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pH-Dependent Micellization of Poly(2-vinylpyridine)-*block*-poly((dimethylamino)ethyl methacrylate) Diblock Copolymers

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ABSTRACT: A series of poly(2-vinylpyridine)-*block*-poly((dimethylamino)ethyl methacrylate) diblock copolymers (P2VP-*b*-PDMAEMA) have been synthesized by living anionic polymerization of the comonomers. Dynamic light scattering (DLS) has been used to study the associative behavior of these copolymers in water as a function of copolymer composition, pH, ionic strength, and temperature. Three association regimes are observed. At low pH, loose aggregates are formed, although both the P2VP and PDMAEMA blocks are protonated. At intermediate pH, micelles are observed that consist of an uncharged hydrophobic P2VP core surrounded by a protonated PDMAEMA corona. At higher pH, the PDMAEMA corona is essentially uncharged and collapses at temperatures higher than 40 °C, which results in unstable micelles. The micelles observed by transmission electron microscopy are spherical.

Introduction

Steadily increasing attention is paid nowadays to water-soluble block copolymer surfactants not only for their supramolecular organization in water but also because of potential applications in quite different fields, such as pigment stabilization in water-borne coatings[1] and drug delivery systems.[2] In most cases, the amphiphilic block copolymer molecules self-associate into micelles that consist of a core formed by the insoluble hydrophobic blocks surrounded by a shell formed by the water-soluble blocks. The field of block copolymer micelles has been recently reviewed by Hamley.[3]

However, the direct dissolution of amphiphilic block copolymers in water is quite a problem and usually requires the temporary use of an organic cosolvent, such as methanol, dimethylformamide, or tetrahydrofuran, for the preparation of stable and well-defined micelles.[4] The organic solvent can play the role of plasticizer for the hydrophobic core, and it increases the unimer/micelle exchange rate.[5] A fast exchange rate is indeed a prerequisite to reach the thermodynamic equilibrium in polymeric micelles. In a second step, the organic solvent is removed, most often by dialysis. Therefore, the final micelles observed in pure water are not in the equilibrium state, but they are rather a kinetically frozen picture of the former equilibrium or quasi-equilibrium established in the water/organic solvent mixture.[6]

A more straightforward way to prepare polymeric micelles in water consists in fixing the pH of the aqueous solution of double hydrophilic diblocks such that one block is made insoluble and results in self-aggregation into micelles. For instance, poly(2-vinylpyridine)-*block*-poly(ethylene oxide) diblock copolymers form unimers at low pH and micelles at pH higher than 4.8,[7] because the poly(2-vinylpyridine) block is then deprotonated and insoluble in water. We recently extended this concept to the pH-dependent micellization of poly(methacrylic acid)-*block*-poly(ethylene oxide) diblocks,[8] and Armes et al. reported similar examples.[9] In these systems, the micelles are thought to be close to the thermodynamic equilibrium, although the way an originally soluble block is made insoluble may have an effect on the micelles morphology. This kind of pH-sensitive diblocks can be used as pH sensors as result of the switching from nonassociated chains into micelles. They also have potential in pH-triggered encapsulation and release of molecules of interest.

pH-dependent micellization is also reported for more complex systems, e.g., block copolymers containing two ionizable blocks. Poly((dimethylamino)ethyl methacrylate)-*block*-poly(methyl methacrylate)-*block*-poly(methacrylic acid) triblocks[10] and poly((dimethylamino)ethylmethacrylate)-*block*-poly(methacrylic acid) diblocks are representative examples.[11−13] These copolymers contain ionizable weak acid and weak basic blocks, which can lead to a polyampholytic system in a limited range of pH. We recently reported on the supramolecular organization of this type of copolymers as a function of pH,[11] and we studied extensively their adsorption at a solid/liquid interface.[14] Basically, these copolymers are pH sensors based on transitions from micelles with a shell of protonated basic blocks at low pH, to soluble or unsoluble interpolyelectrolyte complexes close to the isoelectric point, and finally to micelles with a corona of ionized acid block at high pH.

Finally, pH-sensitive micellization is the rule whenever two ionizable weak basic (acid) blocks of different pK_a's are associated in the same molecule. In this respect, Armes et al. synthesized poly(2-(diethylamino)ethyl methacrylate)-*block*-poly(2-(dimethylamino)ethylmethacrylate) copolymers that formed micelles in water above a critical pH, as result of the slight difference in the pK_a's of the two aminated blocks.[15] In the present paper, poly(2-vinylpyridine)-*block*-poly((dimethylamino)ethyl methacrylate) diblocks (P2VP-*b*-PDMAEMA) are studied. This system has the advan-

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Table 1. Molecular Characteristic Features of the P2VP-*b*-PDMAEMA Diblock Copolymers

entry	$\bar{M}_n$ P2VP	$\bar{M}_n$ diblock	$\bar{M}_w/\bar{M}_n$ diblock	diblock composition (P2VP wt %)
1	3500	7300	1.3	48
2	5000	9000	1.3	68
3	8000	10800	1.2	74

tage of a larger difference in the pK_a's of the two basic blocks compared to the diblock studied by Armes et al. Finally, this copolymer is expected to be a pH sensor, in relation to a change in the structure of the self-aggregates.

Experimental Part

Polymer Synthesis. The diblock copolymers were synthesized by sequential living anionic copolymerization, with rigorously purified and dried monomers and solvents. Briefly, the monomers were purified by distillation over triethylaluminum. The glass reactor containing the required amount of LiCl (10/1 LiCl/initiator molar ratio) was flame-dried under vacuum, purged with nitrogen, added with the solvent (tetrahydrofuran distilled over benzophenone sodium), and cooled to −78 °C. Diphenyl methyl potassium was used to initiate the polymerization of 2VP at −78 °C. Thirty minutes later, an aliquot was picked out from the reactor and analyzed by size exclusion chromatography (SEC). DMAEMA was then added and polymerized for 2 h at −78 °C. The copolymerization medium was then quenched with methanol. The copolymers were characterized by SEC and nuclear magnetic resonance (NMR). SEC was performed in tetrahydrofuran added with 1% (v/v) triethylamine, using a Hewlett-Packard 1050 liquid chromatograph equipped with two Plgel columns (1000 and 10 000 Å, respectively) and a Hewlett-Packard 1047A refractive index detector. Polystyrene standards were used for calibration. ^{1}H NMR spectra were recorded at 400 MHz with a Bruker AM 400 spectrometer. $\bar{M}_n$ of the second block was calculated from the ^{1}H NMR spectrum of the copolymer and $\bar{M}_n$ of the first block. The (co)polymers were purified by dialysis against regularly replaced distilled water for 1 week. Water was finally removed by lyophilization. The molecular characteristics of all the copolymers considered in this study are listed in Table 1.

Aqueous solutions of the copolymers were prepared by dissolution of known amounts of copolymers in pH-adjusted bidistilled water. The copolymer concentration was generally set to 1 g/L, unless specified. pH was controlled by using 50 mM phosphate buffer.

Dynamic Light Scattering (DLS). DLS measurements were performed with a Brookhaven Instruments Corp. DLS apparatus that consists of a BI-200 goniometer, a BI-2030 digital correlator, and an Ar ion laser (LEXEL Lasers) with a wavelength of 488 nm. The scattering angle used for the measurements was 90°. A refractive index matching bath of filtered decalin surrounded the scattering cell, and the temperature was controlled at 25 °C. Prior to sample loading, appropriate glass vessels were soaked overnight in sulfochromic solution, thoroughly cleaned by bidistilled water, and dried in a vacuum oven.

The scattering angle was 90°, and the second-order correlation function $G_2(t)$ was measured. In the case of single-exponential decay, $G_2(t)$ can be expressed by eq 1:

$$G_2(t) = B[1 + \beta \exp(-2\Gamma t)] = B[1 + \beta|G_1(t)|^2] \qquad (1)$$

where B is the baseline, β is an optical constant that depends on the instrument, Γ is the decay rate for the process, t is time, and $G_1(t)$ is the first-order correlation function. Γ is given by

$$\Gamma = Dq^2 \qquad (2)$$

where D is the translation diffusion coefficient, and q is the absolute value of the scattering vector

$$q = [4\pi n \sin(\theta/2)]/\lambda \qquad (3)$$

n is the refractive index of the solvent, θ is the diffusion angle, and λ is the wavelength of the incident light.

The diffusion coefficient extrapolated to zero concentration (D_0) for spherical particles is related to the hydrodynamic radius, R_h, by the Stokes−Einstein equation:

$$D_0 = k_B T/6\pi\eta R_h \qquad (4)$$

where k_B is the Boltzmann constant, T is the absolute temperature, and η is the viscosity of the solvent.

The polydispersity index of the micellar aggregates was estimated from the μ_2/Γ^2 ratio, in which μ_2 was determined by analysis of the first-order correlation function by the method of the cumulants.

$$G_1(t) = \exp[-\Gamma t + (\mu_2/2)t^2 - (\mu_3/3!)t^3 + ...] \qquad (5)$$

Transmission Electron Microscopy (TEM). TEM observations were carried out with a Philips CM 100 operating at a voltage of 100 kV. A Gatan 673 CCD camera was used to directly record the TEM pictures which were then transferred to a computer equipped with the Kontron KS 100 software.

Samples were prepared by dipping Formvar-coated copper TEM grid into the aqueous copolymer solution added with a very small amount of $HAuCl_4$ (10 mol % of the aminated groups). The excess of copolymer solution was wiped off with a paper filter, and the grid was dried under ambient atmosphere for 1 h.

Results and Discussion

The association behavior of diblock copolymers consisting of two weak basic blocks of different pK_a's was studied by Gast et al. in the case of poly(2-(diethylamino)ethyl methacrylate)-*block*-poly(2-(dimethylamino)ethyl methacrylate) (PDEAEMA-*b*-PDMAEMA) diblocks.[15b] Potentiometric titration, fluorescence spectroscopy, DLS, and small-angle neutron scattering confirmed the formation of micelles in water whenever the degree of protonation of the copolymer chains exceeded a critical value. However, once the micelles were formed, their characteristic features were independent of the ionic strength, which suggested the formation of nonionic micelles that consist of a insoluble PDEAEMA core surrounded by an uncharged PDMAEMA corona. The vicinity of the pK_a's of the PDEAEMA and PDMAEMA blocks thus prevented polyelectrolyte-type micelles from being formed. In contrast, the diblocks investigated in this study should lead to the formation of polyelectrolyte micelles with a hydrophobic P2VP core and a partially protonated PDMAEMA corona in a limited pH range, as result of the substantial difference in the pK_a's of P2VP (pK_a ∼ 5)[7,16] and PDMAEMA (pK_a ∼ 8).[10] At higher pH, micelles with a neutral PDMAEMA corona are expected to be formed.

This paper is divided into five sections. First, the association of the P2VP-*b*-PDMAEMA diblocks has been studied as a function of pH and copolymer composition, with some references to the pH-dependent behavior of the constitutive homopolymers. Several association regimes have been accordingly identified. The effect of temperature has been then examined in the different association regimes. The effect of concentration has also been investigated in order to measure the critical micellar concentration (cmc). Additional information about the micellar structure has been collected by probing the effect of the ionic strength. Finally, the

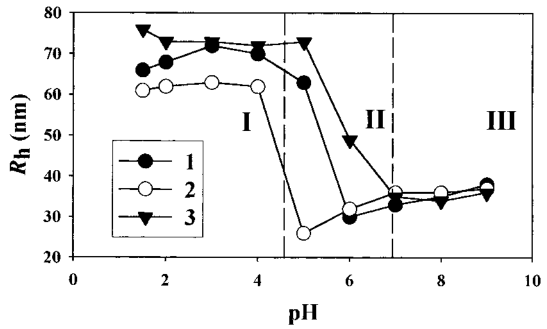

Figure 1. R_h as a function of pH for the investigated P2VP-*b*-PDMAEMA diblocks ($C = 1$ g/L). For the sake of comparison, the three aggregation regimes (I, II, and III) have been indicated.

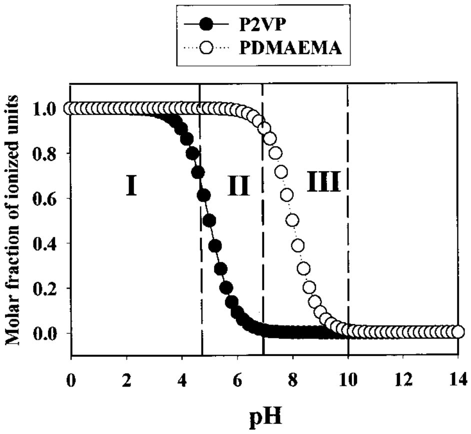

Figure 2. Theoretical dependence of the molar fraction of the ionized units in P2VP and PDMAEMA as a function of pH. For the sake of comparison, the three aggregation regimes (I, II, and III) have been indicated.

morphology of the micelles formed in each association regime has been directly observed by TEM.

pH-Dependent Association of P2VP-*b*-PDMAEMA Diblock Copolymers. The hydrodynamic radius (R_h) of the self-associates formed by the three investigated diblocks has been plotted as a function of pH in Figure 1. At pH < 5, aggregates have been observed with R_h in the 60−75 nm range (regime I). This observation is quite surprising since, in this pH range, both the P2VP and PDMAEMA blocks are protonated (Figure 2). A possible explanation might be found in the complex ionization of P2VP. Indeed, a transition in the P2VP conformation was observed at a degree of neutralization of 0.5.[17] This critical neutralization degree was molecularly explained by the sharing of one proton by two neighboring 2VP units, and it was identified, e.g., by a sharp increase in the light scattering turbidity and in the intensity (I) dissymmetry ratio ($I_{45°}/I_{135°}$).[18] Moreover, it was suggested that aggregates could be formed at intermediate neutralization degrees because of the coexistence of uncharged hydrophobic 2VP units and charged ones, which engage themselves in self-aggregation. Indeed, the uncharged units were assumed to self-assemble into hydrophobic cores surrounded by the ionized units.[17] Because this aggregation could happen intra- or/and intermolecularly and charged units could be entrapped into the hydrophobic cores, loose aggregates were expected to be formed. The same behavior of the P2VP blocks of the diblocks may not be precluded in this study, so accounting for the aggregation observed at low pH. A second association regime is observed in the $4.5 < \text{pH} < 7$ range, in which aggregates with R_h of ca. 30 nm are formed. These aggregates are thought to be micelles with an hydrophobic P2VP core and a protonated PDMAEMA corona (regime II). In the $7 < \text{pH} < 10$ range, the PDMAMEA block is almost deprotonated and micelles with a hydrophobic P2VP core and an essentially uncharged PDMAEMA corona are formed (regime III). Finally, at pH > 10, the copolymers become insoluble.

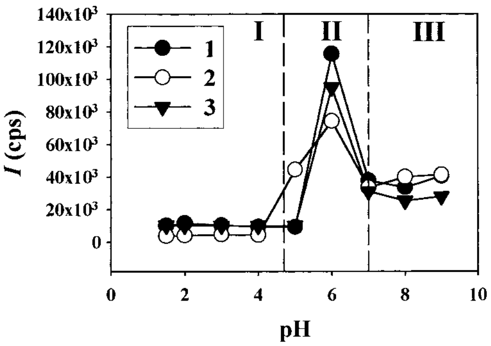

Figure 3. Scattered intensity (I) as a function of pH for the investigated P2VP-*b*-PDMAEMA diblocks ($C = 1$ g/L). For the sake of comparison, the three aggregation regimes (I, II, and III) have been indicated.

To give credit to this proposal of three association regimes, Figure 2 shows how the protonation degree of P2VP and PDMAEMA depends on pH. The validity of these curves is however limited by the approximation that the pK_a's of P2VP (5) and PDMAEMA (8) are independent of the ionization degree. Nevertheless, the qualitative comparison of the ionization of each block and the aggregation regimes is quite consistent as shown in Figure 2. At pH < 4.5, both the P2VP and PDMAEMA blocks are quasi-completely charged (regime I). In regime II, the charge of the P2VP blocks decreases rapidly with increasing pH, in contrast to the charge of the PDMAEMA block which remains essentially constant. Finally, in regime III, the P2VP block is no longer charged, and the charge density of the PDMAEMA block decreases dramatically as the pH is increased.

Additional information has been extracted from the dependence of the scattered intensity on pH, as shown in Figure 3. In the first association regime, the scattered intensity is low, in agreement with a small number of aggregates and/or formation of loose aggregates. When the micellization starts, a strong upturn in intensity is observed for each copolymer under consideration. Finally, the micelles are characterized by a scattered intensity significantly higher that the one observed at low pH. From the data reported in Figures 1 and 3, it appears that the characteristic features of the micelles or aggregates do not depend on the copolymer composition, at least for regimes I and III. Moreover, no clear tendency has been observed for the charged micelles formed in regime II (see data at pH = 5 and 6 in Figure 1). These observations contrast to the common report that the size and/or morphology of copolymer micelles change with the copolymer composition.[19] However, the restricted number of samples examined in the present study impedes a clear conclusion from being drawn.

The size distribution of the aggregates/micelles formed by the copolymers has been estimated from the μ_2/Γ^2 ratio, which is plotted as a function of pH in Figure 4. This figure confirms the formation of two different types

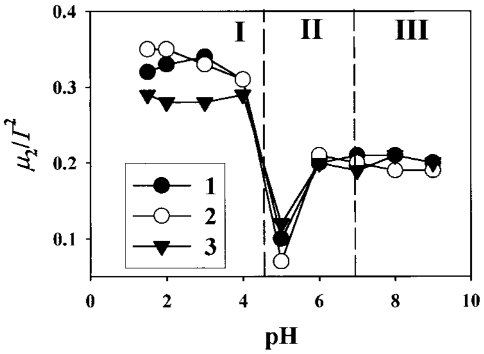

Figure 4. μ_2/Γ^2 as a function of pH for the investigated P2VP-*b*-PDMAEMA diblocks ($C = 1$ g/L). For the sake of comparison, the three aggregation regimes (I, II, and III) have been indicated.

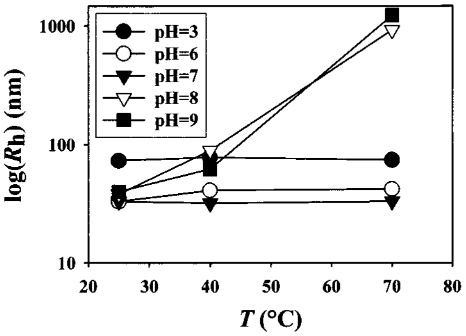

Figure 5. R_h as a function of temperature (T) for the diblock **3** ($C = 1$ g/L) at different pH's.

of aggregates/micelles depending on the pH. Polydisperse aggregates, with μ_2/Γ^2 of ca. 0.3, are formed in regime I, whereas micelles with μ_2/Γ^2 of ca. 0.2 are observed at pH higher than 6. Micelles with a low μ_2/Γ^2 of ca. 0.1 are detected in regime II (Figure 4). It must be noted that the micelles in regime II scatter light more strongly than the micelles or aggregates in regimes I and III (Figure 3) and that their size is smaller (Figure 1). These experimental observations are consistent with the formation of well-defined dense micelles in regime II and suggest a critical pH at which the segregation of the P2VP and PDMAEMA blocks is sharp and leads to monodisperse dense micelles. According to Figures 1, 3, and 4, this critical pH would be in the $5 < \text{pH} < 6$ range, i.e., in the range where the difference in the ionization degrees of the two blocks is in the extreme (no ionization for P2VP and complete ionization for PDMAEMA, as shown in Figure 2). A less sharp demixing of the constitutive blocks in regimes I and III would account for formation of micelles that are larger (see Figure 1), less dense (see the decrease in scattered intensity in Figure 3), and much more polydisperse (Figure 4) than in regime II.

Effect of Temperature. The effect of temperature can contribute to elucidate the micellar structure. Indeed, uncharged PDMAEMA is known for a cloud point at ca. 40 °C.[13] Therefore, micelles consisting of an uncharged PDMAEMA corona must precipitate out from the solution or flocculate above 40 °C, as result of the collapse of the PDMAEMA steric barrier. Figure 5 shows the effect of temperature on the diblock **3** at different pH's, the same dependence being observed for the two other diblocks (data not shown). According to these data, the aggregates formed at pH = 3 (regime I) are insensitive to temperature, which strongly indicates that they are not stabilized by uncharged PDMAEMA blocks. The same conclusion holds for the micelles formed at pH = 6 and 7 (regime II), which therefore contain an essentially protonated PDMAEMA corona. A marked effect of temperature is reported for the micelles formed at pH = 8 and 9 (regime III). A substantial increase in the micellar size is observed at 40 °C. At higher temperatures, the size measured by DLS goes on increasing until micrometer-sized colloidal particles are formed. In parallel, the solutions turn highly turbid. These observations are strong evidence for the formation of micelles stabilized by an essentially uncharged PDMAEMA corona in regime III.

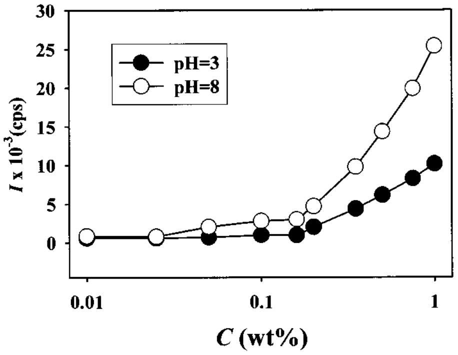

Figure 6. I as a function of concentration (C) of diblock **1** at different pH's.

Table 2. Cmc Determined by DLS for the Investigated P2VP-*b*-PDMAEMA Copolymers at pH = 3, 6 and 8

	1	2	3
cmc (g/L), pH = 3	0.18	0.11	0.05
cmc (g/L), pH = 6	0.17	0.10	0.03
cmc (g/L), pH = 8	0.17	0.12	0.04

Effect of Concentration. DLS was used to determine the critical micelle concentration (cmc) by plotting the scattered intensity as a function of the logarithm of concentration.[20] A sharp break in this curve was assigned to the cmc. Figure 6 shows the dependence of the scattered intensity on the diblock **1** concentration at two pH's. A break in the scattered intensity is clearly seen at the two investigated pH's. Therefore, a cmc can be assigned to the aggregates formed at low pH and to the micelles observed at higher pH. The very close vicinity of the two cmc's must be pointed out. The cmc's measured by DLS at pH = 3 (regime I), 6 (regime II), and 8 (regime III) are listed in Table 2 for the investigated diblocks. For all the samples, the cmc's measured at these three pH's are essentially the same, although the cmc strongly depends on the copolymer composition. Indeed, the higher the P2VP content is, the lower the cmc. This observation is consistent with the trend commonly reported in the scientific literature for amphiphilic diblocks, according to which the cmc decreases when the hydrophobic content of the copolymers is increased.[21]

Effect of the Ionic Strength. Addition of a salt is a very simple way to modulate the ionic strength of a colloidal solution and to give consistency to stabilization by an electrostatic mechanism. Indeed, addition of salt results in the compression of the electrical double layer that protects the particles and the ultimate flocculation. Therefore, whenever a polyelectrolyte corona stabilizes micelles, the increase in the ionic strength results in decreasing electrostatic repulsions between neighboring charged units in the same chain or not, which occurs at the expense of the stretching of the corona-forming

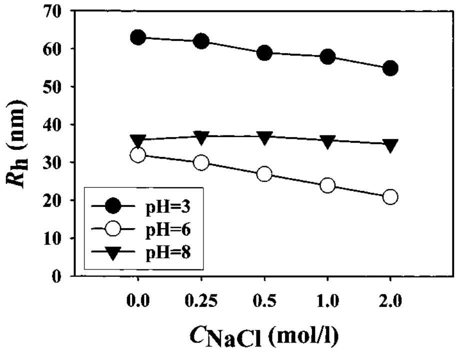

Figure 7. R_h as a function of NaCl concentration (C_{NaCl}) for the diblock **3** (C = 1 g/L) at different pH's.

blocks and results in smaller R_h.[22] In some cases, the addition of salt is a prerequisite for the micelle formation because the electrostatic repulsion between the polyelectrolyte blocks is too strong for micelles to be stable.[23]

The experimental data plotted in Figure 7 show that the aggregates formed in regime I (pH = 3) are sensitive to the ionic strength, because their size decreases when the NaCl concentration is increased. The same conclusion is valid to the micelles observed at pH = 6 (regime II), which are thought to consist of a hydrophobic P2VP core surrounded by a protonated PDMAEMA corona. Finally, the size of the micelles formed at pH = 8 (regime III) is independent of NaCl concentration, which confirms that basically uncharged components are involved; i.e., uncharged hydrophobic P2VP forms, the core which is surrounded by an essentially uncharged water-soluble PDMAEMA corona.

Morphology of the Micelles Formed by the P2VP-*b*-PDMAEMA Diblocks. Formation of micelles by the P2VP-*b*-PDMAEMA diblocks has been confirmed by TEM. For this purpose, micellar solutions were added with $HAuCl_4$, which is known for selective interaction with amines.[24] Small amounts of $HAuCl_4$ were added, so that the pH of the buffered micellar solutions was not significantly perturbed. This staining did not perturb the micellar structure, as confirmed by DLS data for stained and unstained samples. These solutions were then deposited on Formvar-coated TEM copper grid and dried under ambient atmosphere. Electron irradiation in the microscope caused reduction of the Au^{3+} salt into gold nanoparticles, as discussed elsewhere.[24b,25] Therefore, the micelles can be considered as templating reactors for the synthesis of gold nanoparticles.[24-26] Because the two blocks of the P2VP-*b*-PDMAEMA copolymers contain amine moieties, both the core and the corona of the micelles should be stained. Figure 8 illustrates the aggregates formed by the diblock **1** at low pH (regime I). Few large and polydisperse aggregates are observed throughout the sample. Although some contrast is observed within these aggregates, it is weak in agreement with the hypothesis of formation of loose aggregates. In sharp contrast, dense micelles are observed for the copolymer **1** at pH = 8 (regime III, Figure 9a). Micelles are observed with a diameter ranging from ca. 70 to 120 nm, which has to be compared to the average hydrodynamic diameter measured by DLS for the same micelles, i.e., 70 nm. Therefore, the micelles tend to spread out on the Formvar grid onto which they are deposited. Another interesting feature may be noted in Figure 9, i.e., the tendency of individual micelles to stick one to each other. Figure 9b shows that several micelles are "trapped" in a continuous film, which might indicate that the unprotonated PDMAEMA corona is soft because of a T_g close to room temperature and tends to act as a glue for the dried particles. Consistently, sticky micelles are not observed at pH = 6 (regime II), thus when the PDMAEMA corona is protonated and of a higher T_g. Finally, it must be noted that essentially the same observations are reported for the diblocks **2** and **3**.

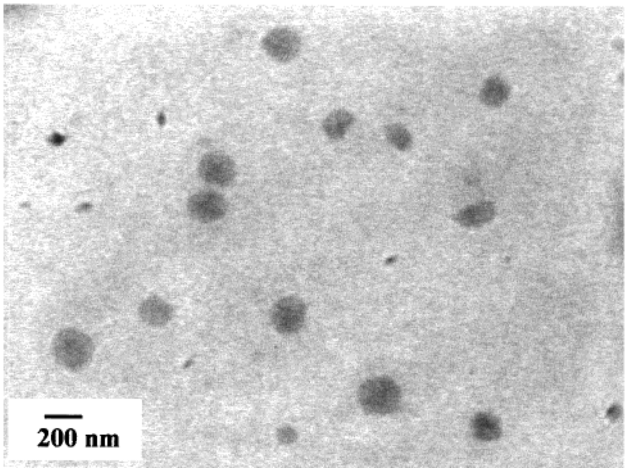

Figure 8. TEM picture for the aggregates formed by the diblock **1** at pH = 3.

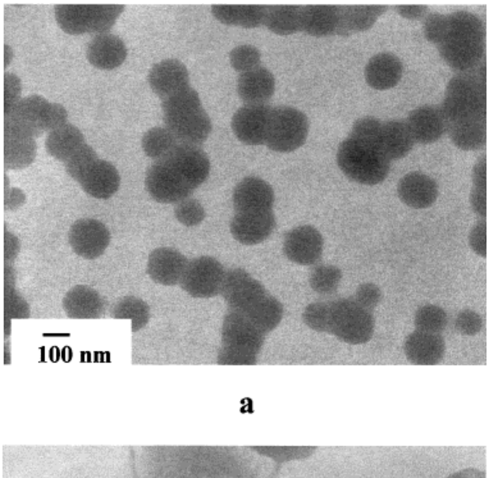

Figure 9. TEM pictures for the micelles formed by the diblock **1** at pH = 8. TEM pictures have been recorded at low magnification (a) and high magnification to show how the micelles stick together (b).

Conclusions

This paper reports on the pH-dependent association of P2VP-*b*-PDMAEMA diblock copolymers. Different types of micelles/aggregates have been detected. At low pH, polydisperse loose aggregates are formed, although the two blocks are protonated. These aggregates are sensitive to the ionic strength but not to the temperature. Their detailed structure is not yet cleared up. At pH of ca. 5, spherical micelles are formed that contain a hydrophobic P2VP core and a protonated PDMAEMA corona. The electrostatic repulsion of the charged coronal chains is reduced by Debye screening. Finally at higher pH, micelles consist of a hydrophobic P2VP core surrounded by an essentially uncharged PDMAEMA corona. Although these micelles are not sensitive to the ionic strength, they flocculate above the cloud point of PDMAEMA (ca. 40 °C), due to the collapse of the protective chains. These copolymers can be seen as pH sensors, in relation to the possible switching between two distinct types of aggregates/micelles.

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