Macromolecules **2005,** *38,* 899−903

Comicellization of Poly(ethylene glycol)-*block*-poly(acrylic acid) and Poly(4-vinylpyridine) in Ethanol

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Received October 13, 2004; Revised Manuscript Received November 22, 2004

ABSTRACT: Comicellization of poly(4-vinylpyridine) and poly(ethylene glycol)-*block*-poly(acrylic acid) in ethanol is studied by static light scattering (SLS), dynamic light scattering (DLS), and scanning electron microscopy (SEM). It is found comicellization takes place due to strong hydrogen bonding between poly(4-vinylpyridine) and the poly(acrylic acid) block when mixing poly(4-vinylpyridine) and poly(ethylene glycol)-*block*-poly(acrylic acid) in ethanol. The resultant micellar complexes are core−corona spheres with the hydrogen-bonded PAA/P4VP as core and the PEG as corona. Compared with typical amphiphilic block copolymer core−shell micelles, the present micellar complexes are much more swollen. Furthermore, it is also found the hydrodynamic diameter D_h, the gyration radius R_g^0, and the mass weight M_w of the micellar complexes can be easily tuned by changing the weight ratio of poly(4-vinylpyridine) to poly(ethylene glycol)-*block*-poly(acrylic acid).

1. Introduction

Micellization of amphiphilic block copolymers in block-selective solvents and the resultant micelles are well documented in scientific literature because of their potential in various applications, such as electrosteric stabilization of latex particles and of pigment dispersion in waterborne paints.[1] Usually, micellization of amphiphilic block copolymers in block-selective solvents is the most popular way to prepare micelles, and the resultant micelles usually consist of a core containing the insoluble block surrounded by a swollen shell of the soluble block.[2] However, it is not an easy thing to design the target amphiphilic block copolymers and then prepare the micelles. For example, for amphiphilic block copolymer of polystyrene-*block*-poly(acrylic acid), the micelles are usually prepared first by dissolving the block copolymer in a common solvent such as *N*,*N*-dimethylformamide (DMF) and then adding block-selective solvent such as water into the block copolymer solution and dialyzing against water to remove the common solvent of DMF at last.[2] Besides micellization of amphiphilic block copolymers in block-selective solvents, another method to prepare micellar aggregates in common solvents through noncovalent hydrogen bonding or electrostatic interaction is also proposed.[3−6] For example, Jiang et al. prepared spherical hollow micellar aggregates by simply mixing two polymers of carboxyl-terminated polyimide and poly(4-vinylpyridine) in their common solvent of chloroform due to hydrogen bonding between poly(4-vinylpyridine) and the carboxyl group of the polyimide;[3] Yoshida and Kunugi found that comicellization occurred when mixing 1,4-butanediamine and poly(vinylphenol)-*block*-polystyrene (PVPh-*b*-PS) in 1,4-dioxane through hydrogen-bonding cross-linking between the PVPh block and 1,4-butanediamine;[4] Wu et al. studied the comicellization of poly(styrene-*co*-4-vinylphenol) and poly(styrene-*co*-4-vinylpyridine) due to hydrogen bonding;[5] Kataoka et al. prepared polyion complex micelles from mixture of a charged block polymer and a oppositely charged compounds such as synthetic ionomers, enzymes, surfactant, and DNA;[6] and Jerome et al. prepared water-soluble micellar complexes of poly(2-vinylpyridinium)-*block*-poly(ethylene oxide) and poly(sodium methacrylate)-*block*-poly(ethylene oxide).[7] Compared with micellization of amphiphilic diblock copolymers in block-selective solvents, the method to prepare micellar aggregates by comicellization of two polymers through noncovalent hydrogen-bonding or electrostatic interaction is more facile by just simply mixing the two components in their common solvent.

Herein, we study the comicellization of block copolymer poly(ethylene glycol)-*block*-poly(acrylic acid) (PEG-*b*-PAA) and homopolymer poly(4-vinylpyridine) (P4VP) in ethanol. It is found the resultant micellar complexes are very stable in ethanol due to the soluble corona-forming PEG block of the micellar complexes, which are very similar to the typical micelles self-assembled by amphiphilic block copolymers in block-selective solvents. Furthermore, the present method has a merit that the size of the resultant micellar complexes can be easily tuned by changing the weight ratio of the homopolymer to the block copolymer.

2. Experimental Section

Materials. Polyethylene glycol monomethyl ether (CH_3O-PEG_{45}-OH) (M_w = 2000 and the polydispersity index PDI = 1.10) was purchased from Fluka. The monomer of methyl acrylate (MA) (99%) was first dried with $MgSO_4$ and then distilled at pressure about 2 mmHg. CuCl and 4-vinylpyridine were purchased from Aldrich and purified according to ref 8. 2,2′-Bipyridine (BPY) (99%) was used as received without further purification. Poly(4-vinylpyridine) (P4VP) was synthesized by atom transfer radical polymerization (ATRP) according to ref 8. The weight-average molecular weight M_w and the PDI of P4VP measured by gel permeation chromatography (GPC) using $CHCl_3$ as the eluent were 16 000 g/mol and 1.27, respectively. Other solvents were analytical chemical reagents and used as received without further purification.

Synthesis of PEG Macroinitiator. Bromide-tailed macroinitiator PEG_{45}-Br was synthesized according to ref 9. The synthetic procedures and the H NMR spectra of CH_3O-PEG_{45}-OH and PEG_{45}-Br can be seen in the Supporting Information.

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10.1021/ma0478761 CCC: $30.25

Synthesis of PEG$_{45}$-*b*-PMA$_{180}$. PEG$_{45}$-*b*-PMA$_{180}$ was synthesized by ATRP. The typical polymerization procedure was introduced as follows. 2.0 g of PEG$_{45}$-Br was added to a reaction flask, and then a 6 mL solvent mixture of butanone and 2-propanol (1:1 by volume) was added. The sample was first stirred with ultrasonic and then degassed under nitrogen purge. Subsequently, the CuCl and BPY catalysts were introduced into the reaction flask. At last, 20.0 g of methyl acrylate was added into the flask and degassed under nitrogen purge. Polymerization was performed at 120 °C for 6 h. The block copolymer PEG$_{45}$-*b*-PMA$_{180}$ was purified by first passing through a Al_2O_3 column to remove the copper catalyst and then deposited in cold ether. The PDI of PEG$_{45}$-*b*-PMA$_{180}$ measured by GPC using $CHCl_3$ as the eluent was 1.32. The composition of the block copolymer PEG$_{45}$-*b*-PMA$_{180}$ was determined by the ^{1}H NMR spectrum, as shown in the Supporting Information.

Hydrolysis of PEG$_{45}$-*b*-PMA$_{180}$. PEG$_{45}$-*b*-PMA$_{180}$ was first hydrolyzed in 10 wt % NaOH aqueous solution at 90 °C for 2 days and then neutralized with 33 wt % HCl aqueous solution until pH at about 2. The sample was then heated to remove all solvent. The product of poly(ethylene glycol)-*block*- poly(acrylic acid) (PEG$_{45}$-*b*-PAA$_{180}$) was received first by extracting with dioxane at room temperature and then depositing in cold ether.

Preparation of the Micellar Complexes. The block copolymer PEG$_{45}$-*b*-PAA$_{180}$ was dissolved in ethanol to make a 0.20 mg/mL polymer solution. P4VP was dissolved in ethanol to make P4VP solution series with different concentrations. Subsequently, 1.0 mL of P4VP solution was added into equal volume of PEG$_{45}$-*b*-PAA$_{180}$ solution at a rate of 1 drop (about 0.1 mL) every 10 s with vigorously stirring. The resultant micellar complexes were characterized by laser light scattering and scanning electron microscopy (SEM) before being kept overnight at room temperature to ensure full complexation between PEG$_{45}$-*b*-PAA$_{180}$ and P4VP.

Light Scattering Measurement. The structure of the micellar complexes was characterized by a combination of static laser scattering (SLS) and dynamic laser scattering (DLS) measurement. In DLS measurement, the Laplace inversion of a 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 relation, $G(\Gamma)$ can be transferred into a transitional diffusion coefficient distribution $G(D)$ since $\Gamma/q^2_{\theta\to 0,C\to 0} \to D$ or a hydrodynamic diameter distribution $f(D_h)$ via the Stokes−Einstein equation

$$D_h = k_b T/(3\pi\eta D) \tag{1}$$

where k_b, T, and η are the Boltzmann constant, the absolute temperature, and the solvent viscosity, respectively. In the present study, $\Gamma/q^2_{\theta\to 0}$ or D^0 of the micelles at given concentration was calculated by extrapolating q^2 to 0, and then the hydrodynamic diameter D_h^0 or the hydrodynamic diameter distribution $f(D_h)$ of the micelles at given polymer concentration was further calculated from eq 1. The radius of gyration R_g, the second virial coefficient A_2, and the weight-average mass weight of the micellar complexes M_w were calculated from SLS. On the basis of SLS theory, for a dilute polymer solution at polymer concentration C (g/mL) 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

$$[KC/R(\theta,C)] = [1/M_w][1 + (R_g^{\,2}q^2)/3] + 2A_2C \tag{2}$$

where K is the optical constant and $K = 4\pi^2n^2(\mathrm{d}n/\mathrm{d}c)^2/(N_A\lambda_0^{\,4})$ with N_A, n, and λ_0 being Avogadro's number, the solvent refractive index, and the wavelength of laser, respectively, $\mathrm{d}n/\mathrm{d}c$ is the specific refractive index increment, q is the magnitude of the scattering wave vector, and $q = (4\pi n/\lambda_0)\sin(\theta/2)$. For a given dilute polymer solution, eq 2 can be expressed as

$$[KC/R(\theta,C)] \approx [1/M_w][1 + (R_g^{\,2}q^2)/3] \tag{3}$$

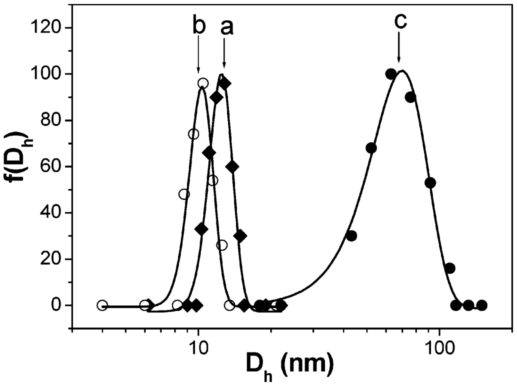

Figure 1. Hydrodynamic diameter distribution $f(D_h)$ of PEG$_{45}$-*b*-PAA$_{180}$ (a) and P4VP (b), where the polymer concentrations were 0.20 and 0.15 mg/mL, respectively, and the micellar complexes formed by dropping 0.15 mg/mL P4VP into equal volume of 0.20 mg/mL PEG$_{45}$-*b*-PAA$_{180}$ (c). All DLS measurements were performed at scattering angle 90° at 25 °C.

Based on eq 3, the apparent gyration radius R_g^0 and apparent weight-average mass weight M_w of the micellar complexes were calculated after measuring $R(\theta,C)$ at a set of θ series.

In this study, dynamic light scattering (DLS) and static light scattering (SLS) experiments were performed on a laser light scattering spectrometer (BI-200SM) equipped with a digital correlator (BI-9000AT) at 514 nm. All samples were prepared by filtering about 1 mL of the micellar complexes solution with a 0.45 μm Millipore filter into a clean scintillation vial and then measured at 25 °C. The detailed method of light scattering can be seen in our recent works or Wu's study.[10]

Scanning Electron Microscopy Observation. Scanning electron microscopy (SEM) was performed on a Hitachi S3500N at 20 kV. The samples for SEM observation were prepared by first dropping about 0.05 mL of the micellar complexes solution on a clean glass slide and then volatilizing the solution at room temperature and finally sputtering a thin gold layer about 3 nm thickness with a Hitachi E-1010 ion sputter machine.

3. Results and Discussion

3.1. Characterizing the Unimers of PEG$_{45}$-*b*-PAA$_{180}$ and P4VP in Ethanol.

Figure 1a,b shows the hydrodynamic diameter distribution $f(D_h)$ of the coils of PEG$_{45}$-*b*-PAA$_{180}$ and P4VP in ethanol. The hydrodynamic diameter D_h of the coils of PEG$_{45}$-*b*-PAA$_{180}$ ranges from 10.3 to 14.9 nm, and the apparent hydrodynamic diameter D_h^{app} can be calculated from $f(D_h)$ by $\int_0^\infty f(D_h)D_h\,\mathrm{d}D_h$, which is about 12.4 nm. Similarly, the apparent hydrodynamic diameter D_h^{app} of the P4VP unimers is about 10.3 nm. Clearly, PEG$_{45}$-*b*-PAA$_{180}$ and P4VP exist as single molecules or unimers in ethanol because ethanol is a good solvent for P4VP and PEG-*b*-PAA.

3.2 Comicellization of PEG$_{45}$-*b*-PAA$_{180}$ and P4VP.

Just as discussed above, PEG$_{45}$-*b*-PAA$_{180}$ or P4VP exists as single molecules or unimers in ethanol. However, it is well-known that PAA is a polyacid and P4VP is a polybase, and there exists strong hydrogen bonding between the polyacid and polybase in ethanol; thus, it is reasonable to think micellar complexes will form and the resultant micellar complexes compose of a hydrogen-bonded PAA/P4VP core and a soluble PEG corona when mixing P4VP and PEG$_{45}$-*b*-PAA$_{180}$ in ethanol. Actually, when dropping P4VP into the PEG$_{45}$-*b*-PAA$_{180}$ solution, micellization does occur as indicated by the appearance of turbidity in the polymer solution. Figure 1c shows the hydrodynamic diameter distribution $f(D_h)$ of the

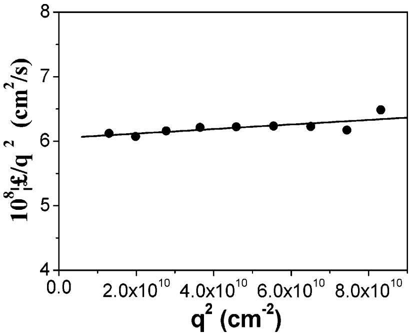

Figure 2. Plot of Γ/q^2 of the micellar complexes vs q^2, where the micellar complexes were prepared by dropping a given volume of 0.15 mg/mL P4VP ethanol solution into equal volume of 0.20 mg/mL PEG_{45}-*b*-PAA_{180} ethanol solution.

micellar complexes formed by dropping 1.0 mL of 0.15 mg/mL P4VP ethanol solution into 1.0 mL of 0.20 mg/mL PEG_{45}-*b*-PAA_{180} ethanol solution. Clearly, the apparent hydrodynamic diameter D_h^{app} of the micellar complexes is about 62 nm, which is much larger than that of the unimers of PEG_{45}-*b*-PAA_{180} and P4VP in ethanol. These results confirm the formation of the micellar complexes.

Figure 2 shows the plot of Γ/q^2 of the micellar complexes discussed above vs q^2 at 25 °C. From the fit line in Figure 2, the translational diffusion coefficient D^0 can be calculated by extrapolating q^2 to 0, which is 6.05×10^{-8} cm^2/s. Based on eq 1, the hydrodynamic diameter D_h of the micellar complexes is calculated, and the value is 66.6 nm. It is also found that the Γ/q^2 value of the micellar complexes is almost independent of q^2, which suggests that the micellar complexes are spherical.[11] In the following study, if specified otherwise, all the values of the hydrodynamic diameter D_h of the micellar complexes are calculated from the translational diffusion coefficient D^0, which is achieved by extrapolating q^2 to 0.

It is interesting that the size of the resultant micellar complexes changes with the weight ratio of P4VP to PEG_{45}-*b*-PAA_{180} [*W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180})]. Figure 3A shows the hydrodynamic diameter D_h of the micellar complexes of PEG_{45}-*b*-PAA_{180} and P4VP with different values of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}). The results show that the hydrodynamic diameter D_h of the micellar complexes increases from 61 to 162 nm and then almost keeps a constant of about 180 nm when the value of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}) increases from 0.5 to 2.5. Figure 3B shows the apparent gyration radius R_g^0 of the micellar complexes with different values of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}). Clearly, the apparent gyration radius R_g^0 of the micellar complexes increases from 36.4 to 106.2 nm when *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}) ranges from 0.5 to 2.5, which is very similar to the change of hydrodynamic diameter D_h of the micellar complexes. Here, it should be pointed out that the micellar complexes formed at *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}) equal to 1.25 (indicated by arrows in Figure 3) have equal moles of 4-vinylpyridine units (4VP) and the acrylic acid units (AA) in the micellar complexes. Clearly, the values of D_h and R_g^0 of the micellar complexes fast increase with the increase of the weight ratio of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}) when the weight ratio is below 1.25 and almost keep a constant when the weight ratio further increases from 1.25 to 2.5, which reflects the complexation between the polybase of P4VP and polyacid of PAA block.

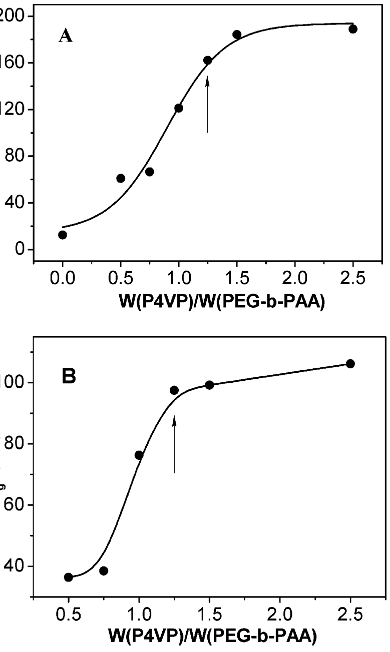

Figure 3. Hydrodynamic diameter D_h (A) and the apparent gyration radius R_g^0 (B) of the micellar complexes vs the weight ratio of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}).

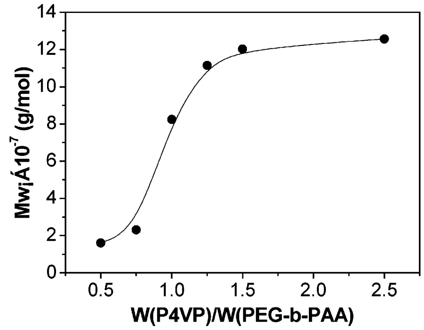

Figure 4. Apparent mass weight M_w of the micellar complexes vs the weight ratio of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}).

Assuming that the specific refractive index increment (d*n*/d*c*) of the micellar complexes can be approximately expressed as[12]

$$dn/dc = w_A(dn/dc)_A + w_B(dn/dc)_B + w_C(dn/dc)_C \quad (4)$$

where w_A, w_B, and w_C represent the weight ratio of the PEG block, the PAA block, and the P4VP unimer in the micellar complexes, respectively, the apparent mass weight M_w of the micellar complexes can be calculated by the Zimm plots of SLS, which is shown in Figure 4. The results show the apparent mass weight M_w of the micellar complexes increases from 1.61×10^7 to 12.6×10^7 g/mol and then almost keeps a constant when the value of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}) increases from 0.5 to 2.5. In the present study, the weight-average molecular weight M_w of PEG_{45}-*b*-PAA_{180} is about 20 000, which is close to that of P4VP. Thus, the total aggregation number N^{agg} of the two polymer chains in micellar complexes can be approximately calculated, which ranges from 900 to 7000 when the value of *W*(P4VP)/*W*(PEG_{45}-*b*-PAA_{180}) increases from 0.5 to 2.5.

It is well-known that the R_g/R_h value can reveal the morphology of particles in solution.[13-17] Clearly, the R_g/

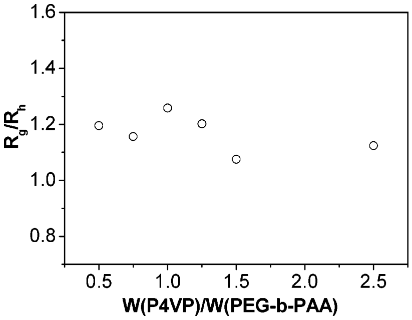

Figure 5. R_g/R_h value of the micellar complexes vs the weight ratio of $W(\mathrm{P4VP})/W(\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180})$.

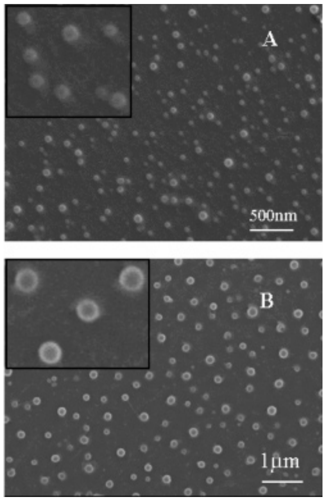

Figure 6. SEM images of the micellar complexes with the weight ratio of $W(\mathrm{P4VP})/W(\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180})$ at 0.75 (A) and 2.5 (B).

R_h value of the micellar complexes as shown in Figure 5 with different values of $W(\mathrm{P4VP})/W(\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180})$ ranges from 1.05 to 1.20. In comparison with that of random coils of homopolyer (~1.50), the R_g/R_h value of the micellar complexes is much smaller, which further confirms the formation of the micellar complexes. However, compared with typical amphiphilic block copolymer crew-cut micelles (<0.775),[12,13] the R_g/R_h value of the micellar complexes is much bigger, which possibly suggests the micellar complexes, especially the core of the micellar complexes, are a little swollen in ethanol.

To further explore the structure of the micellar complexes, scanning electron microscopy (SEM) was used to observe the morphology of the micellar complexes. Parts A and B of Figure 6 show the typical SEM images of the micellar complexes with the weight ratio of $W(\mathrm{P4VP})/W(\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180})$ at 0.75 (A) and 2.5 (B), respectively. Clearly, the diameter of the spheres in parts A and B of Figure 6 is about 50 and 150 nm, respectively. It must be noted that the values of the hydrodynamic diameter D_h of the micellar complexes measured by DLS are a little larger than those observed by SEM. This is because the micellar complexes are swollen in ethanol, while SEM observation shows the diameter of the dried aggregates of the micellar complexes. For the micellar complexes with the weight ratio of $W(\mathrm{P4VP})/W(\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180})$ ranging from 0.5 to 2.5, spheres with average diameter ranging from about 40 nm to 150 nm are also observed by SEM. These results further confirm the formation of the spherical micellar complexes when dropping P4VP into the $\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180}$ solution with the weight ratio of $W(\mathrm{P4VP})/W(\mathrm{PEG}_{45}\text{-}b\text{-}\mathrm{PAA}_{180})$ ranging from 0.5 to 2.5.

Therefore, the possible mechanism of comicellization of poly(ethylene glycol)-*block*-poly(acrylic acid) and poly(4-vinylpyridine) in ethanol due to hydrogen bonding between homopolymer of P4VP and PAA block and the formation of spherical micellar complexes can be schemed out in Figure 7.

4. Conclusions

Comicellization takes place due to strong hydrogen bonding between poly(4-vinylpyridine) and poly(acrylic acid) block when mixing poly(4-vinylpyridine) and poly(ethylene glycol)-*block*-poly(acrylic acid) in ethanol. The resultant micellar complexes are core−corona spheres with the hydrogen-bonded PAA/P4VP as core and the PEG block as corona. The hydrodynamic diameter D_h,

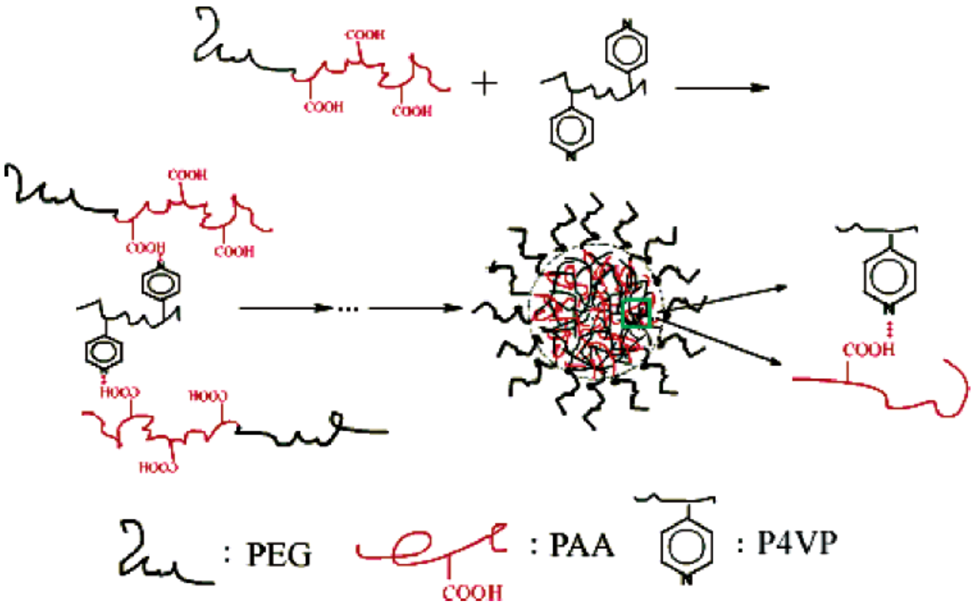

Figure 7. Schematic mechanism of comicellization of poly(ethylene glycol)-*block*-poly(acrylic acid) and poly(4-vinylpyridine) in ethanol due to hydrogen bonding between poly(4-vinylpyridine) and poly(acrylic acid) block.

apparent gyration radius R_g^0, and the apparent mass weight M_w of the micellar complexes increase from 61 to 185 nm, from 36.4 to 106.2 nm, and from 1.61×10^7 to 12.6×10^7 g/mol, respectively, when the weight ratio of W(P4VP)/W(PEG$_{45}$-*b*-PAA$_{180}$) ranges from 0.5 to 2.5. Compared with typical amphiphilic block copolymer core−shell micelles with the insoluble block as core, the R_g/R_h value of the micellar complexes is much higher since the core of the micellar complexes is composed of the swollen hydrogen-bonded PAA/P4VP blocks.

Acknowledgment. The financial support by Development Fund for Excellent Doctors of Nankai University, National Natural Science Foundation of China (No. 50273015) and Chinese Education Ministry Foundation for Nankai University, and Tianjin University Joint Academy is gratefully acknowledged.

Supporting Information Available: Text giving synthetic procedures for the macroinitiator PEG$_{45}$-Br; figures showing ^{1}H NMR spectra of CH$_3$-PEG$_{45}$-OH, PEG$_{45}$-*b*-P4VP$_{56}$, and PEG$_{45}$-Br. This material is available free of charge via the Internet at http://pubs.acs.org.

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