NOVEL "CORE-SHELL-CORONA" ARCHITECTURES VIA COMPLEXATION OF MICELLES OF IONIC AMPHIPHILIC DIBLOCK COPOLYMERS WITH OPPOSITELY CHARGED POLYELECTROLYTES

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Introduction

Self-assembly of ionic amphiphilic block copolymers in aqueous solutions results in the formation of micelles, each containing a compact hydrophobic core formed by non-polar blocks and a swollen hydrophilic corona formed by polyelectrolyte blocks. Being charged, such macromolecular assemblies are naturally expected to interact with oppositely charged polyions, generating interpolyelectrolyte complexes (IPECs). Although IPECs formed by oppositely charged linear polyelectrolytes were thoroughly investigated during the last decades[1,2], the interactions of micelles of ionic amphiphilic block copolymers with oppositely charged macromolecules has received only little attention both experimentally[3a] and theoretically.[3b]

This paper demonstrates that this interaction can result in the formation of novel polymeric "core-shell-corona" architectures which can find promising applications as nano-containers and nano-reactors and it summarizes our recent studies[4] on the complexation of micelles formed in aqueous solutions of polyisobutylene-*block*-poly(sodium methacrylate) diblock copolymers with quaternized poly(4-vinylpyridine)s.

Experimental

Materials. Polyisobutylene-*block*-poly(*tert*-butyl methacrylate) diblock copolymers (PIB_X-b-$PtBMA_Y$) with different lengths of the PIB and PtBMA blocks (X and Y denote the number-average degrees of polymerization of the corresponding blocks: X =20, Y = 100, 280, 425; X = 25, Y = 2850; X = 75, Y = 615, 1590) were synthesized via a combination of living cationic and anionic polymerizations.[5] In order to prepare polyisobutylene-*block*-poly(methacrylic acid) diblock copolymers (PIB_X-b-$PMAA_Y$), the *tert*-butyl methacrylate groups of PIB_X-b-$PtBMA_Y$ were hydrolyzed with HCl in dioxane at 80 °C.

Poly(N-ethyl-4-vinylpyridinium bromide)s (PVP·EtBr) with M_w = 110,000 and 660,000 g/mol (DP_w = 500 and 3000, respectively) were synthesized from the corresponding samples of poly(4-vinylpyridine) (Polysciences Inc.) via their exhaustive quaternization with a 10-fold excess of ethyl bromide at 60 °C.

Methods and Instrumentation. Turbidimetric titrations were carried out in isoionic regime at λ = 500 nm with a Hitachi 150-200 UV-vis spectrophotometer. Sedimentation experiments were carried out with a Beckman (Spinco, Model E) analytical ultracentrifuge equipped with a UV-vis absorption optical detector. Steady-state fluorescence spectra of the air-equilibrated solutions were recorded with a Hitachi F-4000 fluorescence spectrophotometer. Small-angle neutron scattering (SANS) measurements were performed with the instrument D11 of the ILL (Grenoble, France) with a neutron wavelength λ = 6 Å at sample-to-detector distances of 1.1, 4, and 16 m. Dynamic light scattering (DLS) measurements were carried out with an ALV DLS/SLS-SP 5022F equipment which consists of an ALV-SP 125 laser goniometer, an ALV 500/E correlator, and a He-Ne laser with wavelength λ = 632.8 nm.

Results and Discussion

On addition of the solution of PVP·EtBr to alkaline solutions of the PIB_X-b-$PMANa_Y$ micelles, no macroscopic phase separation is observed until the charge ratio in the mixtures of the oppositely charged polymeric components, Z = [+] / [-], exceeds a certain maximum value, Z_M (**Figure 1a**), at low concentration of NaCl ([NaCl] ≤ 0.1 M), the values of Z_M being comparable with those obtained for mixtures of the reference homopolyelectrolyte, PMANa (DP_n = 400), and PVP·EtBr. Sedimentation patterns obtained for the homogeneous mixtures of PIB_X-b-$PMANa_Y$ and PVP·EtBr at λ = 270 nm (at

this wavelength, the cationic polyelectrolyte absorbs light while the diblock copolymers posses nearly no absorbance) shows the existence of only type of species whose sedimentation velocity is much higher than that of individual cationic macromolecules (**Figure 1b**). They can be associated with particles of water-soluble IPEC resulting from the interaction of the PIB_X-b-$PMANa_Y$ micelles with PVP·EtBr, all cationic macromolecules being incorporated in such particles and evenly distributed among them.
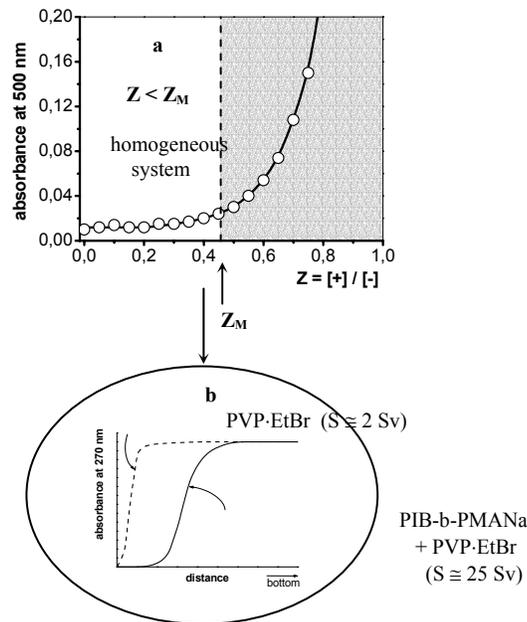

Figure 1. (a) Turbidimetric titration curve of the solution of the PIB_{20}-b-$PMANa_{100}$ micelles with the solution of PVP·EtBr (DP_w = 500); **(b)** Sedimentation profiles detected after 15 min for a with Z = [+]/[-] = 0.4 (——) and for the reference solution of PVP·EtBr (DP_w = 500) (---); 0.1 M NaCl, 0.01 M TRIS (pH 9).

The particles of the formed water-soluble IPECs were found to solubilize pyrene, which was used as a fluorescence polarity probe. This fact indicates that these particles, as well as the original PIB_X-b-$PMANa_Y$ micelles, contain cores formed by the PIB blocks, pyrene being solubilized by such cores (reference experiments carried out under the same conditions with solutions of the reference homopolyelectrolyte PMANa as well as with solutions of IPECs formed upon its interaction with PVP·EtBr show no solubilization of pyrene). Additionally, the intensity of pyrene fluorescence in solutions of the complex species is lower than that measured under the same conditions in solutions of the original PIB_X-b-$PMANa_Y$ micelles, steeply falling with the rising content of the cationic polyelectrolyte and approaching a limiting value already at low Z (e.g., for IPECs resulting from the interaction of the PIB_{20}-b-$PMANa_{100}$ micelles with PVP·EtBr of DP_w = 500 already at Z ≈ 0.1). This effect can be accounted for by quenching of pyrene fluorescence by pyridinium groups of the cationic polyelectrolyte and indicates that cationic macromolecules prefer to be located in the vicinity of the PIB cores.

The scattering curves obtained by means of SANS for particles of the formed water-soluble IPECs demonstrate a higher intensity and a larger slope at intermediate values of the scattering vector as compared to the original PIB_X-b-$PMANa_Y$ micelles, becoming more pronounced with increasing Z (as an example, the scattering curves for the PIB_{20}-b-$PMANa_{100}$ micelles and water-soluble complex species resulting from their interaction with PVP·EtBr are given in **Figure 2**). These findings point to a larger size of the dense nucleus for the particles of the water-soluble IPECs as compared to the micel-

lar core of the original micelles, the size of the nucleus increasing with the rising content of the cationic polyelectrolyte.
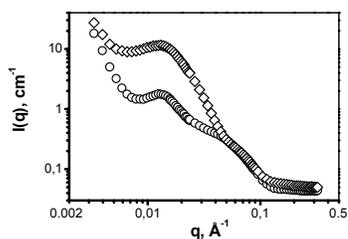
Figure 2. SANS intensity as a function of the scattering vector, q, for solutions of PIB_{20}-b-$PMANa_{100}$ micelles (○) and their IPEC formed with PVP·EtBr ($DP_w = 500$) at Z = [+]/[-] = 0.4 (◊); [PIB_{20}-b-$PMANa_{100}$] = 1.0% (wt); 0.1 M NaCl, 0.01 M TRIS (pH 9).

All these results considered in a combination suggest that the water-soluble complex species formed upon the interaction of the PIB_X-b-$PMANa_Y$ micelles with PVP·EtBr represent peculiar "onion"-like micelles whose hypothetical architecture is schematically depicted in **Figure 3**. Each micelle consists of a PIB core (**A**) surrounded by a shell assembled from the coupled oppositely charged polyelectrolyte fragments (**B**) and an ionic corona (**C**) built up from the excess fragments of the PMANa blocks not involved in the interpolyelectrolyte complexation.
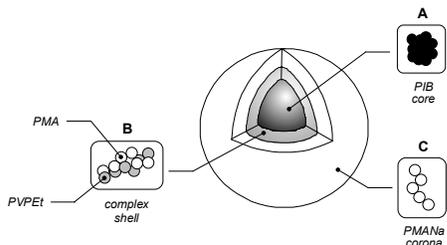
Figure 3. Core-shell-corona architecture of IPEC particles.

The scattering curves presented in **Figure 2** were quantitatively analyzed on the basis of a "core-shell" model to compare the structural parameters (core radius, R_c, and aggregation number, N_{agg}) of the original PIB_{20}-b-$PMANa_{100}$ micelles and particles of the water-soluble micellar IPECs formed upon their interaction with PVP·EtBr. In the framework of this model, the scattering length densities for the core of the particle and the solvent are taken constant while the scattering length density of the shell is assumed to gradually decrease with rising distance from the core. For the water-soluble complex species, the scattering contributions from the PIB core and the complex shell cannot be meaningfully separated under the contrast condition used (D_2O was used as a solvent). Therefore, a nucleus of each complex particle is considered to contain the PIB blocks and the corresponding (according to Z) amount of the stoichiometric (including the opposite charges in 1:1 ratio) IPEC.

The values of R_c and N_{agg} (evaluated under the assumption that the density of the PIB core coincides with that for PIB in the bulk) resulting from the analysis are given in **Table 1**. It is remarkable that the number of PIB_{20}-$PMANa_{100}$ macromolecules incorporated in particles of the water-soluble micellar IPEC formed even at Z = 0.4, which is close to Z_M, is only slightly (within 5%) higher than N_{agg} for the original PIB_{20}-b-$PMANa_{100}$ micelles, while the core radius rises by a factor of 2.

The results of DLS (**Table 1**) show that hydrodynamic radius, R_h, of the water-soluble complex species is measurably but not pronouncedly lower than that of the original PIB_{20}-b-$PMANa_{100}$ micelles, confirming that no intermicellar aggregation or a significant change of N_{agg} upon their interaction with the cationic polyelectrolyte takes place. The observed decrease in the size of particles of the water-soluble micellar IPECs compared to the original PIB_{20}-b-$PMANa_{100}$ micelles can be explained by a collapse of the formerly stretched PMANa blocks when they complex with PVP·EtBr.

Thus, the obtained results suggest that cationic macromolecules interacting with the PIB_X-b-$PMANa_Y$ micelles prefer to penetrate deeply inside their coronas via polyion exchange reactions[2] to be finally localized in the vicinity of the PIB cores, the structure of the original micelles being apparently not affected by this complexation.

Table 1. Structural Parameters the PIB_{20}-b-$PMANa_{100}$ Micelles and the Particles of the Water-Soluble Micellar IPEC Formed Upon Their Interaction with PVP·EtBr ($DP_w = 500$) at Z = [+] / [-] = 0.4; 0.1 M NaCl, 0.01 M TRIS (pH 9).

Micelles			IPEC		
R_c [a], nm	N_{agg} [a]	R_h [b], nm	R_c [a,c], nm	N_{agg} [a]	R_h [b], nm
3.4	84	22.5	6.3	88	19

[a] SANS; c = 1.0 % (wt); [b] DLS; c = 0.02 % (wt); [c] Radius of the two-phase nucleus consisting of the PIB core surrounded by the IPEC shell.

At relatively high concentrations of NaCl (e.g., at [NaCl] > 0.3 M for the mixtures of PIB_X-b-$PMANa_Y$ and PVP·EtBr of $DP_w = 500$), the intensity of the scattering curves obtained by means of SANS for the water-soluble micellar IPECs decreases with the increasing ionic strength, the curves gradually approaching to those observed for the PIB_X-b-$PMANa_Y$ micelles under the same conditions. This can be accounted for by dissociation of the water-soluble complex species due to effect of small ions screening the interaction between the oppositely charged polymeric components.

Conclusions

Interaction of PIB_X-b-$PMANa_Y$ micelles with quaternized poly(4-vinylpyridine) leads to water-soluble IPECs in which part of the corona of the original micelles apparently plays a lyophilizing part. Each particle of such IPECs is considered to be a peculiar complex micelle consisting of a two-phase hydrophobic nucleus formed by a PIB core surrounded by a shell of the coupled oppositely charged polyelectrolyte fragments and an ionic corona built up from fragments of PMANa blocks not involved in the interpolyelectrolyte complexation. Thus, these water-soluble micellar complex species represent novel polymeric architectures of "core-shell-corona" ("onion"-like) structure. At relatively high ionic strength of the surrounding medium the water-soluble micellar IPECs dissociate due to the screening of the interpolyelectrolyte interaction by small ions.

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