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# Water-Soluble Complexes of Star-Shaped Poly(acrylic acid) with Quaternized Poly(4-vinylpyridine)

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The interaction of star-shaped poly(acrylic acid) having various numbers of arms (5, 8, and 21) and a strong cationic polyelectrolyte, viz., poly(*N*-ethyl-4-vinylpyridinium bromide), was examined at pH 7 by means of turbidimetry and dynamic light scattering. Mixing aqueous solutions of the oppositely charged polymeric components was found to result in phase separation only if their base-molar ratio  $Z = [N^+]/[COO^- + COOH]$  exceeds a certain critical value  $Z_M$  ( $Z_M < 1$ ); this threshold value is determined by the number of arms of the star-shaped polyelectrolyte and the ionic strength of the surrounding solution. At  $Z < Z_M$ , the homogeneous aqueous mixtures of the oppositely charged polymeric components contain two types of complex species clearly differing in their sizes, with the fractions of these species appearing to depend distinctly on the number of arms of the star-shaped poly(acrylic acid), the base-molar ratio of the oppositely charged polymeric components in their mixtures, and the ionic strength of the surrounding solution. The small complex species (major fraction) are assumed to represent the particles of the water-soluble interpolyelectrolyte complex whereas the large complex species (minor fraction) are considered to be complex aggregates.

## Introduction

The design of novel generations of macromolecular architectures as well as a detailed study of their structure and properties is one of the current challenges of polymer science. One possible approach to this problem is to use macromolecular coassembly processes in multicomponent polymeric systems. Such processes take place, for example, upon mixing aqueous solutions of oppositely charged polyelectrolytes. As a result of this electrostatically driven macromolecular coassembly, so-called interpolyelectrolyte complexes (IPECs) are generated. IPECs are mainly stabilized via cooperative system of interpolymer salt bonds, though hydrogen bonding, hydrophobic interactions, charge-transfer interactions, and van der Waals forces can also considerably contribute to their stabilization. The structure and properties of IPECs are determined by a number of factors: the characteristics of the polymeric components (e.g., nature of their ionic groups, degrees of polymerization, charge densities, etc.) and their concentrations, the ratio between amounts of oppositely charged groups of polyelectrolytes, the conditions of the surrounding solution (e.g., ionic strength, pH, temperature, etc.) and in some cases the method of the preparation of such macromolecular assemblies. The formation and properties of IPECs generated due to the interaction between oppositely charged linear polyions have been investigated in detail by a great number of research groups and exhaustively reviewed elsewhere. (See, for example, reviews in refs 1 and 2.)

Apart from the other factors, the topology of polymeric components taking part in interpolyelectrolyte complexation is also thought to have an influence on this process as well as the properties of the resulting polymeric assemblies. Until now,

however, ionic dendrimers representing regularly branched treelike structures have been mostly used as ionic polymers with nonlinear structure, and their complexation with oppositely charged macromolecules, both synthetic and natural, has been investigated.<sup>3–14</sup> At the same time, the interaction of other nonlinear ionic polymers, such as star-shaped polyelectrolytes, polyelectrolyte bottle brushes, hyperbranched polyelectrolytes, has received only scarce attention. To the best of our knowledge, only one paper dealt with a so-called anionic/nonionic polyelectrolyte prototype copolymer brush, viz., poly(ethylene oxide)/partially sulfonated polystyrene, interacting with a linear cationic polyelectrolyte, viz. poly(*N*-methyl-4-vinylpyridinium iodide); this interaction was shown to generate rod-shaped anionic/nonionic polyelectrolyte prototype copolymer brush aggregate/polycation complexes as a result of the abundant binding of such anionic/nonionic brushes with the cationic polyelectrolyte.<sup>15</sup>

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**Table 1. Molecular Characteristics of the Star-Shaped Poly(acrylic acids)**

sample <sup>a</sup>	X	DP <sub>n,arm</sub> <sup>b</sup>	M <sub>n,star</sub> , g/mol <sup>c</sup>	PDI <sub>star</sub> <sup>c</sup>	DP <sub>n,arm</sub> <sup>c</sup>
(PAA <sub>90</sub> ) <sub>5</sub>	5	86	36 900	1.04	100
(PAA <sub>100</sub> ) <sub>8</sub>	8	101	67 200	1.05	114
(PAA <sub>100</sub> ) <sub>21</sub>	21	97	161 500	1.02	104

<sup>a</sup> The designations of the samples are given in ref 21. <sup>b</sup> Expected degree of polymerization from monomer to initiation site ratio and monomer conversion.<sup>21</sup> <sup>c</sup> Derived from M<sub>n</sub> of methylated star-shaped poly(acrylic acid) determined by means of MALDI-TOF mass spectrometry.<sup>21</sup>

In our previous studies, we have investigated the interaction of starlike micelles of ionic amphiphilic diblock copolymers, viz., polyisobutylene-*block*-poly(sodium methacrylate), each consisting of a compact hydrophobic core surrounded by a corona of ca. 100 polyelectrolyte chains with a strong linear cationic polyelectrolyte, viz., poly(*N*-ethyl-4-vinylpyridinium bromide).<sup>16–20</sup> The results of those investigations have provided evidence that electrostatically driven coassembly in such systems can result in the formation of peculiar core–shell corona (onionlike) macromolecular architectures with a shell assembled from the oppositely charged polyelectrolyte fragments and a corona in which excess polyelectrolyte segments apparently play a lyophilizing part.

This communication reports on our recent study on the interaction of star-shaped poly(acrylic acid) with a strong cationic polyelectrolyte, viz., poly(*N*-ethyl-4-vinylpyridinium bromide), in aqueous media and describes some properties of the complex species generated by this interaction.

## Experimental Section

**Materials.** Star-shaped poly(acrylic acid) ((PAA<sub>N</sub>)<sub>X</sub>, with *N* and *X* indicating the degree of polymerization and the number of arms, respectively) with 5, 8, and 21 arms was synthesized via atom-transfer radical polymerization of *tert*-butyl acrylate (the “core-first” approach using initiators derived from α-D-glucose, saccharose, and β-cyclodextrin) followed by subsequent treatment of the resulting polymer with trifluoroacetic acid in dichloromethane at room temperature as described elsewhere.<sup>21</sup> The molecular characteristics of the used samples of (PAA<sub>N</sub>)<sub>X</sub> are presented in Table 1 (with the values of *N* being given in ref 21).

Poly(*N*-ethyl-4-vinylpyridinium bromide) (PVP•EtBr) was synthesized from poly(4-vinylpyridine) (Aldrich) with M<sub>w</sub> = 60 000 g/mol (DP<sub>w</sub> ≈ 570; the polydispersity of the sample is not specified by the manufacturer) via its exhaustive quaternization with a 10-fold excess of ethyl bromide at 60 °C in methanol. According to the IR spectrum (characteristic absorbance of pyridine units at 1600 cm<sup>−1</sup>, characteristic absorbance of quaternized pyridine units at 1640 cm<sup>−1</sup>), the molar fraction of quaternized pyridine units in the resulting polymer was about 0.9, corresponding to ca. 510 charged monomer units per polymer chain.

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Low-molecular-weight compounds TRIS (2-amino-2-(hydroxymethyl)-1,3-propanediol, Aldrich), TRIS•HCl (2-amino-2-(hydroxymethyl)-1,3-propanediol hydrochloride, Aldrich), and NaCl (Merck) were used as received.

**Sample Preparation.** The stock solutions of (PAA<sub>N</sub>)<sub>X</sub> and PVP•EtBr were prepared by their direct dissolution in water. Then, the pH of their solutions was adjusted to 7 by the addition of 0.5 M NaOH (pH was controlled with a pH-ionometer Ecotest-120 calibrated with three buffers of pH 4.01, 7.00, and 9.21). The base-molar concentration of the stock solutions of (PAA<sub>N</sub>)<sub>X</sub> and PVP•EtBr was 0.05 M. These stock solutions were afterward diluted with 0.01 M TRIS/TRIS•HCl (pH 7), and then a 4 M solution of NaCl in 0.01 M TRIS/TRIS•HCl (pH 7) was added to provide the desired ionic strength. The stock solutions prepared by such a method were stirred over at least a day prior to use.

The sample solutions containing both the star-shaped anionic polyelectrolyte and the cationic polyelectrolyte were prepared according to two different procedures. Method A (mostly used in this work) is a dropwise addition of the concentrated solution of PVP•EtBr to the solution of the (PAA<sub>N</sub>)<sub>X</sub> star; this was carried out at constant pH and ionic strength as well as under continuous stirring. Method B is mixture of the concentrated solutions of the (PAA<sub>N</sub>)<sub>X</sub> star and PVP•EtBr at high ionic strength ([NaCl] > 2 M) followed by a dilution of the prepared mixture by the solvent, viz., 0.01 M TRIS/TRIS•HCl (pH 7).

## Methods

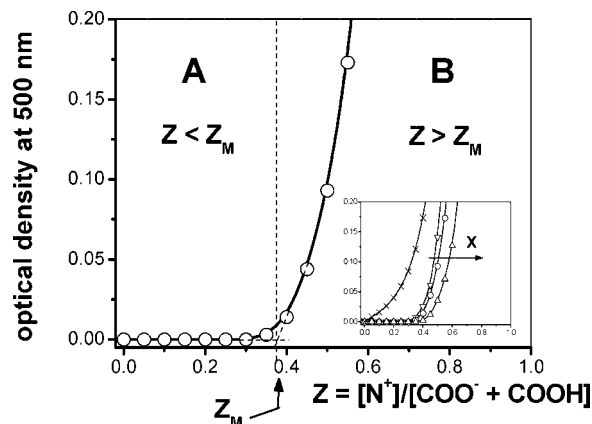
**Turbidimetric Titrations.** Turbidimetric titrations of solutions of (PAA<sub>N</sub>)<sub>X</sub> with solutions of PVP•EtBr were carried out in the isoionic regime at pH 7 (according to potentiometric titration curves, this pH at comparable values of ionic strength corresponds to a degree of ionization of (PAA<sub>N</sub>)<sub>X</sub> of ca. 0.9) at the wavelength λ = 500 nm with a Hitachi 150-20 UV–vis spectrophotometer. At this wavelength, the polymers used do not absorb light; therefore, the optical density results from light scattering only. The titrations were run under continuous stirring, and the time interval between subsequent additions of a titrant was equal to 1 min.

**Dynamic Light Scattering.** Dynamic light scattering (DLS) measurements were performed in sealed cylindrical cells with the use of ALV DLS/SLS-SP 5022F equipment consisting of an ALV-SP 125 laser goniometer, an ALV 5000/E correlator, and a He–Ne laser as a wavelength of λ = 632.8 nm. The prepared sample solutions were thoroughly filtered by being passed at least three times through nylon filters (13-HV, Millipore) with a pore size of 0.45 μm. The autocorrelation functions measured at 90° were analyzed by the CONTIN method.

**Static Light Scattering.** Static light scattering (SLS) measurements were performed in sealed cylindrical cells with the use of a Sofica goniometer equipped with a He–Ne laser at a wavelength of λ = 632.8 nm. The prepared sample solutions were thoroughly filtered by being passed at least three times through nylon filters (13-HV, Millipore) with a pore size of 0.45 μm. A Zimm plot was used to evaluate the measurements. Differential refractometer DnDC2010/620 (PSS) was used to determine the refractive index increment, dn/dc, for the mixtures of oppositely charged polymeric components at a wavelength of λ = 620 nm. Dialysis against an aqueous solution with the same pH and ionic strength for at least three days was carried out to obtain a solvent for dilution of the samples needed for dn/dc measurements.

## Results and Discussion

Figure 1 shows a typical turbidimetric titration curve of a solution of the (PAA<sub>100</sub>)<sub>8</sub> star with a concentrated solution of PVP•EtBr. As is seen, on addition of the cationic polyelectrolyte

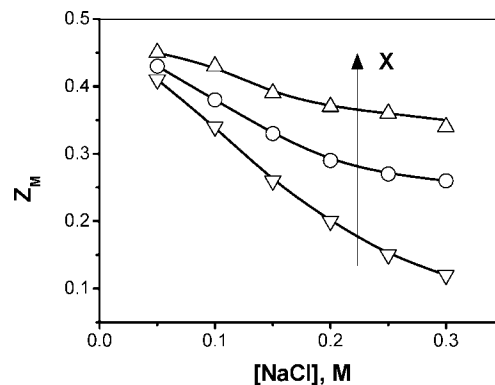


**Figure 1.** Turbidimetric titration curve of the aqueous solution of the  $(\text{PAA}_{100})_8$  star with the aqueous solution of  $\text{PVP}\cdot\text{EtBr}$  ( $\text{DP}_w \approx 570$ ). (A) Homogeneous system. (B) Heterogeneous system; 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS $\cdot$ HCl),  $[(\text{PAA}_{100})_8] = 0.002$  base-mol/L. The inset shows the corresponding turbidimetric titration curves for aqueous solutions of the  $(\text{PAA}_N)_X$  stars with  $X = 5$  ( $\nabla$ ), 8 ( $\circ$ ), and 21 ( $\triangle$ ) as well as for linear PAA with  $\text{DP}_n = 500$  ( $\times$ ); 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS $\cdot$ HCl),  $[(\text{PAA}_N)_X] = 0.002$  base-mol/L.

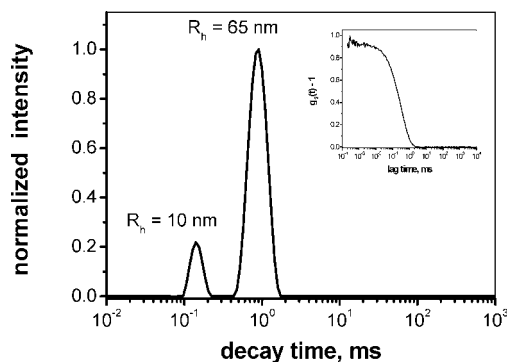
to the solution of the star-shaped anionic polyelectrolyte no phase separation is observed unless the base-molar ratio  $Z$  of the polymeric components,  $Z = [\text{N}^+]/[\text{COO}^- + \text{COOH}]$ , exceeds a certain value  $Z_M$  (defined as illustrated in Figure 1, that is, as an intercept of a line drawn through the initial points with the constant optical density and a line drawn through the two points with optical density demonstrating distinct deviations from that of the initial points). At  $Z < Z_M$ , the mixtures of the  $(\text{PAA}_{100})_8$  star and  $\text{PVP}\cdot\text{EtBr}$  are transparent, strongly suggesting the formation of water-soluble complex species due to the interaction between the oppositely charged polymeric components.

Qualitatively similar behavior was also observed for  $(\text{PAA}_{90})_5$  and  $(\text{PAA}_{100})_{21}$  stars, with the values of  $Z_M$  distinctly increasing with an increasing number of arms (Figure 1, inset). At the same time, the transparent solutions of PAA arms ( $\text{DP}_n = 100$ ) cleaved from the  $(\text{PAA}_{100})_8$  star or even PAA with  $\text{DP}_n = 500$  ( $\text{PDI} = 1.1$ ) become turbid after the addition of the first portion of the concentrated solution of  $\text{PVP}\cdot\text{EtBr}$ , that is, at  $Z \approx 0.05$  (Figure 1, inset). This finding means that the  $(\text{PAA}_N)_X$  stars, in contrast to their cleaved arms or even linear PAA with  $\text{DP}_n = 500$ , can play a lyophilizing part in the water-soluble complex species formed at  $Z < Z_M$ . It should be noted that previous studies by Kabanov and co-workers show that in salt-containing solutions a linear polyelectrolyte can play a lyophilizing part only if its DP considerably exceeds the DP of the polymeric counterpart: the interaction between the oppositely charged polymeric components results in the formation of water-soluble IPECs if this condition is met. (See, for instance, the review in ref 22.)

Figure 2 demonstrates the dependences of  $Z_M$  on the concentration of NaCl for the  $(\text{PAA}_N)_X$  stars. As is seen, the values of  $Z_M$  gradually decrease with rising ionic strength, but this effect becomes less pronounced with an increasing number of arms. This tendency is reasonably attributed to a lowering of the lyophilizing strength of the  $(\text{PAA}_N)_X$  stars as a result of the more effective screening of their charge by small counterions at higher ionic strength. Such a salt-induced decrease in  $Z_M$  was also described previously for mixtures of linear poly(sodium methacrylate) (PMANa) and  $\text{PVP}\cdot\text{EtBr}$  with an excess of the anionic polymeric component, provided that  $\text{DP}_{\text{PMANa}}$  consider-



**Figure 2.** Dependence of the threshold base-molar ratio  $Z_M$  of the mixtures of the  $(\text{PAA}_N)_X$  stars and  $\text{PVP}\cdot\text{EtBr}$  ( $\text{DP}_w \approx 570$ ) on the concentration of NaCl for the  $(\text{PAA}_N)_X$  stars with  $X = 5$  ( $\nabla$ ), 8 ( $\circ$ ), and 21 ( $\triangle$ ); pH 7 (0.01 M TRIS/TRIS $\cdot$ HCl),  $[(\text{PAA}_N)_X] = 0.002$  base-mol/L.



**Figure 3.** Intensity distribution of decay times obtained at  $90^\circ$  for the mixture of  $(\text{PAA}_{100})_8$  with  $\text{PVP}\cdot\text{EtBr}$  ( $\text{DP}_w \approx 570$ ) at the base-molar ratio  $Z = 0.2$ ; 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS $\cdot$ HCl),  $[(\text{PAA}_{100})_8] = 0.002$  base-mol/L. The inset shows the original autocorrelation function.

ably exceeds  $\text{DP}_{\text{PVP}\cdot\text{EtBr}}$ .<sup>23</sup> It is remarkable that the slight dependence of  $Z_M$  on the ionic strength of the surrounding medium, which is observed for the  $(\text{PAA}_{100})_{21}$  star with the highest number of arms, was also detected for micelles of polyisobutylene-*block*-poly(sodium methacrylate) diblock copolymers interacting with the same cationic polyelectrolyte;<sup>20</sup> that is, the increasing number of arms of the  $(\text{PAA}_N)_X$  stars causes them to behave, at least in this aspect, similarly to starlike micelles generated by ionic amphiphilic diblock copolymers in aqueous media.

The homogeneous mixtures of  $(\text{PAA}_N)_X$  stars with  $\text{PVP}\cdot\text{EtBr}$  were further examined by means of DLS. As a typical example, an intensity distribution of decay times obtained at  $90^\circ$  for the mixture of  $(\text{PAA}_{100})_8$  with  $\text{PVP}\cdot\text{EtBr}$  at the base-molar ratio  $Z = 0.2$  at 0.1 M NaCl and pH 7 is demonstrated in Figure 3. As is seen, the distribution is clearly bimodal, strongly suggesting that two types of scattering species exist in these mixtures. At the polymer concentration used, the pure  $(\text{PAA}_{100})_8$  stars show negligible scattering; therefore, the detected species can be undoubtedly attributed to particles of IPECs formed upon interaction with  $\text{PVP}\cdot\text{EtBr}$ , with their base-molar stoichiometries being apparently different from the base-molar ratio  $Z = [\text{N}^+]/[\text{COO}^- + \text{COOH}]$  of the mixture of  $(\text{PAA}_{100})_8$  with  $\text{PVP}\cdot\text{EtBr}$ .

From this distribution, one can easily obtain the apparent hydrodynamic radii,  $R_{h,\text{app}}$ , of the IPEC particles coexisting in

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**Table 2. Hydrodynamic Radii  $R_h$  of the Individual  $(PAA_N)_X$  stars, Apparent Hydrodynamic Radii  $R_{h,app}$  of the Small and Large IPEC Particles Formed in the Mixtures of  $(PAA_N)_X$  with PVP•EtBr ( $DP_w \approx 570$ ), and the Fraction of the Area of the Peak Corresponding to the Large Complex Species ( $Z = 0.2$ ; 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS•HCl);  $[(PAA_N)_X] = 0.002$  base-mol/L)**

X	$(PAA_N)_X$	IPEC ( $Z = 0.2$ )		
		$R_{h,app}$ , nm <sup>b</sup>		$\{A_{large}/(A_{large} + A_{small})\}^c$
		small	large	
5	8	not detected <sup>d</sup>	72 ± 6	≈ 1
8	5	10 ± 2	65 ± 3	0.89 ± 0.03
21	10	12 ± 1	63 ± 7	0.25 ± 0.05

<sup>a</sup> Determined at an angle of  $6 \div 7^\circ$ . <sup>b</sup> Determined at an angle of  $90^\circ$ . <sup>c</sup> Calculated from the intensity distributions of  $R_h$ . <sup>d</sup> Not detected by means of DLS.

the mixture of  $(PAA_{100})_8$  with PVP•EtBr, which are found to be ca. 10 and 65 nm. The value of  $R_h$  for the small complex species is close to the hydrodynamic radius found for the individual  $(PAA_{100})_8$  stars,  $R_h \approx 8$  nm (determined by means of DLS at the small angle of  $6 \div 7^\circ$ ), whereas the value of  $R_h$  for the large complex species considerably exceeds the size of the individual  $(PAA_{100})_8$  stars.

Table 2 shows that a similar result was obtained for the mixture of  $(PAA_{100})_{21}$  with PVP•EtBr; it also comprises two types of IPEC particles with distinctly different sizes, the small complex species being of comparable size to the individual  $(PAA_{100})_{21}$  stars whereas the large complex species is larger by a factor of ca. 6 than the individual  $(PAA_{100})_{21}$  stars. At the same time, for the mixture of  $(PAA_{90})_5$  with PVP•EtBr the contribution of the large complex species to the intensity of the scattered light is dominant, with their size considerably exceeding (by a factor of ca. 9) the size of the corresponding individual  $(PAA_{90})_5$  stars. In the latter case, however, one cannot exclude the formation of the small complex species: the contribution of the small IPEC particles to the scattering of light is masked by a dominant contribution from the larger ones. Indeed, the fraction of the area of the peak associated with the large complex species,  $A_{large}/(A_{large} + A_{small})$ , obtained from the corresponding intensity distributions of  $R_h$  significantly increases with decreasing X from 21 to 5 (Table 2), indicating that the fraction of the large IPEC particles in the mixtures of  $(PAA_N)_X$  with PVP•EtBr increases.

It should be noted that although the large complex species make a major (or in some cases at least significant) contribution to the intensity of scattered light, their mass-weighted fraction appears to be considerably lower than that of the small complex species. Indeed, the mass-weighted fraction of the large complex species roughly estimated with the use of CONTIN software from the intensity distribution presented in Figure 3 is within only 0.06; that is, they obviously represent the minor fraction of all complex species formed upon the interaction of  $(PAA_{100})_8$  with PVP•EtBr.

As demonstrated in Table 3, the increasing content of the cationic polyelectrolyte in the mixture of  $(PAA_{100})_8$  with PVP•EtBr leads to an increasing fraction of large IPEC particles whereas the sizes of the both small and large complex species appear to be virtually constant except for the IPEC particles formed in the mixtures of the oppositely charged polymeric components at  $Z = 0.1$ : the size of both types of complex species in the latter case is larger by  $20 \div 30\%$  than the corresponding values of  $R_{h,app}$  obtained for the other mixtures of  $(PAA_{100})_8$  with PVP•EtBr. At the same time, the fraction of large IPEC particles significantly increases with increasing values of Z.

A similar increase in the fraction of the large IPEC particles can be reached by the rising concentration of NaCl (Table 3).

**Table 3. Apparent Hydrodynamic Radii  $R_{h,app}$  (Measured at  $90^\circ$ ) of Small and Large IPEC Particles Formed in Mixtures of  $(PAA_{100})_8$  with PVP•EtBr ( $DP_w \approx 570$ ) and the Fraction of the Area of the Peak Corresponding to the Large Complex Species (pH 7 (0.01 M TRIS/TRIS•HCl);  $[(PAA_{100})_8] = 0.002$  base-mol/L)**

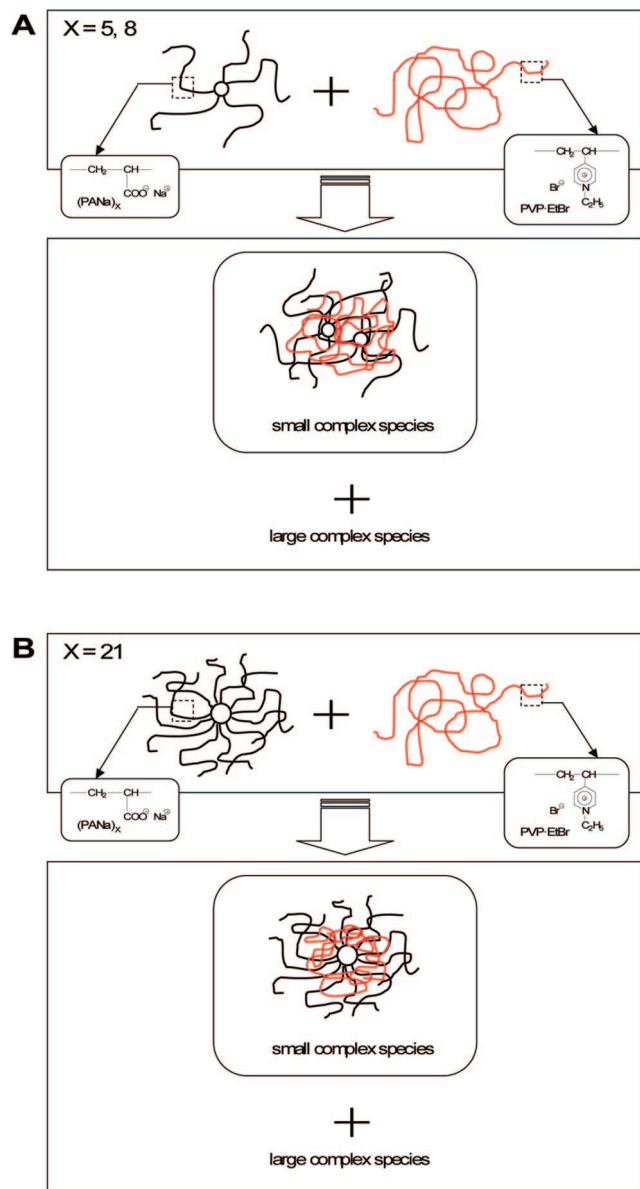
Z	[NaCl], M	$R_{h,app}$ , nm		$\{A_{large}/(A_{large} + A_{small})\}^a$
		small	large	
0.1	0.1	12 ± 1	79 ± 3	0.55 ± 0.01
0.15	0.1	11 ± 2	65 ± 7	0.56 ± 0.06
0.2	0.1	10 ± 2	65 ± 3	0.89 ± 0.03
0.25	0.1	10 ± 2	59 ± 2	0.95 ± 0.02
0.3	0.1	not detected <sup>b</sup>	60 ± 4	≈ 1 <sup>c</sup>
0.2	0.05	11 ± 2	79 ± 7	0.85 ± 0.03
0.2	0.15	10 ± 2	62 ± 4	0.94 ± 0.02
0.2	0.2	8 ± 2	64 ± 3	0.97 ± 0.01 <sup>d</sup>

<sup>a</sup> Calculated from intensity distributions of  $R_h$ . <sup>b</sup> Not detected by means of DLS. <sup>c</sup> Mass-weighted fraction of the large complex species roughly estimated using CONTIN software is within 0.35 even for the mixture of  $(PAA_{100})_8$  with PVP•EtBr at  $Z = 0.3$ . <sup>d</sup> Mass-weighted fraction of the large complex species roughly estimated using CONTIN software is within 0.15 even for the mixture of  $(PAA_{100})_8$  with PVP•EtBr at 0.2 M NaCl.

Again, the values of  $R_{h,app}$  of both the large and small complex species remain nearly constant. It should be noted that the position of the peak corresponding to the small IPEC particles is rather ill-defined when its fraction becomes sufficiently low; therefore, the error in the determination of  $R_{h,app}$  might be relatively high. With the increasing concentration of NaCl, the values of the ratio  $A_{large}/(A_{large} + A_{small})$  demonstrate a distinct tendency to increase, providing clear evidence that the fraction of large IPEC particles becomes larger.

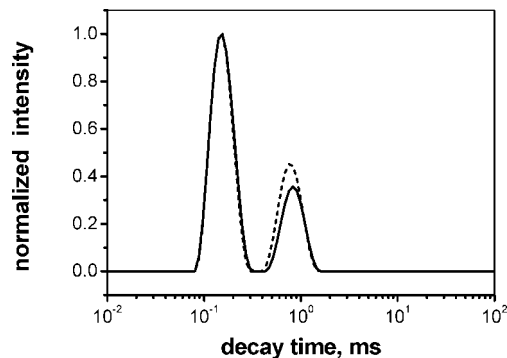
On the basis of the obtained results, one can suppose that the small complex species dominantly formed in the mixtures of  $(PAA_N)_X$  with PVP•EtBr most likely represent particles of water-soluble IPEC whereas the minor large complex species are apparently stable on the colloidal-level aggregates that are assumed to be peculiar precursors of insoluble IPEC formed upon further increasing content of the cationic polyelectrolyte in the mixtures of the oppositely charged polymeric components. Such aggregates are thought to comprise many chains of the cationic polyelectrolyte and the  $(PAA_N)_X$  stars, with their base-molar stoichiometry being thought to be close to 1:1.

Because the hydrodynamic sizes of the small complex species are rather close to those measured for the corresponding  $(PAA_N)_X$  stars, they are expected to be assembled from a few macromolecules of the oppositely charged polymeric components. In the case of the  $(PAA_{90})_5$  and  $(PAA_{100})_8$  stars interacting with PVP•EtBr, that is, when the total numbers of ionic groups on individual macromolecules of the oppositely charged polymeric components are comparable, each small IPEC particle in the simplest case might be assumed to comprise only a single chain of the cationic polyelectrolyte but should include several macromolecules of the star-shaped polyelectrolyte to be soluble in aqueous media. Thus, the addition of PVP•EtBr to solutions of  $(PAA_N)_X$  stars with  $X = 5$  and 8 can induce the assembly of macromolecules of the star-shaped polyelectrolyte. In the case of the  $(PAA_{100})_{21}$  stars interacting with PVP•EtBr, that is, when the total number of carboxylate and carboxylic groups on an individual macromolecule of the  $(PAA_{100})_{21}$  star considerably (for a factor of ca. 4) exceeds the total number of pyridinium groups on an individual macromolecule of PVP•EtBr, each small IPEC particle in the simplest case might be thought to comprise only a single  $(PAA_{100})_{21}$  star and from one to two chains of the cationic polyelectrolyte, depending on the value of Z and the ionic strength of the surrounding medium. Possible scenarios of complexation between  $(PAA_N)_X$  and PVP•EtBr are schematically represented in Figure 4A ( $X = 5, 8$ ) and Figure 4B ( $X = 21$ ).



**Figure 4.** Hypothetical Representation of Interpolyelectrolyte Complexation between  $(PAA_N)_X$  (in the Form of Its Sodium Salt) and PVP•EtBr for  $(PAA_N)_X$  with  $X = 5, 8$  (A) and  $(PAA_N)_X$  with  $X = 21$  (B).

The reason for the coexistence of two types of complex species in aqueous mixtures of the  $(PAA_N)_X$  stars with PVP•EtBr at  $Z < Z_M$  is not clear. It should be noted, however, that a nonuniform distribution of chains of “guest” polyelectrolyte among chains of the lyophilizing (or “host”) polyelectrolyte, leading to the formation of two types of complex species with considerably different base-molar stoichiometries, was previously observed for a number of systems of oppositely charged linear polyelectrolytes at  $Z \approx Z_M$  (cf., for instance, the review in ref 22 and references therein). In those cases, one of the types of complex species represented an IPEC of ca. 1:1 base-molar stoichiometry whereas the other population of the complex species was found to be a particle water-soluble IPEC with base-molar stoichiometry considerably deviating from 1:1. The complex species with base-molar stoichiometry close to 1:1 rapidly underwent secondary aggregation, and finally macroscopic phase separation took place in the mixtures of the oppositely charged polymeric components. Thus, previously a nonuniform distribution of chains of the guest polyion among chains of the lyophilizing (host) polyion was



**Figure 5.** Intensity distributions of decay times obtained at  $90^\circ$  for the mixture of  $(PAA_{100})_{21}$  with PVP•EtBr ( $DP_w \approx 570$ ) at the base-molar ratio  $Z = 0.2$  prepared according to method A (—) and method B (---); 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS•HCl),  $[(PAA_{100})_{21}] = 0.002$  base-mol/L.

generally associated with the macroscopic phase separation of such systems. In the case of the  $(PAA_N)_X$  stars interacting with PVP•EtBr, a nonuniform distribution of the chains of the cationic polyelectrolyte (guest polyelectrolyte) among macromolecules of the  $(PAA_N)_X$  stars (lyophilizing or host polyelectrolyte) is, however, already observed at  $Z < Z_M$  and is not accompanied by concomitant macroscopic phase separation in the system.

Another possible reason that we cannot exclude and that might, at least to some extent, explain the formation of the large complex species is the probable high PDI of PVP•EtBr, leading to the presence of longer chains of the cationic polyelectrolyte that are expected to generate large complex species upon their interaction with  $(PAA_N)_X$ . A detailed investigation on effect on DP of the linear cationic polyelectrolyte with narrow MWD on its complexation with  $(PAA_N)_X$  will be the subject of our forthcoming publication.

The distinct coexistence of two populations of the complex species does not allow carrying out SLS to determine the molecular weights and radii of gyration of the formed IPEC particles. In one case however, viz., when one can neglect the contribution of the small complex species to the intensity of scattered light, such measurements are feasible, for example, for the mixture of  $(PAA_{90})_5$  with PVP•EtBr at  $Z = 0.2$  (Table 2). The results obtained point to a rather high weight-average molecular weight of the large complex species of  $M_w \approx 8 \times 10^6$  g/mol and their radius of gyration of  $(R_g^2)^{0.5} \approx 75$  nm ( $R_g/R_h \approx 1$ ) as well as a negative value of the second virial coefficient  $A_2 \approx -1.67 \times 10^{-4}$  (mole  $\times$  mL)/g<sup>2</sup>. These findings support our inferences made above that such large complex species represent rather compact aggregates. Such aggregates may be considered to be IPEC particles with base-molar stoichiometry close to 1:1, and they are dense because of the mutual charge neutralization of the chains of the oppositely charged polymeric components incorporated and stabilized against further progressive aggregation by adsorption on their surfaces of excess  $(PAA_{90})_5$  stars, thus making such particles stable on the colloidal level. Under this assumption, each large IPEC particle is roughly estimated to comprise ca. 85  $(PAA_{90})_5$  stars and ca. 70 chains of the cationic polyelectrolyte.

All factors that lower the lyophilizing strength of the  $(PAA_N)_X$  stars (viz., decreasing the number of arms, increasing the content of the cationic polyelectrolyte, or with the increasing ionic strength of the surrounding solution) are expected to increase the fraction of the large complex species formed in the mixtures of  $(PAA_N)_X$  with PVP•EtBr. Indeed, the corresponding variations of all aforementioned factors result in an increase in the fraction of large species (Tables

**Table 4. Apparent Hydrodynamic Radii  $R_{h,app}$  (Measured at 90°) of Small and Large IPEC Particles Formed in the Mixtures of (PAA<sub>100</sub>)<sub>21</sub> with PVP•EtBr ( $DP_w \approx 570$ ) and the Fraction of the Area of the Peak Corresponding to the Large Complex Species ( $Z = 0.2$ ; 0.1 M NaCl, pH 7 (0.01 M TRIS/TRIS•HCl), [(PAA<sub>100</sub>)<sub>21</sub>] = 0.002 base-mol/L)**

method	$R_{h,app}$ , nm		$\{A_{large}/(A_{large} + A_{small})\}^a$
	small	large	
A	12	63	0.25
B	12	59	0.32

<sup>a</sup> Calculated from intensity distributions of  $R_h$ .

2 and 3) being in satisfactory agreement with our considerations of interpolyelectrolyte complexation between (PAA<sub>N</sub>)<sub>X</sub> and PVP•EtBr.

It is remarkable that the size and the fraction of both small and large IPEC particles formed in the mixtures of the (PAA<sub>N</sub>)<sub>X</sub> stars and PVP•EtBr appear to be independent of the method of preparation of such mixtures. Figure 5 presents the intensity distribution of decay times of the complex species detected in the mixtures of the oppositely charged polymeric components prepared by addition of the concentrated solution of PVP•EtBr to the solution of (PAA<sub>100</sub>)<sub>21</sub> at 0.1 M NaCl (method A, solid line), as well as the intensity distribution of decay times of the complex species obtained when the mixtures of the oppositely charged polymeric components were prepared via a different route, viz., by mixing the concentrated solutions of (PAA<sub>100</sub>)<sub>21</sub> and PVP•EtBr at high ionic strength ([NaCl] > 2 M), at which the electrostatic interaction is completely suppressed by the screening effect of small ions, followed by a dilution of this mixture by the solvent leading to the same salt concentration in the final mixture of (PAA<sub>100</sub>)<sub>21</sub> with PVP•EtBr, that is, 0.1 M NaCl (method B, dashed line). As is seen, the decay time distributions obtained for both cases are very similar: both distributions are clearly bimodal; furthermore, the values of  $R_{h,app}$  of the complex species and the values of the fractions of areas

of the peaks derived from these intensity distributions are in a reasonable accordance with each other (Table 4). This finding suggests that the IPEC particles formed in the mixtures of the oppositely charged polymeric components are apparently in equilibrium, at least under the specific experimental conditions applied.

## Conclusions

Mixing aqueous solutions of star-shaped poly(acrylic acid) with different number of arms (5, 8, and 21) and poly(*N*-ethyl-4-vinylpyridinium bromide) results in the formation of two coexisting populations of complex species considerably differing in size. The mixtures of the oppositely charged polymeric components remain transparent until their base-molar ratio exceeds a certain threshold value depending on the number of arms of the star-shaped poly(acrylic acid) and the ionic strength of the surrounding solution. The small complex species (major fraction) are assumed to represent the particles of water-soluble IPEC whereas the large complex species (minor fraction) are considered to be complex aggregates with base-molar stoichiometry close to 1:1. The fractions of these complex species but not their sizes distinctly depend on the number of arms of the star-shaped poly(acrylic acid) and the base-molar ratio of the oppositely charged polymeric components in their mixtures as well as the ionic strength of the surrounding solution.

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