

Novel Water-Soluble Micellar Interpolyelectrolyte Complexes<sup>†</sup>

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The interaction of polyisobutylene-*block*-poly(sodium methacrylate) diblock copolymer micelles with a strong cationic polyelectrolyte, poly(*N*-ethyl-4-vinylpyridinium bromide), in alkaline media was examined by means of turbidimetry, analytical ultracentrifugation, and fluorescence spectroscopy. It was shown that the diblock copolymer micelles and the cationic polyelectrolyte, taken at charge ratios  $Z = [+]/[-]$  not exceeding a certain critical value  $Z_M < 1$ , form peculiar water-soluble micellar complex species, each containing a two-phase hydrophobic nucleus and a hydrophilic corona. The nucleus consists of a polyisobutylene core and a shell assembled from the fragments of the water-insoluble interpolyelectrolyte complex. The corona is formed by the excess fragments of poly(sodium methacrylate) blocks not involved in the complexation with poly(*N*-ethyl-4-vinylpyridinium bromide).

## Introduction

The electrostatic interaction between oppositely charged macromolecules drives them to form interpolyelectrolyte complexes (IPECs). Such macromolecular assemblies have received considerable attention not only from a fundamental point of view but also because of their numerous promising potential applications as new smart polymeric reagents and materials for industry, ecology, biotechnology, and medicine. The formation, structure, and properties of IPECs were thoroughly investigated in a great number of studies, which have been exhaustively reviewed.<sup>1–3</sup>

Block copolymers with one of the blocks being a polyelectrolyte can also be used as components in interpolyelectrolyte complexation. The use of such copolymers provides an attractive opportunity for a design of novel complex macromolecular architectures. For example, it has been demonstrated in a number of publications<sup>4–7</sup> that the interaction of ionic diblock copolymers containing nonionic hydrophilic blocks, e.g., poly(ethylene glycol),<sup>4</sup> poly(ethylene oxide),<sup>5,7</sup> or poly(glycerol methacrylate),<sup>6</sup> with oppositely charged macromolecules, e.g., synthetic homopolyelectrolytes,<sup>5a,6,7</sup> natural polyelectrolytes<sup>4b–d,5b</sup> as well as ionic diblock copolymers,<sup>4a</sup> results in the formation of micellar IPECs also called polyion complex micelles<sup>4</sup> or block ionomer complexes.<sup>5</sup> The particles of such IPECs were found to have a “core–shell” structure with a core assembled from the fragments of the insoluble interpolyelectrolyte complex surrounded by a corona built up from nonionic hydrophilic blocks.

Being amphiphilic, ionic block copolymers containing non-ionic hydrophobic blocks are well-known to self-assemble in

aqueous solutions to generate micelles, each micelle consisting of a compact hydrophobic core formed by the nonpolar blocks and a swollen hydrophilic corona formed by the polyelectrolyte blocks. Such macromolecular assemblies are expected to interact with oppositely charged polyelectrolytes to form IPECs. Up to now, however, the interpolyelectrolyte complexation in such systems has received only little attention both experimentally<sup>8</sup> and theoretically.<sup>9</sup>

This paper considers the interaction of polyisobutylene-*block*-poly(sodium methacrylate) diblock copolymer micelles with a strong cationic polyelectrolyte, poly(*N*-ethyl-4-vinylpyridinium bromide), in alkaline media and the properties of IPECs resulting from this interaction.

## Experimental Section

**Materials.** A polyisobutylene-*block*-poly(*tert*-butyl methacrylate) diblock copolymer (PIB-*b*-PtBMA) was synthesized via a combination of living cationic and anionic polymerizations as described elsewhere.<sup>10,11</sup> The molecular weight distributions of the PIB precursor (measured separately) and PIB-*b*-PtBMA were determined by means of size exclusion chromatography (SEC) with the use of PIB and PtBMA standards. For the diblock copolymer, a weighted average of the homopolymer calibration curves was used. SEC was performed using PSS SDV-gel columns (5  $\mu$ m, 60 cm, 1  $\times$  linear (10<sup>2</sup>–10<sup>5</sup> Å), 1  $\times$  100 Å) with THF as eluent at a flow rate of 1.0 mL/min at room temperature using UV ( $\lambda$  = 230 and 260 nm) and RI detection.

The values of number-average molecular mass,  $\bar{M}_n$ , for PIB and PtBMA blocks were found to be 1100 g/mol ( $\overline{DP}_n \approx 20$ ) and 14 500 g/mol ( $\overline{DP}_n \approx 100$ ), respectively; the estimated polydispersity index of PIB-*b*-PtBMA was 1.16. To prepare polyisobutylene-*block*-poly(methacrylic acid) (PIB-*b*-PMAA), the *tert*-butyl methacrylate groups of PIB-*b*-PtBMA were hydrolyzed with hydrochloric acid in dioxane at 80 °C.<sup>11</sup>

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Poly(*N*-ethyl-4-vinylpyridinium bromide) (PVP·EtBr) was synthesized from poly(4-vinylpyridine) (Polysciences Inc.) with weight-average molecular mass  $\bar{M}_w = 50\,000$  g/mol ( $\overline{DP}_w \approx 480$ ) via its exhaustive quaternization with a 10-fold excess of ethyl bromide at 60 °C. As determined by  $^1\text{H}$  NMR spectroscopy, the molar fraction of quaternized pyridine units in the resulting polymer was close to 0.9, corresponding to about 430 charged monomer units per polymer chain.

**Sample Preparation.** *Stock Solutions.* To prepare a stock solution of the copolymer, PIB-*b*-PMAA was dissolved in 0.1 M NaOH at 50–60 °C under continuous stirring. The concentration of sodium carboxylate groups in the resulting alkaline stock solution of PIB-*b*-PMANa was 0.1 M. A stock solution of PVP·EtBr was prepared by dissolving the cationic polyelectrolyte in water. The concentration of pyridinium groups in the resulting stock solution of PVP·EtBr was 0.05 M.

*Sample Solutions.* Sample solutions of PIB-*b*-PMANa were prepared by an appropriate dilution of the stock copolymer solution with a 0.01 M aqueous solution of 2-amino-2-(hydroxymethyl)-1,3-propanediol (Tris, Fluka) of pH 9. Sample solutions containing both PIB-*b*-PMANa and PVP·EtBr were obtained by mixing the stock solutions of these polymers in the presence of NaCl with a subsequent appropriate dilution of such mixtures by 0.01 M Tris. The ionic strength of the sample solutions was adjusted by an addition of 4 M NaCl (ICN).

**Methods and Instrumentation.** *Turbidimetric Titration.* Turbidimetric titrations of PIB-*b*-PMANa solutions with solutions of PVP·EtBr were carried out in an isoionic regime at the wavelength  $\lambda = 500$  nm with a Hitachi 150-20 UV–vis spectrophotometer. At this wavelength, the polymers used do not absorb light; therefore, the values of optical density resulted from light scattering only. The titrations were run under continuous stirring; the time interval between subsequent additions of a titrant was equal to 1 min.

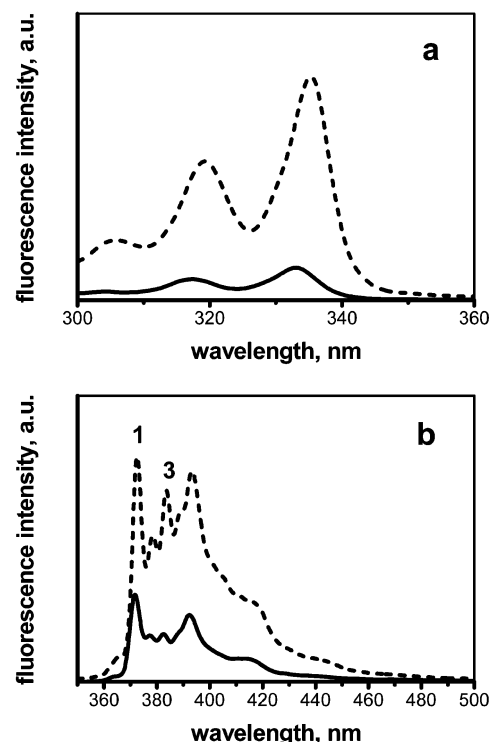
*Analytical Ultracentrifugation.* Sedimentation experiments were carried out in the scan mode with a Beckman (Spinco, model E) analytical ultracentrifuge equipped with a UV–vis absorption optical detector. The sedimentation profiles were recorded at  $\lambda = 270$  nm, and the speed of rotor rotation was 48 000 rpm.

*Fluorescence Spectroscopy.* The samples for fluorescence measurements were prepared according to a procedure similar to that described elsewhere.<sup>12</sup> Certain aliquots of a solution of pyrene (Aldrich) in acetone were carefully dropped into empty dark vials by a Hamilton microsyringe, and afterward acetone was evaporated by gentle heating. Then the sample solutions were added. To equilibrate pyrene, the samples were kept at 40–50 °C for 2 days under intensive stirring. The final concentration of the fluorescent probe in the prepared samples was kept constant at  $5 \times 10^{-7}$  M, that is, only slightly below the saturation concentration of pyrene in water at 22 °C.

Steady-state fluorescence spectra of the air-equilibrated samples were recorded with a Hitachi F-4000 fluorescence spectrophotometer (right angle geometry, 1 cm  $\times$  1 cm quartz cell). The widths of slits were chosen to be 3 and 1.5 nm for excitation and emission, respectively.

## Results and Discussion

**Determination of Critical Micellization Concentration of PIB-*b*-PMANa in Aqueous Solutions.** The photophysical properties of pyrene are known to be strongly dependent on the polarity of its environment.<sup>13</sup> This feature has allowed using this fluorophore as a probe to determine critical micellization concentrations (cmc) for some nonionic and ionic amphiphilic

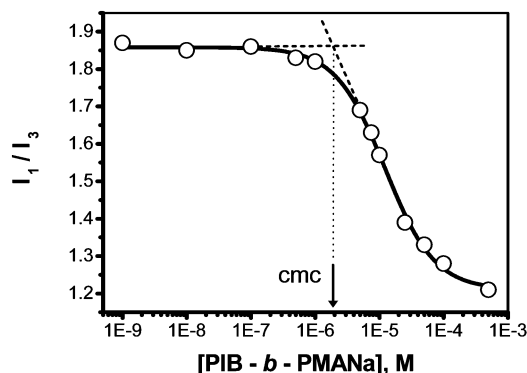


**Figure 1.** Excitation (a) and emission (b) spectra of pyrene in solutions of PIB-*b*-PMANa at the copolymer concentrations equal to  $1 \times 10^{-9}$  M (12  $\mu\text{g/L}$ ; solid line) and  $5 \times 10^{-4}$  M (6 g/L; dashed line) (0.05 M NaCl, 0.01 M Tris). (a) The emission wavelength is 383 nm; (b) the excitation wavelength is 333 nm.

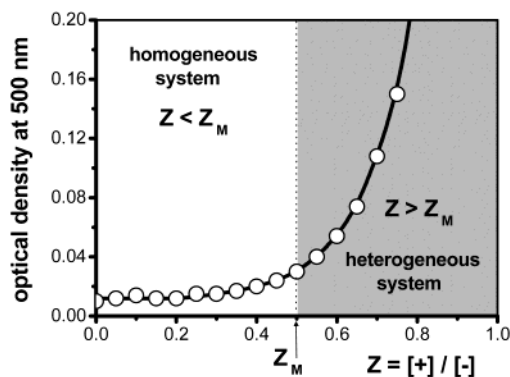
block copolymers in aqueous solutions.<sup>12,14,15</sup> In particular, the fine structure of the emission spectrum of pyrene, especially the ratio between the intensities of first and third vibrational bands,  $I_1/I_3$ , is rather sensitive to the polarity of its surrounding medium: this ratio was demonstrated to decrease if the environment of the fluorescent probe becomes less polar.<sup>13</sup>

Figure 1 shows the excitation and emission spectra of pyrene in the solutions of PIB-*b*-PMANa at two considerably different copolymer concentrations:  $1 \times 10^{-9}$  M (12  $\mu\text{g/L}$ ) and  $5 \times 10^{-4}$  M (6 g/L) (here and below the molar concentration of the copolymer is expressed as the molar concentration of single macromolecules). The distinct shift of the excitation maximum to the longer wavelength region and the pronouncedly increasing overall intensity of the excitation spectrum provide evidence for a transfer of the fluorescent probe from a polar to a nonpolar environment upon the rise in the copolymer concentration (Figure 1a). This process is accompanied by a considerable decrease of  $I_1/I_3$ : this ratio falls from 1.85, which is characteristic for pyrene in the pure solvent (0.01 M Tris), to 1.20 (Figure 1b). The observed changes indicate the formation of macromolecular micelles in the PIB-*b*-PMANa solution of the higher copolymer concentration, the fluorescent probe being solubilized by the hydrophobic cores of such micelles.

The complete dependence of  $I_1/I_3$  on the concentration of PIB-*b*-PMANa is presented in Figure 2. The values of  $I_1/I_3$  remain fairly constant at low concentrations of the copolymer, this ratio being very close to that obtained for pyrene in the pure solvent ( $I_1/I_3 \approx 1.85$ ). Above a certain concentration of PIB-*b*-PMANa, the values of  $I_1/I_3$  demonstrate a pronounced fall upon the rising concentration of the copolymer. The concentration determined as the intersection of tangent to the dependence curve of  $I_1/I_3$  on PIB-*b*-PMANa concentration at its inflection with horizontal tangent through points corresponding to low concentrations of PIB-*b*-PMANa can be considered as cmc. As is seen, the molar



**Figure 2.** Dependence of the intensity ratio  $I_1/I_3$  on the molar concentration of PIB-*b*-PMANa (0.05 M NaCl, 0.01 M Tris); the excitation wavelength is 333 nm.

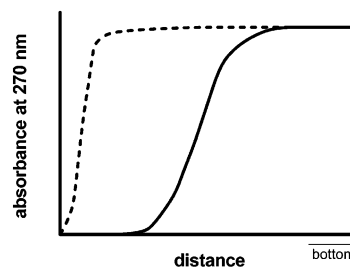


**Figure 3.** Turbidimetric titration curve of the solution of PIB-*b*-PMANa micelles with the solution of PVP•EtBr (0.1 M NaCl, 0.01 M Tris).

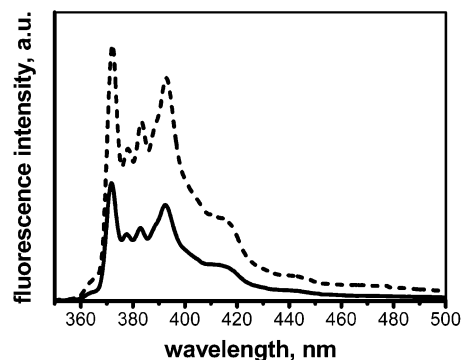
value of cmc is around  $2 \times 10^{-6}$  M (24 mg/L). This value is comparable to those for polystyrene-*block*-poly(sodium acrylate) diblock copolymers with lengths of hydrophobic and ionic blocks similar to the corresponding lengths of PIB-*b*-PMANa.<sup>14</sup> However, as expected, the determined value is much higher than the molar values of cmc obtained for PIB<sub>70</sub>-*b*-PMANa<sub>x</sub> ( $x = 52, 70$ ) and PIB<sub>134</sub>-*b*-PMANa<sub>x</sub> ( $x = 145, 288$ ), that is, for the diblock copolymers with considerably longer hydrophobic blocks (the subscripts denote the number-average degrees of polymerization of the corresponding blocks). Indeed, for those copolymers the molar values of cmc were evaluated to be in the range of  $10^{-9}$ – $10^{-8}$  M ( $<0.3$  mg/L).<sup>11</sup>

**Formation and Properties of Water-Soluble IPECs Resulting from Interaction of PIB-*b*-PMANa Micelles With PVP•EtBr.** The investigation on the interaction of the copolymer micelles with PVP•EtBr was carried out at a copolymer concentration that is 1 order of magnitude higher than the observed cmc, that is,  $c = 2 \times 10^{-5}$  M (0.24 g/L). Figure 3 demonstrates a curve of turbidimetric titration of a solution of the PIB-*b*-PMANa micelles with a solution of PVP•EtBr. On addition of the cationic polyelectrolyte to the solution of the copolymer micelles, a phase separation is only observed when the charge ratio of the polymeric components,  $Z = [+]/[-]$ , exceeds a certain value,  $Z_M$ . At  $Z < Z_M$ , the mixtures of the PIB-*b*-PMANa micelles and PVP•EtBr remain homogeneous. Such homogeneous mixtures were further examined by means of analytical ultracentrifugation and fluorescence spectroscopy.

A typical sedimentation pattern obtained for the homogeneous mixtures of the PIB-*b*-PMANa micelles and PVP•EtBr in the scanning mode at  $\lambda = 270$  nm is given in Figure 4. At this



**Figure 4.** Sedimentation profiles detected after 15 min for a mixture of PIB-*b*-PMANa and PVP•EtBr with  $Z = [+]/[-] = 0.4$  (solid line) and for the reference solution of PVP•EtBr (dashed line) (0.2 M NaCl, 0.01 M Tris).



**Figure 5.** Emission spectra of pyrene in a solution of PIB-*b*-PMANa (dashed line) and in a mixture of PIB-*b*-PMANa and PVP•EtBr with  $Z = [+]/[-] = 0.4$  (solid line) (0.05 M NaCl, 0.01 M Tris); the excitation wavelength is 333 nm.

wavelength, the cationic polyelectrolyte absorbs light while the copolymer demonstrates nearly no absorbance. As is seen, only one type of species is detected in the pattern, their sedimentation velocity being considerably higher than that of the individual macromolecules of PVP•EtBr. Thus, these species can be considered as particles of water-soluble IPEC resulting from the interaction of the copolymer micelles with the cationic polyelectrolyte. The high value of the evaluated sedimentation coefficient  $S$  of the formed IPEC species,  $S \approx 25$  Sv, which pronouncedly exceeds that obtained for PVP•EtBr ( $S \approx 2$  Sv) provides evidence for their relatively large mass. As is additionally seen from the sedimentation pattern, all polycations are incorporated in the IPEC particles and evenly distributed among them.

Figure 5 (solid line) shows the fluorescence spectrum of pyrene in a solution of the IPEC. The evaluated value of  $I_1/I_3$  is equal to 1.65 which is distinctly lower than the value of  $I_1/I_3$  obtained for pyrene in the pure solvent ( $I_1/I_3 \approx 1.85$ ), indicating that the formed IPEC species solubilize pyrene. The reference experiments carried out under the same conditions with the solution of the corresponding linear anionic homopolyelectrolyte, poly(sodium methacrylate) (PMANa), as well as with the solution of IPEC resulting from the interaction between PMANa and PVP•EtBr show no solubilization of pyrene: the values of  $I_1/I_3$  for such solutions are nearly equal to 1.85. These findings point out that the IPEC particles formed upon the interaction of the PIB-*b*-PMANa micelles with PVP•EtBr, as well as the pure copolymer micelles, contain hydrophobic cores consisting of polyisobutylene blocks.

At the same time, the value of  $I_1/I_3$  for the solution of IPEC is pronouncedly higher than the value obtained for the corresponding solution of the PIB-*b*-PMANa micelles ( $I_1/I_3 = 1.45$ ). Moreover, the fluorescence intensity of pyrene in the solution of IPEC is considerably (ca. 2–2.5 times) lower than that



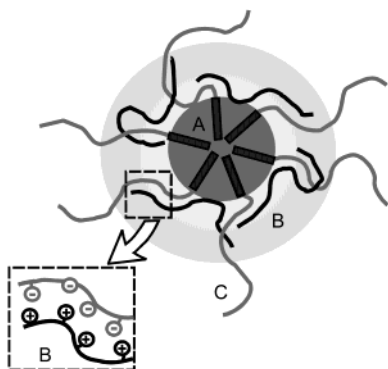


Figure 6. Hypothetical architecture of IPEC particles.

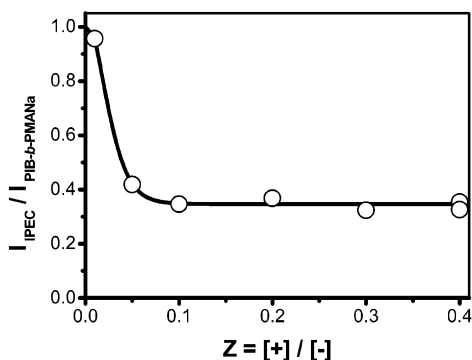


Figure 7. Dependence of the relative intensity  $I_{3,IPEC}/I_{3,PIB-b-PMANa}$  of the third vibrational band of the fluorescence spectrum of pyrene in IPEC solutions on the charge ratio  $Z = [+]/[-]$  (0.05 M NaCl, 0.01 M Tris); the excitation wavelength is 333 nm.

measured under the same conditions for the reference solution of the copolymer (Figure 5). The above differences could be accounted for by quenching of emission of the fluorescence probe by pyridinium groups of the polycations located in the vicinity of polyisobutylene cores. In such a case, a contribution of pyrene molecules being not solubilized by the IPEC particles, that is, existing in the polar environment, to the overall fluorescence spectrum of pyrene is naturally increased, increasing the  $I_1/I_3$  ratio.

Thus, the obtained results suggest that the IPEC species can be considered as a peculiar complex micelle whose hypothetical onionlike structure is schematically depicted in Figure 6. Each species is assumed to consist of a polyisobutylene core (A), surrounded by a shell (B) formed by interacting oppositely charged polyelectrolyte fragments, and the ionic corona (C) formed by fragments of polyelectrolyte blocks not involved in the interpolyelectrolyte complexation. The ionic corona apparently stabilizes the whole complex micelle in aqueous media.

Figure 7 presents the dependence of relative fluorescence intensity of pyrene in solutions of IPECs,  $I_{IPEC}/I_{PIB-b-PMANa}$ , on  $Z$ . The values of  $I_{IPEC}/I_{PIB-b-PMANa}$  steeply fall with the rising content of PVP·EtBr in the mixtures of the oppositely charged copolymer micelles and the cationic polyelectrolyte, approaching the limiting value already at relatively low  $Z$  ( $Z \approx 0.1$ ). The observed trend is consistent with the proposed architecture of

the complex micelle, suggesting that the polycations prefer to be located in the vicinity of its polyisobutylene core.

## Conclusion

It was demonstrated that the polyisobutylene-*block*-poly(sodium methacrylate) diblock copolymer micelles interacting with poly(*N*-ethyl-4-vinyl pyridinium bromide) form a novel type of water-soluble IPEC in which the polyelectrolyte component of the original micelles apparently plays a lyophilizing part. The IPEC species is hypothesized to be a peculiar, complex, onionlike micelle consisting of a two-phase hydrophobic nucleus formed by a polyisobutylene core surrounded by a shell of coupled oppositely charged polyelectrolyte fragments and an ionic corona formed by fragments of poly(sodium methacrylate) blocks not involved in the interpolyelectrolyte complexation.

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