# Sizing of PDADMAC/PSS Complex Aggregates by Polyelectrolyte and Salt Concentration and PSS Molecular Weight

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ABSTRACT: Herein we report on the influence of salt and polyelectrolyte (PEL) concentration, molecular weight, and mixing ratio on the size and size distribution of polyelectrolyte complex (PEC) particles composed of cationic poly-(diallyldimethylammonium chloride) and anionic poly(styrene sulfonic acid). The unusual salt concentration dependence of PEC particle sizes was observed. This behavior was explained by competition of two processes both related to the charge screening: swelling/shrinking of the outer shell formed by the excess PEL molecules and increasing/decreasing of the aggregation rate of colloidal PEC particles. The results on the size regulation of PEC particles by varying PEL concentration reflect both competitive processes as well. The regulation of the mixing ratio of PEL allows producing PEC particles with different charges, and it does not affect significantly the PEC particle size regulation by salt concentration. The PEC size dependence on the molecular weight of polymer was shown to be power and an exponent value of $\alpha \approx 0.13$ was obtained for the spherical PEC particles. This value is lower than one for polymer particles with a compact globular structure with exponent values of $\alpha = 0.33$. However, the molecular weight of only one polymer component of a two-component PEC particle was varied.
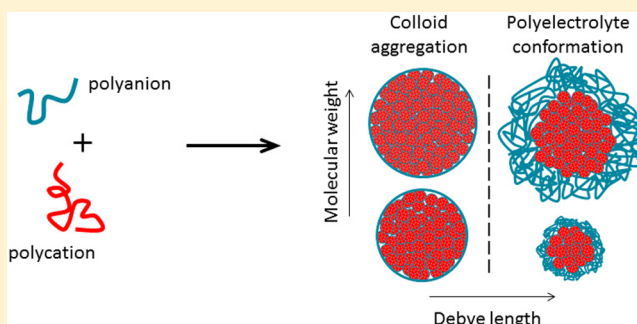
INTRODUCTION

Dispersions of polyelectrolyte complexes (PEC) formed by the direct mixing of polycation and polyanion solutions are established as their own class of polymer nanoparticles.[1−4] However, the practical applications of these nanoparticles in areas like drug delivery[5,6] demand some key requirements like reproducible preparation, monomodality of size distribution, and possibility to obtain particles of controllable and graded sizes ("sizing"), which still have not been sufficiently addressed or fulfilled up to now. Many early works concerning controlled sizing of PEC particles, e.g., from Dautzenberg,[7] are devoted to the influence of medium parameters like polyelectrolyte (PEL) concentration on the processes of formation of the PEC dispersion. A recent review on sizing of PEC particles can be found in ref 8.

In the past new concepts of PEC preparation providing improved reproducibility and monomodality were elaborated. One of them implies consecutive steps of centrifugation/separation of the freshly prepared raw PEC dispersion, which we have successfully applied to the system of poly-(diallyldimethylammonium chloride)/poly(maleic acid-co-α-methylstyrene) (PDADMAC/PMA-MS) with nonstoichometric ratios of either $n_-/n_+ = 1.50$ or 0.66 with respect to their charged monomer units.[9] It allowed the polydispersity of the system to decrease significantly due to elimination of the fraction of small primary complex particles with particle radii ≤20 nm, whereas secondary particles with radii ≥100 nm

remained in dispersion. Recently, this process was addressed by DLS and AFM experiments and by computer simulations based on the PDADMAC/poly(styrenesulfonate) (PSS) system as a function of ionic strength.[10] According to this approach, the process of PEC particle formation involves two stages, which are schematically depicted in Figure 1: formation of primary PEC particles from mixed PEL solutions (molecular level) and formation of secondary PEC particles as a result of aggregation of the primary particles (colloid level). The simulations of the second process were performed by variation of the Debye length λ as the main parameter. However, conformational
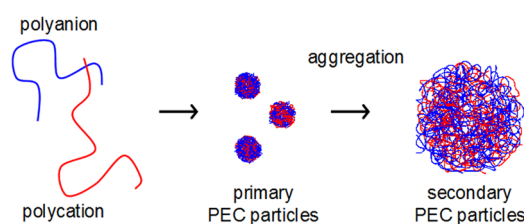
Figure 1. Schematic presentation of the processes occurring during mixing of PEL solutions and formation of PEC particles.

processes of PEL molecules were also found to play an important role.

Herein we present experimental results obtained for the standard PEC system PDADMAC/PSS concerning the influence of various additional parameters beside ionic strength on the formation and final size of the PEC particles. These experimental data confirm the assumption about the PEC particle structure and are in harmony with our previous results.[10] Again current data will serve as an input for future simulations. The article is organized as follows. First, results on the influence of variations of salt concentration (C_s) before and after mixing the PEC components at various molecular weights of PSS (M_w^{PSS}), a comparison with simulation data from ref 10, and two different mixing ratios are presented and discussed. Second, the influence of PEL concentration (C_{PEL}) at various M_w^{PSS} is studied. Finally, the direct dependence of PEC particle size versus M_w^{PSS} is represented by a simple scaling law and the obtained exponent values are tentatively assigned and discussed.

■ **MATERIALS AND METHODS**

Polyelectrolyte Solutions. Poly(diallyldimethyl-ammonium chloride) (PDADMAC; 20% water solution Aldrich Chemical Co., Inc., Milwaukee, WI; Figure 2a) and
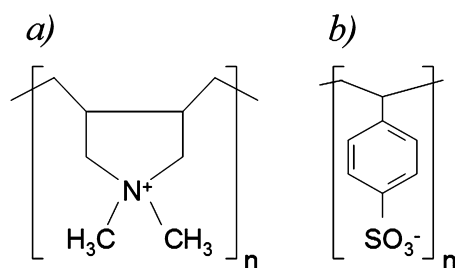
Figure 2. Structural formulas of PELs: (a) poly-(diallyldimethylammonium chloride) and (b) poly(styrene sulfonate).

poly(styrene sulfonic acid) (PSS; Polysciences, Inc., Warrington, PA; Figure 2b) were used without further purification. The molecular weight of PDADMAC was 200 - 350 kg/mol and four different samples of PSS with M_w^{PSS} = 4600, 70 000, 400 000, and 1 117 000 g/mol were used. PEL solutions (0.00005, 0.0001, 0.0005, 0.001, 0.0015, and 0.002 M) were prepared using deionized refined water (Millipore GmbH, Eschborn, Germany). The salt concentration of PEL solutions was adjusted by variation of NaCl (Merck KG, Darmstadt, Germany) concentration, which was taken as C_s = 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, and 0.075 M.

Preparation of PDADMAC/PSS Nanoparticles. PEL solutions of equal PEL concentration (concentration of polyanion was equal to concentration of polycation) and salt concentration were mixed in a glass beaker using a home-built setup consisting of a peristaltic pump and a stirring panel. The salt was added to PEL solution before mixing (except for the case when the effect of sequential salt addition was studied). The stoichiometric mixing ratio, related to the charged monomer units, was n_-/n_+ = 1.50 and 0.66 (further denoted as PEC-1.50 and PEC-0.66, respectively). Typically, 10 mL of PDADMAC solution (minority component) was added dropwise to 15 mL of PSS solution (excess component) under continuous stirring for 20 min.

Centrifugation, Evaporation. In order to separate the excess of polymer and primary particles from the secondary particles, the dispersions were centrifuged for 20 min at 11 000 rpm (Centrifuge 5416, Eppendorf AG, Hamburg, Germany) in accordance with the procedure described in ref 9. In the case of dispersions produced at very low polymer concentration, the PEC dispersions require additional processing in order to provide sedimentation of the small PEC particles. Such systems were concentrated using a rotational evaporator.

Dynamic Light Scattering. The size of PEC particles was checked by dynamic light scattering (DLS). DLS data were recorded by a Zetasizer 3000 (632.8 nm, 10 mW He−Ne Laser, Malvern Instruments, Worcestershire, U.K.) and the Nano S 633 (Malvern Instruments Ltd.) applying the scattering angle of 90°. The samples were held in 10 mm cuvettes. The mean particle radius r_m was estimated as the hydrodynamic radius using the Stokes−Einstein equation. The shown errors are related to the standard deviations of at least three different measurements. For PEC dispersions prepared with the lowest C_{PEL} = 0.00005 M, the DLS method was limited due to too low values of the countrate, whereas for high C_{PEL} the method was limited due to too high values of the countrate caused by larger PEC aggregates.

Atomic Force Microscopy (AFM). PEC samples for AFM experiments were precipitated onto a silicon substrate and dried. The measurements were carried out by means of ultramicroscope (Nanostation II, SIS GmbH, Herzogenrath, Germany) provided with an optical dark field microscope and AFM device. AFM measurements were performed in the noncontact mode using tips from nanosensors (Darmstadt, Germany).

■ **RESULTS AND DISCUSSION**

PEC Particles Size Regulation Varying the Ionic Strength of the Solution. *Salt Addition during the Mixing Process.* In this work PEC nanoparticles were prepared by mixing PDADMAC and PSS solutions at defined stoichiometric ratios of either n_-/n_+ = 1.50 or 0.66. Figure 3 shows the dependence of PEC particle mean radius r_m versus salt concentration C_s (upper x axis) or versus Debye length λ (lower x axis), respectively, for four different values of M_w^{PSS}.

In this case the Debye length was used as the main parameter in order to take into account the effect of salt concentration (C_s), as well as concentration of PEL (C_{PEL}), since not only C_s but also C_{PEL} contributes to charge concentrations and thus λ. This was pointed out by Wandrey[10] and the formula for λ given therein was used

$$\lambda = [4\pi N_A l_B (\chi^{-1} C_{PEL} + 2C_s)]^{-1/2}$$

where l_B is the Bjerrum length (l_B = 0.712 nm in water), N_A is the Avogadro constant, and χ is the Manning parameter (we assumed χ = 2.69, details can be found in ref 10).

The upper x axis shows salt concentrations corresponding to the values of λ. PEC particles with the mixing ratio n_-/n_+ = 1.5 were used and PSS was the excess PEL component. Figure 3 shows that all of the curves go through a minimum, approximately at C_s = 0.005 M. Correspondingly, PEC particles of higher radii are observed at very low or very high C_s. This effect was already discussed in our previous theoretical paper,[10] where the results of computer simulation based on the theory of colloidal particle aggregation were compared with experimental data.[9] It was shown that both aggregation processes and
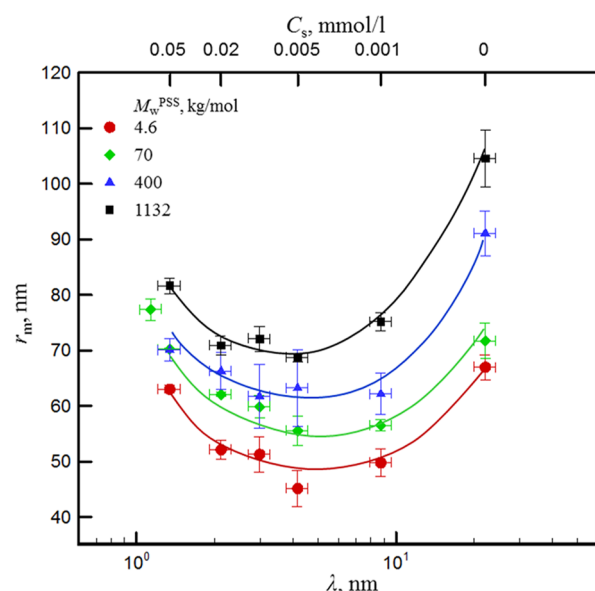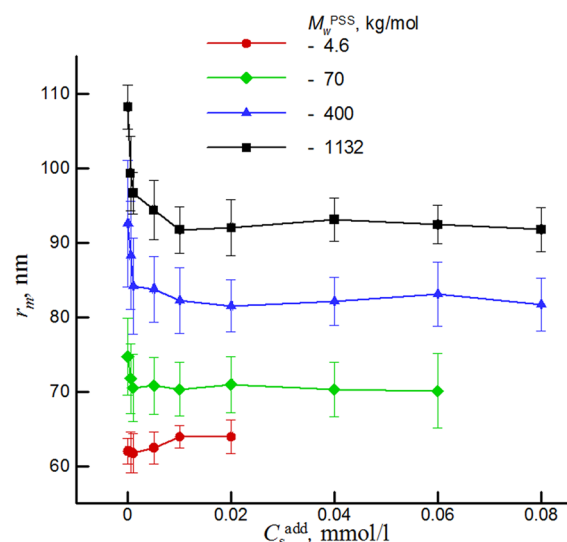
Figure 3. Dependence of the size of PEC particles r_m on Debye length λ (lower x axis) and salt concentration C_s (upper x axis) for different molecular weights of PSS, M_w^{PSS} (C_{PEL} = 0.001 M, n_-/n_+ = 1.5).

Figure 4. Salt concentration C_s^{add} dependence of PEC particle radius r_m for different molecular weight values M_w^{PSS}. C_s^{add} means that the salt was added after mixing of PELs (C_{PEL} = 0.001 M, n_-/n_+ = 1.5).

conformation of PEL molecules play a very important role in PEC particle formation process. It was assumed in ref 10 that increase of λ value (decrease of C_s) results in reduction of the aggregation rate of primary PEC particles due to decreasing electrostatic screening. But at the same time the PEL molecules become more stretched. It follows from the minimum in Figure 3 that a kind of a competition between the aggregation processes and the conformational changes in PEL molecules takes place. On the other hand, the Debye length profiles of PEC particle sizes shift constantly to higher levels with increase of M_w^{PSS}. Such a shift means that the higher the value of M_w^{PSS} the bigger primary particles are formed, but the competition between primary particle aggregation and PEL shell swelling remains, thus it is independent of M_w^{PSS}. Moreover, Figure 3 shows that differences in size upon M_w^{PSS} variation are larger at high λ than at low λ. The stronger size effect at high λ values can be explained by the influence of M_w^{PSS} on the size of the PSS molecule,[11] whereas according to the assumed core–shell morphology of PEC particles, increasing PSS dimensions cause increase of PEC particle shell thicknesses. The lower size effect (low λ) can be explained by the fact that the primary PEC particles have very thin shells of the excess PSS molecules through coiling caused by salt,[12−14] which also lowers electrosteric repulsion interactions and increases the rate of aggregation. Therefore, no strong particle size dependence on M_w^{PSS} is expected for secondary PEC particles formed by aggregation of the primary PEC particles. In other words, PEC particles with the shells of highly coiled excess PEL molecules show only weak M_w^{PSS} dependence.

Salt Addition after the Mixing Process. While Figure 3 shows r_m versus salt concentration C_s dependence for PEC particles formed in the presence of the salt, Figure 4 shows the r_m versus C_s dependence when the salt was added after formation of PEC.

The different amount of salt was added after the gradual preparation of PEC dispersion with various values of M_w^{PSS}. Thus, it was assumed to mark out the effect related to changes in the shell size. It should be noted that addition of salt after the

preparation of PEC dispersion affects rather the particle surface than the particle core. As can be seen from Figure 4, the particle sizes for all molecular weight values start to decrease with the salt addition. The PEC particle shells shrink at high C_s. With further increasing of C_s the particle size reaches the permanent value. After the critical C_s value, the fast aggregation process starts and large flakes are precipitating rapidly. Moreover, the higher is the M_w^{PSS} value, the higher difference between the initial particle radius value and the permanent value was observed. This complements and explains well the data of our previous work[10] dealing with the influence of PEL conformation on PEC particle shell size.

Actually in order to proof the suggestion of core–shell structure of PEC particles we modified the model which was developed and described in our previous paper.[10]

Figure 5 shows the comparison between the experimental results, results of a previous model, and a modified one. The model consists of the aggregation of PEC particles from the colloidal point of view (details can be found in ref 10). Nontrivial Debye length dependence of PEC particle sizes was shown experimentally (Figure 3, also it was described in ref 10). Namely, at λ > 5 nm the r_m grows with increasing λ, whereas colloid theory predicts a decrease of particle sizes with increasing λ,[10] and it is evident that the conformation of PEL molecules was not taken into account. Results which are demonstrated in Figures 3 and 4 corroborate the aforementioned statements: the particles have a core–shell structure and their sizes can be regulated by changing the screening length in solution. Thus, the idea to modify the model was very simple. We have introduced to the model the shell around the colloid particles, and the size of the shell, d_{shell}, was dependent on the Debye screening length, λ. As a first approximation we have chosen the power dependence

$$d_{shell} = B\lambda^{\gamma}$$

This extremely simple assumption surprisingly results in a very good correspondence with experimental data. As can be seen in Figure 5, the line with circles corresponds to the modified model and the line with squares corresponds to experimental data. Parameter B was chosen as 2.22; γ = 1.0.

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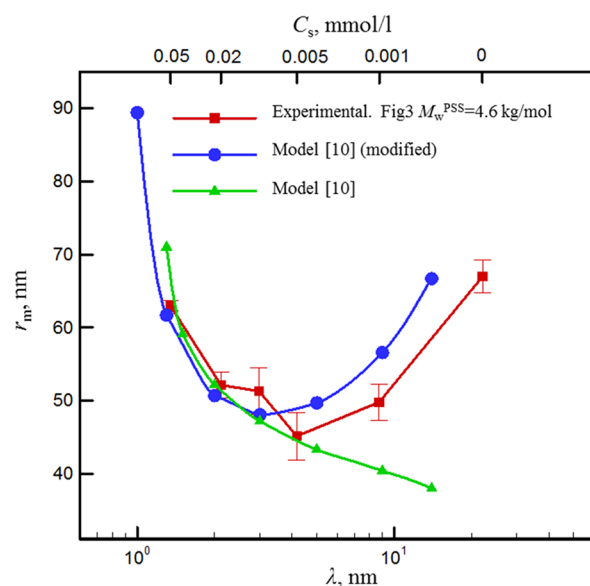
Figure 5. PEC particle sizes r_m versus Debye length λ (lower x axis) and salt concentration C_s (upper x axis). It is a comparison of experimental result from Figure 3 at M_w^{PSS} = 4.6 kg/mol (squares), our previous simulation results from ref 10 (triangles), and modified simulation results from ref 10 (circles).

Of course Figure 5 gives only a qualitative picture, whereas the real physics of the process is not clear at the moment. For example, one of the further questions can be directed to the conformational behavior of the confined PEL, namely the loops and tails of excess PEL which probably form the shell around the PEC particles. Nevertheless, the rough comparison in Figure 5 is an evidence of core−shell assumption and presence of two competitive processes of colloid aggregation and PEL conformation during the formation process of PEC particles.

Influence of Salt Concentration at Two Mixing Ratios. Figure 6 shows the Debye length dependence of PEC particle
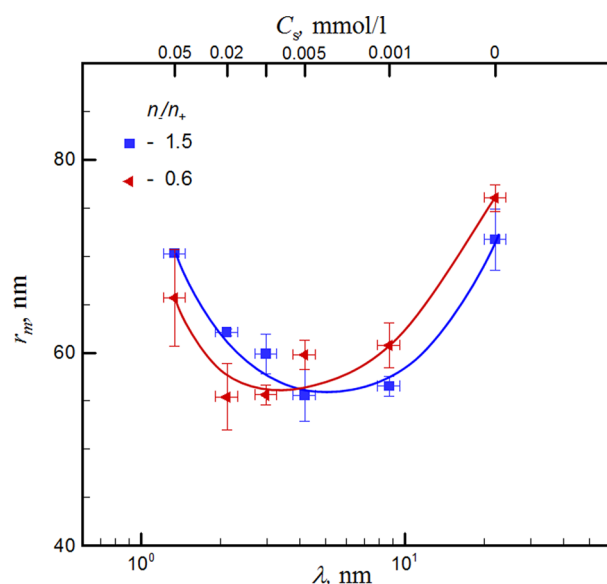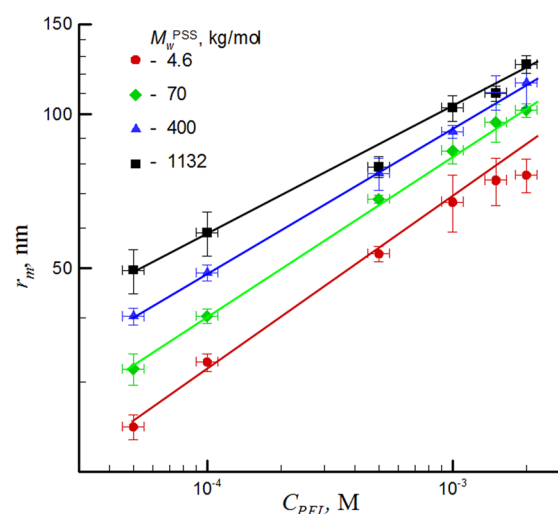

Figure 6. The dependence of PEC particle sizes r_m on Debye length λ (lower x axis) and salt concentration C_s (upper x axis) for different nonstochiometric mixing ratio n/n_+ (C_{PEL} = 0.001 M, M_w^{PSS} = 70 kg/mol).

radius at different values of nonstoichiometric ratio n_-/n_+. The dependencies are similar to the ones which are shown on Figure 3 and serve as comparison of two symmetric cases of formation of positively and negatively charged particles.

In the case of n_-/n_+ = 1.5, negatively charged PEC particles are produced, because the PSS polyanion is the excess PEL during mixing and PSS molecules form a shell around PEC core and thus, define the negative surface charge of those PEC particles. In the case of n_-/n_+ = 0.66, the polycation PDADMAC defines the sign of PEC particle surface charge. The curves demonstrate almost the same behavior for both negatively and positively charged particles. Both curves pass through a minimum in the range of Debye length values between 3 and 6 nm. This fact means that charge of excess polymer plays a minor role during the PEC formation process. It is principally possible to create PEC particles of both types following similar procedures of preparation and regulate their size by regulation of the same parameters.

Influence of PEL Concentration on the Size of PEC Particles. The PEL concentration (C_{PEL}) dependencies of PEC particle radius r_m for different molecular weights of PSS and constant molecular weight of PDADMAC (200−350 kg/mol) are shown in Figure 7.

Figure 7. PEL concentration dependence of PEC particle sizes r_m at different M_w^{PSS} (C_s = 0 M, n_-/n_+ = 1.5).

Generally, as can be seen in Figure 7 the initial value of C_{PEL} considerably affects the size of the secondary PEC particles. PEC particles with noticeably different sizes can be prepared by adjustment of M_w^{PSS} and C_{PEL}. For example, relatively small size of PEC particles with r_m of nearly 23 nm can be obtained for M_w^{PSS} = 4.6 kg/mol and C_{PEL} = 0.00005 M; and PEC particles with r_m of nearly 125 nm for M_w^{PSS} = 1132000 g/mol and C_{PEL} = 0.002 M. An explanation of the $r_m(C_{PEL})$ profiles is not straightforward, since the PEC formation process depends not only on the aggregation of primary particles, but also on polymer conformation and electrostatic conditions in solution as it was discussed before. Increasing of polymer concentration and thus, concentration of primary particles accelerates the aggregation and increases the size of the secondary particles.[15,16,10] Generally, according to Wandrey,[17] the concentration of charges increases and the Debye length value decreases with increaseing C_{PEL}. It has two effects: first, the conditions of aggregation of colloid particles change,[10] and

second, the conformation of PEL molecules also changes.[12−14] In accordance with the theory of colloid aggregation, the concentration of particles at the moment (and, as a consequence, the size of particles) depends on initial concentration of the primary particles according to

$$\nu(t) = \frac{\nu_0}{1 + t/\theta}$$

where ν is the current number concentration of particles, ν_0 is the initial number concentration of particles, t is the time of the process, and θ is the half aggregation time.

If the PEC particle is homogeneous (nonfractal) and consists of N_p primary particles, then its radius r_m scales as $r_m \approx N_p^{1/3}$. N_p depends on the initial concentration of particles, because the higher the initial concentration is, the higher the rate of aggregation. Thus, in accordance with the equation given above $r_m \approx \nu_0^{1/3}$ (of course, it is a function of time). According to refs 12−14, both experimental and theoretical dependences of the PEL molecule sizes presented in literature obey the exponential law.

Variation of the Width of Distribution Function of PEC Particle Radii. Obviously, production of rather small particles with radius down to 23 nm is possible for a strong PEL at low C_{PEL}. This might be rationalized by the decrease of the relative width $\Delta r/r_m$ of the particle size distribution function (Figure 8)
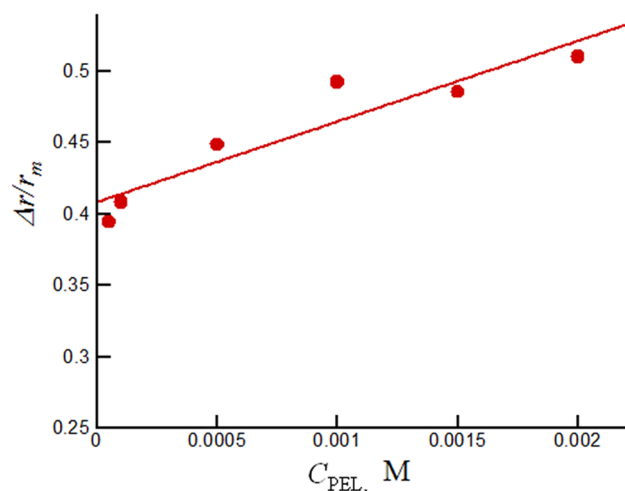
Figure 8. Dependence of the half width of distribution function $\Delta r/r_m$ versus PEL concentration C_{PEL} (C_s = 0.001 M, M_w^{PSS} = 70 kg/mol).

with decreasing C_{PEL}. The dependence presented in Figure 8 can be explained by approaching the ideal system at low polymer concentrations. It means that reduction of interaction between two neighbor molecules and reduction of the rate of aggregation result in decrease of the width of PEC particle distribution function.

Influence of Molecular Weight of Negatively Charged Excess PEL. The surprising experimental result in this work is the dependence of the mean PEC particle radius r_m versus molecular weight of PSS (M_w^{PSS}). Four different C_{PEL} values are shown in Figure 9. Generally, the PEC particle radii increase with increasing M_w^{PSS}. This effect reflects the general trend of uncomplexed polymers, as far as their size parameters like end-to-end distance, gyration radius or hydrodynamic radius increase with increasing polymerization degree N according to Flory theory. For real polymers the hydrodynamic radius is proportional to $N^{3/5}$ accounting for the balance of excluded
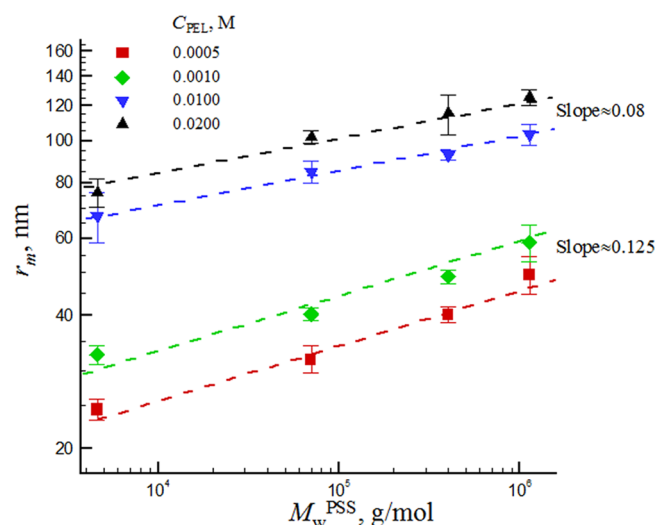

Figure 9. Dependence of mean PEC particle radius r_m on the molecular weight M_w^{PSS} at different polymer concentrations C_{PEL} (C_s = 0 M).

volume interactions between monomers and entropy loss due to the swollen chain conformations.[18] It may be assumed, that for compact spherical PEC particles like particles of PDADMAC/PSS the hydrodynamic radius scales as $N^{1/3}$ assuming, that the number of PDADMAC and PSS molecules regardless of their molecular weight remains constant. However, in our case the molecular weight of only one PEL component (PSS component) in PEC particle (consisting of two PEL components) was varied. Intuitively in this case, one might also expect power dependence between r_m and N, i.e.

$$r_m \sim N^\alpha$$

Moreover, Figure 9 shows that the r_m (M_w^{PSS}) dependence is getting weaker with increasing of C_{PEL}. Indeed, we have fitted the double logarithmic data in Figure 9 by a power function $r_m \approx (M_w^{PSS})^\alpha$ and have found, that exponent value $\alpha \approx 0.125$ for low concentrations of PEL (C_{PEL} = 0.00005 and 0.0001 M) falls within α = 1/9 (0.111) and α = 1/6 (0.166), whereas it is $\alpha \approx$ 0.08 for C_{PEL} = 0.001 and 0.002 M. Such deviation of the exponent values might reflect both the colloid aggregation of the primary PEC particles to the secondary ones and swelling of PEL shells. The lower is PEL concentration, the weaker is the aggregation tendency and the larger is the PEL shell expansion. The higher is PEL concentration, the stronger is the aggregation tendency and the smaller is the shell expansion. Therefore, the M_w^{PSS} dependence is steeper ($\alpha \approx 0.125$) for low concentrations, since primary and secondary PEC particles have larger shell sizes in comparison to the sizes of PEC core. For high C_{PEL} dependence of M_w^{PSS} is less steep (value $\alpha \approx 0.08$), since primary and secondary PEC particles have smaller PEC shell sizes in comparison to the sizes of PEC core size. This result is also in line with the findings concerning the salt influence on the size of PEC particles (data presented in Figure 4). Here, the colloid contribution (aggregation of primary particles) is less pronounced at low ionic strengths and the PEC particles are of larger size due to shell expansion. However, it is matter for further discussions about the correlations between the molecular weight of polymer and actually the number of molecules which form the PEC particle.

Reduction of Particle Size Distribution. Of course from the point of view of real application of PEC particles one would
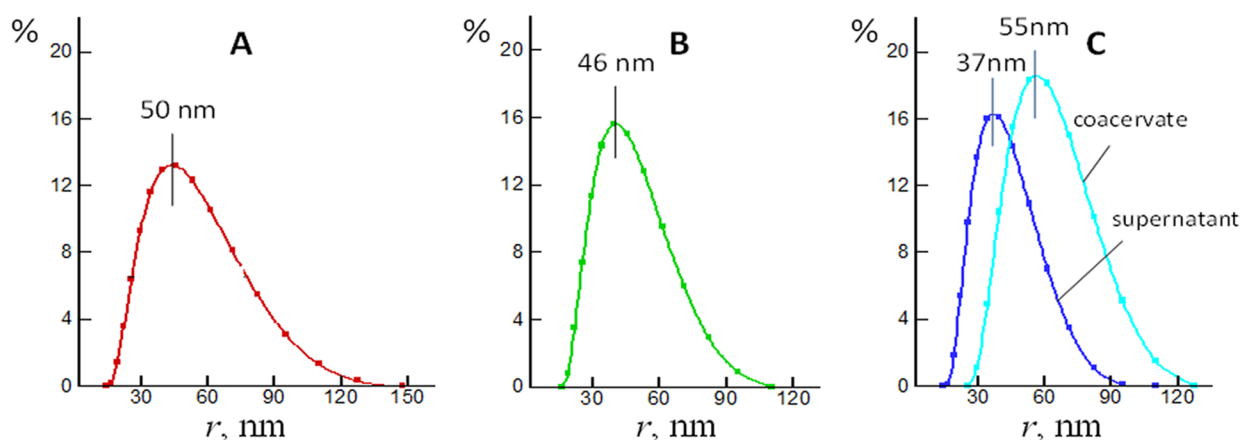
Figure 10. Particle size distributions. (A) after the preparation of dispersion at $C_{PEL} = 0.00005$ M; (B) after evaporation of water; (C) after centrifugation of supernatant and coacervate. $M_w^{PSS} = 70$ kg/mol.

think about very narrow size distribution. It was shown in the Figures 7 and 9 that creation of extremely small PEC particles (down to $r_m = 23$ nm) is possible during mixing at very low C_{PEL}. Additionally, in Figure 8 it was found, that with decreasing of C_{PEL} during mixing smaller values of the half-width of the distribution function were obtained. Finally, it is possible to produce very small particles with a narrow size distribution function. However in this case centrifugation cannot be applied for separation of PEC particles from the excess PEL and for reduction of polydispersity.[9] Evaporation of the solvent (concentrating) of the initial PEC dispersion was found to be efficient. In this case the PEC dispersion was prepared using very dilute PEL solutions ($C_{PEL} = 5 \times 10^{-6}$ M) and then dispersion medium (water) was evaporated. Thereby, concentration of solution was increasing during the process by 10 to 20 times.

Figure 10 shows the behavior of the distribution functions during the process. It was not possible to centrifuge the dispersion and to reach separation of phases directly after its preparation. But after concentrating dispersion becomes dense and may be centrifuged. Probably, during centrifugation of a very dilute dispersion the PEC particles spread throughout in solution according to the sedimentation theory. But when particle concentration exceeds a certain value, the particles of colloidal size start to contact one with another resulting in a secondary minimum according to DLVO theory. Finally, they form a coacervate phase, which can be easily destroyed by gentle shaking resulting in the reformation of a stable dispersion, which is due to a low energetic expense to escape the shallow secondary minimum.

Figure 11 shows an AFM image of such a PEC particle, which looks like an aggregate of small particles. The concept offered before[10] is based on the assumption, that aggregation of primary particles takes place in PEC dispersion. The AFM image in Figure 11 confirms this assumption. As can be seen primary PEC particles ($r_m \leq 20$ nm) is not detected due to the resolution limit of the AFM method. Nevertheless, the conception of aggregation of small particles to larger ones on a larger length scale is supported here. Assuming self-similarity of such PEC systems, one might extrapolate this actual picture also to lower length scales.
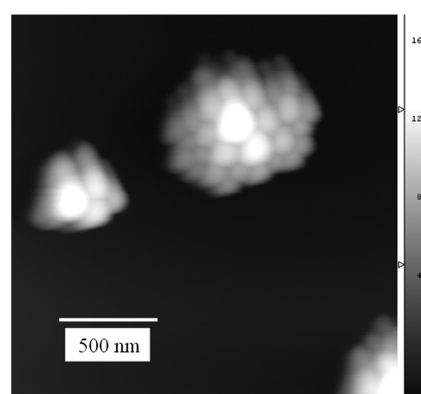
Figure 11. AFM image of PEC particles prepared by evaporation and centrifugation method.

■ CONCLUSIONS

The experimentally observed effects and interplay of typical external (solution) and internal PEL parameters evidence that PEC dispersions are multiscale colloidal systems. Herein we emphasize the existence of two important regimes of PEC dispersions, where different processes dominate: one is colloid aggregation and the other one is conformational changes of PELs.

We have found, that the courses of the radius r_m of refined PDADMAC/PSS particles as a function of ionic strength of solution passed through a rather distinct minimum at around $C_s = 0.005$ M for various values of M_w^{PSS}. This was explained by the competition of swelling process of the outer excess PEL shell of PEC particles and the aggregation process of the primary PEC particles.

Increasing of PEL concentration C_{PEL} resulted in monotonous increases of r_m for different M_w^{PSS}, which reflects both increase of the number of PEL molecules and charge screening, respectively. No significant effect of the mixing ratio was observed, it makes possible creation of PEC particles with different sign of the surface charge without changing the preparation protocol.

The molecular weight dependence of the PEC size was shown to be power and an exponent value of $\alpha \approx 0.13$ was obtained for the spherical PEC particles. This value is below the value for polymer particles with compact globular structure with exponent values of $\alpha = 0.33$. However, the M_w of only one

polymer component (PSS) of a two-component PEC particle was varied.

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Notes

The authors declare no competing financial interest.

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