Onion-Type Micelles from Polystyrene-*block*-poly(2-vinylpyridine) and Poly(2-vinylpyridine)-*block*-poly(ethylene oxide)

Maria Ruela Talingting, Petr Munk,* and S. E. Webber*

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

Zdenek Tuzar

Institute of Macromolecular Chemistry, Academy of Sciences of Czech Republic, Heyrovsky Sq. 2, 162 06, Prague 6, Czech Republic

Received August 11, 1998; Revised Manuscript Received December 17, 1998

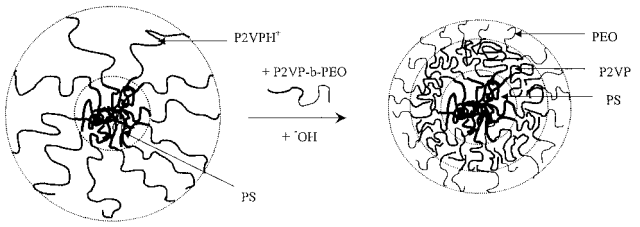
ABSTRACT: Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-PVP) was synthesized by anionic polymerization. Micellization of PS-*b*-PVP was accomplished by dissolving the polymer in a 45:50:5 volume ratio methanol:dioxane:water mixture followed by a stepwise dialysis into a 0.1 M HCl solution. The hydrophobic PS blocks form the core of the micelles, and the protonated $PVPH^+$ forms the outer shell. Addition of poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PVP-*b*-PEO) and titration to a pH above 10 causes a coprecipitation of the PVP blocks of both copolymers, forming three-layered micelles that we refer to as "onion" micelles. The micellar structures were investigated by static and dynamic light scattering and transmission electron microscopy. The weight ratio of PVP-*b*-PEO to PS-*b*-PVP was varied during the onion micelle preparation to study the fraction of PVP-*b*-PEO that is adsorbed on the PS-*b*-PVP "core micelle". The stability with respect to dilution of the micelles formed from PS-*b*-PVP and of the onion micelles was studied.

Introduction

Studies on polymer micelles have been actively pursued by a variety of groups for the past 30 years.[1] Our group has particularly emphasized micelles comprised of a glassy core and a polyelectrolyte corona in aqueous media.[2] One motivation for the study of polymer micelles in water is their potential as drug carrier systems.[3,4,5] We are also interested in micelles of different architectures, and this paper focuses on a type of three-layered micelles that we have denoted "onion-skin" or "onion-type" micelles.[6] Three-layered micelles of a triblock copolymer ABC have been reported recently.[7] Multilayered micelles may provide for innovative applications, and an understanding of the structure and dynamics of this type of micelle may also influence general concepts about polymer stabilization of colloids and the self-organization of polymers. We note the recent papers from the Eisenberg group that describe unusual copolymer aggregate morphologies that are produced by the addition of a nonsolvent (water) to an organic solution (DMF) of the copolymer.[8] This process is analogous to the titration method discussed later. For our polymers the lengths of the hydrophobic and hydrophilic chains are roughly equal, while for the Eisenberg work the hydrophilic chain is relatively short (so-called "crew-cut" copolymer aggregates).

The onion-type micelles we discuss herein are similar to the poly(*tert*-butyl acrylate)-*b*-poly(2-vinylpyridine) system published earlier.[6] They are formed from two different diblock copolymers AB and BC containing a common block B by a two-step process. First, the copolymer that will form the inner part of the final micelle (AB) is converted to micelles, and these are brought into a solvent in which the second copolymer (BC) is molecularly soluble. Then the BC copolymer is added, and the solvent environment is changed to reduce the solubility of the block B common to both copolymers. These blocks collapse together, presumably forming a layer around the core A. The remaining, unique block C of the second polymer remains soluble and forms the corona of the final micelle (see Scheme 1). This process is analogous to colloid stabilization but is distinct because of the simultaneous collapse and interpenetration of the common polymer blocks. In the present paper characterization of these micelles is accomplished using static and quasi-elastic light scattering and TEM techniques. The results of a small-angle neutron scattering study that provide a deeper insight into the onion-type particle structure will be reported in a separate paper.[9]

Scheme 1



Experimental Section

Chemicals and Instrumental. *General Materials.* Styrene and 2-vinylpyridine monomers and THF solvent were purchased from Aldrich and were purified extensively before use (Supporting Information).

Poly(2-vinylpyridine)-*block*-poly(ethylene oxide) (PVP-*b*-PEO) was purchased from Polymer Source Inc., Dorval, Quebec, Canada. According to the manufacturer, the molecular weight of the PVP block was 14 200 and of the PEO block 15 400; M_w/M_n was 1.06 (this value was verified independently in our laboratory).

Gel Permeation Chromatography. The GPC system consisted of a Waters pump (model 510) and four Waters Millipore μStyragel columns (10^5, 10^4, 10^3, and 500 Å, in order of flow)

10.1021/ma981269u CCC: $18.00 © 1999 American Chemical Society
Published on Web 02/11/1999

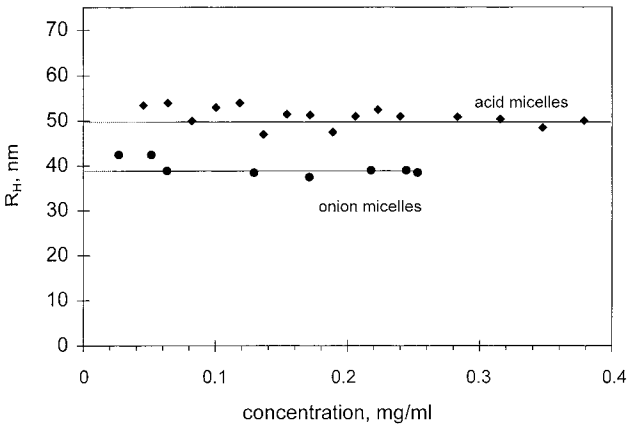


Figure 1. R_H for PS-*b*-PVPH$^+$ (acid micelles) and PS-*b*-PVP/PVP-*b*-PEO (onion micelles) as a function of concentration.

using a Hewlett-Packard 1050 UV-vis diode array detector and a Waters differential refractometer R401 for detection. THF was used for the mobile phase at a flow rate of 1.5 mL/min. Polystyrene standards (Scientific Polymer Products) of molecular weights 17K, 35K, 70K, and 135K were used for calibration.

NMR Measurements. All NMR spectra were obtained using a Bruker AC-300 spectrometer (300 MHz). The proton spectra were referenced to residual solvent ($CDCl_3$) protons.

Static Light Scattering (SLS). For these measurements we use a modified FICA 50 instrument. The data were analyzed using Zimm plots which yield the weight-average molecular weight M_w, radius of gyration R_G, and the second virial coefficient A_2. The refractive index increments for the solutions in aqueous solutions were estimated as weighted averages on the basis of the copolymer composition and literature data[10] for refractive index increments (in mL/g) of the homopolymers (PS latexes in water, dn/dc = 0.257; PVP in methanol, dn/dc = 0.27; PEO in water, dn/dc = 0.13). The weight average for PS-*b*-PVP is 0.268 ≈ 0.27 (w_{PS} = 0.392). The refractive index increment for the PS-*b*-PVP copolymer in THF as measured with Brice-Phoenix differential refractometer was 0.167.

Quasi-Elastic Light Scattering (QELS). These measurements employed a Zeta Plus instrument with a model BI-9000 AT digital correlator (Brookhaven Instruments). For the evaluation of the quality of a micelle preparation we use the cumulant analysis as described by Kiserow and Prochazka,[2g] which yields the hydrodynamic radius R_H. For characterization of particle size distributions we have employed the CONTIN method of analysis supplied as part of the software by Brookhaven. This method in most instances produced a distribution of hydrodynamic radii that had a well-developed narrow peak corresponding to the micelles studied.

TEM Sample Preparation and Instrumentation. In all cases a given micelle solution was diluted sufficiently to yield well-separated particles, and approximately 0.1 mL of the solution was placed on a carbon−copper TEM grid that had been chilled in liquid nitrogen. The solution froze immediately and was transferred into a vacuum chamber for freeze-drying. For the PS-*b*-PVPH$^+$ micelles the dilution medium was 0.1 M HCl (PVPH$^+$ is the protonated polypyridine). For the PVP-*b*-PEO and PS-*b*-PVP/PVP-*b*-PEO onion micelles the dilution medium was pure H_2O rather than 0.1 M NaCl (i.e., the background salt after the titration) because the NaCl crystals would seriously compromise the TEM images. It was verified by QELS that R_H did not change under low salt conditions. The sample was stained by exposure to RuO_4 vapor in a closed reaction vessel. Ruthenium tetraoxide was produced in situ by reacting ruthenium dioxide hydrate with excess sodium periodate. The resulting TEM micrograms were subjected to statistical image analysis using a NIH image (version 1.6, public domain) to produce the histograms discussed later (Figure 3). Obviously, the TEM images correspond to micelles with collapsed shells. TEM pictures were taken using a Philips

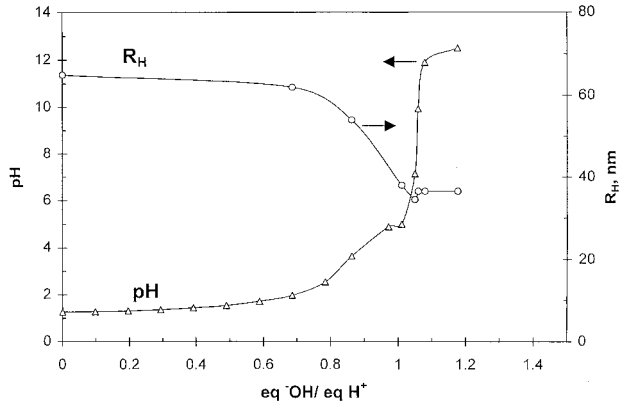


Figure 2. Titration of PS-*b*-PVP/PVP-*b*-PEO (onion) with c_B/c_A = 2.0 illustrating the change in R_H that occurs as the onion micelle forms. NaOH (0.5 M) is used as the base.

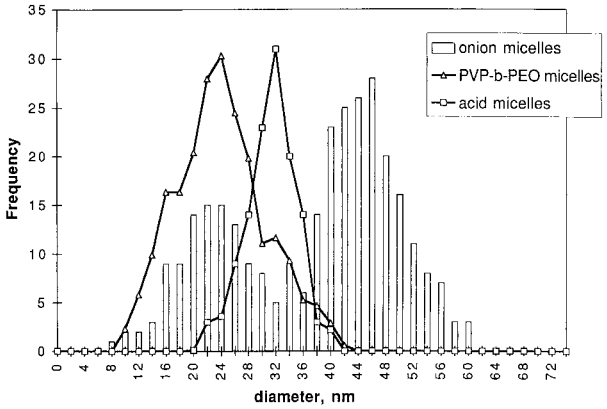


Figure 3. Histograms of micellar diameters in TEM for (a) PS-*b*-PVPH$^+$ and (b) PVP-*b*-PEO and PS-*b*-PVP/PVP-*b*-PEO onion (c_B/c_A = 3.0 in Table 1). The histograms are based on two or three independently prepared samples.

model EM208 with an accelerating voltage of 80 kV. TEM experimentation was facilitated by John Mendenhall, Cell Research Institute, University of Texas at Austin.

Measurement of Concentration by UV Absorbance. During the process of dialysis the concentration of the micellar solutions is changed due to the change of the volume of the dialysis bag, adsorption of the micelles on the dialysis membrane, etc. When such solutions are to be measured by SLS or any other method requiring the precise knowledge of concentration, it is necessary to employ some method of measurement following dialysis. For our system UV absorption proved to be convenient. For solutions of high molecular weight particles light scattering makes a sizable contribution to the apparent absorbance. Therefore, we had to dissolve our micelles in a solvent in which micelles are molecularly dissociated. The absorbance of the pyridine moiety is different for the protonated and unprotonated forms. Thus, the solution must have either very high or very low pH. We have selected as the solvent ethanol containing 5 vol % of 0.1 M NH_3. To a cell containing 2.5 mL of the solvent (and utilized as the blank) were added several aliquots of the analyte (the maximum total addition was 40 μL), and the spectra were recorded. Both our copolymers exhibited a flat baseline and a linear concentration dependence of the absorption at the absorption maximum (262 nm). Calibration was accomplished by adding known concentrations of pure polymers dissolved in THF. We obtained the following extinction coefficients at 262 nm: 1.975×10^4 mL/(g cm) for PS-*b*-PVP and 1.448×10^4 mL/(g cm) for PVP-*b*-PEO. (Note: the fact that PS-*b*-PVP is molecularly soluble in ethanol is somewhat surprising, but it was reproduced experimentally. Evidently, the concentrations employed are under the critical micelle concentration for this solvent.)

Synthesis of PS-*b*-PVP. The polymerization reactor is fairly standard and has been described elsewhere.[11] It permits

Table 1. Apparent Molecular Weights, Radii of Gyration, Second Virial Coefficients, and Hydrodynamic Radii of the Dominant Particles[a,b]

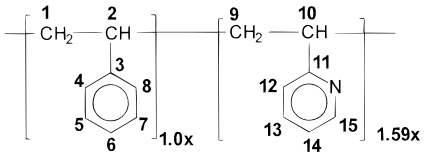
sample[b]	$M_{app} \times 10^{-6}$	R_G, nm	R_H, nm	R_G/R_H	$A_2 \times 10^5$, mol mL/g^2
PS-*b*-PVP core micelles[e]	13.4	33.8	49	0.690	1.19
PVP-*b*-PEO micelles, 5 mg/mL[c,e]	1.73	13.1	20	0.66	−16.2
PVP-*b*-PEO micelles, 10 mg/mL[c,e]	1.73	13.2	19	0.70	−8.6
PVP-*b*-PEO micelles, 20 mg/mL[c,e]	1.73	13.0	19	0.68	−3.5
onion micelles,[f] $c_B/c_A = 0.5$[d]	47.2	65.4	36	1.8	−0.86
onion micelles,[f] $c_B/c_A = 1.0$	37.8	53.0	34	1.6	−0.24
onion micelles,[f] $c_B/c_A = 2.0$	24.5	29.4	35	0.84	0.22
onion micelles,[f] $c_B/c_A = 3.0$	29.4	23.7	35	0.68	0.83
onion micelles,[f] $c_B/c_A = 4.0$	24.5	20.0	34	0.59	0.45

[a] The light scattering constants K used for evaluation of the SLS data were calculated with dn/dc = 0.27 (applicable for the PS-*b*-PVP copolymer) for all samples with the exception of the PVP-*b*-PEO micelles for which dn/dc = 0.194 was used. All values from the Zimm analysis are considered to have a precision of ±3−4%. [b] Core micelles were dissolved in 0.1 M HCl; all other micelles in 0.1 M NaCl at pH 10. [c] Concentration during titration by NaOH. [d] Micelles marginally stable (see text). [e] Values cited represent true ones, not apparent values (cf. onion micelles, see text). [f] For all these experiments c_A = 3.82 mg/mL where A refers to the PS-*b*-PVP copolymer.

sequential additions of reactants and removal of aliquots without exposure of the reaction to ambient conditions. Polystyrene-*block*-poly(2-vinylpyridine) (PS-*b*-PVP) was synthesized via anionic polymerization using cumylpotassium as the initiator. The order of monomer addition was styrene followed by 2-vinylpyridine. An aliquot of PS was removed before the addition of the 2-vinylpyridine, for molecular weight characterization. The details of this polymerization are available as Supporting Information.

Characterization of PS-*b*-PVP. *GPC Characterization.* The polystyrene homopolymer (first block) weight-average molecular weight was 36 000 (DP(PS) = 346) with an overall polydispersity of 1.11. The diblock copolymer elution volume corresponded to a M_w of 70 000 (based on the polystyrene calibration curve) with a polydispersity of 1.14 (Supporting Information).

Nuclear Magnetic Resonance. ^{13}C NMR using gated decoupling was used to quantitatively determine the ratio of PS to PVP.[12] A comparison of areas under the ST carbon peak at the sixth position and VP carbon peak at 15th position was made. The ratio of C(6) at 125.6 ppm and C(15) at 164.2 ppm was found to be 1.0:1.59 (see structure **1**). This corresponds to a PS-*b*-PVP molecular weight of 93 000 and DP(PVP) = 550, assuming DP(PS) = 346 from the GPC characterization.



A similar calculation was done with normal ^{1}H NMR spectra of the copolymer. The peak integrations at 8−8.5 ppm (one proton at C(15) position for VP) and 6−7.5 ppm (three and five aromatic protons of VP and styrene, respectively) were used to calculate the PS to PVP ratio. This was cross-referenced with the peaks at 1−3.0 ppm, which is the integration of the six protons at the backbone chain. The mass ratio obtained was PS:PVP 1.0:1.52, which corresponds to a molecular weight of 91 000 (DP(PVP) = 526). (All NMR spectra are available as Supporting Information.)

SLS Characterization. SLS measurement of the copolymer in THF revealed a molecular weight of 100 000, using the refractive index increment of PS-*b*-PVP as 0.167 mL/g. This corresponds to a DP(PVP) = 610, but we prefer the values obtained from NMR because they reflect the ratio of PS to PVP more accurately. If we accept the SLS molecular weight and the composition from NMR, we obtain DP(PS) = 377 ± 6 and DP(PVP) 580 ± 5 (error bars from average of two NMR methods). (Zimm plots are available as Supporting Information.)

Polymer Micelle Preparation and Characterization. *PS-b-PVPH$^+$ "Core" Micelles.* The first step was to determine the best set of conditions for preparing the PS-*b*-PVPH$^+$ micelles (PVPH$^+$ = protonated PVP blocks). Discovering these conditions for most micelles involves enlightened trial and error. Attempts to dissolve the polymer directly in 90:10 and 80:20 dioxane:0.1 M HCl water mixtures were unsuccessful. (The polymer did not dissolve.) Replacement of the 0.1 M HCl by water led to formation of micelles, but they were rather polydisperse. In an earlier study Procházka et al. used methanol as a cosolvent.[6] We have therefore prepared mixtures of methanol and dioxane in different volume ratios and added the polymer. Micelles were formed instantly in 50:50% (by volume) methanol:dioxane mixture at room temperature, but they were found to precipitate after 24 h. This is probably the result of insufficient segregation of the two blocks within the micelle. Addition of a small amount of water to the solvent mixture produced stable micelles with a low polydispersity. The optimal mixture found was 45:50:5 methanol:dioxane:water.

We were interested in obtaining the highest possible micelle concentration. We found that micelles can be prepared reproducibly up to polymer concentration 6.5 mg/mL in the 45:50:5 methanol:dioxane:water solvent mixture. In all cases the micellar solution was gradually dialyzed to 0.1 M HCl. The core micelles were studied by static and quasi-elastic light scattering at pH 1. The CONTIN analysis of the QELS data produced a dominant micellar peak accompanied by a minuscule amount (about 1%) of smaller material. The Zimm plot of the light scattering intensity as a function of both concentration and scattering angle was constructed using the estimated refractive index increment 0.27 mL/g (Supporting Information). The resulting values of M_w, A_2, and R_G values are presented in Table 1 together with the value of R_H of the dominant peak from QELS measurements. We note that the size of this polymer micelle is relatively large because its corona is a polyelectrolyte (cf. the onion micelle later).

We expected that the PS-*b*-PVPH$^+$ micelles would be very stable in aqueous environments due to the presence of the highly hydrophobic micellar core. To verify this expectation, we prepared a series of very dilute micellar solutions and analyzed them using the QELS method. Both the hydrodynamic radius and the ratio of the intensity to concentration were virtually constant down to concentrations of about 5×10^{-2} mg/mL (Figure 1). At lower concentrations the signal/noise ratio was too low for valid measurements of R_H. Thus, we conclude that the cmc is below 5×10^{-2} mg/mL for this polymer micelle system.

PVP-b-PEO Micelles. The preparation of these micelles by titration has been described in an earlier publication.[13] However, as we needed reliable data for our analysis, we repeated the measurements. Three different solutions of the copolymer having concentrations 5, 10, and 20 mg/mL were prepared in 0.1 M HCl. Each solution was titrated to pH 10 by 1 M NaOH. For the SLS measurements all these micellar solutions were diluted to the same final concentration. The value of dn/dc was estimated to be 0.194 g/mL for this polymer. The results of the SLS and QELS measurements are presented in Table 1. (A Zimm plot is available as Supporting Information.)

As observed previously, the titration curve displayed a clear pH plateau between pH 5.0 and 5.1 accompanying the micelle formation.[13] If QELS measurements are attempted at or immediately above the pH of micelle formation, large aggregates are formed over time. This phenomenon was observed repeatedly on various systems and is undoubtedly related to so-called "anomalous micellization".[1a]

We tested the stability of the PVP-*b*-PEO micelles by the dilution experiment described above for the core micelles. However, the molecular weight of the PVP-*b*-PEO micelles is almost an order of magnitude smaller than that of the core micelles, and the intensity of the light scattering signal was insufficient to yield meaningful data for the most dilute solutions. No change in R_H and the scattering intensity-to-concentration ratio was observed down to 0.2 mg/mL, and the Zimm plot was well-behaved down to 0.2 mg/mL (Supporting Information). Therefore, it seems that the cmc for PVP-*b*-PEO micelles is below 0.2 mg/mL.

PS-b-PVP/PVP−PEO "Onion" Micelles. PVP-*b*-PEO was molecularly dissolved in 0.1 M HCl and added to the solution of core micelles, also in 0.1 M HCl. The mixture was titrated with 1 M NaOH solution to raise the pH to 10 and deprotonate the $PVPH^+$. In addition to pH, R_H was monitored during the titration. A typical titration curve (for a PS-*b*-PVP to PVP:PEO 1:2 mass ratio in 0.1 M HCl) of pH and the hydrodynamic radius R_H of the dominant particles is shown in Figure 2. As the pH rises to the equivalence point (near pH 5), R_H drops from >50 to 36.5 nm. Once again there was a pH plateau when the $PVPH^+$ chains were deprotonated. This plateau occurred between pH 4.9 and 5.0, i.e., slightly lower than for the PVP-*b*-PEO micelles. The onset of onion micelle formation was clearly manifested by a sudden deepening of the bluish appearance of the solution which is characteristic of the increased light scattering of the more massive onion micelle.

In a separate experiment, we prepared a set of solutions using different weight ratios of the two copolymers (c_B/c_A), but exactly the same concentration of the core micelles ($c_A = 3.82$ mg/mL), and studied the solutions by the QELS and SLS methods. The sample with the lowest mass ratio of PVP-*b*-PEO/PS-*b*-PVP copolymers proved unstable. The QELS measurement carried out immediately after the sample preparation demonstrated a well-behaved micellar solution. However, after standing overnight, some precipitate formed. Even after clarification by filtration, the SLS data suggested some aggregation. The other samples were stable. The experimental results (including data for the presumably aggregated sample) are presented in Table 1. We assumed that the onion micelles were accompanied in the solution by the much smaller PVP-*b*-PEO micelles and tried to establish their presence by the CONTIN analysis of the QELS data. However, the contribution of the smaller micelles to the overall scattered intensity was small (see later discussion), and the QELS experiments did not yield any clear answer.

As in the study of the PS-*b*-$PVPH^+$ micelles, we have characterized the stability of the onion micelles by determining R_H as a function of concentration. The much stronger light scattering intensity of these massive micelles allowed us to ascertain that the micelles were stable for days to months down to a concentration 1×10^{-2} mg/mL (Figure 1). However, samples of onion micelles that were even more diluted tended to develop aggregates over the course of many months.

TEM Studies. The PS-*b*-$PVPH^+$ micelles were fairly monodisperse with a diameter of ca. 31 ± 4 nm (standard deviation). The PVP-*b*-PEO micelle diameter is ca. 20 ± 3 nm. For the PS-*b*-PVP/PVP-*b*-PEO onion micelle (mass ratio 3:1, see Table 1) the TEM size distribution is clearly bimodal. The larger and smaller components are similar to the PS-*b*-$PVPH^+$ micelles and PVP-*b*-PEO, respectively (see Figure 3). In Figure 4 we present an example of the images of the PS-*b*-$PVPH^+$ and PS-*b*-PVP/PVP-*b*-PEO onion micelles (the latter also contains PVP-*b*-PEO micelles). The onion micelles in Figure 4b do not stain as evenly as PS-*b*-$PVPH^+$ or PVP-*b*-PEO micelles. This has also been the experience of others, using I_2 staining (S. Förster, private communication). Our main objective in examining the TEM images is to verify the presence of well-formed PVP-*b*-PEO micelles, as is demanded by our analysis of the light scattering results discussed later. We note that the polyelectrolyte corona of PS-*b*-$PVPH^+$ is collapsed under the conditions of the TEM experiment, such that the TEM diameters are in line with the molecular weight differences.

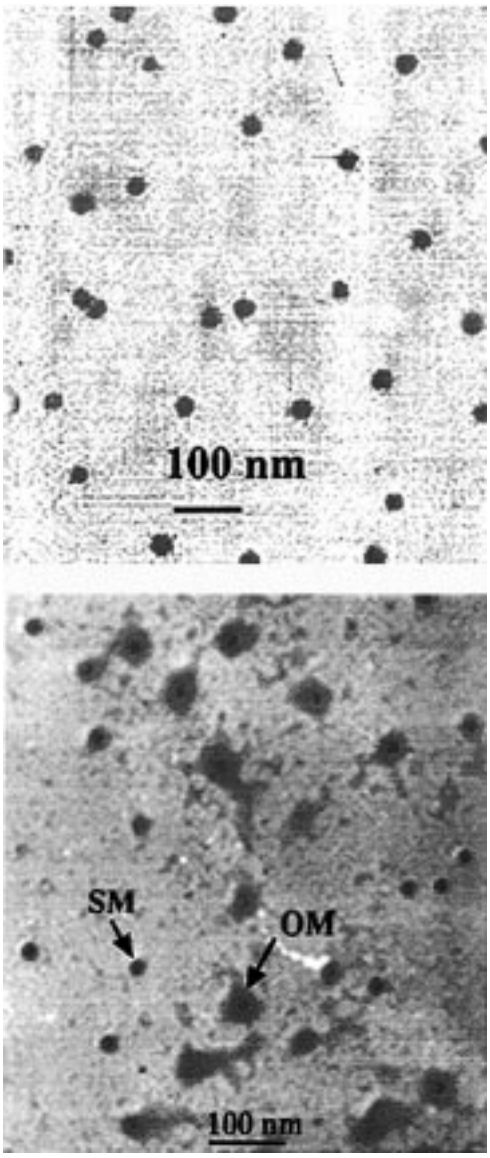


Figure 4. TEM images of (a, top) PS-*b*-$PVPH^+$ "core" and (b, bottom) PS-*b*-PVP/PVP-*b*-PEO "onion" micelles. In the latter case both the "onion" (OM) and PVP-*b*-PEO "small" micelles (SM) are observed.

Discussion

Our analysis follows that presented in ref 6 on a similar system containing poly(*tert*-butyl acrylate)-*block*-poly(2-vinylpyridine) (PBA-*b*-PVP) as the core micelle copolymer and the same sample of PVP-*b*-PEO that we are using herein. We conclude that the solution containing onion micelles also contains smaller PVP-*b*-PEO micelles formed by the excess PVP-*b*-PEO copolymer (see later). In this case, the experimental values obtained from light scattering for the onion micelles are only apparent ones, and a more involved analysis of the scattering data is required.

In the following we consider first the two simple micelles composed of PS-*b*-$PVPH^+$ and PVP-*b*-PEO alone and then analyze the properties of the onion micelle. In the Appendix we present a detailed discus-

sion of our approach to the analysis of the weight ratio of PVP-*b*-PEO to PS-*b*-PVP in the onion micelles.

Structure of PS-*b*-PVPH$^+$ Core Micelles. The experimental results for the core micelles are fully compatible with the model of a micelle having a homogeneous spherical core surrounded by an expanded polyelectrolyte shell. The micelle core is formed by polystyrene, which does not swell in aqueous solution, and may be assumed to be compact. The spherical nature of the micelle is unequivocally manifested by the experimental ratio $R_G/R_H = 0.69$. This ratio for coiled molecules is larger than unity. The theoretical value for homogeneous spheres is 0.775. Our lower value supports the concept of a micellar structure in which the segment density in the shell is much smaller than in the core. Employing the procedures described in the Appendix and the experimental value for the molecular weight, R_G, and R_H, we have calculated the expected ratios for three models of the shell structure: homogeneous, coiled, and stretched. The theoretical values were 0.619, 0.581, and 0.531, respectively. Thus, none of these simple models seem to fit the experimental result. We explain the discrepancy by the polydispersity of the micellar aggregation numbers that is small but not negligible (see ref 9). The polydispersity tends to shift the average values of R_G to higher values more than it shifts the R_H values. Thus, polydisperse systems are expected to exhibit increased values of R_G/R_H.

Dividing the molecular weight of the PS-*b*-PVPH$^+$ micelles by the polymer molecular weight ($93-100 \times 10^3$) yields an aggregation number in the range 134−144. From the micellar weight ($M_{micelle}$) one may calculate the core radius (R_c):

$$x_{PS}M_{micelle} = (4\pi/3)R_c^3\rho_{PS}N_{Av} \quad (1)$$

In this equation x_{PS} is the mole fraction of the PS core, ρ_{PS} is the density (assumed to be that of the pure bulk polymer), and N_{Av} is Avogadro's number. We obtain 12.6 nm for R_c assuming that PS is not swollen. This is very close to the value obtained from small-angle neutron scattering ($R_c = 12.0$ nm).[9]

From the difference of R_H and R_c the thickness of the shell d_s can be estimated to be 36.4 nm. The length L of the stretched shell forming block is about 138 nm based on the average polymerization degree of the PVP block of 550 and 0.25 nm per monomeric unit. Thus, the coiling ratio of the polyelectrolyte chains is about 3.8. If we assume that the thickness of the shell is approximately equal to the average end-to-end distance of the coil $d_S = (NA^2)^{1/2}$ and $L = NA$ (N represents the number of statistical segments of length A), we find $A = d_S^2/L = 9.6$ nm. This is much larger than typical values for common polymers, and it reflects the polyelectrolyte brush effect.[14] From R_c and the aggregation number we compute the area per PVP chain at the PS interface to be 13.9 nm^2, larger than the value of 9.8 nm^2 per poly(methacrylic acid) chain for PS-*b*-PMA micelles.[15]

The observed apparent second virial coefficient for the core micelles is of the order of 10^{-5} mol mL/g^2. When light scattering produces virial coefficients of this magnitude, a correction due to the turbidity of the solution should be applied.[16] In the present case the correction calls for subtracting about 0.8×10^{-5} mol mL/g^2, leading to the second virial coefficient equal to 0.4×10^{-5} mol mL/g^2. Values of this magnitude are to be expected if we use a model based on the volume exclusion of noninteracting hard spheres for the analysis of the thermodynamic properties.[2c]

Structure and Properties of the PVP-*b*-PEO Micelles. In a previous paper we have studied the micellization process of the same sample of PVP-*b*-PEO as used here.[13] We previously found that the average R_H of the micelles increased with the concentration of the copolymer in the solution that was titrated. This increase was modest for the pure copolymer sample, but it was very dramatic if some PVP homopolymer was present. In the present paper we used a much more sensitive SLS technique, and we did not observe any meaningful differences among three samples titrated at concentrations in the ratio 1:2:4 (Table 1).

The relatively high negative second virial coefficients derived from the Zimm plot varied systematically with preparation conditions. All other properties of the micelles were virtually identical. Any interpretation of this puzzling phenomenon would be highly speculative, and we refrain from it. Nevertheless, we believe that this observation merits further research.

For the analysis of the structure of the PVP-*b*-PEO micelles we will adopt the averaged data from Table 1, namely $M_w = 1.73 \times 10^6$, $R_G = 13.1$ nm, and $R_H = 19$ nm. Comparison of the molecular weights of the micelles and the unimers leads to an aggregation number of approximately 58. The ratio R_G/R_H is 0.69, consistent with a spherical particle. From the molecular weight of the micelle and the composition of the copolymer we find the radius of the core (R_c) to be 6.67 nm. Applying again the relations from the Appendix for homogeneous, coiled, and stretched coronas, we obtain R_G/R_H values of 0.524, 0.502, and 0.474, respectively. These theoretical values are even smaller than those for the core micelles because the shell material has a much smaller refractive index increment than the core.

The PEO block of the copolymer has a degree of polymerization of approximately 350, which corresponds to an extended length about 130 nm. The thickness of the shell d_s ($= R_H - R_c$) is 12.3 nm, which leads to a coiling ratio about 10. From these values the apparent length of the statistical segment is found to be 1.16 nm, approximately 3 times larger than for unperturbed PEO.[17] The area per PEO chain is computed from R_c and the aggregation number to be 9.64 nm^2, slightly smaller than for PVP chains in the PS-*b*-PVPH$^+$ micelles and similar to PMA chains in PS-*b*-PMA micelles.

Structure and Properties of the Onion Micelles. During the titration of the mixture of the core micelles with the PVP-*b*-PEO copolymer, R_H starts decreasing even before the pH of micellization is reached. This is consistent with diminished stretching of the PVPH$^+$ blocks as they are deprotonated. The collapsing PVP chains remove pyridine from the dissociation equilibrium which leads to the appearance of the plateau on the titration curve, as we have explained previously.[6] At the same time, the PVP blocks from the two copolymers may interpenetrate to form a single intermediate layer of the onion micelles while PS is expected to form the inner micellar core and PEO forms the onion micelle corona. The small difference between the pH values in the plateau region for the collapsing PVP chains in the PVP-*b*-PEO copolymer and in the shell of the PS-*b*-PVP micelles is experimentally reproducible and significant. In the micellar shells the pyridine moieties are much closer to each other than in chains of a simple linear

Table 2. Results of Modeling the Onion Micelles

experimental data[a]			model 1			model 2				
c_B/c_A	$M_{app} \times 10^{-6}$	R_G/R_H	$M_A \times 10^{-6}$	$M_{tot} \times 10^{-6}$	N	$c_{B,ad}/c_A = \delta$	$M_{onion} \times 10^{-6}$	R_{G1}, nm	R_{G1}/R_H	R_{oc}, nm
0.5	47.2	1.82	25.5	38.3	1.906	1.238				
1.0	37.8	1.56	12.8	25.6	0.955	0.944	26.1	53.2	1.6	19.8
2.0	24.5	0.84	4.13	12.4	0.308	0.436	19.2	31.5	0.90	18.6
3.0	29.4	0.68	2.95	11.8	0.220	0.593	20.9	26.1	0.74	19.0
4.0	24.5	0.59	1.63	8.16	0.122	0.361	18.2	22.2	0.65	18.4

[a] From Table 1, for ease of comparison.

$PVPH^+$, which may lead to the change of the effective pK of the pyridine moiety. We have analyzed this situation in a previous publication.[18] As a result, the shells of the core micelles may start collapsing sooner than the PVP-*b*-PEO. During this process the PVP chains of PVP-*b*-PEO can be adsorbed in the newly formed intermediate layer before or during formation of PVP-*b*-PEO micelles.

As we have already mentioned, the attempt to find the presence of smaller particles by QELS in the solutions of the onion micelles was inconclusive. This is because the onion micelle has much more scattering power than the PVP-*b*-PEO micelle, based on their respective molecular weights and dn/dc values (see later).

We will use the light scattering results to estimate the amount of PVP-*b*-PEO that is incorporated into the onion structure. The true behavior of the system will be then assessed from the plausibility of the results.

Model 1. We will assume that both copolymers are fully incorporated into the observed particles. This is the first model treated in the Appendix (following eq A10 for $c_B - c_{B,ad} = 0$). In Table 2 we have compiled the derived values of the mass of the core copolymer A in the particles M_A, the total mass of the micelles M_{tot}, and the apparent number of the core micelles per particle, $N = M_A/M_{cm}$ (M_{cm} is the molecular weight of the core micelles). It is obvious that the model has some plausibility when the c_B/c_A ratio is 0.5 or 1.0. It could be interpreted as a small number of the core micelles forming quite asymmetric clusters (large R_G/R_H ratios). However, for larger c_B/c_A ratios the model fails badly, predicting that only a small fraction of a core micelle is present in each particle.

Model 2. This model represents most closely our picture of the onion micelles. We assume that each PS-*b*-PVP micelle forms exactly one onion micelle that is stabilized by trapped PVP-*b*-PEO chains. It is further assumed that any excess PVP-*b*-PEO forms another set of micelles that are identical with the PVP-*b*-PEO micelles formed in the absence of the PS-*b*-PVP micelles and presented in Table 1. This yields the following equation for the apparent molecular weight of a solution containing both the onion micelles and PVP-*b*-PEO micelles (also see the Appendix, eq A10):

$$M_{app} = M_A[1 + (c_{B,ad}/c_A)(dn/dc_B)/(dn/dc_A)]^2 + M_B[(c_B - c_{B,ad})/c_A][(dn/dc_B)/(dn/dc_A)]^2 \quad (2)$$

In this equation M_A is the molecular weight of the core PS-*b*-PVP micelle and M_B is the molecular weight of the PVP-*b*-PEO micelle. c_A and c_B are the concentrations of PS-*b*-PVP and PVP-*b*-PEO, respectively. $c_{B,ad}$ is the amount of PVP-*b*-PEO adsorbed onto the core micelle and in the context of this model is the only unknown. Equation 2 is a quadratic equation in $c_{B,ad}/c_A$ ($\equiv\delta$), so obtaining δ as a function of c_B/c_A is straightforward (see eq A11 of the Appendix). The molecular weight of the onion micelle is given by

$$M_{onion} = (1 + \delta)M_A \quad (3)$$

For $c_B/c_A > 1$ the δ values have an average value of 0.46 $\pm$ 0.12. Comparing the light scattering power of the onion and the PVP-*b*-PEO micelles (the first and second term on the right-hand side of eq 2), we find that the PVP-*b*-PEO micelles account for less than 10% of the scattering intensity.

Once δ is evaluated, we may calculate the radius of gyration for the onion micelles using eq A12 from the Appendix. The resulting values of δ, M_{onion}, R_G, and R_G/R_H are collected in Table 2 for the onion micelles. While the results for the larger c_B/c_A ratios are quite plausible, for $c_B/c_A = 0.5$ the result is physically meaningless. The δ value for $c_B/c_A = 1$ is physically possible, but the ratio R_G/R_H is not compatible with a spherical model. It is more likely that the values for $c_B/c_A = 1$ are corrupted by aggregation. For the larger c_B/c_A ratios R_G/R_H for the onion micelle are reasonably consistent with spherical particles; this is also seen from the TEM pictures.

The onion core radius R_{oc} corresponds to the sum of the radius of the inner PS core and the contribution of the intermediate PVP layer. These quantities are easily evaluated from the known masses and densities of these portions. The data presented in Table 2 are based on an assumption that the PVP layer is unswollen. In fact, PVP does swell slightly in water, so R_{oc} is a lower limit. We can compare the coiling ratio of the PEO chains in the shell and the apparent statistical segment size with the PVP-*b*-PEO micelles. From the thickness of the PEO shell ($d_s = R_H - R_{oc}$) and the PEO extended length of 130 nm, we find the coiling ratio to be about 8 and the average statistical segment length of 2.0 nm. This is twice as large as for the same chains forming the shell of the PVP-*b*-PEO micelles and 6 times that of unperturbed PEO. It is plausible that this is a result of the crowding of the PEO chains when they are attached to a surface with a larger radius of curvature. Characterization of onion micelles as a function of the size of the core micelle and the block lengths of the corona polymer would be a reasonable approach to the study of polymer brushes on curved surfaces.

Summary

Anionically synthesized polystyrene-*block*-poly(2-vinylpyridine) could be converted to micelles with a polystyrene core using mixed solvents. By a stepwise dialysis, we transferred these micelles into 0.1 M HCl, where the protonated poly(vinylpyridine) chains formed a polyelectrolyte corona with estimated length of statistical segments about 10 nm, i.e., about 1 order of magnitude longer than typical flexible polymer chains.

When these micelles were mixed with a molecular solution of poly(2-vinylpyridine)-*block*-poly(ethylene ox-

ide) in 0.1 M HCl and titrated to a basic or neutral pH, the protonated poly(vinylpyridine) chains collapsed around the polystyrene cores capturing the sister chains of the PVP-*b*-PEO, while the water-soluble PEO kept the whole complex in solution. We refer to these multilayered micelles as "onion micelles". These materials represent a new class of self-assembled polymers.

The analysis of the light scattering data revealed that an excess of the PVP-*b*-PEO copolymer is needed in order to form stable spherical onion micelles. Otherwise, complexes containing several core micelles may be also formed.

We have found that the final onion micelles incorporated a relatively small portion of the PVP-*b*-PEO present. Typically, the ratio of masses of PVP-*b*-PEO to PS-*b*-PVP within the onion micelles was about 0.5 (average value 0.46 ± 0.12). We presume this value represents the best compromise between chain crowding and steric stabilization of the onion micelles and micelle formation by PVP-*b*-PEO alone. The extent to which this optimal value represents kinetic vs thermodynamic control of the co-micellization is not known.

Acknowledgment. This work has been supported by the U.S. Army Office of Research (Grant DAAH04-95-1-0127) and the Robert A. Welch Foundation (F-356). P.M. and Z.T. acknowledge the support of the Czechoslovak-American Science and Technology Fund Grant No. 95010.

Appendix

When studying light scattering of our system of onion micelles mixed with another type of smaller micelles, we are faced with several tasks. First, we need to understand light scattering of particles composed of two spatially separate materials (e.g., cores and shells). Second, we need to find a way how to obtain from the scattering data the composition of particles composed from two different copolymers. Third, we need to understand the behavior of systems containing two types of particles differing in composition, structure, and size. We will now treat these three problems separately. Parts of the following treatment were already utilized in our previous publications.[6,19]

First, we will consider light scattering of particles that are composed of two parts, A and B, at zero angle and in the limit of vanishing concentration. In this limit the scattered intensity is an algebraic sum of intensities scattered by individual particles. For the solution containing A and B we assume the change of refractive index is given by

$$\Delta n = (\mathrm{d}n/\mathrm{d}c_A)c_A + (\mathrm{d}n/\mathrm{d}c_B)c_B \qquad \text{(A1)}$$

which yields the Rayleigh ratio extrapolated to zero angle and zero concentration:

$$R(0) = [(4\pi^2 n_0^{\,2}/\lambda_0^{\,4} N_{Av})(\mathrm{d}n/\mathrm{d}c_A)^2] \times [1 + (c_B/c_A)(\mathrm{d}n/\mathrm{d}c_B)/(\mathrm{d}n/\mathrm{d}c_A)]^2 c_A M_A \qquad \text{(A2)}$$

where M_A is the mass of particle A, λ_0 is the wavelength of the light in vacuo, c_i is the mass per volume concentration of the ith component, and n_0 is the refractive index of the solvent.

Equation A2 is also useful when dealing with particles composed of two different types of molecules, as when evaluating sorption of small molecules onto large particles or when analyzing particles composed from two types of macromolecules such as those in the present investigation. The first bracket of eq A2 is the light scattering constant K_A calculated with the refractive index increment of component A, $\mathrm{d}n/\mathrm{d}c_A$. The ratio c_B/c_A is the ratio of concentrations of components A and B within the particles. When M_A and the ratio of refractive index increments $(\mathrm{d}n/\mathrm{d}c_B)/(\mathrm{d}n/\mathrm{d}c_A)$ are known, the ratio (c_B/c_A) can be evaluated from eq A2 rearranged to

$$R(0)/K_A c_A \equiv M_{app} = M_A[1 + (c_B/c_A)(\mathrm{d}n/\mathrm{d}c_B)/(\mathrm{d}n/\mathrm{d}c_A)]^2 \qquad \text{(A3)}$$

When the SLS for a single-material particle is evaluated using the Zimm technique, the radius of gyration R_G is evaluated from the scattering shape of the scattering function. However, when the scattering particle is composed from two materials, the experimental value does not represent the true radius of gyration but only an apparent one, $R_{G,app}$. The theory of light scattering leads to the following expression for $R_{G,app}$ of particles composed of two materials having different refractive increments.[20]

$$R_{G,app}^{\,2} = R_{G,A}^{\,2} w_A(\mathrm{d}n/\mathrm{d}c)_A/(\mathrm{d}n/\mathrm{d}c) + R_{G,B}^{\,2} w_B(\mathrm{d}n/\mathrm{d}c)_B/(\mathrm{d}n/\mathrm{d}c) + \Delta^2 w_A w_B(\mathrm{d}n/\mathrm{d}c)_A(\mathrm{d}n/\mathrm{d}c)_B/(\mathrm{d}n/\mathrm{d}c)^2 \qquad \text{(A4)}$$

Here $R_{G,A}$ and $R_{G,B}$ are the radii of gyration of the materials A and B, w_A and w_B are their mass fractions, $(\mathrm{d}n/\mathrm{d}c)_A$ and $(\mathrm{d}n/\mathrm{d}c_B)$ are their refractive increments, $(\mathrm{d}n/\mathrm{d}c)$ is the refractive increment for the composite particle, and Δ is the distance between the centers of mass of the two materials. The overall refractive increment can be expressed as

$$\mathrm{d}n/\mathrm{d}c = w_A(\mathrm{d}n/\mathrm{d}c)_A + w_B(\mathrm{d}n/\mathrm{d}c)_B \qquad \text{(A5)}$$

For random copolymers, the spatial distribution of both monomeric units is the same, and the apparent radius of gyration is equal to the true one. In block copolymers dissolved in solvents good for both blocks, the blocks may occupy different regions, and all three terms in eq A4 are significant. Most block copolymer micelles are spherically symmetrical such that the Δ value is zero, and only the first two terms of eq A4 contribute. For micelles that have a well-defined core−shell boundary, the gyration radii of the two components may be expressed as a function of the radius of the core R_c and of the whole micelle R_m. We will designate the insoluble core block as A and the soluble corona one as B. It is reasonable to assume that the micellar cores are essentially homogeneous such that

$$R_{G,A}^{\,2} = (3/5)R_c^{\,2} \qquad \text{(A6)}$$

R_G of the shells depends on the spatial distribution of the shell forming chains. We consider three cases:

(1) The segment density is uniform:[21]

$$R_{G,B}^{\,2} = (3/5)(R_m^{\,5} - R_c^{\,5})/(R_m^{\,3} - R_c^{\,3}) \qquad \text{(A7)}$$

(2) The segment density within the shell is inversely proportional to the distance from the micelle center (this approximates the situation when the shell chains adopt a conformation of ideal coils attached to a surface):

$$R_{G,B}{}^2 = (1/2)(R_m{}^4 - R_c{}^4)/(R_m{}^2 - R_c{}^2) \quad \text{(A8)}$$

(3) The segment density within the shell is inversely proportional to the square of the distance from the micelle center (stretched chains):

$$R_{G,B}{}^2 = (1/3)(R_m{}^3 - R_c{}^3)/(R_m - R_c) \quad \text{(A9)}$$

The molecular weight of the core is easily calculated if the micellar weight is known together with the composition of the copolymer. From the molecular weight of the core, the density of the core polymer, and the known or assumed swelling of the core, R_c is obtained. R_m can be taken to be the hydrodynamic radius of the micelle, R_H. Therefore, the experimental ratio $(R_{G,app}{}^2)^{1/2}/R_H$ ($\equiv R_G/R_H$) can be compared to the values calculated using various assumptions about the structure of the micelle and eq A4.

We will now turn to the problem of composition of complex particles. In one model we will assume that we have a system composed from two different materials: material A that forms the nucleus of the scattering particles and all of material B is adsorbed on this nucleus. In our present case, A is our PS-*b*-PVPH$^+$ micelles and B is the solubilizing copolymer (PVP-*b*-PEO). This model is rather general and is also applicable to polymer solutions in mixed solvents, where A is the individual polymer molecule and B is the preferentially adsorbed solvent component.

Equation A3 is applicable for this model. If we know the molecular weight of material A within the complex particles and the apparent molecular weight M_{app} then, we can calculate the mass ratio of the two components. This situation applies both to the polymers in mixed solvents and to our onion-type micelles when we assume that each particle contains just one core micelle. If the molecular weight of the A portion of the complex particle is not known originally, it could be obtained from eq A3 provided that we can make a plausible assumption about the ratio of the polymers in the particles.

For a system with two types of scatterers in the limit of zero concentration, eq A3 must be modified to recognize the light scattering of the excess component B. A convenient form of the equation reads

$$R(0)/K_A c_A \equiv M_{app} = M_A[1 + (c_{B,ad}/c_A)(dn/dc_B)/(dn/dc_A)]^2 + M_B[(c_B - c_{B,ad})/c_A][(dn/dc_B)/(dn/dc_A)]^2 \quad \text{(A10)}$$

In this equation we use subscript A for the material forming the nucleus of the complex particles (e.g., the core micelle formed from PS-*b*-PVP) and subscript B for the material (e.g., the PVP-*b*-PEO copolymer) that either is adsorbed onto the nucleus (concentration $c_{B,ad}$) or forms independent particles (concentration ($c_B - c_{B,ad}$), where c_B is the total concentration of B in the solution). We will analyze two simple models for this situation.

In the first model we will assume that all B is adsorbed onto the complex particles, i.e., $c_{B,ad} = c_B$. Then the second term in eq A10 vanishes, and the equation may be solved for M_A, the molecular weight of A in the complex particle. The molecular weight of the whole particle is then obtained as $M_{tot} = M_A(1 + c_B/c_A)$.

For the second model we will assume that the properties of the core micelle are known, and the material B is distributed between the complex particles and the outside solution. In this situation it is convenient to define a fractional adsorption $\delta = c_{B,ad}/c_A$ and evaluate it from eq A10 which is quadratic in δ. The solution reads

$$\delta = a/2 - b + [b^2M' + a^2/4 - ab - ac]^{1/2} \quad \text{(A11)}$$

where $M' = M_{app}/M_A$, $a = M_B/M_A$, $b = (dn/dc_A)/(dn/dc_B)$, and $c = c_B/c_A$.

How can we interpret the observed radius of gyration in this case? It is again possible only if a plausible assumption can be made about the particle structure. In the case of onion-type micelles in the absence of any other significant scatterers, the procedure is straightforward. From the above analysis we already know the masses of the individual layers and can calculate the boundaries of the layers. Assuming that the central and intermediate portions of the micelles are collapsed and homogeneous, we may calculate their contribution to the radius of gyration using eqs A6 and A7, respectively. The contribution of the outer shell is obtained from eqs A7−A9. Then from the comparison of experimental and calculated R_G/R_H ratio, we may again evaluate the behavior of the outer shell layer.

For our second model we need first to separate the contributions of both types of particles to the apparent radius of gyration. The separation is based on a relation that is general for any solution containing two types of scattering particles, namely

$$R_{G,app}{}^2 = \frac{M_1 w_1 (dn/dc_1) R_{G1}{}^2 + M_2 w_2 (dn/dc_2) R_{G2}{}^2}{M_1 w_1 (dn/dc_1) + M_2 w_2 (dn/dc_2)} \quad \text{(A12)}$$

In this relation the subscripts 1 and 2 refer to the two types of particles, and w_1 and w_2 are the corresponding mass fractions. In our second model (all excess B forms particles with known $R_{G2}{}^2$) the mass fractions follow from the extent of adsorption δ. All other quantities in eq A12 are known, so $R_{G1}{}^2$ is evaluated. It can be then further analyzed using the procedure described after eq A11.

Supporting Information Available: Description of the polymerization conditions and figures showing the GPC elution curve for PS-*b*-PVP, a ^{13}C NMR spectrum of PS-*b*-PVP, and Zimm plot of PS-*b*-PVPH$^+$, PVP-*b*-PEO, and onion micelle. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Tuzar, Z.; Kratochvil, P. In *Surface and Colloid Science*; Matijevic, E., Ed.; Plenum Press: New York, 1993; Vol. 15, p 1. (b) Riess, G.; Hurtrez, G.; Bahadur, P. In *Encyclopedia of Polymer Science and Engineering*, 2nd ed.; Mark, H. F., Bikales, N. M., Overberger, C. G., Menges, G., Eds.; Wiley: New York, 1985; Vol. 2, pp 324−436. (c) *Solvents and Self-Organization of Polymers*; Webber, S. E., Munk, P., Tuzar, Z., Eds.; NATO ASI Series E; Kluwer Academic Publishers: Dordrecht, 1996; Vol. 327.

(2) (a) Karymov, M. A.; Procházka, K.; Mendenhall, J. M.; Martin, T. J.; Munk, P.; Webber, S. E. *Langmuir* **1996**, *12*, 4748. (b) Martin, T. J.; Webber, S. E. *Macromolecules* **1995**, *28*, 8845. (c) Qin, A.; Tian, M.; Ramireddy, C.; Webber, S. E.; Munk, P.; Tuzar, Z. *Macromolecules* **1994**, *27*, 120. (d) Chan, J.; Fox, S.; Kiserow, D. J.; Ramireddy, C.; Munk, P.; Webber, S. E. *Macromolecules* **1993**, *26*, 7016. (e) Tian, M.; Qin, A.; Ramireddy, C.; Webber, W. E.; Munk, P.; Tuzar, Z.; Procházka, K. *Langmuir* **1993**, *9*, 1741. (f) Procházka, K.; Kiserow, D.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 454. (g) Kiserow, D.; Procházka,

K.; Ramireddy, C.; Tuzar, Z.; Munk, P.; Webber, S. E. *Macromolecules* **1992**, *25*, 461. (h) Cao, T.; Munk, P.; Ramireddy, C.; Tuzar, Z.; Webber, S. E. *Macromolecules* **1991**, *24*, 6300.
(3) Ropert, C.; Lavignon, M.; Dubernet, C.; Couvreur, P.; Malvy, C. *Biochem. Biophys. Res. Commun.* **1992**, *183*, 879.
(4) Seki, K.; Tirrell, D. *Macromolecules* **1984**, *17*, 1692.
(5) (a) Yokoyama, M. In *Biorelated Polymers and Gels*; Academic Press: New York, 1998; Chapter 6, pp 193−229. (b) Cammas, S.; Kataoka, K. In *Solvents and Self-Organization of Polymers*; Webber, S. E., Munk, P., Tuzar, Z., Eds.; NATO ASI Series E; Kluwer Academic Publishers: Dordrecht, 1996; Vol. 327, Chapter 6, pp 83−114. (c) Harada, A.; Kataoka, K. *Adv. Drug Delivery Rev.* **1995**, *16*, 295. (d) Harada, A.; Kataoka, K. *Macromolecules* **1995**, *28*, 5294. (e) Scholz, C.; Iijima, M.; Nagasaki, Y.; Kataoka, K. *Macromolecules* **1995**, *28*, 7295. (f) Bader, J. H.; Rin, H.; Schmidt, B. *Angew. Makromol. Chem.* **1984**, *123*, 457.
(6) Procházka, K.; Martin, T. J.; Webber, S. E.; Munk, P. *Macromolecules* **1996**, *29*, 6526.
(7) Kriz, J.; Masar, B.; Plestil, J.; Tuzar, Z.; Pospisil, H.; Doskocilova, D. *Macromolecules* **1998**, *31*, 41.
(8) (a) Yu, H.; Eisenberg, A. *Macromolecules* **1998**, *31*, 3509. (b) Zhang, L.; Eisenberg, A. *Science* **1995**, *268*, 1728.
(9) Plestil, J.; et al., manuscript in preparation.
(10) *Polymer Handbook*, 3rd ed.; Brandrup, J., Immergut, E. H., Eds.; Wiley-Interscience: New York, 1989; pp VII, 409−484.
(11) (a) Martin, T. J. Ph.D. Dissertation, The University of Texas at Austin, May 1996. (b) Ramireddy, C.; Tuzar, Z.; Procházka, K.; Webber, S. E.; Munk, P. *Macromolecules* **1992,** *25*, 2541.
(12) NMR data using gated decoupling was facilitated by Dr. Ben Shoulders, NMR Facility, Department of Chemistry and Biochemistry, UT Austin.
(13) Martin, T. J.; Procházka, K.; Munk, P.; Webber, S. E. *Macromolecules* **1996**, *29*, 6071−73.
(14) Lyatskaya, Yu. V.; Leermakers, F. A. M.; Fleer, G. J.; Zhulina, E. B.; Birshtein, T. M. *Macromolecules* **1995**, *28*, 3562.
(15) See ref 2c, Table 6 (for an unswollen PS core); 9.8 nm^2 is the average of the 12 values given there.
(16) Munk, P.; Tian, M. *Polymer* **1995**, *36*, 1975.
(17) Lee, J.; Martic, P. A.; Tan, J. S. *J. Colloid Interface Sci.* **1989**, *131*, 252.
(18) Munk, P.; Tuzar, Z.; Procházka, K. *Collect. Czech. Chem. Commun.* **1997**, *62*, 1730.
(19) (a) Tian, M.; Arca, E.; Tuzar, Z.; Webber, S. E.; Munk, P. *J. Polym. Sci., Polym. Phys.* **1995**, *33*, 1713−1722. (b) Munk, P.; Rangelov, S.; Tuzar, Z. *Int. J. Polym. Anal. Characterization*, in press.
(20) Benoit, H.; Froelich, D. In *Light Scattering from Polymer Solutions*; Huglin, M. B., Ed.; Academic Press: London, 1972; pp 467−501.
(21) Tuzar, Z.; Plestil, J.; Konak, C.; Hlavata, D.; Sikora, A. *Makromol. Chem.* **1983**, *184*, 2111.

MA981269U