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# Migration of cationic polymer between anionic polymer microspheres

**Kirill I. Yuzhanin,*[a,b] Irina G. Panova,[a,b] Natalia N. Shevchenko[b,c] and Alexander A. Yaroslavov[a,b]**

[a] *Department of Chemistry, M. V. Lomonosov Moscow State University, 119991 Moscow,*
*Russian Federation. Fax: +7 495 939 0174; e-mail: 0073158@mail.ru*
[b] *Yaroslav-the-Wise Novgorod State University, 173003 Veliky Novgorod, Russian Federation*
[c] *Institute of Macromolecular Compounds, Russian Academy of Sciences, 199004 St. Petersburg,*
*Russian Federation*

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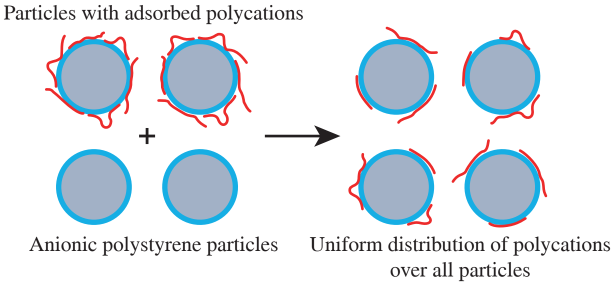
**In aqueous solution, the cationic polymers poly(diallyldimethylammonium chloride) and poly-L-lysine hydrobromide are electrostatically adsorbed onto anionic polystyrene microspheres, which are used as a model of microplastics. The adsorbed polymers are able to migrate between the particles, resulting in a uniform distribution of macromolecules over all particles in the system. Interparticle migration should be taken into account when discussing the spread of toxicants associated with micron-sized vectors.**



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The accumulation of polymer waste is an unsolved global problem.[1] As a result of polymer degradation, huge amounts of microplastics (MP), particles 5 mm or smaller in size, are formed.[2,3] MP are found everywhere: from soil and water to animals and food products.[4–6] The greatest danger is posed by submicron plastic particles (<1 μm), which can penetrate cell membranes and cause various negative consequences.[3,7]

In addition to the original MP particles, their conjugates (complexes) with toxic substances can be potentially dangerous. These include heavy metals,[8,9] antibiotics,[8,10] persistent organic pollutants[3,8] and dyes.[11] MP can bind polymeric substances of both natural (proteins) and synthetic origin. Among the latter, cationic poly(diallyldimethylammonium chloride) (PDADMAC) and polylysine can be mentioned. The first is a reagent (flocculant) for water purification,[12,13] the second is used in the food industry,[14,15] cosmetics and medicine.[16,17] Both polymers demonstrate high toxicity towards microorganisms.[15,17–19] Binding of a cationic polymer to MP can lead to the formation of new toxic particles, and the redistribution of the polymer between the components of the system will increase the number of toxic particles. This hypothetical, but quite plausible picture forces us to study the migration of cationic macromolecules between MP species.

Considering the experimental difficulties associated with the isolation and characterization of MP particles, especially small ones,[8,20] real MP is often replaced by model objects with reproducible characteristics: chemical composition, xenobiotic capacity, size, surface charge, *etc.* Following this approach, we complexed two cationic polymers, PDADMAC and poly-L-lysine hydrobromide (PL), with model MP particles, polystyrene microspheres (PSMs) with carboxyl surface groups, and investigated the migration of adsorbed polymers between the microspheres. PDADMAC with an average molecular weight $M_w < 100$ kDa and a degree of polymerization DP < 620 (Sigma-Aldrich) and PL with $M_w = 15.7$ kDa and DP = 75 (Sigma-Aldrich) were used. PSMs were synthesized as described elsewhere,[21] their average size (hydrodynamic diameter, $D_h$) was 400 nm, electrophoretic mobility (EPM) of PSMs, a parameter related to their surface charge, was –6 μm cm s$^{-1}$ V$^{-1}$. The polymer concentration [N$^+$] was expressed as moles of amino or ammonium groups per liter, the PSM concentration [COO$^-$] as moles of carboxyl groups per liter, participating in complexation with polycations at pH 7 (for details, see Online Supplementary Materials).

Complexation of polymers with PSMs was carried out in 1 mM Tris aqueous solution (pH 7) additionally containing 5 mM NaCl (Tris–NaCl buffer), while the charge-to-charge ratio $Z = [\text{N}^+]/[\text{COO}^-]$ was varied from 0 to 2. Addition of PDADMAC solution or PL solution to PSMs solution led to neutralization of the PSM charge that was accompanied by a change in the EPM of particles in the system [Figure 1(*a*), curves *1* and *2*]. In both cases, complete neutralization of the PSMs charges was observed at $Z \approx 1$, and a further increase in $Z$ led to the formation of positively charged polycation–PSM complexes with an excess of adsorbed polycation. Measurements of the size (hydrodynamic diameter, $D_h$) of the complex particles [Figure 1(*b*)] correlated well with the EPM data. Initially, neutralization of the PSM charge was accompanied by a progressive loss of aggregate stability and an increase in $D_h$, reaching a maximum value at EPM = 0. Then the complex particles acquired a positive charge, which ensured their

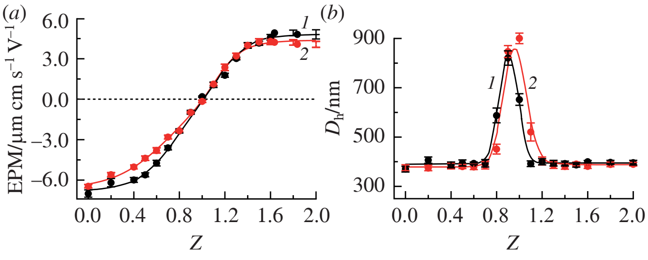

**Figure 1** Dependences of (*a*) EPM and (*b*) hydrodynamic diameter $D_h$ of PSMs in complexes with (*1*) PDADMAC and (*2*) PL on the value of $Z = [\text{N}^+]/[\text{COO}^-]$ at a PSM concentration of $1.6\times10^{-6}$ M in Tris–NaCl buffer (pH 7).

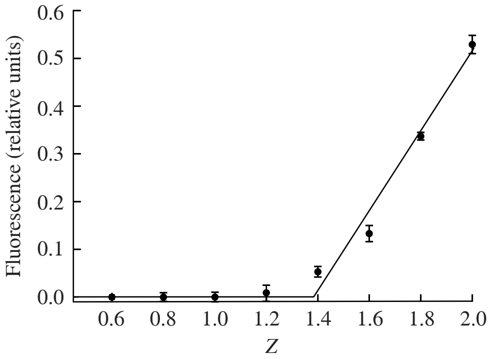

**Figure 2** Dependence of the relative fluorescence of the PL*–PSM complex on the value of $Z = [N^+]/[COO^-]$ at a PSM concentration of $1.6\times10^{-6}$ M in Tris–NaCl buffer (pH 7).

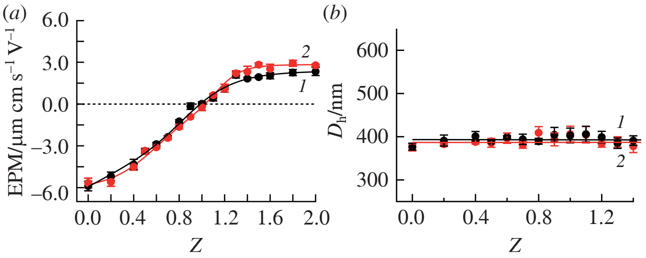

**Figure 3** Dependences of (*a*) EPM and (*b*) hydrodynamic diameter $D_h$ of PSMs in complexes with (*1*) PDADMAC and (*2*) PL on the value of $Z = [N^+]/[COO^-]$ at a PSM concentration of $1.6\times10^{-7}$ M in Tris–NaCl buffer (pH 7).

stability and a decrease in $D_h$. Such behavior is typical for mixed polymer–colloid systems.[22]

The efficiency of the polycation–(anionic colloid) interaction has been discussed in the literature.[23,24] It has been shown that the electrostatic complexation of oppositely charged macroions is irreversible: all added polycations bind to the particle surface until the entire accessible particle area is covered by adsorbed macromolecules.[25,26] Typically, macromolecules bearing hundreds and thousands of cationic units are considered. PDADMAC with DP < 620 satisfies this condition, but PL containing only 75 repeating cationic units at first glance may bind to particles *via* a reversible mechanism. To test this assumption, PL with fluorescein isothiocyanate covalently attached to the amino groups (PL*) was used, and its DP was close to that of unlabeled PL (for details, see Online Supplementary Materials). Briefly, PSM solutions were mixed with PL* solutions such that the *Z* value varied from 0 to 2. The PL*–PSM complexes were then centrifuged, and the supernatant was analyzed fluorimetrically at an emission wavelength of $\lambda_{em} = 525$ nm (excitation wavelength $\lambda_{ex} = 490$ nm). The relative fluorescence *vs.* *Z* plot (Figure 2) shows no signal (no free PL*) in the supernatant up to $Z = 1.4$, indicating complete polymer binding at $Z \leqslant 1.4$, while a positively charged complex is formed in the range $1 < Z \leqslant 1.4$.

A simple and visual method for demonstrating the migration of an adsorbed polymer between PSMs is as follows. The first important criterion for the migration process is monitoring the EPM value of the complex particles. For this purpose, a positively charged polymer–PSM complex containing no free polycations was prepared, mixed with the original negatively charged PSMs, and after some time, the EPM of the particles in the system was recorded (for details, see Online Supplementary Materials). In the case of uniform redistribution of macromolecules between all PSMs, the recorded EPM should be equal to the EPM value determined according to the EPM dependence on *Z* [see Figure 1(*a*)] for the *Z* value formally corresponding to the final state of the system. A large amplitude of the EPM values, from –6 up to +4 μm cm $s^{-1}$ $V^{-1}$, allows reliable recording of the EPM during the experiment.

However, there is another important criterion for polymer migration between individual PSMs: the final size of the complex particles should be close to the size of the initial PSMs. If the final size is larger, then we can only talk about partial redistribution of the polymer within the polymer–PSM aggregates. For this reason, the increase in the size of the polymer–PSM complexes recorded for the interval $0.8 < Z < 1.2$ [see Figure 1(*b*)] did not allow maintaining the small size of the particles during the redistribution process.

Aggregation in binary colloid–ligand systems can be minimized by decreasing the concentrations of the components. Following this concept, we reduced the PSM concentration by one order of magnitude but maintained the polymer to PSMs ratio, *i.e.*, the *Z* value. The EPM *vs.* *Z* profiles [Figure 3(*a*)] also demonstrated a wide range of EPM variations, while the polymer–PSM complexes retained their size up to $Z = 1.4$ [Figure 3(*b*)], which corresponded to a saturated positively charged complex. The size of the complex particles did not change during the 30 min required to complete the migration experiments (see below).

In migration experiment 1 (ME-1), the PDADMAC–PSM complex with $Z = 1.4$ was prepared and mixed with an equal amount of the original PSMs, so that the final *Z* value was 0.7. Additionally, in migration experiment 2 (ME-2), the PDADMAC–PSM complex with $Z = 1.2$ was mixed with an equal amount of the original PSMs, which gave a final *Z* value of 0.6. The EPM and size of the particles in solution were monitored for 30 min after mixing. The EPM changed from positive to negative within 10 min after adding the PSM solution to the complex solution, and then slightly changed to more negative EPM values (Table 1). After 30 min, the EPM reached –2.63 μm cm $s^{-1}$ $V^{-1}$ in ME-1 and –3.04 μm cm $s^{-1}$ $V^{-1}$ in ME-2. According to the plot of EPM *vs.* *Z* for the PDADMAC–PSM complex [Figure 3(*a*), curve *1*], the EPM values obtained in the migration experiments corresponded to *Z* values of 0.65 and 0.57 in ME-1 and ME-2, respectively. They are in excellent agreement with the *Z* values calculated based on the migration experiment procedure: 0.7 and 0.6 in ME-1 and ME-2, respectively. During the migration experiments, the key parameter, particle size, remained unchanged for 30 min (see Table 1). The electrophoresis and light scattering data clearly indicate the migration of PDADMAC macromolecules between the PSMs, resulting in a uniform redistribution of PDADMAC over all PSMs.

Migration experiments were then performed with PSMs and another cationic polymer, PL. In this series, a saturated PL–PSM complex with $Z = 1.4$ was prepared and mixed either with an equal amount of the original PSMs in migration experiment 3 (ME-3), giving a final *Z* value of 0.7, or with twice the amount of the original PSMs in migration experiment 4 (ME-4), giving a final *Z* value of 0.47. The EPM and size of the particles in solution recorded 30 min after mixing are shown in Table 2. In both cases, the EPM changed from positive to negative and reached $-2.73\pm0.11$ and $-4.27 \pm 0.35$ μm cm $s^{-1}$ $V^{-1}$ in ME-3 and ME-4, respectively. The plot of EPM *vs.* *Z* for the PL complex [Figure 3(*a*), curve *2*] shows that these EPM values correspond to *Z* values of

**Table 1** Time-dependent changes in EPM and hydrodynamic diameter of PDADMAC–PSM complexes after mixing with the original PSMs (see text for details).

| Time after mixing/min | EPM/μm cm $s^{-1}$ $V^{-1}$ | | $D_h$/nm | |
|---|---|---|---|---|
| | ME-1 | ME-2 | ME-1 | ME-2 |
| 0 (before mixing) | 1.93 ± 0.06 | 0.99 ± 0.34 | 427 ± 38 | 429 ± 13 |
| 10 | –1.71 ± 0.28 | –2.77 ± 0.22 | 452 ± 2 | 387 ± 19 |
| 20 | –2.87 ± 0.38 | –2.64 ± 0.47 | 461 ± 16 | 427 ± 30 |
| 30 | –2.63 ± 0.17 | –3.04 ± 0.48 | 399 ± 29 | 397 ± 14 |

**Table 2** Changes in EPM and hydrodynamic diameter of PL–PSM complexes after mixing with the original PSMs (see text for details).

| Time after mixing/min | EPM/μm cm s$^{-1}$ V$^{-1}$ | | $D_h$/nm | |
|---|---|---|---|---|
| | ME-3 | ME-4 | ME-3 | ME-4 |
| 0 (before mixing) | 2.32 ± 0.40 | 2.21 ± 0.25 | 403 ± 21 | 418 ± 15 |
| 30 | –2.73 ± 0.11 | –4.27 ± 0.35 | 396 ± 4 | 417 ± 5 |

0.65 and 0.45, respectively, which are close to the calculated $Z$ values of 0.7 and 0.47 in ME-3 and ME-4, respectively. The particle size measured 30 min after mixing was consistent with that before mixing. Thus, migration of PL macromolecules between PSMs was proven.

In summary, it was found that complexation of a cationic polymer (PDADMAC or PL) with anionic PSMs (the latter were taken at a concentration of $1.6\times10^{-6}$ M) results in aggregation of polycation–PSM complexes under conditions of complete neutralization of the negative charges of the PSMs by the positive charges of the polycations. With a decrease in the PSM concentration by an order of magnitude, the polycation–PSM complexes retain aggregate stability over the entire range of component ratios. Under these conditions, adsorbed polycation macromolecules are able to migrate between individual PSMs that leads to a uniform distribution of the polymer over all PSMs. The transfer of macromolecules from one particle to another could occur *via* two mechanisms: by direct contact of the PSMs or as a result of desorption of macromolecules from one particle, their diffusion through the solution and adsorption on another particle. The above-described quantitative binding of the polymers on the PMS surface indicates a contact exchange mechanism. The driving force of the process is the increase in the entropy of the system as a result of the distribution of polymers between all particles. The migration of adsorbed polycations between colloidal particles is a pathway for the spread of toxic compounds in the environment and should be taken into account when discussing the negative impact of microplastics on biological objects.

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*Online Supplementary Materials*

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7585.

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