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Thermoresponsive core–shell–corona micelles of poly(ethyleneglycol)-*b*-poly(*N*-isopropylacrylamide)-*b*-polystyrene

Wangqing Zhang*, Xiaowei Jiang, Zhenping He, Dean Xiong, Peiwen Zheng,
Yingli An, Linqi Shi*

Key Laboratory of Functional Polymer Materials of Ministry of Education, Institute of Polymer Chemistry, Nankai University, Tianjin 300071, China

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Abstract

Core–shell–corona micelles with a thermoresponsive shell self-assembled by triblock copolymer of poly(ethyleneglycol)-*b*-poly(*N*-isopropylacrylamide)-*b*-polystyrene (PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46}) are studied by ^1H NMR, light scattering and atomic force microscopy. The thermoresponsive triblock copolymer, which has a relatively short hydrophobic PS block, can disperse in water at room temperature to form core–shell–corona micelles with the hydrophobic PS block as core, the thermoresponsive PNIPAM block as shell and the hydrophilic PEG block as corona. At temperature above lower critical solution temperature (LCST) of the PNIPAM block, the PNIPAM chains gradually collapse on the PS core to shrink the size and change the structure of the resultant core–shell–corona micelles with temperature increasing. It is found that there possibly exists an interface between the PNIPAM shell and PEG corona of the core–shell–corona micelles at temperature above LCST of the PNIPAM block.

Keywords: Core–shell–corona micelles; Self-assembly; Thermoresponsive

1. Introduction

Micelles self-assembled by amphiphilic block copolymer in block-selective solvent stimulate a great deal of interest in physical chemistry and polymer science for the past 30 years [1]. Core–shell micelle is the most common one and it is usually self-assembled by diblock copolymer in block-selective solvent, where the insoluble block forms the core and the soluble block forms the shell. For example, various morphological core–shell micelles self-assembled by amphiphilic diblock copolymers such as polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) [2], polystyrene-*block*-poly(ethylene oxide) (PS-*b*-PEO) [3], poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (P2VP-*b*-PEO) [4], polystyrene-*block*-poly(4-vinyl pyridine) (PS-*b*-P4VP) [5], polystyrene-*block*-poly(2-cinnamoylethyl methacrylate) (PS-*b*-PCEMA) [6], poly(methyl vinyl ether)-*block*-poly(isobutyl vinyl ether) (PMVE-*b*-PIBVE) [7] and poly(*t*-butyl methacrylate)-*block*-poly(2-diethylaminoethyl methacrylate) [8] have been extensively studied.

Besides core–shell micelles, another type of three-layered micelles such as "onion-type" micelles and core–shell–corona micelles have also been studied. These three-layered micelles may provide innovative applications, and understanding of the structure and dynamics of micelles and also may influence general concepts about polymer stabilization of colloids and the self-organization of polymers [9,10]. Compared with core–shell micelles, core–shell–corona micelles are scarcely studied, which is possibly due to the difficulty in synthesis of the triblock copolymer and partly due to the complicated structure of three-layered micelles. Generally, three strategies are proposed to prepare core–shell–corona micelles. The first general method is the micellization of amphiphilic ABC triblock copolymer [11–20]. For example, Jerome et al. prepared pH responsive core–shell–corona micelles from triblock copolymer of polystyrene-*block*-poly(2-vinyl

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* Corresponding authors. Tel.: +86 22 23509794; fax: +86 22 23503510 (W.Z.).
E-mail address: wqzhang@nankai.edu.cn (W. Zhang).

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pyridine)-*block*-poly(ethylene oxide) (PS-*b*-P2VP-*b*-PEO) [9,20]; Eisenberg and Kriz et al. produced core–shell–shell micelles from poly(styrene)-*block*-poly(methyl methacrylate)-*block*-poly(*tert*-butylacrylate) and poly(2-ethylhexyl acrylate)-*block*-poly(methyl methacrylate)-*block*-poly(acrylic acid) [10]. The second method suggested by Munk and Webber is the coprecipitation of a core–shell micelle of AB block copolymer and a linear BC block copolymer [21]. Complexation between a core–shell micelle and linear polymer chains is the third method to prepare core–shell–corona micelles. For example, Kabanov et al. prepared multilayer nanoparticles in aqueous solution through complexation between block ionomer micelles of polystyrene-*block*-poly(*N*-ethyl-4-vinylpyridiniumbromide) (PS-*b*-PEVP) and a linear polyanion of poly(sodium methacrylate) (PMANa) [22]. Recently, we have also proposed a facile method to prepare three-layered core–shell–corona micelles in ethanol from complexation between PS-*b*-PAA core–shell micelles and poly(ethylene glycol)-*block*-poly(4-vinyl pyridine) (PEG-*b*-P4VP) [23]. Usually, the identification of the core layer, shell layer and corona layer of core–shell–corona micelles is very difficult or complex. Transmission electron microscopy (TEM) and atomic force microscopy (AFM) measurements are possibly the most popular ways to identify a core–shell–corona micelle. However, a core–shell–corona micelle is usually observed to be a sphere by TEM or AFM, which is just like a core–shell one. Today, how to characterize core–shell–corona micelles is still a challenge to polymer scientists.

Herein, we prepare and characterize the thermoresponsive core–shell–corona micelles from self-assembly of a triblock copolymer of poly(ethyleneglycol)-*b*-poly(*N*-isopropylacrylamide)-*b*-polystyrene (PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46}) in water. The present triblock copolymer can self-assemble into core–shell–corona micelles by directly dispersing in water since the hydrophilic blocks of PEG and PNIPAM are much longer than the hydrophobic PS block. Furthermore, the resultant core–shell–corona micelle has an advantage that it has a thermoresponsive PNIPAM shell and can give responsive to temperature stimulus.

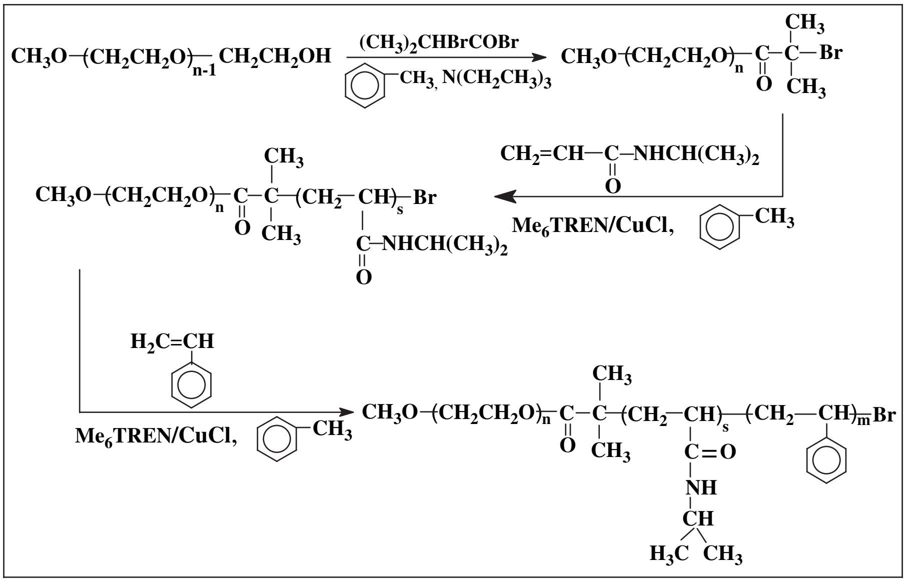
2. Experimental section

2.1. Materials

Polyethylene glycol monomethyl ether (CH_3O-PEG_{45}-OH) ($M_w = 2000$ g/mol and the polydispersity index PDI = 1.05) was purchased from Fluka. CuCl was purchased from Aldrich and purified according to Ref. [24]. The monomer of *N*-isopropylacrylamide (NIPAM, Acros Organics) was purified by recrystallization from a benzene/*n*-hexane mixture and dried carefully in a vacuum. Styrene was purchased from Tianjin Chemical Reagent Corporation and purified firstly by dried with $CaSO_4$ and then distilled at vacuum pressure. Tris-[2-(dimethylamino)ethyl]amine (Me_6TREN) was synthesized according to Ref. [24]. Heavy water (D_2O) was obtained commercially from Beijing Chemical Plant and used as received. All water used in this study was purified with a Millipore Mill-Q system and the resistivity was above 16 MΩ cm. Other analytical reagents were used as received.

2.2. Synthesis and characterization of the triblock copolymer

The triblock copolymer of PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} was synthesized by sequential atom transfer radical polymerization of *N*-isopropylacrylamide and styrene using PEG_{45}-Br as the macroinitiator. The synthesis is illustrated in Scheme 1. Firstly, the macroinitiator PEG_{45}-Br was synthesized according to Ref. [23]. Secondly, the PEG_{45}-*b*-$PNIPAM_{168}$-Br was synthesized according to Ref. [25]. Thirdly, PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} was synthesized by atom transfer radical polymerization of styrene using PEG_{45}-*b*-$PNIPAM_{168}$-Br as



Scheme 1. Synthesis of PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46}.

macroinitiator. The detailed process was introduced as below. PEG_{45}-*b*-$PNIPAM_{168}$-Br (2.0 g) was added into a reaction flask and then 5 mL of toluene was added. The sample was first stirred and then degassed under nitrogen purge. Subsequently, 0.016 g of CuCl and 0.080 g of Me_6TREN were introduced into the reaction flask. At last, 0.50 g of styrene was added into the flask and degassed under nitrogen purge again. Polymerization was performed at 130 °C for 6 h and the conversion is over 80%. The resultant triblock copolymer PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} was purified by first passing through an Al_2O_3 column to remove the copper catalyst and then precipitated in a mixture of 80 vol% *n*-hexane and 20 vol% toluene.

PEG_{45}-Br, PEG_{45}-*b*-$PNIPAM_{168}$ and PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} were characterized by a Waters gel permeation chromatography (GPC) analysis system (Waters 1525 binary HPLC pump, Waters 2414 refractive index detector and waters 717_{plus} autosampler), where THF was used as eluent and narrow-polydispersity polystyrene was used for calibration standard. The GPC traces for PEG_{45}-Br, PEG_{45}-*b*-$PNIPAM_{168}$ and PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} are shown in Fig. 1. The polydispersity index PDI of PEG_{45}-Br, PEG_{45}-*b*-$PNIPAM_{168}$ and PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} measured by GPC is 1.05, 1.28 and 1.21, respectively. A VARIAN UNITY PLUS-400 spectrometer was used to characterize the triblock copolymer, where the polymer was dissolved in $CDCl_3$ at appropriate concentrations and ^1H NMR spectra were recorded at 25 °C. The composition of the triblock copolymer is determined by ^1H NMR spectra as shown in Fig. 2A.

Summarily, the parameters of the triblock copolymers and its precursors are listed in Table 1.

2.3. Preparation and characterization of the core–shell–corona micelles

The core–shell–corona micelles are prepared by directly dispersing the triblock copolymer in water or heavy water D_2O at room temperature. Stir can accelerate the dispersion of the triblock copolymer. The core–shell–corona micellar solution was kept at room temperature for over a week and then characterized by dynamic laser scattering (DLS) and static laser scattering (SLS), AFM and ^1H NMR. DLS and SLS measurements were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 514 nm, where the sample was first prepared by filtering about 1 mL of the aqueous solution with a 0.45 μm Millipore filter into a clean scintillation vial and then heated at a given time for about half an hour. The detailed method of DLS and SLS measurements can be found elsewhere [26]. AFM measurement was conducted by using a Digital Instrumental Nanoscope IV atomic force microscope in tapping mode, whereby a small drop of core–shell–corona micellar solution was first dispersed on a clean silicon wafer and then dried in a vacuum oven at 20 °C. For ^1H NMR measurement of the core–shell–corona micelles, a given amount of the triblock copolymer was first dispersed in D_2O to form 0.05 mg/mL micellar solution, then the micellar solution was heated at a given temperature for about half an hour and then ^1H NMR spectra were recorded.

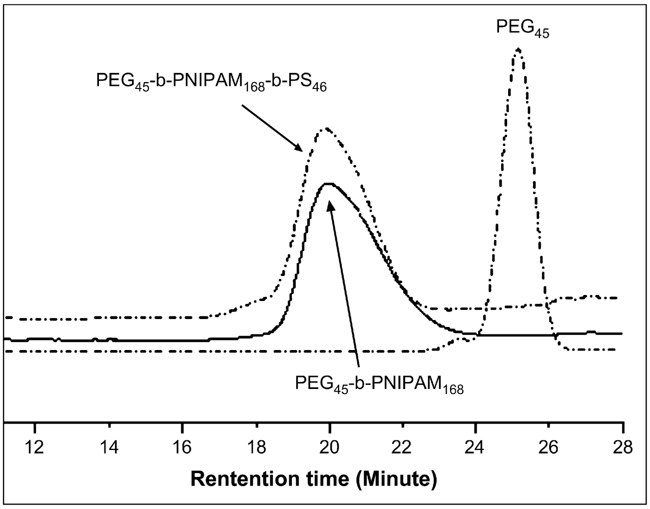


Fig. 1. GPC traces for PEG_{45}-Br, PEG_{45}-*b*-$PNIPAM_{168}$ and PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} in THF at room temperature.

The lower critical solution temperature (LCST) [27] of the PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} micelles was determined by measuring the absorbance or transmittance at 500 nm on a TU-8110 UV–vis spectrophotometer. The samples with different block copolymer concentrations were heated by directly immersing in preheated water at a given temperature and then the absorbance or transmittance was measured. The LCST of the PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} micelles was defined as the temperature at the initial break point in the resulting transmittance versus the temperature curve.

3. Results and discussion

Generally, star micelles of amphiphilic block copolymer can be prepared by directly dissolving the block copolymer in a solvent selective for the relatively long block [28]. Similarly, the present micelles of PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} is prepared by dispersing the copolymer in water at room temperature, since the hydrophilic blocks of PEG and PNIPAM are much longer than the hydrophobic PS block. The critical micelle concentration of the triblock copolymer in aqueous solution at 25 °C is about 5 μg/mL. The resultant micelles are very stable in water at room temperature and no aggregation is observed in six months. The micelles are predicted to have a core–shell–corona structure, where the insoluble PS block forms the core, the soluble PNIPAM block forms the shell and the PEG block forms the corona of the resultant micelles. Fig. 2A shows the ^1H NMR spectra of the triblock copolymer in $CDCl_3$ at 25 °C. Clearly, all characteristic ^1H NMR signals of PS block (peak d at $\delta = 6–7.2$ and peak c at $\delta = 1.2–1.4$), PNIPAM block (peak e at $\delta = 4.0$, peak b at $\delta = 1.4–2.5$ and peak f at $\delta = 1.2$) and PEG (peak a at $\delta = 3.6$) can be clearly observed. This means that the triblock copolymer exists as single chains in $CDCl_3$ since $CDCl_3$ is a good solvent of the triblock copolymer. Compared with Fig. 2A, the distinctness of the ^1H NMR spectra shown in

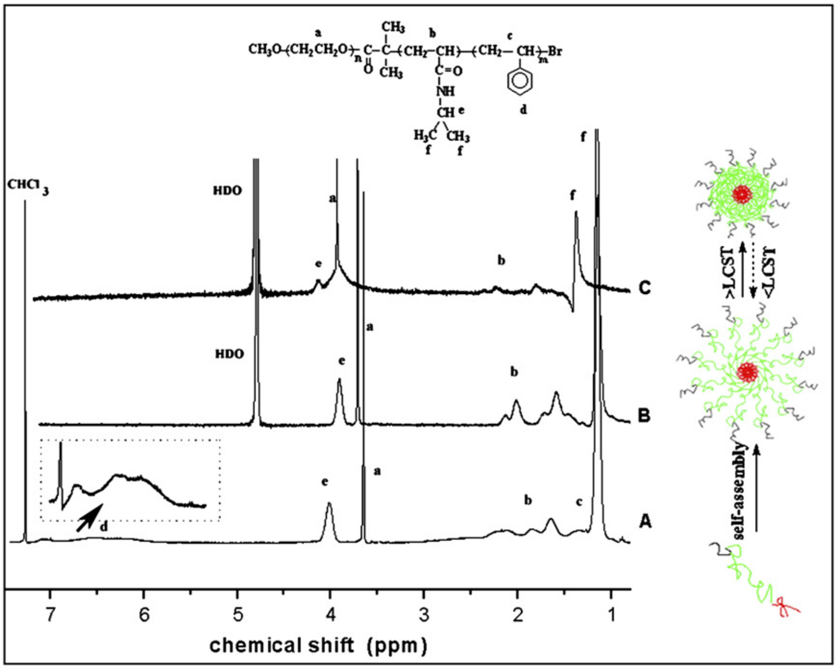


Fig. 2. The ^{1}H NMR spectra of the triblock copolymer in $CDCl_3$ at 25 °C (A) and in D_2O at 25 °C (B) and 45 °C (C). Wherein, the spectra in the dashed rectangle directed by a black arrow in the down left of the figure is magnification of the spectra with chemical shift ranging from 5.8 to 7.2 in 2A. The right part shows the schematic micellization of the triblock copolymer, where the red, green and black lines denote the PS, PNIPAM and PEG chains, respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Fig. 2B is that the peaks d and c corresponding to the PS block disappear. This suggests that the triblock copolymer self-assembles into micelles with the PS block as core in water at 25 °C. When the micellar solution is heated at 45 °C, peaks b and f as shown in Fig. 2C are much attenuated due to the PNIPAM chains collapsing on the PS core to form core–shell–corona micelles at temperature above LCST of the PNIPAM block [29]. These results confirm the hypothesis that the triblock copolymer self-assembles into core–shell–corona micelles with PS block as core, PNIPAM block as shell and PEG block as corona in water. Furthermore, the peaks b, c and f as shown in Fig. 1C are just much attenuated but do not disappear, which suggests that there possibly exists an interface [30] between the PNIPAM shell and PEG corona in the core–shell–corona micelles at 45 °C and which will be further discussed subsequently. Due to the temperature limit of the spectrometer, the ^{1}H NMR spectra performed at higher temperature are not recorded. But it is believed that the characteristic ^{1}H NMR signals of peaks b, c and f due to the PNIPAM block and the interface between the PNIPAM shell and PEG corona will mostly disappear [31]. Summarily, the schematic self-assembly of the triblock copolymer into thermoresponsive core–shell–corona micelles are inserted at the right side in Fig. 2.

Table 1
Characteristics of the polymers used in this study

Polymer	M_w (g/mol)[a]	M_n (g/mol)[b]	PDI[a]
PEG-Br	3.14×10^3	2.00×10^3	1.05
PEG-*b*-PNIPAM	2.53×10^4	2.10×10^4	1.28
PEG-*b*-PNIPAM-*b*-PS	2.89×10^4	2.60×10^4	1.21

[a] The weight-average molar mass M_w and the polydispersity index PDI of the polymers are determined by GPC.

[b] The number-average molar mass M_n of the polymer is calculated from ^{1}H NMR.

Fig. 3 shows the temperature dependence of light transmittance of the aqueous solutions of the PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46} micelles with different block copolymer concentrations. When the triblock copolymer concentration is 0.20 mg/mL, the micelles show a LCST at about 33 °C. When the triblock copolymer concentration decreases to 0.050 mg/mL, the LCST of the micelles slightly increases to 35 °C. It is found that the present micelles are very stable and can keep suspending in

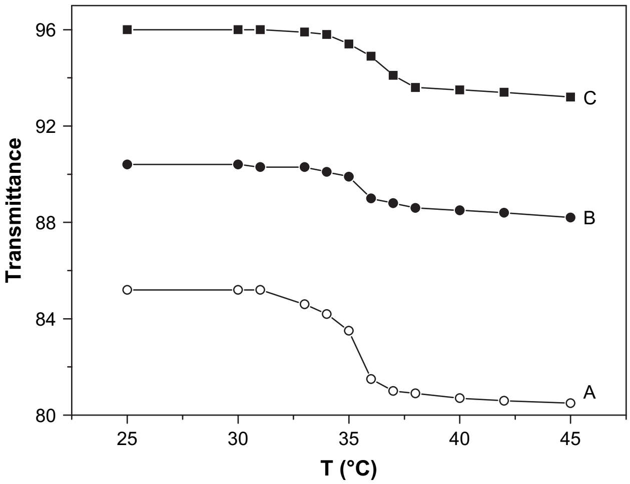


Fig. 3. Temperature dependence of light transmittance of the aqueous solutions of the core–shell–corona with the block copolymer concentration at 0.20 (A), 0.10 (B) and 0.050 mg/mL (C).

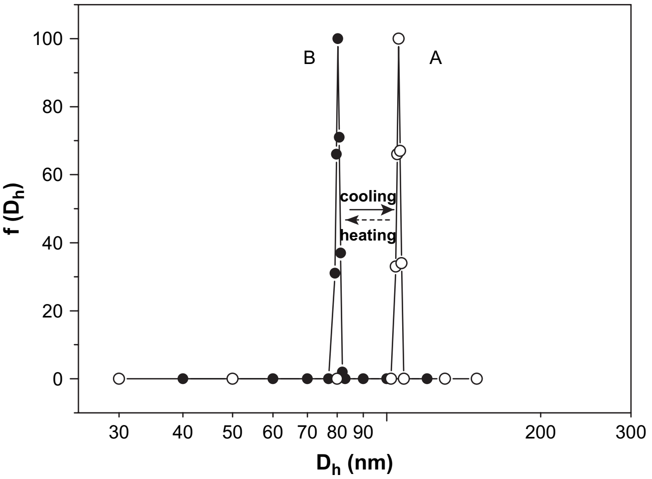


Fig. 4. The hydrodynamic diameter distribution $f(D_h)$ of the core–shell–corona micelles in water with copolymer concentration at 0.050 mg/mL at 25 °C (A) and 50 °C (B).

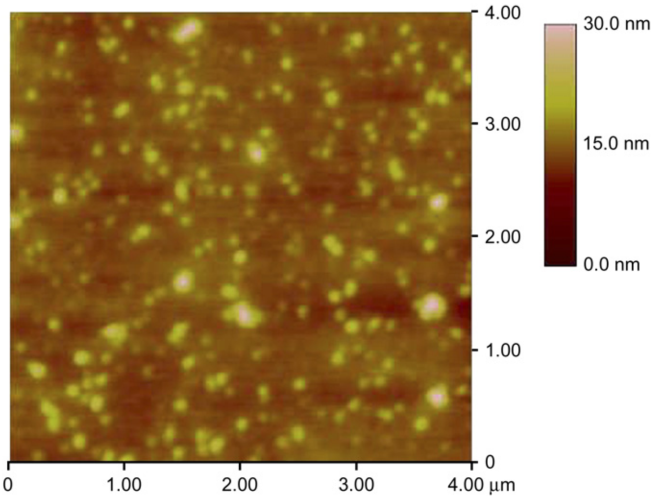


Fig. 5. The AFM image of the core–shell–corona micelles formed on silica wafer.

water at temperature much higher than LCST, which is ascribed to the hydrophilic PEG block.

Fig. 4A shows the hydrodynamic diameter distribution $f(D_h)$ of the core–shell–corona micelles in water with copolymer concentration at 0.050 mg/mL at 25 °C. Clearly, the hydrodynamic diameter D_h of the micelles is much narrowly distributed. The apparent hydrodynamic diameter D_h^{app} can be calculated from $f(D_h)$ by $\int_0^\infty f(D_h)D_h dD_h$. It is also found that the hydrodynamic diameter of the core–shell–corona micelles remains a constant in the copolymer concentration range from 0.010 to 0.20 mg/mL. When temperature increases above LCST of the shell-forming PNIPAM block, the solubility of the PNIPAM chains decreases and the PNIPAM chains gradually collapse on the PS core of the core–shell–corona micelles, which decreases the hydrodynamic diameter of the resultant micelles. Fig. 4B shows the hydrodynamic diameter distribution $f(D_h)$ of the core–shell–corona micelles with copolymer concentration at 0.050 mg/mL at 50 °C. Compared with the core–shell–corona micelles at 25 °C, the hydrodynamic diameter D_h of the resultant micelles at 50 °C is also narrowly distributed, but the diameter becomes smaller about 25 nm due to the collapse of the shell-forming PNIPAM chains above LCST. When temperature decreases back to 25 °C, the hydrodynamic diameter of the core–shell–corona micelles gradually increases. It must be noted that the hydrodynamic diameter of the resultant micelles at copolymer concentration higher than 0.20 mg/mL will increase when the core–shell–corona micellar solution is heated above LCST of PNIPAM block. The possible reason is that the core–shell–corona micelles at high polymer concentration aggregate to form micellar clusters at temperature above LCST of the PNIPAM block [18], which will be further studied in future.

Fig. 5 shows the AFM image of the core–shell–corona micelles formed on a silica wafer. As discussed above, the core–shell–corona micelles are expected to be spheres in water. Whereas, the observed micelles on silica surface are uniform flat spheres. The reason, just as Schubert et al. deduced [32], is that the AFM image shows the dried core–shell–corona micelles on the surface of silica, where the PNIPAM shell and PEG corona chains are no longer swollen by the solvent but to be oriented flat on the surface of silica. Based on the diameter and height of the flat spheres, the present core–shell–corona micelle can be shrunk into a dried sphere with diameter about 50 nm. Herein, it must be noted that the values of the hydrodynamic diameter of the core–shell–corona micelles measured by DLS are larger than those observed by AFM. This is because the core–shell–corona micelles are water swollen due to the soluble PEG and PNIPAM blocks, while AFM observation shows the diameter of the dried aggregates.

Fig. 6A shows the hydrodynamic diameter of the core–shell–corona micelles in water with copolymer concentration at 0.050 mg/mL at different temperatures. Clearly, the hydrodynamic diameter of the core–shell–corona micelles almost keeps a constant of about 130 nm at temperature below 35 °C. When temperature increases, the hydrodynamic diameter decreases gradually till to a smaller constant about 105 nm at 50 °C. Herein, the LCST of the shell-forming block is about 35 °C, which is little higher than that of homopolymer PNIPAM [29]. The possible reason is that the hydrophilic PEG block enhances the solubility of the PNIPAM. Besides, the ^{1}H NMR results as shown in Fig. 2C suggest that there exists an interface between the PNIPAM shell and PEG corona at 45 °C. From the difference between the hydrodynamic diameters of the core–shell–corona micelles at 45 and 50 °C, the thickness of the interface is calculated to be about 4 nm. When temperature is above 50 °C, the interface disappears and the hydrodynamic diameter almost keeps a constant. Fig. 6B shows the apparent gyration radius R_g of the core–shell–corona micelles formed at 0.050 mg/mL at different temperatures. Clearly, the R_g of the resultant micelles decreases from a constant about 63–41 nm as temperature increases from 25 to 50 °C, which is very similar to the change of hydrodynamic diameter of core–shell–micelles as discussed in Fig. 5A.

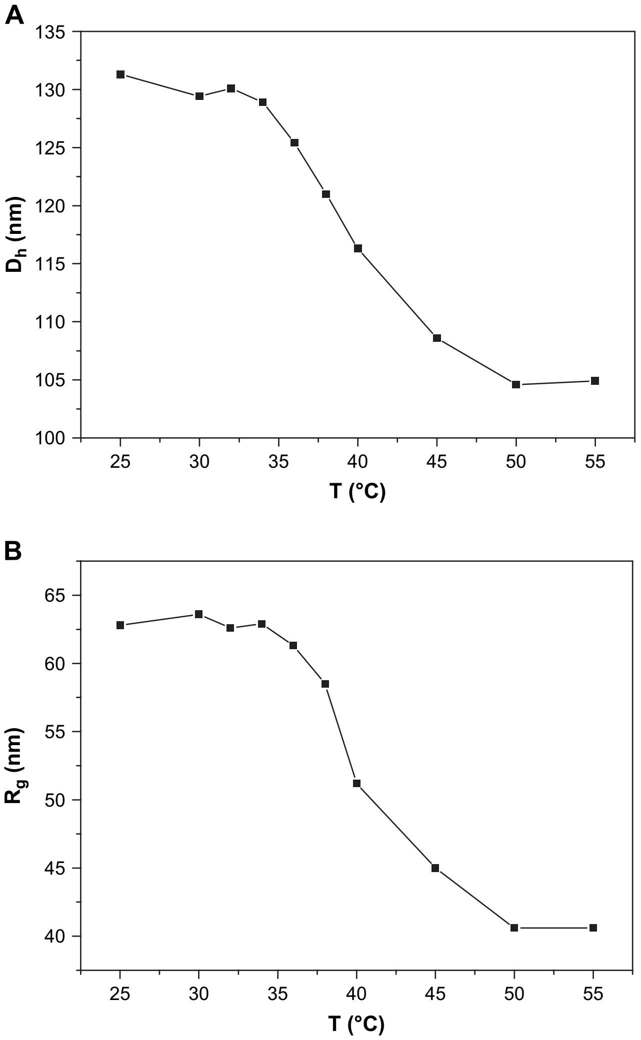


Fig. 6. The temperature dependence of the hydrodynamic diameter D_h (A) and gyration radius R_g (B) of the core–shell–corona micelles formed in water with copolymer concentration at 0.050 mg/mL.

It is well known that the R_g/R_h value, where R_h is the hydrodynamic radius, indicates the particle shape in solution [33]. For example, the R_g/R_h values of typical amphiphilic block copolymer crew-cut micelles and star micelles are approximately 0.77 and 1.0, respectively [26,33,34]. The R_g/R_h value of the core–shell–corona micelles as shown in Fig. 7 decreases from 0.96 to 0.77 when temperature increases from 25 to 50 °C. At temperature below LCST, the shell-forming PNIPAM block is soluble and the total length of the hydrophilic blocks of PEG and PNIPAM is much longer than that of the hydrophobic PS block, thus the present core–shell–corona micelle is just like a star one and has a higher R_g/R_h value at about 0.96. At 50 °C, the shell-forming PNIPAM block becomes hydrophobic and the length of the hydrophilic block is much shorter than that of the hydrophobic, therefore the core–shell–corona micelle is just like a crew-cut one and has a lower R_g/R_h value at about 0.77.

Conclusively, the thermoresponsive triblock copolymer of PEG_{45}-*b*-$PNIPAM_{168}$-*b*-PS_{46}, which has a relatively short hydrophobic PS block, can directly disperse in water at room temperature to form star-like core–shell–corona micelles with the hydrophobic PS block as core and the thermoresponsive PNIPAM block as shell and the hydrophilic PEG block as corona. At temperature above LCST of the PNIPAM block, the shell-forming PNIPAM chains gradually collapse on the PS core to shrink the size of the micelle and change the star-like core–shell–corona micelle to a crew-cut one.

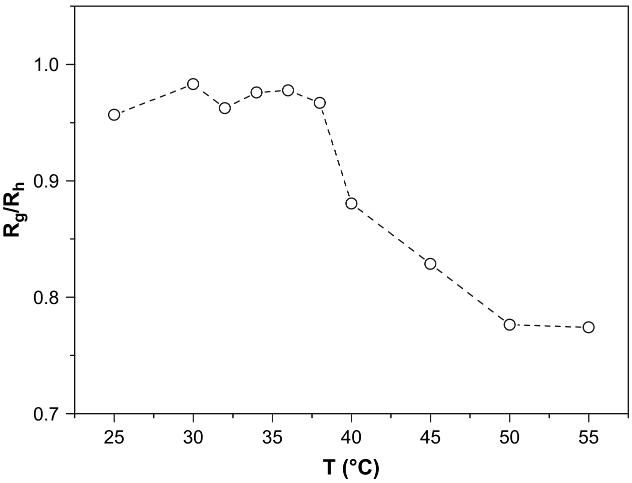


Fig. 7. The temperature dependence of the R_g/R_h value of the core–shell–corona micelles formed in water with copolymer concentration at 0.050 mg/mL.

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Appendix. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.polymer.2006.09.053.

References

[1] Webber SE, Munk P, Tuzar Z. Solvents and self-organization of polymers. In: NATO ASI series E. Kluwer Academic Publishers; 1996.

[2] (a) Zhang L, Eisenberg A. Science 1995;268:1728;
(b) Yu K, Eisenberg A. J Am Chem Soc 1997;119:8383;
(c) Zhang W, Shi L, An Y, Gao L, Wu K, Ma R. Macromolecules 2004;37:2551.

[3] (a) Yu K, Eisenberg A. Macromolecules 1996;29:6359;
(b) Zhao C, Winnik MA, Riess G, Croucher MD. Macromolecules 1990;6:514;
(c) Xu R, Winnik MA, Hallett FR, Riess G, Croucher MD. Macromolecules 1991;24:87.

[4] Martin TJ, Prochazka K, Munk P, Webber SE. Macromolecules 1996;29:6071.

[5] (a) Khougaz K, Gao Z, Eisenberg A. Macromolecules 1994;27:6341;
(b) Shen H, Zhang L, Eisenberg A. J Am Chem Soc 1999;121:2728.

[6] (a) Underhill RS, Ding J, Birss VI, Liu G. Macromolecules 1997;30:8298;
(b) Ding J, Liu G. Macromolecules 1999;32:8413;
(c) Tao J, Stewart S, Liu G, Yang M. Macromolecules 1997;30:2738.

[7] Verdoncka B, Gohy J-F, Khousakounb E, Jerome R, Du Prez F. Polymer 2005;46:9899.

[8] Maoa BW, Gana LH, Gana YY, Tamb KC, Tan OK. Polymer 2005;46:10045.

[9] (a) Gohy J-F, Willet N, Varshney S, Zhang J-X, Jerome R. Angew Chem Int Ed 2001;17:3214;
(b) Lei L, Gohy J-F, Willet N, Varshney S, Zhang J-X, Varshney S, et al. Macromolecules 2004;37:1089.

[10] (a) Yu G, Eisenberg A. Macromolecules 1998;31:5546;
(b) Kriz J, Masar B, Plestil J, Tuzar Z, Pospisil H, Doskocilova D. Macromolecules 1998;31:41.

[11] Riess G, Schlienger M, Marti S. J Macromol Sci 1980;B17:355.

[12] Patrickios CS, Lowe AB, Armes SP, Billingham NC. J Polym Sci Part A Polym Chem 1998;36:617.

[13] (a) Matsushita Y, Tamura M, Noda I. Macromolecules 1994;27:1267;
(b) Nagazawa H, Ohta T. Macromolecules 1993;26:5503.

[14] Gido SP, Schwark DW, Thomas EL, Goncalves MC. Macromolecules 1993;26:2636.

[15] Auschra C, Stadler R. Macromolecules 1993;26:2171.

[16] Chen WY, Alexandridis P, Su CK, Patrickios CS, Hertler WR, Hatton TA. Macromolecules 1995;28:8604.

[17] Zhang W, Shi L, Ma R, An Y, Xu Y, Wu K. Macromolecules 2005;38:8850.

[18] Kyriacou MS, Hadjiyannakou SC, Vamvakaki M, Patrickios CS. Macromolecules 2004;37:7181.

[19] Sugihara S, Kanaoka S, Aoshima S. J Polym Sci A 2004;42:2601.

[20] (a) Lei L, Gohy J-F, Willet N, Zhang J-X, Varshney S, Jerome R. Polymer 2006;47:2723;
(b) Lei L, Gohy J-F, Willet N, Zhang J-X, Varshney S, Jerome R. Polymer 2004;45:4375.

[21] Talingting RM, Munk P, Webber SE. Macromolecules 1999;32:1593.

[22] (a) Lysenko EA, Chelushkin PS, Bronich TK, Eisenberg A, Kabanov VA, Kabanov AV. J Phys Chem B 2004;108:12352;
(b) Pergushov DV, Remizova EV, Gradzielski M, Lindner P, Feldthusen J, Zezin AB, et al. Polymer 2004;45:367.

[23] (a) Zhang W, Shi L, Gao L, An Y, Wu K. Macromol Rapid Commun 2005;26:1341;
(b) Zhang W, Shi L, Miao Z, Wu K, An Y. Macromol Chem Phys 2005;206:2354.

[24] Xia J, Zhang X, Matyjaszewski K. Macromolecules 1999;32:3531.

[25] Zhang W, Shi L, Wu K, An Y. Macromolecules 2005;38:5743.

[26] (a) Zhang W, Shi L, An Y, Gao L, Wu K, Ma R, et al. Phys Chem Chem Phys 2004;6:109;
(b) Tu Y, Wan X, Zhang D, Zhou Q, Wu C. J Am Chem Soc 2000;122:10201;
(c) Wu C, Fu J, Zhao Y. Macromolecules 2000;33:6340.

[27] (a) Fujishige S, Kubota K, Ando I. J Phys Chem 1989;93:3311;
(b) Cao Z, Liu W, Gao P, Yao K, Li H, Wang G. Polymer 2005;46:5268.

[28] Nakamura K, Endo R, Takena M. J Polym Sci Polym Phys ED 1976;14:1287.

[29] (a) Virtanen J, Holappa S, Lemmetyinen H, Tenhu H. Macromolecules 2002;35:4763;
(b) Wu C, Zhou S. Macromolecules 1995;28:5388;
(c) Schild HG. Prog Polym Sci 1992;17:163;
(d) Wu C, Qiu X. Phys Rev Lett 1998;80:620.

[30] Riess G. Prog Polym Sci 2003;28:1107.

[31] (a) Larsson A, Kuckling D, Schonhoff M. Coll Surf A 2001;190:185;
(b) Sun P, Li B, Wang Y, Ma J, Ding D, He B. Eur Polym J 2003;39:1045.

[32] Guerrero-Sanchez C, Wouters D, Fustin C, Gohy J-F, Lohmeijer BGG, Schubert US. Macromolecules 2005;38:10185.

[33] Wu C, Zuo J, Chu B. Macromolecules 1989;22:633.

[34] Zhang W, Shi L, An Y, Gao L, He B. J Phys Chem B 2004;108:200.