

Polymer Micelles with Hydrophobic Core and Ionic Amphiphilic Corona. 2. Starlike Distribution of Charged and Nonpolar Blocks in Corona

Evgeny A. Lysenko,^{*,†} Alevtina I. Kulebyakina,[‡] Pavel S. Chelushkin,[§] Artem M. Rumyantsev,^{||} Elena Yu. Kramarenko,^{||} and Alexander B. Zezin[†]

[†]Chair of Polymer Sciences, Department of Chemistry, M.V. Lomonosov Moscow State University, Moscow 119991, Russia

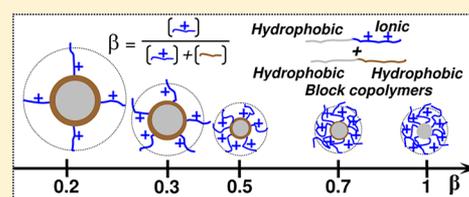
[‡]National Research Center "Kurchatov Institute", Moscow 123182, Russia

[§]Institute of Macromolecular Compounds of the Russian Academy of Sciences, St. Petersburg 199004, Russia

^{||}Chair of Polymer and Crystal Physics, Department of Physics, M.V. Lomonosov Moscow State University, Moscow 119991, Russia

S Supporting Information

ABSTRACT: Mixed polymer micelles with hydrophobic polystyrene (PS) core and ionic amphiphilic poly(4-vinylpyridine)/poly(N-ethyl-4-vinylpyridinium bromide) corona (P4VP/PEVP) spontaneously self-assembled from mixtures of PS-*b*-PEVP and PS-*b*-P4VP macromolecules in dimethylformamide/methanol/water selective solvent. The fraction of PEVP units in corona was $\beta = [\text{PEVP}]/([\text{PEVP}] + [\text{P4VP}]) = 0.05\text{--}1.0$. Micelles were transferred into pure water via dialysis technique and pH was adjusted to 9, where P4VP blocks are insoluble. Structural characteristics of micelles as a function of corona composition β were investigated. Methods of dynamic and static light scattering, electrophoretic mobility measurements, sedimentation velocity, transmission electron microscopy, and UV spectrophotometry were applied. Spherical morphology with core (PS)–shell (P4VP)–corona (PEVP) organization was postulated. Micelles demonstrated a remarkable inflection in structural characteristics near $\beta \sim 0.5\text{--}0.7$. Above this region, aggregation number (m), core and corona radii of mixed micelles coincided with those of individual PS-*b*-PEVP micelles. When β decreased below 0.5, dramatic growth of aggregation number was observed, accompanied by growth in micelle size and stretching PEVP chains. At β below 0.2, dispersions of mixed micelles were unstable and easily precipitated upon addition of NaCl. Scaling relationships between micelle characteristics and β were obtained via minimization the micelle free energy, taking into account electrostatic, osmotic, volume, and surface contributions. Theoretical estimations predicted dramatic influence of β on aggregation number, $m \sim \beta^{-3}$. This result is in general agreement with experimental data and confirms the correctness of the core–shell–corona model. The inflection in micelle characteristics entails drastic changes in micelle dispersion stability in the presence of oppositely charged polymeric (sodium polymethacrylate) or amphiphilic (sodium dodecyl sulfate) complexing agents.



1. INTRODUCTION

Self-assembly is a physicochemical process of formation of well-defined structures via noncovalent interactions of components of the system. Amphiphilic block copolymers belong to self-assembling species.¹ Their main feature is formation of segregated structures, where several different domains coexist within the space of single particle.² In the simplest case of amphiphilic AB diblock copolymers (A is nonpolar and B is polar block) in selective media, the formation of two-layered "core–corona" micelles is observed.^{3–6} Both core and corona may be used for binding and storage of various substances, while corona may also serve for adhesion and targeted transportation of micelles themselves.^{1–3}

One of the intriguing challenges of modern chemistry is the design of polymer micelles with hierarchical structure.^{1,7} It means that the core or corona in its turn segregates onto smaller domains with different properties. Thus, micelles with heterogenic core/corona roughly mimic protein globules,

composed of various subdomains with several different properties, environments, and functions in close proximity.⁸ It is unnecessary to discuss the importance of disclosing main principles of self-assembly of hierarchical micelles.⁹

First descriptions of polymer micelles with heterogeneous core and/or corona started to appear during the previous decade.^{10–12} Major attention was drawn to micelles, soluble in aqueous media, that is, consisting from hydrophobic or amphiphilic core and amphiphilic or hydrophilic corona. To create such micelles, three general approaches have been advanced: (a) synthesis of multiblock (primary triblock) copolymers;¹³ (b) synthesis of amphiphilic copolymers with joint block and random distribution of polar and nonpolar units along the chain;¹⁴ (c) hybridization (comicellization) of several

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diblock copolymers.¹⁵ Brief description of these approaches can be found in the introductory part of our preceding publication.¹⁶

Water-soluble polymer micelles with hydrophobic core from A units and heterogeneous corona from charged B and nonpolar C units constituted the object of our interest. The main question was how the fraction and distribution pattern of charged and nonpolar units in corona influence the structure, dispersion stability, and binding properties of copolymer micelles. To solve this task, we investigated micelle characteristics as a function of the fraction of charged B units $\beta = [B]/([B] + [C])$ and the character of their distribution in corona (statistical vs starlike). We studied micelles both experimentally and theoretically and compared the results.

In a preceding publication, we have focused on a statistical distribution of B and C units in corona. Peculiarities of self-assembly of A-B/C copolymers (B/C is amphiphilic block bearing statistically distributed quenched charges and nonpolar units) in water-organic and aqueous media were systematically studied. The main result consisted in the existence of a jump-point near $\beta \sim 0.6$ – 0.7 , where structural characteristics and most micelle properties abruptly changed, while below or above this point micelle parameters were constant or changed insignificantly. The physical meaning of this point seemed to lay in inversion of the balance between electrostatic and hydrophobic interactions between micelle units as a function of corona composition.¹⁶

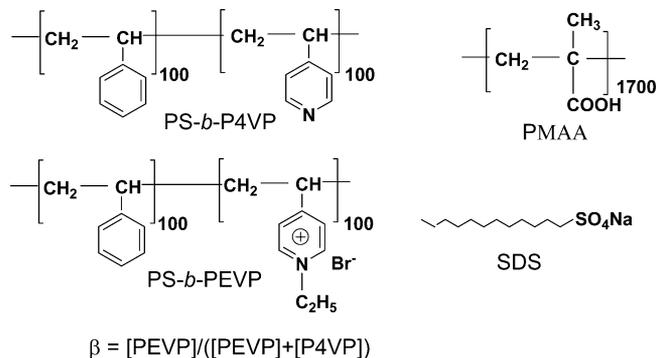
In the present publication, we address another distribution pattern of corona units. This time B and C units are separated into different blocks and belong to different macromolecules though still attached to homogeneous A core. For such distribution, we obtained hybrid (mixed) micelles via joint micellization (hybridization) of AB and AC diblock copolymers in selective water-organic solvent. In hybrid micelles, both charged and nonpolar blocks are emerged from joint A core in a starlike fashion. We have found essential differences in behavior of A-B/C and mixed A-B/A-C micelles upon variation of β . In the case of hybrid micelles, no jump-point is observed. Nevertheless, micelle features change very steeply when β drops below some threshold value of 0.7 – 0.5 . These differences emerge from distinction in distribution and association character of C units in the corona, which entails differences in micelle structure, aggregation stability, and binding properties.

2. EXPERIMENTAL SECTION

2.1. Materials. Block copolymer of PS and poly(4-vinylpyridine) (P4VP), PS-*b*-P4VP, was synthesized by sequential anionic polymerization.¹⁷ Lengths of both blocks equaled 100 units; polydispersity index was 1.12. The exhaustively quaternized by ethyl bromide PS-*b*-P4VP (PS-*b*-PEVP) was synthesized according to procedure, described elsewhere.¹⁸ Poly(methacrylic acid) (PMAA) was obtained via radical polymerization; the fraction with weight average polymerization degree of 1700 units ($M_w = 146\,000$) was used.¹⁶ PMAA was neutralized by equivalent amount of NaOH and used in the form of sodium polymethacrylate (PMANa). In our investigation, we also employed sodium dodecyl sulfate (SDS), sodium chloride (NaCl), dimethylformamide (DMF), methanol, ethyl bromide, tris-(hydroxyethyl)aminomethane (TRIS), sodium hydroxide (NaOH) (all purchased from Sigma-Aldrich) and doubly distilled water. Chemical structures of investigated materials are presented in Chart 1.

2.2. Sample Preparation. Aqueous dispersions of individual PS-*b*-PEVP and hybrid PS-*b*-P4VP/PS-*b*-PEVP micelles (further designated as PS-*b*-P4VP/PS-*b*-PEVP- β , where $\beta = [\text{PEVP}]/([\text{PEVP}] + [\text{P4VP}])$ is micelle composition) were prepared using dialysis technique.

Chart 1. Polymers and Surfactant Used in This Investigation



Initially, individual PS-*b*-PEVP and PS-*b*-P4VP were dissolved in a mixed DMF/methanol (80/20 v/v) solvent at polymer concentration of 50 g/L and stirred for 1 day. For preparation of hybrid micelles, the next step consisted in mixing both solutions at appropriate ratio β . After that, water was added dropwise under vigorous stirring. At water content 33 vol %, the mixture was left for 1 day to reach equilibrium. Afterward another portion of water was added until its content reached 67 vol %. The mixture was stirred additionally for 1 day. Finally, the water-organic mixture was dialyzed against pure water during 1 week using membrane tubing (molecular weight cutoff is 12–14 kDa) to remove organic solvents. The concentration of polymers after dialysis (3–5 g/L) was determined from UV spectrophotometry measurements.¹⁶

All investigations were conducted at room temperature (25 °C) in TRIS buffer solution (0.01 M, pH 9) to keep P4VP blocks completely uncharged. To evaluate dispersion stability of micelles in the presence of NaCl, PMANa or SDS micelle dispersions were mixed with aqueous solutions of corresponding compounds and vigorously stirred for 1 day. In the case of precipitation, the insoluble phase was separated from supernatant via preparative ultracentrifugation using Eppendorf centrifuge during 15 min at $\omega = 13\,000$ rpm. The concentration of micelles in supernatant was determined by UV spectrophotometry technique.

2.3. Measurements. UV spectra were recorded on a UV-vis spectrophotometer, Lambda-25 (Perkin-Elmer), in 10 mm quartz cells.

Static (SLS) and dynamic (DLS) light scattering (LS) measurements were carried out with a Photocor spectrometer at 25 °C. A 25 mW He-Ne laser operating at 630 nm wavelength was used as a light source. Light scattering angles varied within 30–150°. Refractive index increments were measured by a KMX-16 differential refractometer (Milton Roy) with a 2 mW He-Ne laser as a light source, $\lambda = 630$ nm. Prior to light scattering measurements, all solutions were filtered 2–3 times through Millipore GS 0.45 μm filters. SLS data were treated by the Zimm method. Weight-average micelle aggregation numbers (number of macromolecules per micelle) m_w were calculated as the ratio M_w/M_0 , where M_w and $M_0 = \beta M_{0(\text{PS-}b\text{-PEVP})} + (1 - \beta)M_{0(\text{PS-}b\text{-P4VP})}$ are molecular masses of micelle and average molecular mass of single macromolecule in a hybrid micelle correspondingly. Diffusion coefficients (D_z) were calculated from DLS data by cumulant analysis of an autocorrelation function of LS intensity fluctuations. Effective hydrodynamic radii (R_h)₀ of micelles were calculated from extrapolated to zero concentration diffusion coefficients (D_z)₀ using the Stokes equation. Primary SLS and DLS data are summarized in Table S1 of the Supporting Information.

Electrophoretic mobility measurements were performed on a ZetaPlus analyzer (Brookhaven Instruments) with a 30 mW solid-state laser operated at a wavelength of 635 nm. ζ -Potential meanings were calculated from electrophoretic mobility values, using the Smoluchowski equation.

The negative staining technique was used for transmission electron microscopy (TEM) studies. Two microliters of sample solution was allowed to settle on a Formvar-coated copper grid for 1 min, the excess of sample was taken away, and the grid was exposed to 1% uranyl

acetate for 20 s. Samples were air-dried and studied with the use of a Hitachi H-7000 microscope.

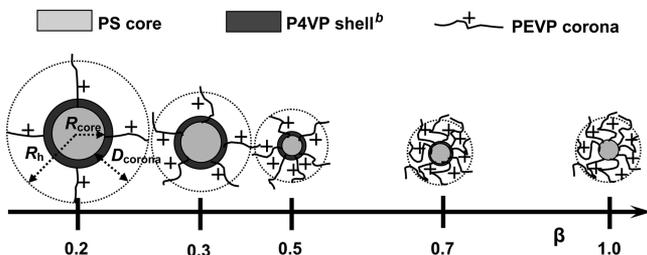
3. RESULTS AND DISCUSSION

The discussion is divided into three sections. First, the influence of β on micelle morphology, molecular mass, hydrodynamic dimensions, electrophoretic mobility, and other characteristics will be regarded, and a qualitative model of micelle structure will be put forward. Second, scaling relationships between β and micelle parameters will be deduced and compared to experimental data. Third, the influence of β on micelle aggregation stability in the presence of inorganic salt (NaCl) and oppositely charged polymeric (PMANa) or amphiphilic (SDS) complexing agents will be discussed. In the concluding section, the structure and properties of A-B/A-C and previously studied A-B/C micelles will be compared.

3.1. Influence of β on PS-*b*-P4VP/PS-*b*-PEVP Micelle Structure. Experimental Data. In our recent publication¹⁹ we have shown that mixing PS-*b*-P4VP with PS-*b*-PEVP in joint water-organic (dimethylformamide/methanol/water, 54/13/33 v/v/v) solvent is accompanied by comicellization of block copolymers and formation of hybrid micelles with a joint PS core and mixed P4VP/PEVP corona. The composition of micelles equals to the composition of copolymer mixture β . The hybridization is favored by thermodynamic reasons. These reasons include the gain in combinatorial entropy of mixing macromolecules,²⁰ the gain in combinatorial entropy of small counterions²¹ and the energetic gain, related to alleviation of electrostatic repulsion of PEVP blocks due to their "dilution" by uncharged P4VP blocks.²² Further replacement of organic solvent by water leads to "freezing" kinetic mobility of the PS core and "fixing" the structure of hybrid micelles.²³

TEM microphotographs demonstrated *spherical* morphology for all PS-*b*-P4VP/PS-*b*-PEVP- β micelles studied. (TEM images and discussion on peculiarities of micelle size distribution can be found in the Supporting Information.) Since P4VP blocks are insoluble in water at pH 9, we suppose a three-layered model of micelle structure. According to this model, micelles consist from insoluble PS core, intermediate spherical layer of contracted P4VP blocks (shell) and the outer lyophilizing corona from charged PEVP units (see Chart 2 below). This "core-shell-corona" structure provides the best stabilization of

Chart 2. Structure of Micelles of PS-*b*-P4VP/PS-*b*-PEVP- β as a Function of β^a



^aBr⁻ counterions are omitted. Dashed circles, indicating boundary of micelle corona, are for eye guide only. ^bPresentation of P4VP shell as a concentric spherical coat around the PS core is a sketch. It designates the layer where collapsed P4VP chains are predominately localized, without further specification its fine structure. We admit this layer may represent itself as separate globules (patches) of P4VP on PS surface at high β , which merge and form a continuous membrane-like nanophase upon decrease of β .

micelles in aqueous media, and was proposed in several recent publications for polymer micelles with chemically heterogenic corona.^{13,15,24}

Micelle characteristics as function of β were obtained from DLS and SLS experiments. Micelles with $\beta = 0.2-1$ were used, supporting NaCl concentration was 0.05 M. Dependences of weight-average molecular mass (M_w) and weight-average aggregation number m_w of micelles vs β are presented in Figure 1. Both dependencies are similar in character. The

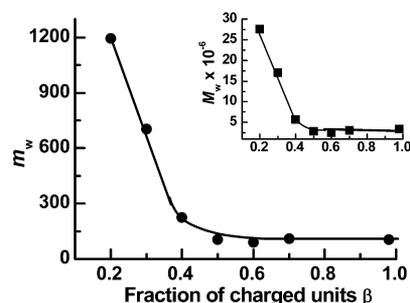


Figure 1. Dependence of weight average aggregation number m_w of PS-*b*-P4VP/PS-*b*-PEVP- β micelles upon β . (Dependence of M_w vs β is depicted in the inset.)

molecular mass of PS-*b*-P4VP/PS-*b*-PEVP-0.2 is more than 6 times higher than that of PS-*b*-PEVP micelles. Such great difference reflects the impact of electrostatic repulsion of PEVP units in the corona onto aggregation number. Within the interval $0.2 \leq \beta < 0.5$, m_w and M_w values drop dramatically, and further at $0.5 \leq \beta \leq 1.0$ these values are small and constant. In other words, the dependence of m_w (M_w) upon β is characterized by an inflection point at $\beta \sim 0.5$.

To understand the essence of structural difference between micelles with various β , we estimated structural and electrophoretic micelle parameters. Figure 2 presents the dependences

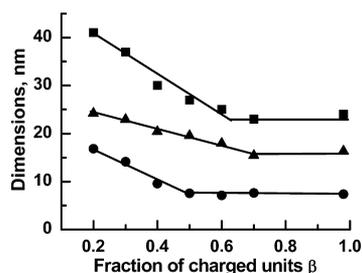


Figure 2. Dependences of hydrodynamic (■), core (●), and corona (▲) radii of mixed PS-*b*-P4VP/PS-*b*-PEVP- β micelles upon β .

of micelle hydrodynamic radius (R_h)₀, radius of the core (R_{core}) and radius of the corona (D_{corona}) on β (see Chart 2 for details). Values of (R_h)₀ were determined from DLS data; values of R_{core} and D_{corona} were calculated as described.¹⁶

From Figures 1 and 2, analogies between changes in micelle dimensions and changes in micelle masses upon variation of β can be noticed. Indeed, within the interval of $\beta = 0.2-0.7$, (R_h)₀ and D_{corona} are monotonously decreasing, while at $0.7 \leq \beta \leq 1.0$ these values are constant. In other words, variation of β has no influence on micelle molecular mass and dimensions, when $\beta \geq 0.7$. Decreasing β below this point induces stretching of PEVP blocks in corona, while at $\beta \leq 0.5$ such stretching is accompanied by remarkable growth of PS core.

Figure 3 shows the dependence of micelle ζ -potential upon fraction of PEVP blocks in hybrid corona. The correlation

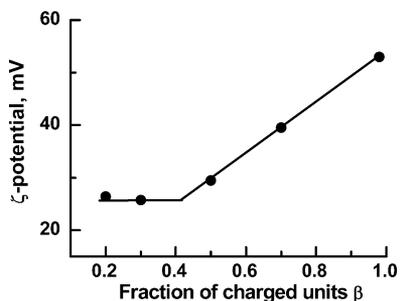


Figure 3. Dependence of ζ -potential of PS-*b*-P4VP/PS-*b*-PEVP- β micelles upon β . $[\text{PEVP}] + [\text{P4VP}] = 3 \times 10^{-5}$ base mol/L.

between ζ -potential and structural changes can be easily established. When $\beta < 0.5$, the ζ -potential is constant, and when $\beta \geq 0.5$, ζ -potential monotonously increases with the growth of β . Here again we have the inflection at $\beta \sim 0.5$.

The integral influence of β on micelle structure is depicted in Chart 2. For convenience of consideration, let us choose PS-*b*-PEVP micelles as initial point and start to substitute PEVP blocks in corona by insoluble P4VP ones. Until the fraction of PEVP blocks is above 0.7, micelle does not “feel” the substitution. The reason of such stability lies in domination of long-range electrostatic repulsion of PEVP units over short-range hydrophobic attraction of PS and P4VP units.

Nevertheless, due to collapse of P4VP blocks, the specific hydrophobic area per one PEVP chain does increase, while net micelle charge and its ζ -potential are decreased (Figure 3). To shield the growing hydrophobic core/shell–corona interface, PEVP chains start to elongate; this is observed as growth of D_{corona} . The effect becomes noticeable at $\beta \leq 0.7$ (Figure 2). When β diminishes below 0.5, the PS core starts to grow (molecular mass increases). The growth of the PS core enables to minimize the specific area per chain for both PS–P4VP and PS/P4VP–water interfaces. The growth of the core means the elongation of PS chains. Elongation of PS chains amplifies the effect of PEVP elongation and enables to sustain ζ -potential and aggregation stability of micelles at some minimum level (Figure 3). The elongation limit for both PS and PEVP chains is defined by their contour lengths (25 nm). From Figure 2, one can see that when $\beta = 0.2$ both blocks practically reach it. This point means the boundary of aggregation micelle stability, since both blocks cannot elongate further. Therefore, when β drops below 0.2, micelles precipitate.

3.2. Influence of β on PS-*b*-P4VP/PS-*b*-PEVP Micelle Structure. Theoretical Approach. Model. Let us consider a dilute salt-free aqueous solution of AB and AC diblock copolymers. We suppose that A, B, and C blocks are flexible chains consisting, respectively, of N_A , N_B , and N_C statistical segments of the same length a . A and C blocks are nonionic and hydrophobic, while B block is strongly dissociating (quenched) polyelectrolyte and $N_B f$ monomeric units of B block carry elementary charge e (f is the fraction of charges in a block). Charges in the B chain appear in the course of dissociation with release of monovalent counterions, and thus, there are $N_B f$ mobile monovalent counterions per chain in the solution. Let β be the fraction of the AB block copolymer in the system, then $(1 - \beta)$ is the fraction of AC chains.

We suppose that diblock copolymers self-assemble into mixed spherical micelles. Hydrophobic A and C blocks are assumed to be “soft” enough to ensure the equilibrium character of self-assembly. The fractions of AC and AB copolymers in a micelle with an equilibrium aggregation number m are equal to $(1 - \beta)$ and β , respectively. The micelle has a three-layered structure. Its core is formed by hydrophobic A blocks of both copolymers. The core is covered by a shell of hydrophobic C blocks, and the micellar corona consists of ionic B blocks. For the reasons of mathematical simplicity, we assume the C shell to be continuous spherical nanophase; that is, we neglect its possible patchlike structure at high β . We also suppose that the radius of the ionic B corona is much larger than the shell thickness and neglect the fact that the shell contains some fraction of B segments passing through it from core to corona. Then, the radius of the dense hydrophobic core, R_{core} , and the radius of the core plus the shell region, R_{shell} , are equal to

$$R_{\text{core}} \cong a(3mN_A/4\pi)^{1/3}$$

$$R_{\text{shell}} \cong a(3m(N_A + (1 - \beta)N_C)/4\pi)^{1/3}$$

The equilibrium value of aggregation number m is determined by a balance between (i) unfavorable contacts of insoluble A and C blocks with each other and with solvent, (ii) elastic stretching of blocks in the corona, (iii) electrostatic interactions, and (iv) the entropy of counterions. Thus, the total micelle free energy per chain in kT units is the sum of four terms:

$$F_{\text{tot}} = F_{\text{surf}} + F_{\text{el}} + F_{\text{el-st}} + F_{\text{ci}} \quad (1)$$

The first term, F_{surf} , describes the surface effects:

$$F_{\text{surf}} \cong m^{-1/3}[G_1 N_A^{2/3} + G_2(N_A + (1 - \beta)N_C)^{2/3}] \quad (2)$$

where $G_i = (36\pi)^{1/3}\gamma_i a^2$, $i = 1, 2$. Here γ_1 and γ_2 are surface tension coefficients of core–shell and shell–corona interfaces, respectively.

Let R_m be the total micelle radius, and hence, the corona radius is equal to $(R_m - R_{\text{core}})$. The energy F_{el} of elastic deformation of corona chains reads:²⁵

$$F_{\text{el}} \cong \frac{3}{2}\beta \frac{(R_m - R_{\text{core}})^2}{N_B a^2} \quad (3)$$

The third term, $F_{\text{el-st}}$, and the fourth term, F_{ci} , in eq 1 are connected with the presence of charges in the system and depend on distribution of counterions in solution. We suppose that only a fraction α of counterions can move freely within the whole volume of solution while $(1 - \alpha)$ is the fraction of counterions kept inside charged micellar corona and partly neutralizing it. The electrostatic energy of a micelle with the charge $Q = \beta \alpha m N_B f$ can be estimated as the energy of uniformly charged ball of the radius R_m

$$F_{\text{el-st}} \cong \frac{1}{m} \frac{Q^2}{\epsilon k T R_m} \cong u \frac{(N_B f \alpha \beta)^2}{R_m/a} m \quad (4)$$

Here ϵ is the dielectric permeability of the solvent. The dimensionless parameter $u = e^2/\epsilon a k T$ describes the strength of electrostatic interactions between two ions at the distance a .

The free energy F_{ci} of the translational motion of counterions within the micellar corona and in outer solution can be written as

$$F_{ci} = N_B \beta f (1 - \alpha) \ln \left(\frac{m N_B \beta f (1 - \alpha)}{(R_m/a)^3} \right) + N_B \beta f \alpha \ln \left(\frac{\Phi N_B \beta f \alpha}{N_A + N_B} \right) \quad (5)$$

where Φ is total volume fraction of all polymeric species in the system.

In the case of $N_A = N_B = N_C = N$ and $G_1 = G_2 = G$, the total free energy per chain reads:

$$F_{tot} = GN^{2/3} m^{-1/3} [1 + (2 - \beta)^{2/3}] + \frac{3}{2} \beta \frac{R_m^2}{Na^2} + u \frac{(Nf\alpha\beta)^2}{R_m/a} m + N\beta f (1 - \alpha) \ln \left(\frac{m N \beta f (1 - \alpha)}{(R_m/a)^3} \right) + N\beta f \alpha \ln \left(\frac{\Phi \beta f \alpha}{2} \right) \quad (6)$$

The equilibrium micellar parameters are calculated via minimization of F_{tot} with respect to R_m , m , and α variables:

$$\begin{cases} \frac{\partial F_{tot}}{\partial R_m} = 0 \\ \frac{\partial F_{tot}}{\partial m} = 0 \\ \frac{\partial F_{tot}}{\partial \alpha} = 0 \end{cases} \quad (7)$$

This system of three equations was solved numerically for $N = 25$, $u = 1$, $G = 17$, $f = 1$, and $\Phi = 10^{-5}$, with these values being close to experimental conditions. Equilibrium aggregation number (m), total micelle radius (R_m), core radius (R_{core}), and the fraction of counterions in outer solution (α) vs β are plotted in Figures 4–6.

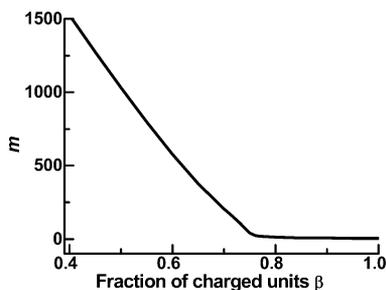


Figure 4. Dependence of equilibrium aggregation number m on β .

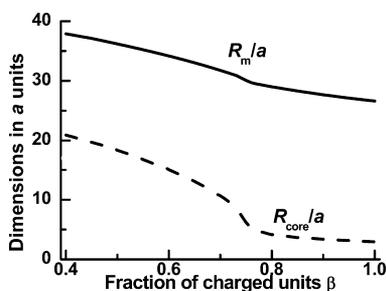


Figure 5. Dependences of micelle R_m/a (solid line) and core R_{core}/a (dashed line) radii on β .

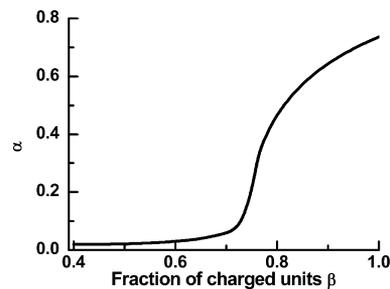


Figure 6. Dependence of fraction α of counterions in outer solution on β .

The distribution of counterions depends strongly on the fraction of ionic block copolymer in the micelle. One can see from Figure 6 that the value of α grows with increasing β ; in a limiting case, micelles with high β can be roughly described in terms of the so-called Pincus regime. In the Pincus regime, small micelles ($m \sim 10$, Figure 4) cannot keep their counterions, all counterions move freely in solution, $\alpha \sim 1$, and the micelle net charge is defined as $Q = N_B f m \beta$. On the contrary, micelles with high fraction of hydrophobic AC chains keep the major fraction of counterions inside the corona. The value of α decreases with decreasing β . In the limiting case $\alpha \sim 0$ all counterions are held within the micellar corona creating osmotic pressure leading to a strong stretching of coronal chains (so-called osmotic regime). Scaling relationships for micellar parameters in the case of starlike micelles ($R_m \gg R_{core}$) can be easily obtained analytically for these two limiting cases of Pincus regime and osmotic regime.

In the *Pincus regime*, the equilibrium length of ionic blocks in the micellar corona is defined by a balance of the Coulomb energy of repulsion of charges in the B block (eq 4) and elastic free energy of coronal blocks (eq 3) preventing chain elongation: $R_m/a \sim u^{1/3} N_B f^{2/3} \beta^{1/3} m^{1/3}$. Then the coronal free energy can be estimated as $F_{el-st} \sim u^{2/3} N_B \beta^{5/3} f^{4/3} m^{2/3}$. Minimizing it together with the surface free energy, we obtain equilibrium micellar parameters in Pincus regime:

$$m \cong u^{-2/3} G(\beta) f^{-4/3} N_B^{-1} \beta^{-5/3}$$

$$R_m/a \cong u^{1/9} N_B^{2/3} f^{2/9} (G(\beta))^{1/3} \beta^{-2/9}$$

where

$$G(\beta) = G_1 N_A^{2/3} + G_2 (N_A + (1 - \beta) N_C)^{2/3}$$

In the *osmotic regime*, the length of coronal blocks is defined by a balance of the elastic free energy (eq 3) and the free energy of translational motion of counterions kept within the micellar corona (the first term in eq 5 with $\alpha = 0$): $R_m/a = N_B f^{1/2}$. Substituting the obtained estimate of R_m into F_{el} (eq 3), we get the coronal free energy $F_{corona} \sim N_B f \beta$, and minimizing it together with the surface contribution we calculate equilibrium micellar parameters in the osmotic regime:

$$m \cong (G(\beta))^3 (f N_B)^{-3} \beta^{-3}$$

$$R_m/a \cong N_B f^{1/2}$$

Comparison Model and Experiment. Experimental data and scaling estimations give a similar principal result: the existence of an inflection point in micellar parameters vs β . Above this point, micelle aggregation number is weakly dependent upon β . Scaling relationships give $m \sim \beta^{-5/3}$; experimentally no

dependence was distinguished. Below the inflection point, the dependence of m upon β is rather steep. Scaling relationships give $m \sim \beta^{-3}$, and experimental points fit this prediction quite satisfactory (see Figures 1 and 4). Calculated dependences of core and micelle radii on β also qualitatively coincide with experimental curves (see Figures 2 and 5). In the limiting case of the Pincus regime, scaling relationships predict very weak dependence of R_m upon β , $R_m \sim \beta^{-2/9}$; experimental data confirm this prediction quite well. At the other end of the osmotic regime, no dependence upon β is observed. Probably, this is because osmotic regime supposes chains are already fully stretched, so their length is no longer dependent upon composition. Such regime may fit experimental data at very small micelle composition, that is, $\beta \leq 0.2$. On the whole, qualitative correlation between theoretical predictions and experimental data confirms the correctness of the “core–shell–corona” model (Chart 2) with segregating PEVP and P4VP blocks for description of the hybrid micelles structure.

3.3. Influence of β on Aggregation Stability of PS-*b*-P4VP/PS-*b*-PEVP Hybrid Micelles in Aqueous Media in the Presence of Ionic Species. Addition of NaCl. Figure 7

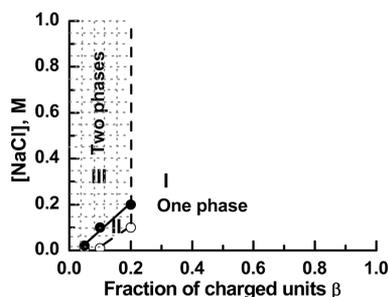


Figure 7. Diagram of aggregation stability of PS-*b*-P4VP/PS-*b*-PEVP- β hybrid micelles in NaCl aqueous solutions. Key: (O) phase separation points, (●) points of quantitative precipitation; [PEVP] = 5×10^{-4} base mol/L.

demonstrates the diagram of micelle aggregation stability upon addition of NaCl. Below the dashed line (region I), micelles are stable, while above it phase separation is observed (region II). The solid line designates the area of quantitative precipitation. Above this line (region III), all micelles are included in the solid phase. It can be easily seen that values of threshold salt concentrations for micelle salting out monotonously increase with increase of $\beta = 0.05$ – 0.2 . Micelles with $\beta \geq 0.3$ do not precipitate even at saturated NaCl concentrations, ca. 5.5 M. The correlation between micelle structure and its ability to persist phase separation is the following. Because of low density of PEVP chains, the hydrophobic core/shell–corona interface is poorly protected against unfavorable contacts with aqueous media when $\beta \leq 0.2$. Therefore, screening electrostatic repulsion of PEVP blocks via addition of NaCl easily trigger intermicellar aggregation. At $\beta \geq 0.3$, the hydrophobic PS/P4VP area is effectively protected by PEVP blocks, and therefore, hybrid micelles do not lose their aggregation stability even at high salt concentrations.

Addition of the Oppositely Charged Polyelectrolyte or Surfactant. If one mixes aqueous dispersions of PS-*b*-PEVP micelles with aqueous solutions of the oppositely charged PMANa or SDS, micelle polyelectrolyte complexes (MPC) do form. Detailed discussion of MPC structure and properties can be found elsewhere.^{18,26–28} The solubility of MPC is defined by

the chemical nature and charge ratio (Z) of the mixing components, $Z = [-]/[+] = [\text{PMANa}]/[\text{PEVP}] = [\text{SDS}]/[\text{PEVP}]$. At stoichiometric ratio, $Z = 1$, insoluble complexes do form, while at $Z \neq 1$, soluble complexes, stabilized by charged units of excessive component, may form. We have studied complexation between PS-*b*-P4VP/PS-*b*-PEVP- β hybrid micelles and PMANa or SDS as a function of Z and β values. When $Z = 1$, both components quantitatively precipitate for any β . It implies that the value of β does not affect the ability of hybrid micelles to form MPC with the oppositely charged species. Nevertheless, β significantly affects the solubility of MPC.

Figures 8 and 9 present diagrams of aggregation stability of MPC between PS-*b*-P4VP/PS-*b*-PEVP- β micelles and PMANa

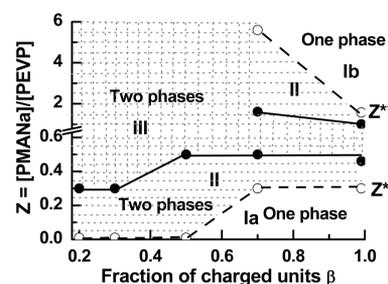


Figure 8. Diagram of aggregation stability of complexes of hybrid PS-*b*-P4VP/PS-*b*-PEVP- β micelles with PMANa. Key: (O) phase separation points, (●) points of quantitative precipitation; [NaCl] = 0.1 M; [PEVP] = 1×10^{-3} base mol/L ($Z \leq 1$) or [PMANa] = 1×10^{-3} base mol/L ($Z \geq 1$).

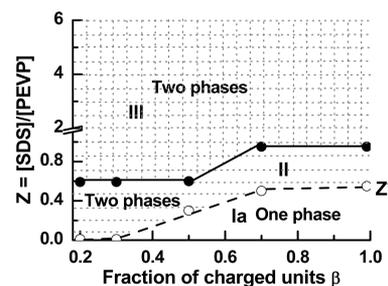


Figure 9. Diagram of aggregation stability of complexes of hybrid PS-*b*-P4VP/PS-*b*-PEVP- β micelles with SDS. Key: (O) phase separation points, (●) points of quantitative precipitation; [NaCl] = 0.01 M; [SDS] = 8×10^{-4} M.

or SDS molecules. The field below the bottom dashed line Z^* (region Ia) corresponds to formation of positively charged soluble MPC, stabilized by excessive PEVP blocks. The shaded field between dashed and solid lines (region II) designates the area of phase separation and partial precipitation of MPC. The shaded field between solid curves (region III) corresponds to quantitative precipitation of MPC. The area above the top dashed line Z^{**} (region Ib) designates the formation of negatively charged (overcharged) soluble MPS, stabilized by excessive PMANa units.

Individual PS-*b*-PEVP micelles can form soluble positively charged ($Z^* = 0.3$) and negatively overcharged ($Z^{**} = 2$) MPC with PMANa. For MPC {PS-*b*-P4VP/PS-*b*-PEVP-0.7–PMANa}, $Z^* = 0.3$ and $Z^{**} = 6$. When $\beta < 0.7$, complexes of hybrid micelles with PMANa precipitate at any Z (Figure 8). In the case of SDS, individual PS-*b*-PEVP micelles can form soluble MPS only at PEVP excess, $Z^* = 0.6$. The substitution of

PEVP blocks onto P4VP ones leads to gradual decrease of Z^* , $Z^* = 0.3$ for $\beta = 0.5$. When β drops below 0.5, complexes of hybrid micelles with SDS precipitate at any Z (Figure 9).

From Figures 8 and 9, one can easily notice that substitution of PEVP blocks onto P4VP ones deteriorates the ability of hybrid micelles to form soluble MPC with oppositely charged species. Again, the inflection region near $\beta \sim 0.5$ – 0.7 can be isolated. Above these β values, soluble MPC may form, while below them soluble MPC do not form. The obtained result implies that individual PS-*b*-PEVP micelles contain some fraction (ca. 30 mol %) of “spare” charged units which are not necessary for keeping micelle aggregation stability. If this fraction of PEVP units is neutralized by an oppositely charged agent, micelles will preserve their aggregation stability. But when β drops below 0.5, all PEVP-units are “involved” in providing micelle aggregation stability. Therefore, charge neutralization even their small part triggers the precipitation.

4. CONCLUSIONS

In the current and preceding papers, we have systematically studied the structure and properties of A-B/C and A-B/A-C polymer micelles as functions of their composition. Micelles consist of an insoluble hydrophobic A core and amphiphilic corona from charged B units and insoluble uncharged C units. Micelles differ by their composition $\beta = [B]/([C] + [B])$ and by character of coronal units distribution (statistical vs starlike). We have found that both types of micelles possess a number of common features: insensitivity to composition variation at high β ; increase in aggregation number upon decrease the fraction of charged B units; and ability to bind oppositely charged polyelectrolytes and surfactants into corona.

At the same time, the character of structural reorganization vs β is quite different for both types of micelles. For A-B/C micelles, the existence of a jump-point has been demonstrated. Below this point, shrinkage of the corona and increase of the core size are observed. For hybrid A-B/A-C micelles, an inflection point can be found. Below this point, steep and monotonous changes of sizes of both core and corona are observed. The differences in a set of micelle parameters can be ascribed to the possibility of spatial segregation of B and C blocks within the corona of hybrid micelles. In the case of A-B/C micelles, B and C units are statistically distributed along one chain, and their spatial separation is hindered.

Overall, the conducted research has shown that polymer micelles with homogeneous core and heterogeneous amphiphilic corona can exist for a wide range of corona compositions. The tendencies in micelle structure and property changes upon variation of composition and distribution pattern of polymer units in corona can be qualitatively predicted as an interplay of electrostatic and hydrophobic interactions of polymer units. We believe these findings may be of certain importance as a part of the fundamental basis for design of multifunctional polymeric micelles with heterogeneous microstructure.

■ ASSOCIATED CONTENT

Supporting Information

Summary of primary SLS and DLS results; TEM and sedimentation velocity data; discussion about peculiarities of micelle size distribution for PS-*b*-PEVP alone and for PS-*b*-P4VP/PS-*b*-PEVP- β mixtures. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: lysenko@genebee.msu.ru.

Notes

The authors declare no competing financial interest.

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