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Synthesis and micellization of thermo- and pH-responsive block copolymer of poly(*N*-isopropylacrylamide)-*block*-poly(4-vinylpyridine)

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Abstract

A novel double-hydrophilic block copolymer poly(*N*-isopropylacrylamide)-*block*-poly(4-vinylpyridine) (PNIPAM-*b*-P4VP) with low polydispersity which could respond to both temperature and pH stimuli in aqueous solution was synthesized by atom transfer radical polymerization. Micellization of the copolymer in aqueous solution was characterized by dynamic and static laser scattering, ^{1}H NMR and transmission electron microscopy. In aqueous solution, the copolymer existed as unimer at pH 2.8 at 25 °C. When the temperature was raised to 50 °C at pH 2.8, the copolymer associated into spherical core–shell micelles with the PNIPAM block forming the core and the P4VP block forming the shell. On the other hand, when pH was increased from 2.8 to 6.5 at 25 °C, the copolymer associated into spherical core–shell micelles with the core formed by the P4VP block and the shell formed by the PNIPAM block. The process was reversible. The critical aggregation temperature of the block copolymer is 36 °C, and the critical aggregation pH value is 4.7.

Keywords: Double-hydrophilic; pH-responsive; Thermo-responsive

1. Introduction

Micellization of double-hydrophilic block copolymers under the influence of a given external stimulus, such as a change in pH, temperature or ionic strength, has attracted considerable interests due to their potential application in areas such as biomimetic chemistry [1], molecular switch [2,3], and controlled drug delivery [4–7]. Many systems, such as poly(ethylene glycol)-*block*-poly(*N*-isopropylacrylamide) (PEG-*b*-PNIPAM) [8], poly(sodium(2-sulfamate-3-carboxylate)isoprene)-*block*-poly(ethylene oxide) [9], poly(styrenesulfonic acid)-*block*-poly(methacrylic acid) [10], and poly(ethylene glycol)-*block*-poly(methacrylic acid) (PEG-*b*-PMAA) [11], have been investigated. Very recently, double-hydrophilic copolymers in which both of the hydrophilic blocks are stimuli-responsive also have been extensively studied for various applications. Armes and Liu prepared a schizophrenic diblock copolymer of poly(4-vinylbenzoic acid)-*block*-poly((2-diethylamino)ethyl methacrylate) (PVBA-*b*-PDEA) which consisted of doubly pH-responsive blocks and underwent reversible micellar association to give either PVBA-core micelles or PDEA-core micelles depending on the pH changes [12]. Similar system of a pH-induced reversible micellization is also reported by Dai et al. [13]. In addition to pH-responsive system, Laschewsky et al., Armes et al. and Maeda et al. also prepared block copolymers consisting of doubly thermosensitive hydrophilic blocks which exhibited a core–shell inversion simply depending on the change in temperature, respectively [14–17]. Laschewsky et al. also prepared a series of amphiphilic diblock and triblock via reversible addition fragmentation chain transfer polymerization and exemplified the concept of multiple-sensitive system [18].

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We report here the synthesis and the micellization of a novel double-hydrophilic copolymer of poly(*N*-isopropylacrylamide)-*block*-poly(4-vinylpyridine) (PNIPAM-*b*-P4VP) consisting of a thermo-responsive block of PNIPAM and a pH-responsive block of P4VP. PNIPAM is a typical thermo-responsive polymer which has a lower critical solution temperature (LCST) at around 32 °C [19]. P4VP is a pH-sensitive polymer which is soluble in water when the pH value is below 4.7, and becomes insoluble when the pH is high [20]. Therefore, the block copolymer PNIPAM-*b*-P4VP could respond to both temperature and pH, i.e., a micelle with a PNIPAM shell and a P4VP core could be formed under the condition of $T <$ LCST and pH > 4.7, and a reverse micelle could be formed under the opposite condition. Our group also reported a triblock copolymer poly(ethylene glycol)-*block*-poly(4-vinylpyridine)-*block*-poly(*N*-isopropylacrylamide) recently which can form various morphological micelles in aqueous solution with combined stimulus of temperature and pH changes because of the existence of PEG block [21]. Compare to the triblock copolymer, the diblock copolymer reported here can easily conduct reversible process without the aid of PEG block.

To the best of our knowledge, in the literature there have been only a small number of such double-hydrophilic diblock copolymers which could respond to changes in both temperature and pH and exhibit a core–shell inversion. These include only poly(propylene oxide)-*block*-poly(2-(diethylamino)ethyl methacrylate) (PPO-*b*-PDEA) and poly(*N*-isopropylacrylamide)-*block*-poly(acrylic acid) (PNIPAM-*b*-PAA) [22,23]. Due to the thermal property of PPO, the PPO-*b*-PDEA copolymer formed a PDEA-core micelle at 5 °C at pH 8.5, and a PPO-core micelle at 40 and 70 °C at pH 6.5. Neither micellar state was stable at ambient temperature, which greatly limited the characterization and applications of the copolymer. With regard to the PNIPAM-*b*-PAA system, it is a regret that no unimer state of the copolymer has been obtained owing to the strong hydrogen bonding between the amide group of PNIPAM and the carboxylic acid group of PAA. It seems that the PNIPAM-*b*-P4VP presented here can overcome the drawback for there is no strong hydrogen bonding interaction between the PNIPAM and P4VP blocks. Furthermore, the critical aggregation temperature of PNIPAM is in a range that is interesting for biomedical applications.

2. Experimental section

2.1. Materials

N-Isopropylacrylamide (NIPAM, Acros Organics, 99%) was recrystallized from an *n*-hexane/benzene mixture and dried under vacuum prior to use. 4-Vinylpyridine (4VP, Acros Organics, 95%) was purified by vacuum distillation. CuCl (Aldrich, 98%) was purified according to a literature procedure [24]. Tris(2-dimethylaminoethyl)amine (Me_6TREN) was obtained as described elsewhere [25]. Water used in this study was purified with a Millipore Mill-Q system and the resistivity was above 16 MΩ cm. 1-Chlorophenylethane (1-PECl, Acros Organics) was used as received. All other regents were used as received.

2.2. Preparation of the macroinitiator PNIPAM-Cl

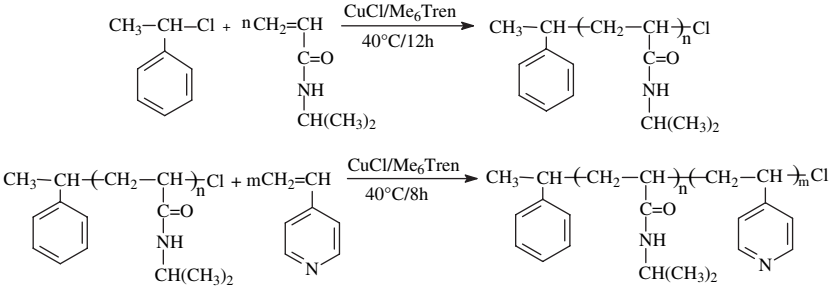
PNIPAM-Cl was synthesized by atom transfer radical polymerization (ATRP) of NIPAM using 1-PECl as the initiator and CuCl as the catalyst. Me_6TREN was used as the ligand in this system. The detailed procedure is described as follows: 0.16 g CuCl and 0.38 g Me_6TREN were added into the reaction flask and 10 mL toluene was then added. The sample was first stirred and then degassed by purging with nitrogen. Subsequently, 10 g NIPAM and 0.15 g 1-PECl were added into the flask and degassed with nitrogen. Polymerization was performed at 40 °C for 12 h and monomer conversion was above 70%. PNIPAM-Cl was purified by passing through an Al_2O_3 column to remove the copper catalyst followed by a precipitation in a toluene/*n*-hexane mixture (3:7 v:v). The precipitate of PNIPAM-Cl was then filtered under vacuum and dried in a vacuum oven at room temperature.

2.3. Preparation of the block copolymer PNIPAM-b-P4VP

PNIPAM-*b*-P4VP was synthesized by atom transfer radical polymerization of 4-vinylpyridine using PNIPAM-Cl as the macroinitiator and CuCl as the catalyst. The detailed procedure is as follows: 0.1 g CuCl and 0.23 g Me_6TREN were added into the reaction flask and then 10 mL solvent mixture of butanone and 2-propanol (7:3 v:v) was added. The sample was first stirred and then degassed under nitrogen purge. Subsequently, 10 g PNIPAM-Cl and 6 g 4-vinylpyridine were added into the flask and degassed under nitrogen purge again. Polymerization was performed at 40 °C for 8 h. The block copolymer was purified by passing through an Al_2O_3 column to remove the copper catalyst and then was precipitated in toluene to remove PNIPAM homopolymer and 4VP monomer. The precipitate was then washed by hot acidic water to remove P4VP homopolymer. Finally, the precipitate was filtered under vacuum and dried in a vacuum oven at room temperature. The synthetic procedure for PNIPAM-Cl and PNIPAM-*b*-P4VP by ATRP is illustrated in Scheme 1.

2.4. Dynamic and static laser scattering (DLS and SLS)

The block copolymer PNIPAM-*b*-P4VP was dissolved in acidic water (pH 2.8) at about 18 °C to obtain a stock solution with a concentration of 0.200 mg/mL. Solutions of different pH values but of the same concentration were prepared by adding sodium hydroxide solutions to the stock solution. Solutions of different concentrations but at the same pH value were prepared by diluting the stock solution with water at pH 2.8. All these samples were then filtered through a 0.45 μm Millipore filter into a clean scintillation vial and characterized by a combination of dynamic (DLS) and static laser scattering (SLS) measurements performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator



Scheme 1. Synthesis of the PNIPAM-*b*-P4VP copolymer by ATRP.

(BI-9000AT) at 514 nm. The specific refractive index increment (dn/dc) was determined with a Wyatt Optilab DSP interferometric refractometer at a wavelength of 514 nm at 25 °C.

In the DLS measurements, the cumulant or Laplace inversion analysis of the measured intensity–intensity time correlation function $G^{(2)}(t,q)$ in the self-beating mode can result in a line-width distribution $G(\Gamma)$. For a pure diffusive relaxation, $G(\Gamma)$ is related to the translational diffusion coefficient D by $G(D)$ since $D = \Gamma/q^2$ at $\theta \to 0$ and $C \to 0$ or a hydrodynamic diameter distribution $f(D_h)$ via the Stokes–Einstein equation $D_h = k_b T/(3\pi\eta D)$, where k_b, T, and η are the Boltzmann constant, the absolute temperature and the solvent viscosity, respectively. In the present study, D^0 of the resultant micelles at a given concentration is calculated by extrapolating q^2 to 0, and then the apparent hydrodynamic diameter D_h^0 and its distribution $f(D_h)$ at given polymer concentration are calculated. On the basis of the SLS theory, for a given dilute polymer solution at concentration C (g/mL) and at the scattering angle θ, the angular dependence of the excess absolute average scattered intensity, known as the excess Rayleigh ratio $R(\theta,C)$, can be approximated as

$$[KC/R(\theta,C)] = [1/M_w]\left[1 + \left(R_g^2 q^2\right)/3\right] \quad (1)$$

where K is the optical constant and $K = 4\pi^2 n^2 (\mathrm{d}n/\mathrm{d}c)^2/(N_A\lambda_0^4)$ with N_A, n and λ_0 being the Avogadro constant, the solvent refractive index and the wavelength of the laser, respectively; and q is the magnitude of the scattering wave vector and $q = (4\pi n/\lambda_0)\sin(\theta/2)$. After measuring $R(\theta,C)$ at a set of θ, the apparent value of radius of gyration R_g and the apparent weight-average molecular weight M_w are determined based on Eq. (1). While the size of the scattering particle is much smaller than the wavelength of incident light, $R(\theta,C)$ has no angular dependence and the M_w can be determined approximately on the basis of the following equation

$$[KC/R(\theta,C)] = [1/M_w] + 2A_2C \quad (2)$$

where A_2 is the second virial coefficient.

2.5. Characterization

The ^{1}H NMR spectra of the copolymers in $CDCl_3$ and D_2O were recorded on a Varian UNITY plus-400 spectrometer operating at 400 MHz for protons. The molecular weights of the polymers were characterized by a Waters 600E gel permeation chromatography (GPC) analysis system equipped with waters Styragel HT column, where $CHCl_3$ was used as the eluent and polystyrene as the calibration standard. Transmission electron microscopy (TEM) was conducted by using a Philips T20ST electron microscopy at an acceleration voltage of 200 kV, whereby the micellar solution was first heated at a given temperature, and then a small drop of micellar solution was deposited onto a preheated carbon-coated copper EM grid and dried at the same temperature at atmospheric pressure.

3. Results and discussion

3.1. Synthesis of PNIPAM-b-P4VP

It is the first time that PNIPAM-*b*-P4VP was synthesized by ATRP. In the ^{1}H NMR spectra for the homopolymer PNIPAM and the copolymer PNIPAM-*b*-P4VP (shown in Supplementary data), the chemical shifts at about 1.1 and 4.1 ppm can be attributed to the methyl and methine protons of the PNIPAM block, respectively. For the copolymer, characteristic peaks of the P4VP block are shown at about 6.5 and 8.5 ppm for the 2,2′ and 3,3′ protons of the pyridine ring, respectively. The polydispersity index (PDI) of PNIPAM and PNIPAM-*b*-P4VP measured by GPC is 1.26 and 1.21, respectively (shown in Supplementary data). Table 1 summarizes the results obtained for PNIPAM and $PNIPAM_{93}$-*b*-$P4VP_{58}$.

3.2. pH-responsive micellization of PNIPAM-b-P4VP

Fig. 1 shows the pH dependence of the normalized intensity of the copolymer solution at 25 °C. Clearly, the sharp increase of the scattering intensity implies the occurrence of

Table 1
Experimental results of PNIPAM and PNIPAM-*b*-P4VP by ATRP

Sample	$M_{n,th}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PDI	$M_{n(PNIPAM)}/M_{n(P4VP)}$ by ^{1}H NMR	Yield (%)
PNIPAM	1.00×10^4	1.05×10^4	1.33×10^4	1.26		72
PNIPAM-*b*-P4VP	1.60×10^4	1.62×10^4	1.97×10^4	1.21	10:6	57

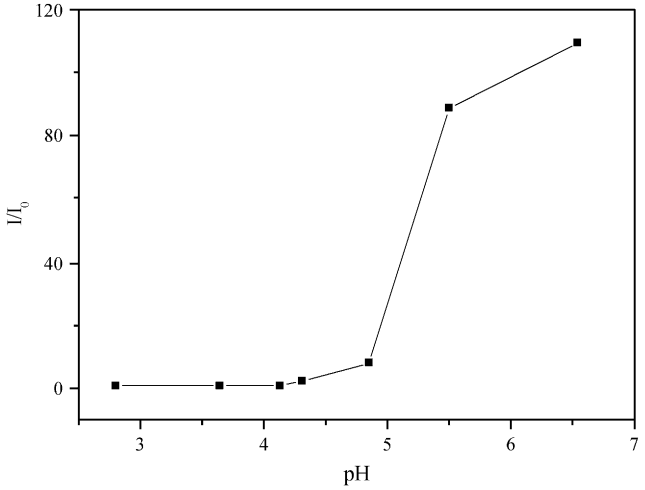


Fig. 1. pH dependence of the normalized intensity I/I_0 of the copolymer solution at 25 °C with copolymer concentration at 0.050 mg/mL.

micellization. From Fig. 1, the onset of the critical aggregation pH of the copolymer is at about 4.7, which is due to the deprotonation of the P4VP block.

Fig. 2A shows the plot of Γ/q^2 versus q^2 of PNIPAM-*b*-P4VP (0.050 mg/mL) at pH 6.5 at 25 °C. From the fitted

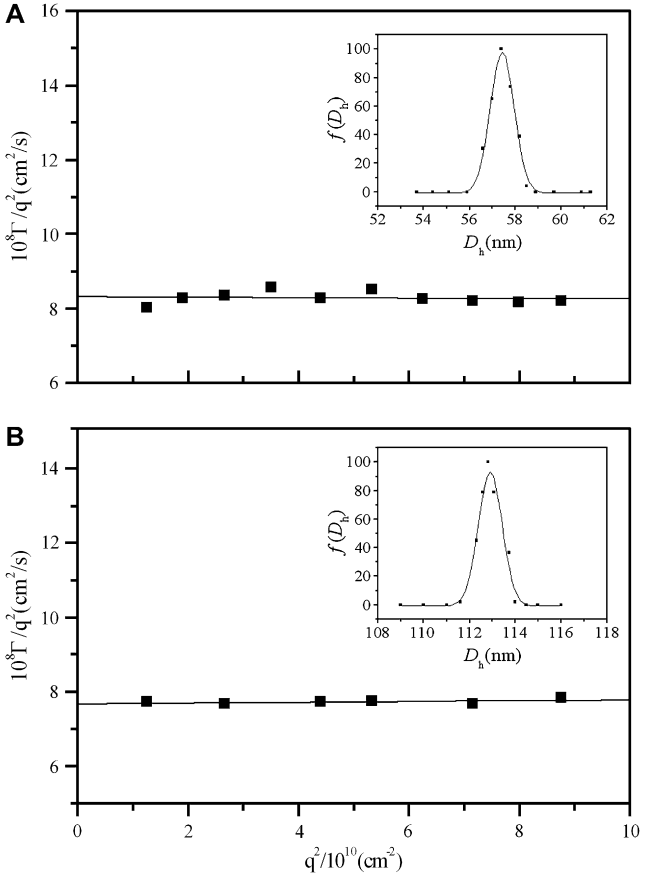


Fig. 2. Plots of Γ/q^2 versus q^2 of the PNIPAM-*b*-P4VP micelles formed with copolymer concentration of 0.050 mg/mL (A) at 25 °C and pH 6.5 and (B) at 50 °C and pH 2.8. Insets: hydrodynamic diameter distribution $f(D_h)$ under the corresponding conditions.

Table 2
Summary of DLS, SLS and TEM results for PNIPAM-*b*-P4VP solution at different pHs and temperatures

	R_h^0 (nm)	μ_2/Γ^2	R_g^0 (nm)	R_g^0/R_h^0	Radius (nm) (TEM)	M_w (SLS)	N_{agg}
pH 2.8 at 25 °C[a]	6.4	0.45	–	–	–	1.86×10^4	
pH 6.5 at 25 °C	30	0.08	24	0.8	25	1.63×10^7	0.87×10^3
pH 2.8 at 50 °C	56	0.04	45	0.81	45	9.80×10^7	5.27×10^3

[a] R_h^0 was measured by DLS at an angle of 135°, and M_w was obtained according to Eq. (2).

straight line in Fig. 2A, the translational diffusion coefficient D^0 can be calculated by extrapolating q^2 to 0, which is 8.43×10^{-8} cm^2 s^{-1}. According to the Stokes–Einstein equation, the apparent hydrodynamic diameter, D_h^0, is calculated to be 59 nm. It is also found that the Γ/q^2 value of the micelle is almost independent of q^2 which suggests that the micelles formed at pH 6.5 are uniform spheres. The apparent radius of gyration R_g^0 of the micelles is about 24 nm. Based on the specific refractive index increment d*n*/d*c* of the micellar solution (0.187 mL/g), the weight-average molar mass M_w and the apparent aggregation number N_{agg} of the micelles are calculated (see Table 2). The R_g^0/R_h^0 value of the micelles, which is about 0.80, also suggests that the micelles are spherical [26]. The inset of Fig. 2A shows the hydrodynamic diameter distribution, $f(D_h)$, of the PNIPAM-*b*-P4VP micelles at pH 6.5, which is measured by DLS at an angle of 90°. Clearly, the size of the micelles is narrowly distributed, and the relative width μ_2/Γ^2 measured by DLS is as low as 0.08. The average hydrodynamic diameter of the micelles is 59 nm. From all the evidence described above, a core–corona structure is expected to be formed with the insoluble P4VP block being the core and the soluble PNIPAM being the corona at pH 6.5.

To prove the conclusion drawn by DLS and SLS, an example of TEM measurements is shown in Fig. 3. Clearly, the aggregates are spheres uniform in size with diameter of ca. 50 nm. It is noted that the diameter of the micelles observed by TEM is lower than the D_h of the micelles measured by DLS. The possible reason is that the micelles collapsed and shrank during the process of water evaporation [27].

3.3. Thermo-responsive micellization of PNIPAM-b-P4VP

The changes in normalized intensity of the copolymer solution were studied as a function of temperature at pH 2.8 with a concentration of 0.050 mg/mL and the results are shown in Fig. 4. Still, the sharp increase of the scattering intensity implies the occurrence of micellization of PNIPAM-*b*-P4VP. From Fig. 4, the critical aggregation temperature of the copolymer is at about 36 °C as the PNIPAM block becomes insoluble. The temperature is higher than the LCST of PNIPAM, 32 °C, reported previously [28]. The possible reason is that the molar mass of the PNIPAM block ($M_n = 10\,500$) here is much lower than that reported in the literature [28]. The result

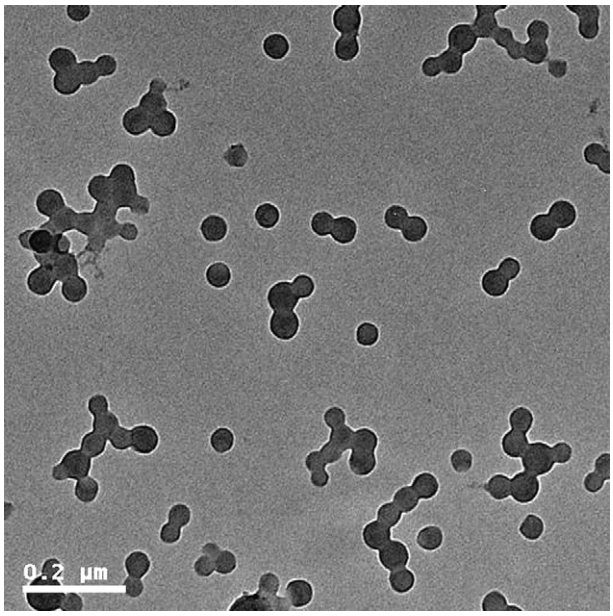


Fig. 3. A TEM image of the micelles formed with a copolymer concentration of 0.050 mg/mL at pH 6.5 at 25 °C.

is consistent with a report by Xia et al. which showed that PNIPAM with a lower molecular weight had a higher LCST [29]. Besides, the soluble P4VP blocks of the copolymer may also contribute to an increased LCST.

Fig. 5 shows the plot of apparent hydrodynamic diameter measured by DLS at an angle of 90° as a function of the concentration of the PNIPAM-*b*-P4VP solution at pH 2.8 at 50 °C. For a concentration range of 0.01–0.05 mg/mL, the apparent hydrodynamic diameter D_h^0 is almost constant at around 110 nm. The critical micelle concentration (CMC) is very low (about 0.0065 mg/mL) as shown in Fig. 5.

Fig. 2B shows the plot of Γ/q^2 versus q^2 of the PNIPAM-*b*-P4VP at pH 2.8 at 50 °C with a copolymer concentration of 0.050 mg/mL. From the line fitting in Fig. 2B, the translational diffusion coefficient D^0 can be calculated by extrapolating q^2

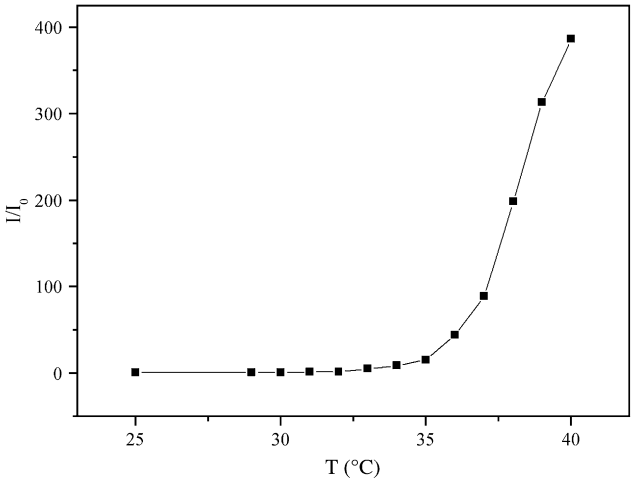


Fig. 4. Temperature dependence of the normalized intensity I/I_0 of the PNIPAM-*b*-P4VP solution at pH 2.8 with the copolymer concentration of 0.050 mg/mL.

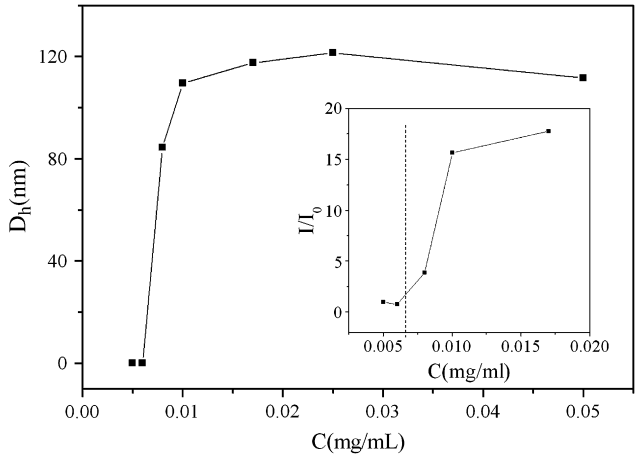


Fig. 5. The plot of apparent hydrodynamic diameter measured at 90° versus the concentration of the PNIPAM-*b*-P4VP solution at pH 2.8 at 50 °C. Inset: the plot of normalized intensity I/I_0 versus the concentration of the copolymer solution at pH 2.8 at 50 °C.

to 0, which is 7.67×10^{-8} cm^2 s^{-1}. According to the Stokes–Einstein equation, the apparent hydrodynamic diameter, D_h^0, is calculated to be 112 nm. It is also found that the Γ/q^2 value of the micelle is independent of q^2, which suggests that the micelles formed at 50 °C at pH 2.8 are uniform spheres. The apparent radius of gyration R_g^0 of the micelles is about 45 nm. The weight-average molar mass M_w and the apparent aggregation number N_{agg} of the micelles are calculated according to Eq. (1) (see Table 2). The R_g^0/R_h^0 value of the micelles, which is about 0.81, also suggests that the micelles are spherical. The inset of Fig. 2B shows the hydrodynamic diameter distribution, $f(D_h)$, of the PNIPAM-*b*-P4VP micelles at 50 °C. Clearly, the size of the micelles is narrowly distributed, and the relative width μ_2/Γ^2 measured by DLS is as low as 0.04. The average hydrodynamic diameter of the micelles is 113 nm.

Fig. 6 shows the TEM image of the dried micelles. Clearly, the aggregates are uniform spheres with a diameter of about

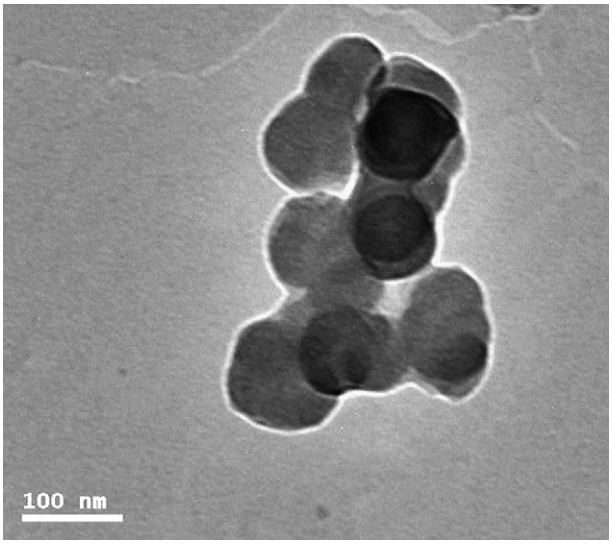


Fig. 6. A TEM image of the micelles formed at pH 2.8 at 50 °C, with a PNIPAM-*b*-P4VP concentration at 0.050 mg/mL.

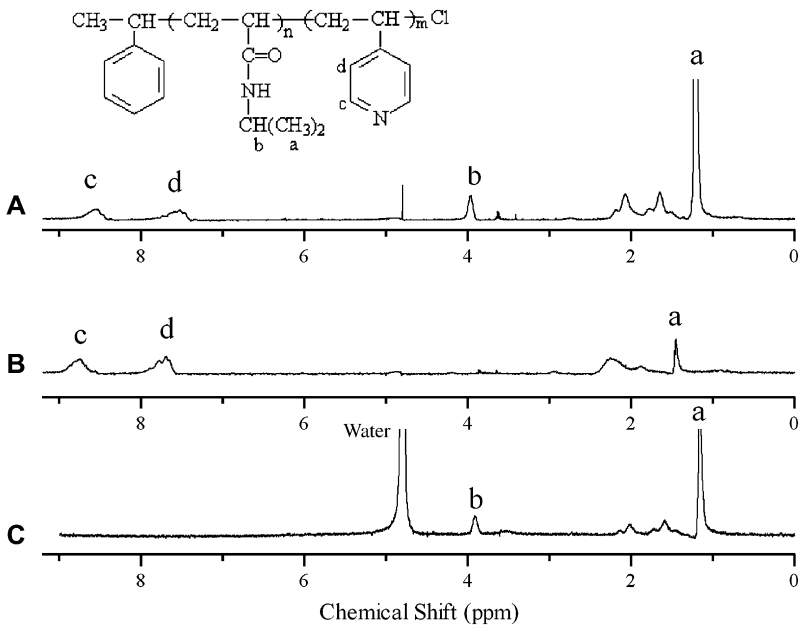


Fig. 7. ^{1}H NMR spectra obtained for PNIPAM-*b*-P4VP in D_2O (A) at pH 2.8 at 25 °C, (B) at pH 2.8 at 50 °C, and (C) at pH 6.5 at 25 °C.

90 nm. These dried particles also show a shrinkage in size in comparison with the hydrated micelles measured by laser scattering.

The micelles formed at pH 2.8 at 50 °C are much larger than those formed at pH 6.5 at 25 °C. This suggests that compound micelles or micelle clusters may be formed under such a condition. These compound micelles disassociated and dissolved into unimer in aqueous solution again by cooling the copolymer solution to 25 °C. Table 2 summarizes the related DLS, SLS and TEM results for PNIPAM-*b*-P4VP solution at different pHs and temperatures.

Fig. 7 shows the ^{1}H NMR spectra recorded for PNIPAM-*b*-P4VP in D_2O at different temperatures and pH values. At pH 2.8 at 25 °C, the diblock copolymer is molecularly dissolved and all the signals due to both blocks are visible (Fig. 7A). When the temperature was raised to 50 °C at pH 2.8, the signals attributed to the methyl and methine protons of PNIPAM block at about 1.2 and 3.9 ppm are greatly suppressed, indicating that the PNIPAM block forms the de-solvated, less mobile micelle core (Fig. 7B). On the other hand, when pH was increased from 2.8 to 6.5 at 25 °C, the signals attributed to the 2,2′ and 3,3′ protons of the pyridine ring of P4VP block at about 7.6 and 8.6 ppm are suppressed, indicating lower mobility and decreased solvation for P4VP block (Fig. 7C).

Based on the results obtained by light scattering, ^{1}H NMR and TEM, Fig. 8 summarizes that the transformation of the copolymer PNIPAM-*b*-P4VP from a water-soluble copolymer under appropriate conditions ($pH < 4.7$ and $T < 36$ °C) can form micelles with a PNIPAM core at a higher temperature or micelles with a P4VP core at a higher pH, while keeping the other conditions constant.

4. Conclusion

The inversion of the micelles formed by PNIPAM-*b*-P4VP upon a change in temperature and/or pH in an aqueous environment provides an example of the interesting transformation of the block copolymer aggregates when exposed to an external stimulus. The concept may be applied to other block copolymer systems that can respond to stimuli such as changes in pH, temperature, ionic strength and presence of bioactive species. The range of temperature and pH of response and the stability of this system are suitable for use in the biomedical fields. The reversibility of this kind of micellar association in aqueous solutions depending on the external conditions may prove to be useful for a variety of applications as mentioned in Section 1.

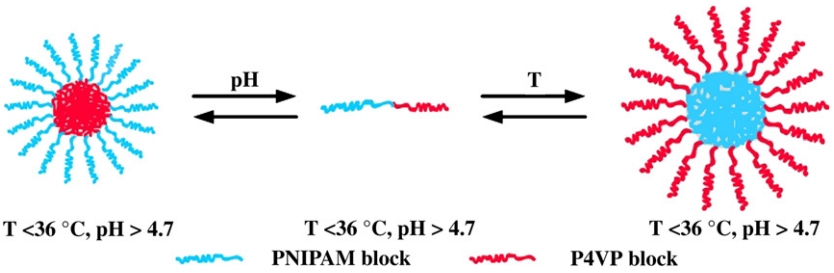


Fig. 8. Schematic representation of the formation of micelles and reverse micelles of PNIPAM-*b*-P4VP in aqueous solutions.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.polymer.2007.01.022.

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