution. The addition of potassium hydroxide to this acidic solution at 20 °C produced a final pH of 8.5 at which the PDEA block becomes substantially deprotonated and therefore hydrophobic, whereas the PMEMA block remained solvated. Thus, micelles comprising the PDEA-core and PMEMA-corona were obtained. Reverse micelles containing PMEMA residues in the core were obtained by selectively salting out the PMEMA block using 1.0 M Na_2SO_4. The synthesis of the second schizophrenic diblock copolymer, poly(propylene oxide-*b*-2-(diethylamino)ethyl methacrylate) (PPO-*b*-PDEA), was reported using atom transfer radical polymerization [2]. The PPO block exhibits a temperature-dependent solubility in water while the PDEA block has a pH-sensitive solubility. The PPO-*b*-PDEA diblock molecularly dissolved at 5 °C and pH 6, because both the PPO and PDEA blocks are soluble in water at these temperatures and pH. Under this condition, the PDEA block has a protonated and cationic form, and the PPO block is hydrated. When the pH of the solution was adjusted to 8.5, the PDEA-core micelles were formed at 5 °C because the PDEA block is insoluble in water at this pH. Alternatively, warming the original solution to 40 °C at pH 6 led to the PPO-core micelles as a result of the PPO block dehydration.

Since then a number of studies have been carried out on schizophrenic micelles [3–22]. Liu and coworkers [3] reported the pH-responsive zwitterionic schizophrenic diblock copolymer, poly(4-vinylbenzoic acid-*b*-2-(diethylamino)ethyl methacrylate) (PVBA-*b*-PDEA). This polymer was synthesized by an atom transfer

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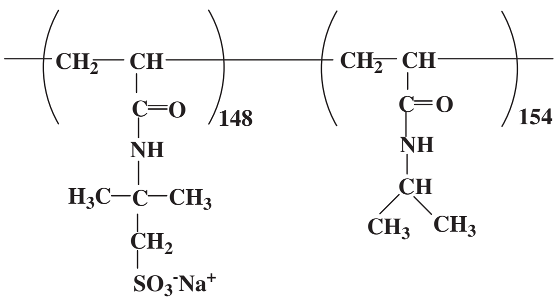
radical polymerization followed by hydrolysis. The PVBA-*b*-PDEA diblock copolymer, reported by this group, forms compact and well-defined PVBA-core micelles at a low pH, whereas it forms PDEA-core micelles at a high pH. Gohy et al. [4] reported that the zwitterionic diblock copolymer, poly(2-(dimethyl amino)ethyl methacrylate-*b*-methacrylic acid) (PDMAEMA-*b*-PMAA), was capable of forming both PDMAEMA-core and PMAA-core micelles under appropriate conditions in aqueous solutions. Recently, Bories-Azeau et al. [5] used the poly(2-(diethylamino)ethyl methacrylate-*b*-succinylethyl methacrylate) (PDEA-*b*-PSEMA) diblock polymer to obtain the PSEMA-core/PDEA-corona micelle at low pH where the tertiary amine of the PDEA block is protonated and become soluble in water. Conversely, the PDEA block becomes hydrophobic in alkaline media forming the core and the PSEMA block becomes anionic forming the corona. Salt-responsive micelle formation and core-corona inversion based on poly(2-(*N*-morphilino)ethyl PAMPS-*b*-PNIPAM Unimer-1-(4-vinylbenzyl)pyridinium betaine) (PMEMA-*b*-PSVBP) in an aqueous solution was studied by Wang et al. [6]. In this polymer, PSVBP is insoluble in pure water, but is readily soluble in the presence of sodium bromide (NaBr) > 0.2 M. Thus, this polymer forms the PSVBP-core and PMEMA-corona in pure water and reverts back to the unimer upon the addition of NaBr (>0.2 M). Conversely, the PMEMA block forms the micelle core in the presence of Na_2SO_4 (>0.6 M) and PSVBP forms the corona in aqueous solution containing NaBr (>0.2 M). Thus, this forms two types of micelles with invertible structures depending on the concentration and type of added salts.

We now report schizophrenic micelles of poly(sodium 2-(acrylamido)-2-methylpropanesulfonate-*b*-*N*-isopropylacrylamide) (PAMPS-*b*-PNIPAM; Scheme 1), which shows different stimuli-responsiveness from the previous schizophrenic polymers [1–22] in aqueous solutions. PAMPS-*b*-PNIPAM gives PAMPS-core micelles at room temperature when the PAMPS block is insolubilized with ferric ion (Fe^{3+}) under acidic conditions (Scheme 2). On the other hand, the PNIPAM-core micelles can be obtained above the lower critical solution temperature (LCST) of PNIPAM (i.e., at temperature > 32 °C [23–26]) in Fe^{3+}–free aqueous solutions. The obtained schizophrenic micelles have been extensively characterized by various techniques including UV–Visible spectrophotometry, dynamic light scattering (DLS), electrophoretic light scattering (ELS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). To the best of our knowledge, this is the first study that employs a metal-ion responsive block in a schizophrenic polymer.

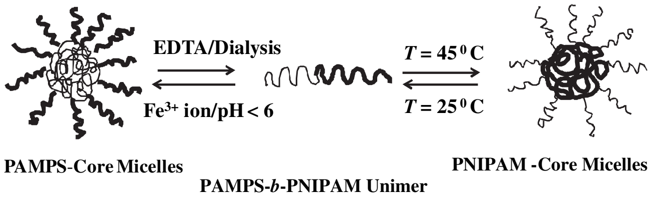
2. Experimental

2.1. Materials

The PAMPS-*b*-PNIPAM diblock copolymer was synthesized according to the previous paper [27]. Details on the synthesis and characterization of PAMPS-*b*-PNIPAM are presented in Supporting Information. The degree of polymerization of PAMPS-*b*-PNIPAM in each block is 148 for PAMPS and 154 for PNIPAM. The molecular weight of the block copolymer is $M_n = 5.16 \times 10^4$.



Scheme 1. Structure of PAMPS-*b*-PNIPAM diblock copolymer.



Scheme 2. Schematic representation of schizophrenic behavior of PAMPS-*b*-PNIPAM diblock copolymer in an aqueous solution.

Ferric chloride hexahydrate ($FeCl_3.6H_2O$) and the ethylenediaminetetracetatic acid (EDTA) sodium salt were purchased from Katayama Chemicals and used without purification.

2.2. Sample preparation

A known amount of PAMPS-*b*-PNIPAM was dissolved in water and gently agitated with a magnetic stirrer at room temperature till a clear solution was obtained. The solution was transferred to a volumetric flask to obtain a stock solution with a concentration of 2 gL^{-1}. A known amount of the stock PAMPS-*b*-PNIPAM solution was then neutralized by titration with a solution of ferric chloride ($FeCl_3$) to produce the working solutions. The amount of added Fe^{3+} is shown by apparent degree of neutralization (DN) which is defined as:

$$\mathrm{DN\%} = \frac{\text{amount of added ferric ion (equivalent)}}{\text{amount of sulfonate ion present (equivalent)}} \times 100 \qquad (1)$$

The pH of the solution was adjusted using 0.01 M sodium hydroxide and 0.01 M hydrochloric acid.

2.3. Turbidity measurements

The turbidity was obtained from the transmittance which was measured using a Hitachi U-3900 and JASCO Ubest-50 spectrophotometers. It is calculated as $(1-T/100)$, where T is the transmittance (%) at 490 nm. It is confirmed that Fe^{3+} ions do not show any absorption at 490 nm, therefore, the decrease in the transmittance is ascribed to the increase in turbidity.

2.4. Dynamic light scattering

DLS measurements were carried out using an Otsuka ELS-8000 electrophoretic light scattering instrument. The scattered light of a vertically polarized He–Ne laser (632.8 nm) was measured at an angle of 90° and was collected by an autocorrelator. The correlation functions were analyzed by the histogram method and used to determine the diffusion coefficient (D) of the samples. Then, hydrodynamic diameter (D_h) was calculated from D using the Stokes–Einstein equation.

$$D_h = k_B T/(3\pi\eta D), \qquad (2)$$

where k_B is the Boltzmann constant, T is the absolute temperature and η is the solvent viscosity. The polydispersity factor of the micelles is represented as μ_2/Γ_2, where μ_2 is the second cumulant of the decay function and Γ_2 is the average characteristic line width.

2.5. Scanning electron microscopy

The SEM measurements were carried out using a Hitachi SU-1500 electron microscope at an accelerating voltage of 15 kV. The samples were prepared by dropping the micelle solution onto a carbon seal (Nisshin Em Co.) attached to the glass plate, followed by drying in air for one day.

2.6. Transmission electron microscopy

The TEM measurements were carried out using a JOEL JEM-1210 at a voltage of 80 kV. The samples were prepared by casting one drop of the micelle solution onto a copper grid on a glass plate, followed by drying in air for one day.

2.7. Zeta-potential measurements

The electrophoretic mobility (EPM) was measured by an Otsuka ELS-8000 apparatus. The zeta-potential (ζ) was calculated from the EPM using the Smoluchowski equation.

$$\mu_E = \zeta\varepsilon/\eta \tag{3}$$

where μ_E is the EPM, ε is the permittivity of the solvent, and η is the viscosity.

3. Results and discussion

3.1. Schizophrenic micellization of PAMPS-b-PNIPAM

It is well-known that the PNIPAM homopolymer dissolves in a cold and dilute aqueous solution while it becomes insoluble above 32 °C (LCST) [23–26]. Thus, increasing the temperature above the LCST is expected to produce PNIPAM-core micelles with the PAMPS-corona. On the other hand, the PAMPS block becomes insoluble in water if Fe^{3+} is bound to this block by electrostatic interaction as will be stated later. Therefore, the addition of Fe^{3+} into the aqueous solution of PAMPS-*b*-PNIPAM may result in the formation of micelles with a PAMPS-core and PNIPAM-corona. Scheme 2 illustrates the expected schizophrenic behavior of the PAMPS-*b*-PNIPAM.

3.2. PNIPAM-core micelles

Hennink et al. [28] found that the micellization of poly(ethylene glycol-*b*-*N*-isopropylacrylamide) at high temperature favors the formation of narrowly distributed micelles for the PNIPAM-core micelles. Thus, we tried to obtain the PNIPAM-core micelles at 45 °C which is much higher than the LCST for the PNIPAM homopolymer.

Fig. 1 represents D_h of the micelles as a function of the PAMPS-*b*-PNIPAM concentration. It is clear from Fig. 1 that the micelle with a hydrodynamic diameter of 170 nm is formed at 0.7 gL^{-1}. The diameter of the micelle is constantly increasing till the polymer concentration increased to 1.4 gL^{-1}. As the value of hydrodynamic diameter (D_h) (300 nm) at higher polymer concentration is too large for a single core-corona type micelle, PNIPAM-*b*-PAMPS may form elongated micelles or multipolymer aggregates due to intermicellar association of the spherical core-corona micelles, as observed by Yusa et al. for PNIPAM-*b*-PAMPS with different block lengths [27].

SEM measurements have been carried out to obtain evidence for the formation of the PNIPAM-core micelle as well as to reveal the morphology of the micelle. A typical image of the samples is presented in Fig. 2. The SEM image clearly shows that micelle particles with a spherical morphology are created.

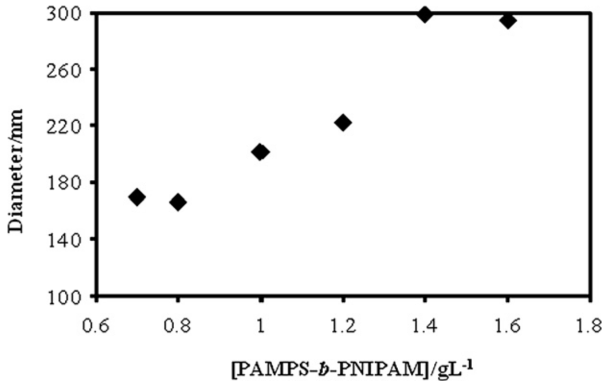


Fig. 1. Hydrodynamic diameter of PNIPAM-core micelles as a function of the concentration of the polymer at $T = 45$ °C.

It should be noted here that the particle size in the SEM image is smaller than that in DLS measurements. This difference may be ascribed to the fact that the former give a size of a dried particle, while the latter gives a hydrodynamic diameter which is calculated from the diffusion coefficient of the particle in an aqueous solution.

3.3. PAMPS-core micelles

To obtain PAMPS-core micelles, we had to find a metal ion that can be reversibly bound to and removed from the PAMPS block. After examining various metal ions (Mg^{2+}, Ca^{2+}, Ba^{2+}, Zn^{2+}, Ag^{+}, Cu^{2+}, Co^{2+}, Fe^{3+}, Zr^{4+} etc.), we found that Fe^{3+} and Zr^{4+} have such a property. Anionic polyelectrolytes possess functional groups, which dissociate in aqueous media to give negatively charged polymer chains. Previous studies [29] on strong and weak polyelectrolytes showed that their stability in presence of multivalent cations depends on the chemical nature of the charged side group of the polymer. For example, for acrylate groups (COO^-), precipitation is observed with inorganic cations having valency 2 or larger. However, for sulfonate groups (SO_3^-) precipitation occurs in presence of inorganic cations of valency 3 or larger. This is the reason why Fe^{3+} and Zr^{4+} insolubilized the PAMPS block that contains SO_3^- side group. Among the cations having valency ≥3, we chose Fe^{3+} because of its high physiological importance.

Fig. 3 shows the turbidity of the PAMPS homopolymer solution as a function of the Fe^{3+} ion concentration. The turbidity is increased with the increasing Fe^{3+} ion concentration. This is due to the decrease in solubility of the PAMPS homopolymer caused by charge cancellation of the anionic PAMPS by the cationic Fe^{3+} ion.

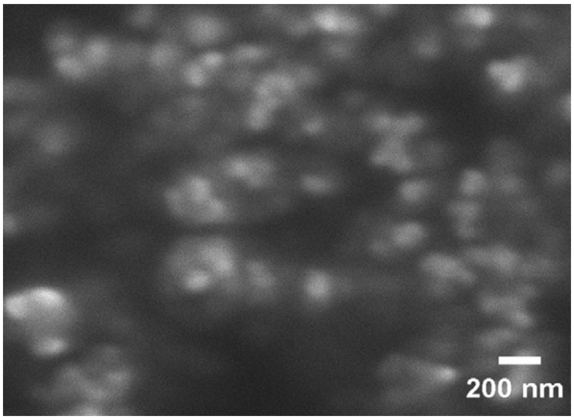


Fig. 2. SEM image of PNIPAM-core micelles. The SEM sample was prepared at 45 °C from the solution with a polymer concentration of 0.8 gL^{-1}.

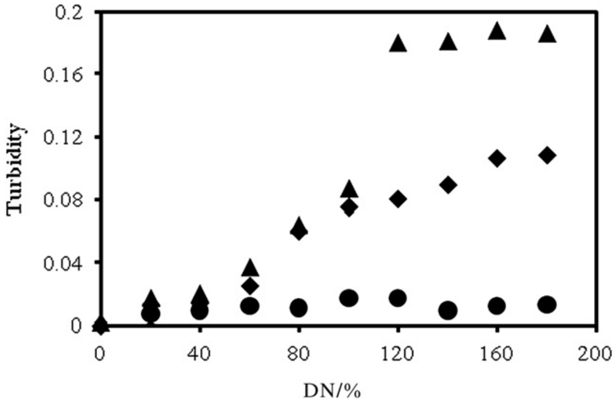


Fig. 3. Turbidity of (▲) PAMPS/Fe3^{+} (0.2 gL^{-1}) (◆) PAMPS-*b*-PNIPAM/Fe3^{+} (0.3 gL^{-1}) solutions as a function of DN. The turbidity of (●) PAMPS/Fe3^{+} (0.2 gL^{-1}) after the addition of EDTA is also shown for comparison. The base-molar concentration of the sulfonic group is the same for the PAMPS and PAMPS-*b*-PNIPAM solutions. The measurements were carried out at 25 °C.

The solution produces a precipitation at a high Fe^{3+} ion concentration (DN > 100%). These data confirmed that the Fe^{3+} ion is effectively bound to the PAMPS homopolymer to insolubilize this polymer. The turbidity change in the PAMPS-*b*-PNIPAM solution is also shown for comparison in Fig. 3. The turbidity increases to some extent with the increase in the DN. However, precipitation did not take place in this case due to the existence of the water-soluble PNIPAM block.

We also carried out experiments to find a way to remove the Fe^{3+} ion from the PAMPS homopolymer, and found that EDTA is an effective reagent for such a purpose. The turbid solution of the Fe^{3+}/PAMPS pair became clear after the addition of EDTA as seen in Fig. 3. This change shows that the Fe^{3+} ion was removed from the PAMPS polymer with EDTA, resulting in the formation of the water-soluble PAMPS homopolymer.

Fig. 4 is a plot of hydrodynamic diameter of the PAMPS-core micelles at 100% DN as a function of the concentration of PAMPS-*b*-PNIPAM. The diameter of the aggregates is high at 0.1 gL^{-1} polymer concentration, but it gradually decreases with an increase in the concentration of the polymer. The decrease in size implies that the core becomes more compact at the higher polymer concentration. The decrease in size with increase in polymer concentration was also reported for another diblock copolymer system [30].

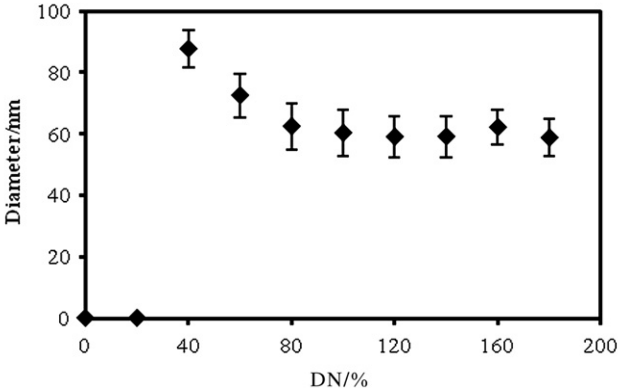


Fig. 5. Hydrodynamic diameter of PAMPS-core micelles as a function of DN at 25 °C. The polymer concentration is maintained at 0.3 gL^{-1}.

Similarly, Fig. 5 shows the plot of the hydrodynamic diameter of the micelles as a function of DN. The formation of the micelles begins at DN of 40%. The size of the micelles decreases with the increasing DN. The decrease in the diameter is explained by a conformational change in the PAMPS block from extended to shrunk forms due to the neutralization of the anionic sulfonic ion (SO_3^-) by the cationic Fe^{3+}. After an 80% DN, the hydrodynamic diameter of the micelles is almost constant, i.e., around 60 nm (±ca. 6 nm). This implies that the conformational change in the PAMPS block is completed at 80% DN.

It should be noted in Figs. 4 and 5 that the values of the hydrodynamic diameter of the the micelles with a polymer concentration of 0.3 gL^{-1} at the DN of 100% are very close to each other, though the samples were prepared by different processes; i.e., by polymer concentration titration in the former and by Fe^{3+} titration in the latter. These cross-check experiments seem to give reliability to the data.

To explore the morphology of the PAMPS-core micelles, SEM measurements were carried out. A typical SEM image of the micelles is shown in Fig. 6. We can see the spherical shape of the particles. The morphologies of the particles at a different DN and different polymer concentration are the same.

We carried out TEM measurements to obtain evidence that the Fe^{3+}/PAMPS pair forms the core of the micelle. A typical image of the micelles is shown in Fig. 7. The dark and small spheres correspond to the PAMPS block of the micelles stained with the Fe^{3+} ion. There are white dots at the center of the dark spheres in some of the micelles. They are the domains which were not stained with Fe^{3+} ions. The faint area around the periphery of the dark spheres may be of PNIPAM-corona of the micelles. This picture provides strong evidence for the binding of the Fe^{3+} ion to the PAMPS block to form the core of the micelle.

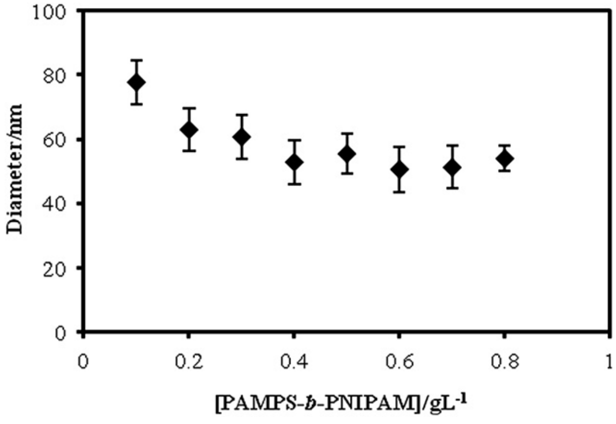


Fig. 4. Hydrodynamic diameter of PAMPS-core micelles as a function of the concentration of the polymer at 25 °C. The DN is maintained at 100% with the Fe^{3+} ion.

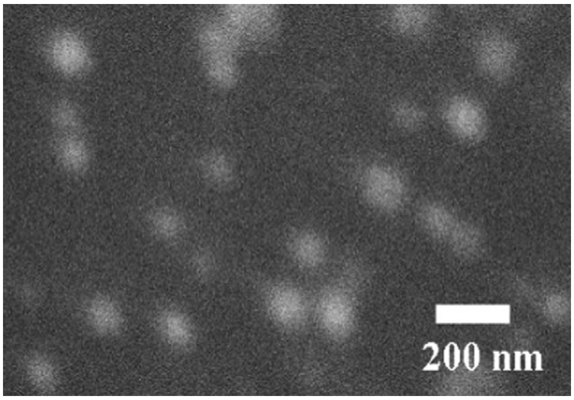


Fig. 6. SEM image of the PAMPS-core micelles. The SEM sample was prepared at 25 °C from the solution with a polymer concentration of 0.06 gL^{-1} and Fe^{3+} concentration of 100% DN.

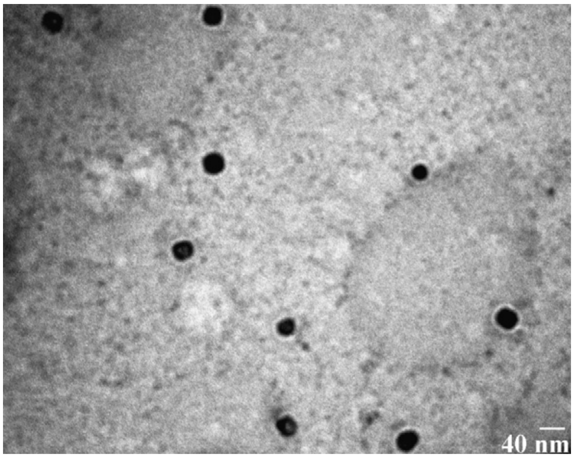


Fig. 7. TEM image of the PAMPS-core micelles. The TEM sample was prepared at 25 °C from the solution with a polymer concentration of 0.4 gL^{-1} and Fe^{3+} concentration of 100% DN.

In order to obtain further evidence for the binding of the Fe^{3+} ion to the PAMPS block, we carried out electrophoresis measurements. In Fig. 8, we plot the ζ-potential of the micelles versus DN at the fixed polymer concentration of 0.3 gL^{-1}. The ζ-potential of the micelles increased from −40 mV to −19 mV when the DN increased from 0 to 100%. This fact indicates that the cationic Fe^{3+} was bound to the anionic SO_3^- group of PAMPS. It should be noted here that the ζ-potential was not zero at 100% DN. The non-zero value of the ζ-potential at 100% DN indicates that all of the added Fe^{3+} ions were not bound to the SO_3^- group of the PAMPS block. It was surprising that the ζ-potential decreased after 100% DN. This implies that the Fe^{3+} ion was removed from the micelles since the free Fe^{3+} ion in aqueous bulk phase does not contribute to the ζ-potential. The addition of $FeCl_3$ after 100% DN increases the concentration of the chloride ion (Cl^-) in the solution, and the anionic Cl^- ion will compete with the SO_3^- ion for the binding to the cationic Fe^{3+} ion. As the Cl^- ion has a smaller hydrated radius than SO_3^-, Cl^- ion will solubilize the Fe^{3+} bound with PAMPS. The present result is similar to that obtained by Khokhlov et al. [31] for the poly(2-acrylamide-2-methyl-1-propanesulfonic acid) linear polymer. However, it is also surprising that the turbidity increases (Fig. 3) even after 100% DN where the Fe^{3+} ion starts to dissociate itself from the PAMPS block. The reason for this is currently unclear. One of the possible reasons is that at a high ionic strength there is less water in the vicinity of the polymer (i.e., the activity of water in the polymer is decreased and the tendency of water to solvate the aggregates diminishes) [32]. This may ultimately increase the turbidity.

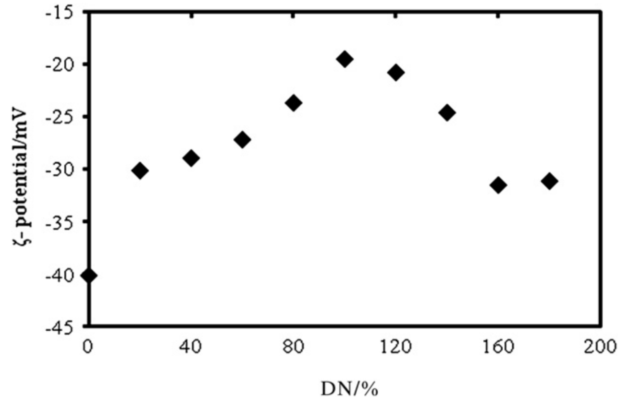


Fig. 8. ζ-potential of PAMPS-core micelles as a function of DN at 25 °C with Fe^{3+} as counter ion. The polymer concentration is maintained constant at 0.3 gL^{-1}.

3.4. Reversible change between PNIPAM-core and PAMPS-core micelles

The schizophrenic behavior of the micelles (i.e., stimuli-induced reversible conversion between PNIPAM-core and PAMPS-core micelles) was checked by various techniques. Fig. 9 shows the results of the SEM measurements. First, the PNIPAM-core micelles were prepared at 45 °C (Step 1, Fig. 9a), and then the temperature was decreased to 25 °C (Step 2) resulting in collapse of the PNIPAM-core micelles. Next, the Fe^{3+} ion was added to the solution to generate the PAMPS-core micelles (Step 3, Fig. 9b). The PAMPS-core micelles were then collapsed by removing the Fe^{3+} ion from the PAMPS block with EDTA (Step 4). Finally, the solution was heated again to 45 °C to get the PNIPAM-core micelles (Step 5, Fig. 9c).

Turbidity data corresponding to each of the above steps is presented in Fig. 10. Concomitantly with the formation or collapse of

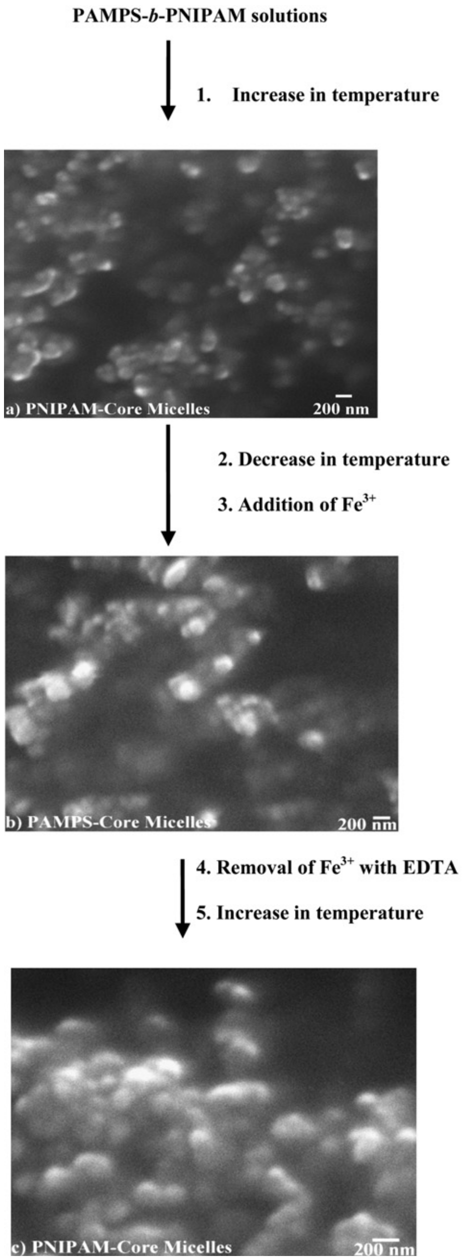


Fig. 9. SEM images showing reversible change between PNIPAM-core and PAMPS-core micelles. See text for details.

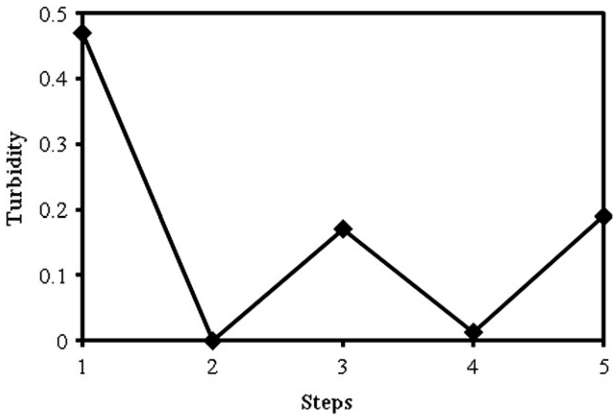


Fig. 10. Turbidity data corresponding to each steps in Fig. 9 showing reversible change between PNIPAM-core and PAMPS-core micelles. (Step 1) $T = 45\ ^\circ\mathrm{C}$, (Step 2) $T = 25\ ^\circ\mathrm{C}$, (Step 3) addition of Fe^{3+}, (Step 4) removal of Fe^{3+} with EDTA, and (Step 5) $T = 45\ ^\circ\mathrm{C}$.

the micelles, the turbidity of the solutions is increased or decreased as seen in Fig. 10. By these experiments, the reversiblity between the two types of micelles was confirmed.

4. Conclusion

New types of schizophrenic micelles were fabricated from PAMPS-*b*-PNIPAM in aqueous solutions; one is the PAMPS-core/PNIPAM-corona micelle and the other is the PNIPAM-core/PAMPS-corona micelle. The former was created by insolubilizing the PAMPS block with the Fe^{3+} ion, and the latter was generated by elevating the temperature higher than the LCST of the PNIPAM block. Switching from the PAMPS-core to the PNIPAM-core micelles was induced by the removal of the bound Fe^{3+} with EDTA, followed by increasing the temperature above the LCST of the PNIPAM. The reverse conversion could be triggered by lowering the temperature below the LCST of the PNIPAM, followed by addition of the Fe^{3+} ion.

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Appendix. Supporting information

Supporting information associated with this article can be found in the online version, at doi:10.1016/j.polymer.2010.05.004.

References

[1] Bütün V, Billingham NC, Armes SP. J Am Chem Soc 1998;120:11818–9.
[2] Liu SY, Billingham NC, Armes SP. Angew Chem Int Ed 2001;40:2328–31.
[3] Liu SY, Armes SP. Angew Chem Int Ed 2002;41:1413–6.
[4] Gohy JF, Creutz S, Garcia M, Mahltig B, Stamm M, Jerome R. Macromolecules 2000;33:6378–87.
[5] Bories-Azeau X, Armes SP, Van den Haak HJW. Macromolecules 2004;37:2348–52.
[6] Wang D, Wu T, Wan X, Wang X, Liu S. Langmuir 2007;23:11866–74.
[7] Bütün V, Sönmez S, Yarligan S, Taktak FF, Atay A, Bütün S. Polymer 2008;49:4057–65.
[8] Fei B, Yang Z, Yang H, Hu Z, Wang R, Xin JH. Polymer 2010;51:890–6.
[9] Arotcarena M, Heise B, Ishaya S, Laschewsky A. J Am Chem Soc 2002;124:3787–93.
[10] Andre X, Zhang MF, Muller AHE. Macromol Rapid Commun 2005;26:558–63.
[11] Schilli CM, Zhang MF, Rizzardo E, Thang SH, Chong YK, Edwards K, et al. Macromolecules 2004;37:7861–6.
[12] Dai S, Ravi P, Tam KC, Mao BW, Gang LH. Langmuir 2003;19:5175–7.
[13] Rao J, Luo Z, Ge Z, Liu H, Liu S. Biomacromolecules 2007;8:3871–8.
[14] Ge Z, Cai Y, Yin J, Zhu Z, Rao J, Liu S. Langmuir 2007;23:1114–22.
[15] Zhang Y, Wu T, Liu S. Macromol Chem Phys 2007;208:2492–501.
[16] Weaver JVM, Armes SP, Bütün V. Chem Commun; 2002:2122–3.
[17] Bütün V, Liu S, Weaver JVM, Bories-Azeau X, Cai Y, Armes SP. React Funct Polym 2006;66:157–65.
[18] Wang D, Yin J, Zhu Z, Ge Z, Liu H, Armes SP, et al. Macromolecules 2006;39:7378–85.
[19] Bütün V, Armes SP, Billingham NC, Tuzar Z, Rankin A, Eastoe J, et al. Macromolecules 2001;34:1503–11.
[20] Jiang X, Ge Z, Xu J, Liu H, Liu S. Biomacromolecules 2007;8:3184–92.
[21] Liu S, Armes SP. Langmuir 2003;19:4432–8.
[22] Rodriguez-Hernandez J, Lecommandoux S. J Am Chem Soc 2005;127:2026–7.
[23] Tanaka F, Koga T, Winnik FM. Phys Rev Lett 2008;101. 028302.
[24] Morimoto N, Winnik FM, Akiyoshi K. Langmuir 2007;23:217.
[25] Aseyev V, Tenhu H, Winnik FM. Adv Polym Sci 2006;196:1.
[26] Heskins M, Guillet JE. J Macromol Sci Chem 1968;A2:1441.
[27] Yusa S, Shimada S, Mitsukami Y, Yamamoto T, Morishima Y. Macromolecules 2004;37:7507–13.
[28] Neradovic D, Soga O, Van Nostrum CF, Hennink WE. Biomaterials 2004;25:2409–18.
[29] Sabbagh I, Delsanti M. Eur Phys JE 2000;1:75–86.
[30] Li Y, Ikeda S, Nakashima K, Nakamura H. Colloid Polym Sci 2003;281:562–8.
[31] Starodoubtsev SG, Lyubimov AA, Khokholov AR. J Phys Chem B 2003;107:12206–11.
[32] Zhang L, Langmuir ME, Bai M, Seitz WR. Talanta 1997;44:1691–8.