Onion-Type Micelles in Aqueous Media

Karel Procházka*

Department of Physical and Macromolecular Chemistry, Faculty of Science,
Charles University in Prague, Albertov 2030, 128 40 Prague 2, Czech Republic

Thomas J. Martin,† Stephen E. Webber,* and Petr Munk*

Department of Chemistry and Biochemistry and Center for Polymer Research,
The University of Texas at Austin, Austin, Texas 78712

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ABSTRACT: Poly(*tert*-butyl acrylate)-*block*-poly(2-vinylpyridine) (PBA-*b*-PVP) in acidic aqueous solutions forms micelles with PBA cores and PVP shells. When this micellar solution is brought to pH higher than 4.8 , the PVP shells collapse and the copolymer precipitates. However, when a sample of acid water soluble poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PVP-*b*-PEO) is present, its PVP blocks coprecipitate with PVP blocks of PBA-*b*-PVP and form a dense outer core. The PEO blocks then stabilize this complex onion-type structure. Static and dynamic light scattering measurements revealed that for small values of the (PVP-*b*-PEO)/(PBA-*b*-PVP) mass ratio the resulting particles are multimicellar clusters. When the ratio is sufficiently large, the solution contains onion-type micelles. However, the outer core of these micelles can incorporate only a limited number of PVP blocks from the PVP-*b*-PEO copolymer. The excess PVP-*b*-PEO molecules then form independent smaller micelles with PVP cores and PEO shells.

Introduction

Within our broad-range studies of block copolymer micellar systems in aqueous media[1] we have been trying to develop new types of micellar structures. In this paper we report our first successful preparation of three-layered micelles.

The interesting and potentially applicable properties of block copolymer micelles are based on their two-layered structure.[2] A typical polymeric micelle consists of a compact core formed by the insoluble blocks and a diffuse shell formed by the soluble blocks. The novel three-layer "onion-type" micelles with a compact inner core surrounded by an outer core formed by another insoluble polymer and a soluble shell, broaden considerably the field of possible applications.

Recently we have synthesized and studied a series of diblock copolymers containing a poly(2-vinylpyridine) block, PVP. Poly(2-vinylpyridine) is protonated and soluble in water at low values of pH and deprotonated and fairly hydrophobic at pH higher than 4.8. The sudden change in hydrophobicity of PVP in a narrow pH region allows for a pH-controlled preparation of polymeric micelles.

In the accompanying paper,[3] we have studied micellization of a poly(*tert*-butyl acrylate)-*block*-poly(2-vinylpyridine), PBA-*b*-PVP, in aqueous buffers. At low pH this copolymer forms spherical micelles with compact PBA cores and protonated PVP shells. The micelles are stable at pH below 4.8 and precipitate at higher pH.

We have also studied micellization of poly(2-vinylpyridine)-*block*-poly(ethylene oxide), PVP-*b*-PEO.[4] This copolymer dissolves molecularly in aqueous solutions at low pH and forms micelles with deprotonated PVP cores at pH above 4.8. The micelles may solubilize a considerable amount of the PVP homopolymer in their cores. Micelles with solubilized PVP are much larger than the original micelles; however, they are still relatively monodisperse.

The precise pH-matching of the precipitation of PBA-*b*-PVP and the appearance of PVP-*b*-PEO micelles suggests that it may be possible to stabilize the PBA-*b*-PVP micelles by the PVP-*b*-PEO copolymer at high pH. Studying the pH behavior of aqueous mixtures of both copolymers, we have found that stable onion-type micelles can be prepared during simple titration.

Experimental Part

Materials. Poly(*tert*-butyl acrylate)-*block*-poly(2-vinylpyridine) (PBA-*b*-PVP) was the same sample as described in the accompanying paper.[3] The poly(vinylpyridine) block had molecular weight M_W = 27 000 and M_W/M_N = 1.07. The copolymer was rather polydisperse with M_W = 79 000 and M_W/M_N = 1.28. The weight fraction of PVP was 0.47.

The sample of poly(2-vinylpyridine)-*block*-poly(ethylene oxide), PVP-*b*-PEO, was purchased from Molecular Sources, Inc., Quebec, Canada. Its PVP block had molecular weight M_W = 14 000 g/mol and M_W/M_N = 1.03. The copolymer had M_W = 29 000 g/mol and M_W/M_N = 1.05. The weight fraction of PVP was 0.48.

Quasi-elastic Light Scattering.[5] The apparent hydrodynamic radii of micelles, R_H, were measured at low, albeit finite concentrations using a Brookhaven BI 2030 apparatus with 72-channel correlator and a He−Ne laser as a source of the incident light (632.8 nm). In the QELS experiment, one measures the intensity−intensity correlation function, $G^{(2)}(t,q)$,

$$G^{(2)}(t,q) = \langle I(t,q)I(0,q)\rangle = A\{1 + \beta[g^{(1)}(t,q)]^2\} \qquad (1)$$

where $I(0,q)$ and $I(t,q)$ are scattering intensities separated by the time interval t and q is the value of the scattering vector, $q = (4\pi n/\lambda_0)\sin(\theta/2)$, where n is the refractive index of the solvent, λ_0 is the wavelength of the light in vacuum, θ is the scattering angle, A is the baseline, and β is a parameter dependent on the coherence area that is detected. In a polydisperse system of scattering particles, the first order correlation function, $g^{(1)}(t,q)$, is related to the characteristic line width distribution function, $G(\Gamma)$

$$g^{(1)}(t,q) = \int_0^\infty G(\Gamma)\exp(-\Gamma t)\,d\Gamma \qquad (2)$$

The method of cumulants was used to treat the experimental correlation curves. In this method, correlation curve $g^{(1)}$-

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* To whom the correspondence should be addressed.

† Present address: CONDEA Vista Chemical, 12024 Vista Park Drive, Austin, Texas 78726-4026.

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(t,q) is expanded into a power series in t

$$g^{(1)}(t,q) = \exp[-\langle\Gamma\rangle t + (\mu_2/2)t^2 - (\mu_3/3!)t^3 + ...] \qquad (3)$$

This approach allows for evaluation of the z-average translation diffusion coefficient of spherical particles, D_T, from the average line width, $\langle\Gamma\rangle$, $D_T = \langle\Gamma\rangle/q^2$, and of the polydispersity index, $\mu_2/\langle\Gamma\rangle^2$. The hydrodynamic radius, i.e., the radius of a hydrodynamically equivalent sphere, R_H, is then calculated using the Stokes–Einstein relation, $R_H = kT/6\pi\eta D_T$ where η is viscosity and kT has its usual meaning. The QELS measurements yield the z-average $\langle R_H^{-1}\rangle_z$ that is very sensitive to the presence of large particles in the samples studied. QELS data also provide information on the sample polydispersity. When the distribution function $G(\Gamma)$ is numerically fitted to a model function using the non-negatively constrained least square algorithm (NNLS), the z-distribution function of particle sizes is obtained.

Static Light Scattering. The time-averaged intensities of the scattered light, I, were also measured using the Brookhaven 2030 apparatus: the total number of counts *per* constant time (proportional to the intensity I) is measured under constant optical conditions. The Rayleigh ratio for vertically polarized light, R_v, is evaluated from the following equation using the literature value for benzene[6] at 632.8 nm, $R_B(\theta{=}90°) = 12.55 \times 10^{-6}$ cm^{-1}

$$R_v(\theta{=}90°) = R_B(\theta{=}90°)(n/n_B)^2\left\{\frac{I - I_S}{I_B - I_D}\right\} \qquad (4)$$

where I is the measured intensity, I_S and I_B are those of the solvent and benzene, respectively, and I_D corresponds to the dark counts.

Values of the refractive index increments were estimated as weighted averages on the basis of the copolymer composition and refractive index increments of homopolymers.[7] Since the particle molar mass of micelles is very high, concentrations for light scattering measurement ranged from 10^{-6} to 10^{-4} g/mL. Solutions for measurement were clarified by centrifugation since we have found that sorption of a copolymer sample on filter material (0.45 μm PVDF) changes the polymer concentration significantly (i.e., the copolymer concentration decreases by ca. 10–25%, depending on concentration, after each repeated filtration step using fresh filters). However, ultrafiltration does not change the measured size and polydispersity of micelles with R_H ca. 55 nm. Filtration by 0.20 mm PVDF filters decreases not only the concentration (by 40–60% depending on the concentration and on the volume filtered) but also the polydispersity. By filtering larger volumes, we have observed saturation, i.e., the larger the volume filtered, the smaller the scattering intensity decrease observed. Micellar sorption on filters is fairly reversible, i.e., micelles may be partially washed out from a filter by pure water or buffers and the original micellar size is recovered.

Results and Discussion

We have studied by light scattering techniques mixtures of PBA-*b*-PVP micelles at constant concentration ($c_0 = 1.54 \times 10^{-4}$ g/mL in 0.1 M HCl) with several concentrations of the PVP-*b*-PEO copolymer. Figure 1 shows the apparent hydrodynamic radii, R_H, and intensities of the scattered light as a function of the concentration of PVP-*b*-PEO. The intensities of the scattered light correspond to the sum of intensities produced by the separate components.Values of R_H decrease with increasing concentration of PVP-*b*-PEO only slightly. This decrease is probably due to electrostatic interactions. As discussed above, the measured values of R_H correspond to the z-average , $<R_H^{-1}>_z$, and are insensitive to the concentration of the unimers of PVP-*b*-PEO that have a molar mass some 2 orders of magnitude smaller than the micelles. Thus no association between the two components has been detected at low concentrations in acidic solutions.

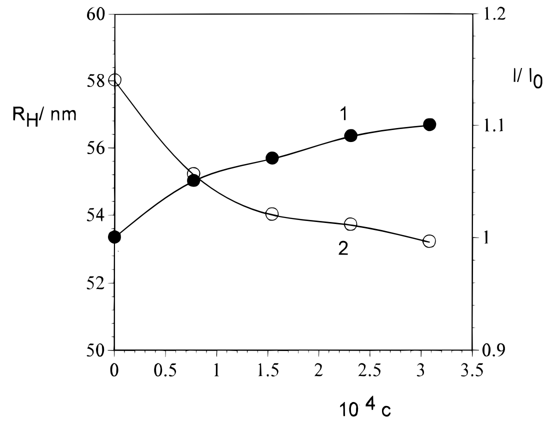

Figure 1. Relative scattering intensities I/I_0 (I_0 measured in the absence of the PVP-*b*-PEO copolymer (curve 1) and hydrodynamic radii (curve 2) of PBA-*b*-PVP micelles ($c_0 = 1.54 \times 10^{-4}$ g/mL in 0.1 M HCl) in the presence of the PVP-*b*-PEO copolymer as a function of the concentration of the latter copolymer, c (in g/mL).

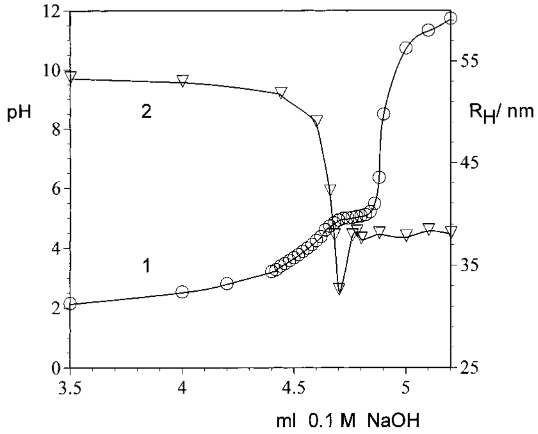

Figure 2. Titration of a mixture (weight ratio 1/1) of PBA-*b*-PVP and PVP-*b*-PEO copolymers in 0.1 M HCl by 0.1 M NaOH. pH of the solution (curve 1) and apparent hydrodynamic radii (curve 2) as a function of the added amount of NaOH.

The onion-type micelles form during the titration of acidic aqueous mixtures of PBA-*b*-PVP micelles and molecularly dissolved PVP-*b*-PEO samples by aqueous solution of NaOH. Figure 2 shows a typical titration curve of a mixture containing PBA-*b*-PVP and PVP-*b*-PEO copolymers (weight ratio 1/1) in 0.1 M HCl by 0.1 M NaOH. Curve 1 shows pH of the solution as a function of the added amount of NaOH. Curve 2 shows the apparent hydrodynamic radii of the micelles measured by QELS. Only the final part of the titration curves is depicted, because the initial part corresponds to the titration of the great surplus of HCl in the solution. The shape of curve 2 may be explained as follows: The protonated PVP blocks in PBA-*b*-PVP micelles are stretched at low pH and the micellar hydrodynamic radius is fairly large (R_H ca. 57 nm in 0.1 M HCl). Values of R_H decrease only little with increasing pH in the region below pH 4 but decrease sharply above pH 4 due to the deprotonation of the PVP blocks that is accompanied by a pronounced diminution of the shell thickness. A minimum value of ca. 32 nm is achieved at pH 4.78. At pH 4.8 the onion-type micelles are formed. Their appearance is clearly manifested by a sudden deepening of the bluish tint due to increased light scattering. At this particular pH, R_H attains a constant value ca. 38 nm and does not change with the further increase in pH. The polydispersity measured by QELS is reasonably low and constant ($\mu_2/\langle\Gamma\rangle^2 < 0.1$).

The titration curves are fully reversible. By adding HCl to alkaline solutions of onion-type micelles, the same curve is obtained in reverse. The onion-type micelles dissociate below pH 4.8 into their components and the original R_{H} of PBA-*b*-PVP micelles is recovered. Repeated back and forth titrations yield onion-type micelles reproducibly with reproducible R_{H} values.

Two things in Figure 2 deserve special mention. (a) Onion-type micelles start appearing when about 15% of the pyridine units are still protonated. (b) The part of the titration curve between the appearance of the onion-type micelles and the neutralization of the remaining protonated groups is much flatter than curves obtained when titrating typical weak polyelectrolytes.[8] In our opinion, these observations are a result of the same phenomenon. When the deprotonization of the pyridinium groups reaches a point at which the PVP chains are no longer soluble, they start to collapse onto the core and form its outer layer. Simultaneously, the PVP blocks of the PVP-*b*-PEO copolymer start being incorporated into the micelles. Because the concentration of PVP chains (polyelectrolyte chains) in this newly forming outer layer of the core is higher than that in the outside solution and the effective dielectric permitivity is lower than that in the outside solution, the effective dissociation constant of the pyridinium moieties increases in the outer core. As a result, the fraction of the deprotonated groups in the outer layer of the core is larger than that in the outside solution. In other words, the outer solution (still containing some PVP-*b*-PEO unimers) becomes depleted with respect to the deprotonated groups and the ratio of the deprotonated and protonated pyridine groups in the outer solution ($c_{\mathrm{D}}/c_{\mathrm{P}}$) decreases. Thus, with progressing titration the newly deprotonated groups enter preferentially the outer core and the ratio $c_{\mathrm{D}}/c_{\mathrm{P}}$ in the outer solution changes much more slowly than if the micelle formation did not take place. As a first approximation, the pH-rise during titration may be expressed by the following formula

$$\mathrm{pH} = \mathrm{p}K'_{\mathrm{a}} + \log(c_{\mathrm{D}}/c_{\mathrm{P}}) \qquad (5)$$

where K'_{a} is the apparent dissociation constant of protonated PVP in the aqueous phase. Since the second term in the right-hand side of eq 5 increases only a little as compared with titrations of soluble polyelectrolytes, the pH rise is very small.

Preliminary experiments indicated that during the preparation of the onion-type micelles only a fraction of the PVP-*b*-PEO copolymer enters the collapsing shell of the PBA-*b*-PVP micelles. In order to get quantitative information on this phenomenon, we have designed the following experiment: We have prepared separate solutions in 0.1 M HCl of the PBA-*b*-PVP micelles and the PVP-*b*-PEO copolymer. Then we mixed identical aliquots of the micelles with various amounts of the PVP-*b*-PEO copolymer and adjusted the volume of the samples by adding 0.1 M NaCl in such a way that during the subsequent titration by 0.1 M NaOH the complete neutralization of the solutions (the steep increase of the titration curve) would occur at the same concentration of the PBA-*b*-PVP micellar component. We then titrated the mixtures under vigorous stirring to pH of about 10. This procedure guaranteed that the onion-type micelles are formed, and their properties are later studied, at the same concentration ($c_0 = 1.54 \times 10^{-4}$ g/mL) of the PBA-*b*-PVP component in all samples. The samples were made dust-free by centrifugation and were studied by QELS, evaluating both the light scattering intensity I and the R_{H} values. These measurements were also performed on the original acidic solution of the PBA-*b*-PVP micelles adjusted to the same concentration (the measured intensity of this reference solution is denoted I_0) and on the alkaline solutions of the PVP-*b*-PEO copolymer at appropriate concentrations. These measurements provide the necessary background intensities for the analysis of the data.

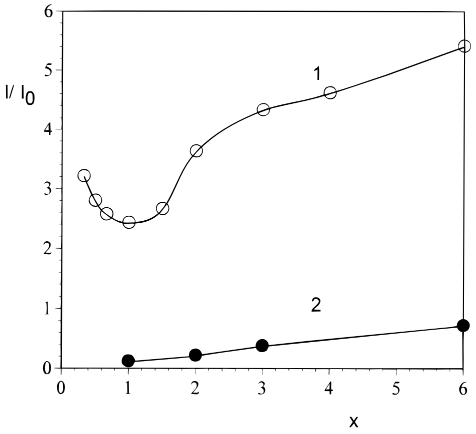

Figure 3. Relative intensity I/I_0 of light scattering of the PVP-*b*-PEO copolymer in the presence (curve 1) and absence (curve 2) of PBA-*b*-PVP micelles in an alkaline solution as a function of relative concentration $x = c/c_0$. I_0 and c_0 refer to the PBA-*b*-PVP micelles (in acidic solution) when PVP-*b*-PEO copolymer is not present; c is the concentration of PVP-*b*-PEO.

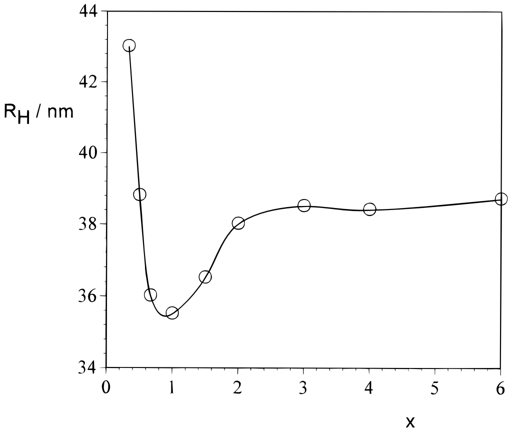

Figure 4. Apparent hydrodynamic radius of particles for the same solutions as in Figure 3 as a function of $x = c/c_0$.

In Figure 3 the relative intensity I/I_0 is plotted as a function of $x = c/c_0$ where c is the concentration of the PVP-*b*-PEO copolymer (curve 1). Curve 2 shows the values obtained for corresponding solutions of PVP-*b*-PEO copolymer in the absence of PBA-*b*-PVP micelles. In solutions of mixed copolymers, the relative scattering intensity, which is large for mixtures with a small amount of PVP-*b*-PEO, decreases with increasing x in the region of low x. It reaches a minimum at the value of x about 1.0 and increases again for large x. The hydrodynamic radius, R_{H} (Figure 4), decreases at first with x, goes through a minimum at $x = 1.0$, then increases again for $x > 2.0$. Polydispersity (not shown) decreases from $\mu_2/\langle\Gamma\rangle^2 = 0.18$ for $x = 0.2$ to $\mu_2/\langle\Gamma\rangle^2 = 0.08$ for $x > 2.0$, and then it is almost constant within the range of experimental errors (0.06−0.09).

For a quantitative discussion of association processes in polymeric systems studied by light scattering, refractive index increments of both polymeric components must be taken into account. Refractive index increments of block copolymers were calculated using the literature values of increments of corresponding homopolymers and mass ratios of blocks in individual copolymer samples.[7] The following values were used: for PVP, d*n*/d*c* = 0.27 g/mL; for PBA, d*n*/d*c* = 0.13 g/mL; for PEO, d*n*/d*c* = 0.13 g/mL. Since the mass ratio in our both PBA-*b*-PVP and PVP-*b*-PEO samples is very close to 1.0, the samples studied have the same value of the refractive index increment, d*n*/d*c* = 0.20.

The shape of experimental curves in Figures 3 and 4 may be explained as follows. In the region of low x, the relative amount of the PVP-*b*-PEO copolymer is not sufficient for stabilization of all individual PBA-*b*-PVP micelles in the form of separate onion-type micelles. The original micelles aggregate and various aggregates are stabilized as larger colloidal particles. The apparent hydrodynamic radius R_H, polydispersity, and the ratio I/I_0 increase with decreasing x. At $x < 0.33$, even the partial stabilization is inefficient and a precipitation of a small fraction of PBA-*b*-PVP is detected. The measured R_H and polydispersity values (less than 0.2) suggest that in the low x region a major portion of both copolymers forms relatively small and compact micellar clusters composed of two, three, etc., micellar cores with combined shells.

Low and almost constant values of R_H are obtained for $x \geq 2.0$ and these values are only slightly larger than the minimum value obtained during titration of mixtures before onion-type micelles are formed. This observation, together with a relatively low polydispersity ($\mu_2/\langle\Gamma\rangle^2 < 0.09$), suggests that micellar clusters are not present to any significant extent in these solutions. Since the relative amount of the stabilizing copolymer PVP-*b*-PEO is high, we assume that individual PBA-*b*-PVP micelles are stabilized as separate onion-type micelles. We propose the following model for this system: The number of onion-type micelles is constant and given by the number of original PBA-*b*-PVP micelles which represent nucleation centers for the three-layer micelle formation. The PBA core from each original PBA-*b*-PVP micelle forms the inner core of the onion type micelle and the middle insoluble layer is formed by collapsed PVP blocks from the original PBA-*b*-PVP micelle and PVP blocks from several tens of PVP-*b*- PEO chains. The outer layer (micellar shell) contains flexible PEO chains.

The thickness of the middle layer is determined by geometric and thermodynamic factors that control the thermodynamic stability of the whole multicomponent system. It means that the number of PVP-*b*-PEO chains for a thermodynamically favorable stabilization of one original micelle of a certain size is under given conditions strictly limited. If the relative concentration of the stabilizing copolymer PVP-*b*-PEO is large, not all chains of the stabilizing copolymer are engaged in formation of onion-type micelles and a certain fraction of them forms "normal" two-layered PVP-*b*-PEO micelles that are smaller than the three-layered micelles. Such micelles with deprotonated PVP cores and PEO shells form also in alkaline solutions in the absence of the PBA-*b*-PVP micelles and they are the subject of a study presented elsewhere.[4]

If we assume that the number of onion-type micelles is equal to the number of original PBA-*b*-PVP micelles for $x > 1.0$, we may treat the formation of onion-type micelles as a special case of the preferential sorption of PVP-*b*-PEO copolymer chains onto PBA-*b*-PVP micelles. This sorption is accompanied by formation of PVP-*b*-PEO micelles that are smaller than the onion-type micelles and make a minor contribution to the total scattering intensity (this contribution will be corrected for, see later). The approach is formally identical to the procedure described in our paper in which we studied the preferential adsorption of mixed solvents onto micelles.[9] In that paper, we have shown that the ratio I/I_0 is related to the extent of adsorption on micelles as

Table 1. Light Scattering Intensity as a Function of Solution Composition and Sorption Ratio

x	I/I_0 [a]	I/I_{cor} [b]	δ [c]	δ_{cor} [c]	N
0.333	3.252				1.83
	3.287				1.85
0.5	2.790				1.24
	2.285				1.02
0.667	2.521	2.510	(0.588)	(0.584)	(0.91)
	2.569	2.560	(0.603)	(0.600)	(0.92)
1.0	2.216	2.210	0.471	0.469	
	2.198	2.193	0.569	0.467	
1.5	2.617	2.498	0.618	0.581	
	2.650	2.532	0.628	0.591	
2.0	3.611	3.463	0.900	0.861	
	3.623	3.475	0.903	0.864	
3.0	4.328	4.070	1.080	1.017	
	4.439	4.185	1.107	1.046	
4.0	4.608	4.225	1.147	1.055	
	4.609	4.225	1.147	1.055	
6.0	5.403	4.778	1.330	1.186	
	5.453	4.829	1.335	1.197	

[a] I—values from alkaline solutions containing mixture of copolymers PBA-*b*-PVP ($c_0 = 1.54 \times 10^{-4}$ g/mL) and PVP-*b*-PEO ($c = xc_0$). I_0—value from the acid solution of PBA-*b*-PVP micelles (concentration c_0). [b] The correction used reflects a non-negligible contribution of PVP-*b*-PEO micelles (that coexist in the solution with the highly scattering onion-type micelles) to the measured intensity of the scattered light. [c] Experimental and corrected values of the ratio of mass of copolymer PVP-*b*-PEO that is sorbed on copolymer PBA-*b*-PVP (see text).

$$\frac{I}{I_0} = \left[1 + \frac{m_{\mathrm{sorb}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{sorb}}}{m_{\mathrm{mic}}(\mathrm{d}n/\mathrm{d}c)_{\mathrm{mic}}}\right]^2 \tag{6}$$

Therefore the relative mass of sorbed copolymer to micelles, δ, is given by

$$\delta \equiv \frac{m_{\mathrm{sorb}}}{m_{\mathrm{mic}}} = \frac{(\mathrm{d}n/\mathrm{d}c)_{\mathrm{mic}}}{(\mathrm{d}n/\mathrm{d}c)_{\mathrm{sorb}}}\,[(I/I_0)^{1/2} - 1] = (I/I_0)^{1/2} - 1 \tag{7}$$

Here m_{mic} and m_{sorb} are the mass of the original micelle and that of adsorbed material onto this micelle, respectively. In the present case (i.e., for the pair of copolymers studied and for their particular compositions), the ratio of the refractive index increments is unity, which permits the final expression in eq 7. As a first approximation, we have evaluated δ from eq 7. The results are given in Table 1. It is apparent that only a part of the PVP-*b*-PEO copolymer is present within the onion-type micelles. The remainder is in the outside solution in the form of small micelles similar or identical to the micelles existing in the solution of the PVP-*b*-PEO copolymer in the absence of the PBA-*b*-PVP copolymer. Obviously, these small micelles scatter the light as well and their contribution to the total intensity I must be subtracted. (This contribution is evaluated as the product of the concentration of the PVP-*b*-PEO copolymer that is not part of the onion-type micelles with the intensity *per* unit concentration of small micelles obtained from an independent experiment—curve 2 presented in Figure 3.) The quantity δ is then reevaluated using the corrected value of I. This corrective process requires approximately two iterations to converge. The corrected data are also shown in Table

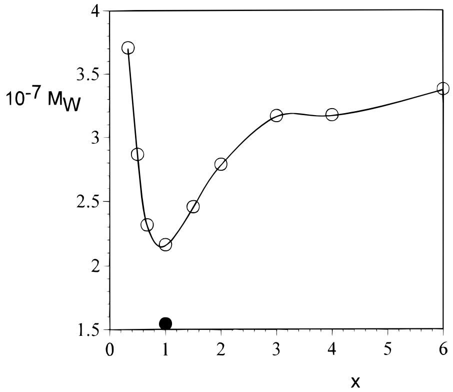

Figure 5. Molar mass of dominant particles in the solutions of onion-type micelles as a function of $x = c/c_0$. The mass of the PBA-*b*-PVP homomicelle is indicated by the filled symbol.

1. It is apparent that the mass of the onion-type micelles rapidly approaches the saturation value with δ ca. 1.2. Of course, this value corresponds only to the two particular samples of copolymers utilized in this study.

As mentioned above, all measurements were performed at low, however, finite, copolymer concentrations and at the constant scattering angle $\theta = 90°$. Measurements in a lower concentration region $10^{-5}-10^{-4}$ g/mL indicate that virial coefficients of the original and onion-type micellar solutions are small and their effects on the ratio I/I_0 are likely to cancel to a large extent. Similarly, the size of stable onion-type micelles is comparable with that of PBA-*b*-PVP micelles and the angular dependences of the measured intensities, which should be taken into account for the precise evaluation of micellar masses, mutually also compensate.

The above described procedure is not applicable for mixtures with $x < 1.0$. It would yield amounts of adsorbed PVP-*b*-PEO copolymer that are larger than those actually present. We therefore assume that all stabilizing copolymer is a part of the complex particles and we easily evaluate the average number ($N = (I/I_0)/(1 + x)^2$) of PBA cores in the micellar clusters that are presumably present in the solution. The results are also presented in Table 1.

The molar mass of PBA-*b*-PVP micelles in acid water, $M_w^{(app)} = 15.4 \times 10^6$ g/mol, was measured by a static light scattering Fica 50 apparatus and evaluated using the Zimm plot (see the preceding paper[3]) . This value was used to recalculate QELS intensities to obtain absolute values of molar masses of the onion-type micelles. We have found it very satisfying that the molecular weight evaluated from the intensity measurements using the Brookhaven 2030 instrument and eq 4 (one point measured at single concentration and single angle) fit quite well into the Zimm plot mentioned above. In separate experiments, we have found that the relative amount of the PVP-*b*-PEO copolymer in the complex micelles does not depend on the total concentration of the copolymers during the titration procedure but rather it depends only on the mass ratio of the two components, *x*. This is in contrast to the comicellization of PVP-*b*-PEO and PVP reported separately.[4]

The dependence of the molar mass of the dominant particles in our mixed system on the parameter *x* is presented in Figure 5. The dominant particles in the region $x < 1$ are multimicellar clusters, for $x > 1$ they are onion-type micelles. These molar masses are significantly higher than the micellar mass of the PVP-*b*-PEO copolymer which we have estimated from the data shown in Figure 3, curve 2, as $M_W = 1.5 \times 10^6$ g/mol, assuming that the structure of PVP-*b*-PEO micelles which form during pH titrations in a pure system (i.e., containing only PVP-*b*-PEO) and in the mixture with the onion-type micelles is the same.

Summary

1. (PBA-*b*-PVP) forms micelles in acidic solutions with PBA cores and PVP shells. When this micellar solution is mixed with molecular solution of PVP-*b*-PEO and brought to pH higher than 4.8 larger micelles are formed.
2. When the relative amount of the PVP-*b*-PEO copolymer is sufficiently large it solubilizes the PBA-*b*-PVP micelles (which have now collapsed PVP blocks) and forms the onion-type micelles.
3. Only a limited amount of the PVP-*b*-PEO copolymer can combine with the collapsed micelles. The excess PVP-*b*-PEO forms smaller micelles with PVP cores and PEO shells.
4. When the relative amount of the PVP-*b*-PEO copolymer is too small, the entities formed are multimicellar clusters.
5. The theory of preferential adsorption onto polymers in mixed solvents can be used successfully to characterize these complex multipolymer systems. For the particular pair of copolymers studied, the mass ratio of the sorbed PVP-*b*-PEO copolymer to PBA-*b*-PVP micelles is approximately 1.2 when the PVP-*b*-PEO copolymer is present in a large excess.

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