

Stabilization of polymer colloid dispersions with pH-sensitive poly-acrylic acid brushes

Baptiste Jaquet · Dan Wei · Bernd Reck ·
Frank Reinhold · Xinya Zhang · Hua Wu ·
Massimo Morbidelli

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Abstract Polyelectrolyte brushes are widely used for surface modification of nano- and colloidal particles because of their ability to dramatically change their conformation, hydrophobicity, polarity, charge, etc., as a response to smooth variations in environmental conditions. In this work, we have studied experimentally the stability behavior of polymer colloids with grafted poly-acrylic acid (PAA) surface brushes. We have measured the Fuchs stability ratio (W) as a function of electrolyte concentrations at different pH. It is observed that at pH < 3, the W values with 1 % and 2 % PAA brushes do not differ significantly from those without PAA, indicating that in their protonated state, the carboxylic groups do not contribute significantly to the colloidal stability. At the intermediate pH ~ 5, the PAA brushes are partially deprotonated, and their contribution to the colloidal stability is substantial and increases as the length of the PAA brushes increases. Under alkaline conditions (pH > 8), since most of the carboxylic groups are ionized, the colloidal stability is much higher than that at pH ~ 5. However, the W values are basically the same with 1 % and 2 % PAA, implying that the contribution of the ionized AA in the two cases is practically the same. This experimental evidence indicates that only the ionized AA groups in the outer region of long brushes contribute to colloidal stability, thus supporting the hypothesis of local electroneutrality in the inner region of long brushes (LEA).

Keywords Polyelectrolyte brush · Fuchs stability ratio · Acrylic acid · pH responsive · LEA

Introduction

When linear polyelectrolyte (PE) chains are densely grafted on a surface, they form so-called surface PE brushes [1]. The strong electrostatic interactions among the highly charged chains within the brushes lead to substantially different properties with respect to surface monolayers of uncharged macromolecular chains. Thus, great attention has been given recently to these systems [2–9].

Weak (or so-called annealing) PEs such as poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA), when exposed to aqueous media, may undergo conformational changes, depending on the system pH and salinity. Under alkaline conditions, due to deprotonation of their carboxylic groups, they are highly charged and hydrophilic, leading to stretching of the backbone and good solubility. Instead, under strongly acidic conditions, because of protonation of the carboxylic groups, they become weakly charged and more hydrophobic with the backbone in a collapsed state, less soluble in water. Accordingly, weak PEs can be used to form brushes on polymeric surfaces, which respond to pH changes in the environment, leading to potential applications in various areas such as nano-scale actuators [10], membrane modifiers for pH-controlled permeation [4, 11], charge-driven reversible polymer and protein adsorption [4, 12–14], nanoparticle stabilization [15], etc.

In this work, we focus on the stability behavior of colloidal particles grafted with PAA brushes. It is known that weak PEs like PAA and PMAA, when grafted on the surface, change substantially their ionization behavior with respect to their un-grafted state in water. Because of the strong electrostatic attraction among the mobile counterions

B. Jaquet · D. Wei · X. Zhang · H. Wu (✉) · M. Morbidelli (✉)
Department of Chemistry and Applied Biosciences, ETH Zurich,
Institute for Chemical and Bioengineering, 8093 Zurich,
Switzerland
e-mail: hua.wu@chem.ethz.ch
e-mail: morbidelli@chem.ethz.ch

D. Wei · X. Zhang
School of Chemistry and Chemical engineering, South China
University of Technology, 510640 Guangzhou, Guangdong, China

B. Reck · F. Reinhold
BASF SE, GKD/T - B001, 67056 Ludwigshafen, Germany

in solution and the opposite charges on the brushes, the concentration of the mobile counterions in the brush-occupied region increases towards the particle surface [16, 17]. It follows that the total local charge density is substantially lower in the inner than in the outer region of the brushes. On this process is based, the so-called local electro-neutrality approximation (LEA) [16, 18], which states that the counterion concentration in the inner region is approximately equal to that of the charged groups on the brushes. As a consequence, the conformation of the brushes in the inner region is different from that in the outer one [19]. In addition, experimental observations reveal that the apparent pKa of surface-grafted PMAA differs from that of PMAA in solution and depends also on both brush thickness and density [20]. In addition to the electrostatic repulsion arising from the charges, the hydrophilicity of the brushes can also contribute to the particle stability *via* steric interactions [21]. These steric interactions arise from the mixing free energy of the polymer chains grafted on the surface [22]. In particular, if the dispersant is a good solvent for the brushes, overlapping between the brushes of two particles would lead to repulsion. The consequence of all the above theoretical and experimental results is that the contribution of the PAA brushes to the stability of colloidal particles is not a trivial function of the AA concentration on the particle surface.

In this work we investigate experimentally the effect of surface-grafted PAA brushes on the stability of polymer colloids at different pH values, i.e., under their different ionization and conformational states. For this, we considered colloidal particles with different thickness of the PAA brushes and measured their Fuchs stability ratio, W , based on the doublet formation kinetics, at different pH values, as a function of electrolyte concentration. In the sequel, we first describe and characterize three types of colloidal particles with different PAA brushes, and measure their W values. Next, we compare the measured W values of the three colloids, and discuss them with respect to the expected conformation of the PAA brushes.

Experimental section

The colloidal systems

The polymer colloids used in this work are three types of butylacrylate-methylmethacrylate-acrylic acid copolymer

latexes, referred to as P1, P2 and P3 in the following, respectively, synthesized ad-hoc by BASF SE (Ludwigshafen, Germany) through emulsion polymerization, using $\text{Na}_2\text{S}_2\text{O}_8$ as initiator and sodium dodecyl sulfate as emulsifier. The characteristics of the three latexes are reported in Table 1. It is seen that the main difference is the amount of acrylic acid (AA): 0 %, 1 % and 2 % for P1, P2 and P3 latexes, respectively. Thus, particles of P1 latex possess only the sulfate ($-\text{OSO}_3^-$) fixed charges, while those of P2 and P3 latexes carry both sulfate and carboxylic ($-\text{COO}^-$) charges.

The SDS (sodium dodecyl sulfate) surfactant present in the original latexes, as well as residual initiator, soluble oligomers and all other possible electrolytes, have been removed completely by ion exchange resin (Dowex MR-3, Sigma-Aldrich), according to a procedure reported elsewhere [23]. After cleaning, the conductivity of the mother liquor is $<10 \mu\text{S}/\text{cm}$ and its surface tension is close to that of deionized water, indicating that the colloidal systems are free of SDS and any other electrolyte. The particle volume fraction for the three latexes after cleaning is about $\phi=20\%$, with pH around 2.7. The cleaning also leads to the counterions, Na^+ of the fixed charges ($-\text{OSO}_3^-$ and $-\text{COO}^-$), being replaced by H^+ (the Na^+ concentration after cleaning measured by atomic absorption spectrometry is equal to about 3 ppm).

The particles characterization has been performed using dynamic and static light scattering (DLS and SLS). The SLS and DLS measurements were carried out using a BI-200SM goniometer system (Brookhaven Instruments, USA), equipped with a solid-state laser, Ventus LP532 (Laser Quantum, U.K.) of wavelength $\lambda_0=532 \text{ nm}$, as the light source, in the scattering angle range of 15° to 150° . When used for DLS, the angle was set to 90° . The reported results are averages of at least 2 independent series of at least 3 measurements. The nominal radius of the particles, R_p , has been evaluated by fitting the measured form factor from the SLS measurements, $P(q)$, defined as $P(q)=I(q)/I(0)$ (where I is the scattered intensity, q is the magnitude of the scattering wavevector, defined as $q=4\pi n_0/\lambda_0 \times \sin[\theta/2]$ with n_0 , λ_0 and θ the refractive index of water, the wavelength of the incident light, and the scattering angle, respectively), with the Rayleigh-Debye-Gans (RDG) theory for spheres. The nominal size of the primary particles after cleaning has been measured under natural pH and 10 mM NaCl, and the results are reported in Table 1.

Table 1 Characteristics of the three latexes used in this work

	Latex name	Composition (weight ratio) ^a	pH	R_p
α —BA: n-butyl acrylate; MMA: methyl methacrylate; AA: acrylic acid; SDS: sodium dodecyl sulfate	P1	BA (50): MMA (50)+0.7 % SDS	5.1	84.1 nm
	P2	BA (49.5): MMA (49.5): AA (1)+0.7 % SDS	4.9	81.0 nm
	P3	BA (49): MMA (49): AA (2)+0.7 % SDS	4.2	90.0 nm

Determination of the fuchs stability ratio W

The contribution of different surface groups to the colloidal stability has been quantified by measuring the Fuchs stability ratio (W) values under different conditions. To this aim, we have conducted all experiments for the W measurements at the particle volume fraction $\phi=5.0\%$ and different pH, using NaCl and H_2SO_4 as the destabilizers.

The principle: The W measurement is based on the observation of the doublet formation kinetics as discussed in previous work [24, 25]. In particular, at the very initial stage of the aggregation, the main process is conversion of primary particles to doublets, and therefore the kinetics of primary particle consumption can be approximated as follows:

$$\frac{dN_1}{dt} = -K_{1,1}N_1^2 \quad (1)$$

where N_1 and $K_{1,1}$ are the primary particle number concentration and doublet formation rate constant, respectively. Introduction of conversion of primary particles to doublets, $x=(N_0-N_1)/N_0$ into Eq. 1, where $(N_0 = 3\phi/[4\pi R_p^3])$ is the initial number concentration of primary particles, yields:

$$\frac{x}{1-x} = K_{1,1}N_0t \quad (2)$$

Thus, from the measured x values as a function of time, t , the slope of the $x/(1-x)$ vs t line leads to the estimation of $K_{1,1}$. Deviations from linear behavior of this line indicate that larger clusters also contribute to the aggregation process, and the experiments have to be repeated at lower conversion values.

From the data above, we can obtain the Fuchs stability ratio, W , based on the following relationship:

$$W = K_B/K_{1,1} \quad (3)$$

where $K_B (=8kT/[3\mu_l])$, with k the Boltzmann constant, T the absolute temperature, and μ_l the viscosity of the dispersant, is the so-called Smoluchowski rate constant, defining the diffusion-controlled collision rate between particles of equal size.

It is clear that to obtain $K_{1,1}$ from Eq. 2, we need measure the x value as a function of t . This is done by taking proper samples of the aggregating system and making SLS measurements. According to the RDG theory [26], the scattered light intensity $I(q)$ for a system containing only primary particles and doublets can be expressed as:

$$\frac{I(q)}{I(0)} = \frac{N_1P_1(q) + 4N_2P_2(q)}{N_1 + N_2} \quad (4)$$

where N_2 is the number concentration of doublets, and $P_1(q)$ and $P_2(q)$ are the form factor of the primary particles and

doublets, respectively. Within the RDG theory, the expression for $P_1(q)$ is given by:

$$P_1(q) = 9 \left[\frac{\sin(qR_p) - (qR_p) \cos(qR_p)}{(qR_p)^3} \right]^2 \quad (5)$$

The expression for $P_2(q)$ depends on whether coalescence occurs or not between the two aggregated particles in the doublet [25]. For the present very soft acrylate copolymer particles ($T_g \approx 15^\circ C$), we have confirmed experimentally, as shown in SI, that coalescence between two particles does occur. Then, considering two primary particles coalescing and forming a new sphere, $P_2(q)$ is given by

$$P_2(q) = 9 \left[\frac{\sin(2^{1/3}qR_p) - (2^{1/3}qR_p) \cos(2^{1/3}qR_p)}{(2^{1/3}qR_p)^3} \right]^2 \quad (6)$$

By substituting Eqs. 5 and 6 into Eq. 4 and considering that $N_1 = (1-x)N_0$ and $N_2 = xN_0/2$, we have:

$$\frac{I(q)}{I(0)P_1(q)} = 1 - \frac{x}{1+x} F(q) \quad (7)$$

Where

$$F(q) = 2 - \frac{1}{2} \left[\frac{\sin(\sqrt[3]{2}qR_p) - (\sqrt[3]{2}qR_p) \cos(\sqrt[3]{2}qR_p)}{\sin(qR_p) - (qR_p) \cos(qR_p)} \right] \quad (8)$$

Therefore, the plot, $I(q)/[I(0)P_1(q)]$ versus $F(q)$, is a straight line, and its slope yields the value of the conversion x .

The experimental procedure: We first mix the latex with a proper electrolyte solution so as to reach a desired particle volume fraction, electrolyte concentration and pH (sulfuric acid and sodium hydroxide were used to tune the pH) to start the aggregation under stagnant conditions. Then, we take samples from the aggregation system at different times and dilute them immediately in Milli-Q water for quenching the aggregation and performing the SLS measurements. In addition, for each aggregating system, pH was measured after the aggregation experiments.

Figure 1 shows typical plots of $x/(1-x)$ vs. t at the very initial stage of the aggregation process for the P2 latex at $\phi=5\%$, using H_2SO_4 as the destabilizer at $C_s=0.116, 0.123$ and 0.130 mol/L. They all are straight lines, whose slopes lead to estimate of the corresponding $K_{1,1}=3.19 \times 10^{-24}, 1.30 \times 10^{-23}$ and $3.23 \times 10^{-23} m^3/s$, and then, based on Eq. 3, to the Fuchs stability ratio values of $W=3.86 \times 10^6, 9.51 \times 10^5$ and 3.82×10^5 , respectively.

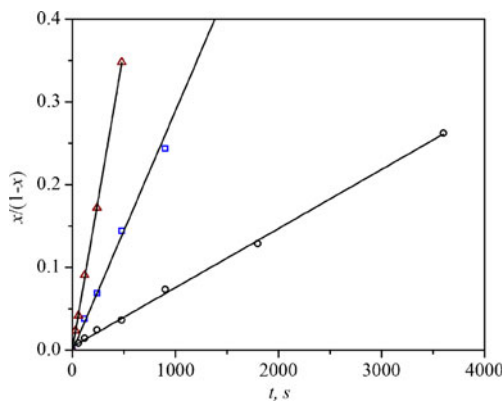


Fig. 1 Examples of the $x/(1-x)$ vs. t plot for the estimate of $K_{1,1}$ based on Eq. 2, in the case of P2 latex using H_2SO_4 as the destabilizer at three concentrations: 0.116 mol/L (\circ), 0.123 mol/L (\square) and 0.130 mol/L (Δ)

Results and discussion

PAA brush conformation behavior

To verify the presence of the PAA brushes on the particles of P2 and P3 latexes with 1 % and 2 % AA, respectively, we have measured the R_h value of the particles by DLS as a function of pH at a controlled ionic strength of 25 mM, and the results are shown in Fig. 2. It is seen that for P3 latex the R_h value increases asymptotically as pH increases and the difference between the smallest and largest R_h values is about 8 nm. These results allow us to conclude that the PAA brushes are indeed attached to the particle surface of P3 latex. In the case of P2 latex, the R_h value increases with pH only marginally, about 2 nm, indicating much shorter PAA brushes. Since the thickness of the brushes of P2 latex with 1 % AA is only 1/4 of P3 latex with 2 % AA, the brush density should be larger for P2 than for P3.

To further confirm the presence of the PAA brushes on the particle surface, we have measured the form factor, $P(q)$ by SLS, at different pH values, and the results are shown in

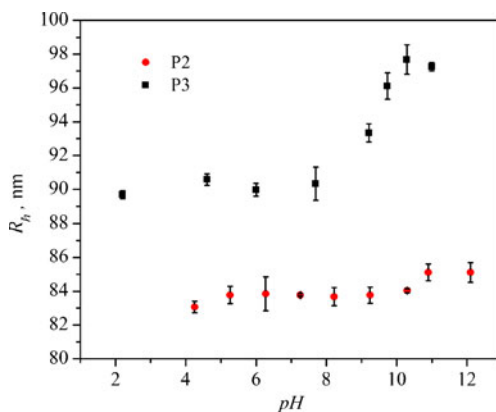


Fig. 2 The hydrodynamic radius, R_h , of the primary particles as a function of pH, determined by DLS, for P2 and P3 latexes after cleaning

Fig. 3a, b for P2 and P3 latexes, respectively. The difference in the $P(q)$ curves obtained at different pH is very small; it follows that the radius of gyration (R_g) of the particles at different pH is also practically the same. Note that for P3, the R_g value does increase about 1 nm with pH in the given pH range, but this is certainly incomparable with the R_h variations in Fig. 2. Therefore, the almost constant R_g and the significant increase in R_h with pH together indicate that the growth in R_h results only from a layer of polymer on the particle surface, instead of swelling of the whole particles. This conclusion arises because from the definition of R_g : $R_g^2 M = \sum r_i^2 m_i$, where M is the total mass, m_i the individual mass and r_i is the distance of m_i from the center, if the whole particle swells as the R_h variation indicates, due to increase in r_i , R_g must vary proportionally with R_h . Instead, since the mass of the particle is dominated by the P(BA-MMA), the variation in the inertia by the 1 or 2 % mass of PAA is really negligible.

Results of zeta-potential measurements showed no clear trend in the pH range, 5 to 9, where ionization and conformation variations of the PAA brushes occur. This is due to the displacement of the slipping plane induced by the transition from the collapsed to stretched state of the brushes [27], making the zeta-potential measurements far from being a good indication of the surface potential.

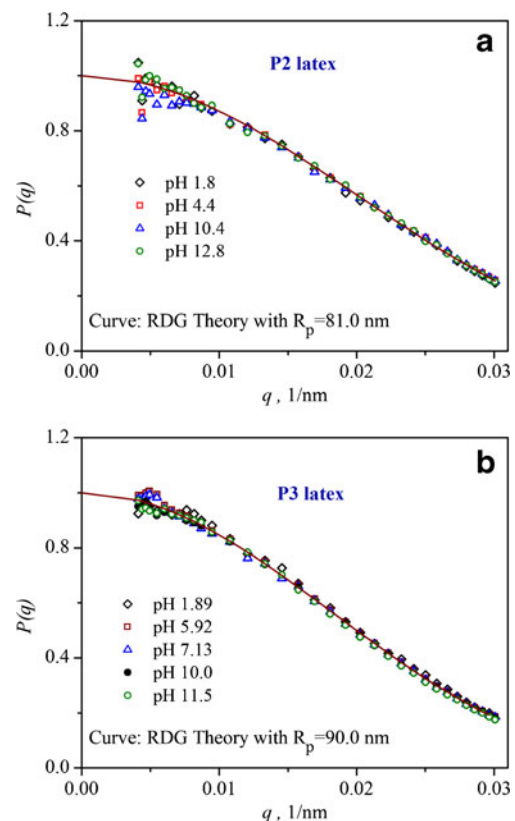


Fig. 3 The form factor of the primary particles, $P(q)$ at various pH values, determined by SLS, for (a) P2 and (b) P3 latexes after cleaning

Further characterization of the PAA brushes of P3 latex by DLS has been carried out by measuring the R_h value of the particles as a function of NaCl concentration at each fixed value of pH in the range, 2.2 to 11.0. These experiments show typical behaviors of the annealing PE brushes. As shown in Fig. 4a, for $\text{pH} \in [2.2, 6.0]$, since most of the AA units are protonated and the brushes are in the collapsed state, the R_h value is insensitive to the salt concentration. At pH 9.1, the initial slight increase in R_h ($C_{\text{NaCl}} < 100$ mM) could indicate a transition from Osmotic Annealing brush regime (Osm_A) to Salted-brush regime (Sd) ($C_{\text{NaCl}} > 100$ mM). In the Osm_A regime, AA ionization in the brush interior is suppressed but increases as the salt concentration increases. The increased osmotic pressure due to the increased counterion concentration in the brush causes the brush swelling. This might explain the slight R_h increase in Fig. 4a. It must be noted that although the observed R_h variations are small, they are larger than the experimental errors. Further increase in C_{NaCl} leads to the Sd regime, where the behavior of the annealing PE brushes becomes similar to that of quenched (strong) PE brushes. In this case, the brush thickness (i.e., R_h) decreases with the salt concentration. At pH 11.0 in Fig. 4a, due to the higher level of AA

ionization, the Sd regime is reached at a much lower C_{NaCl} value. In fact, we can observe only the decreasing part, which merges with the same trend of the case at pH 9.1 in the high C_{NaCl} region. When the data in Fig. 4a are plotted in the form of brush thickness, δ in Fig. 4b, the slope in the Sd regime is about $-1/3$, in good agreement with theoretical and experimental results in the literature [17, 28].

It must be noted that we have also measured R_h at extremely low pH (1.5) for P3 latex, and we have reported only one R_h value in Fig. 4a at $C_{\text{NaCl}} = 10$ mM. Further increase in C_{NaCl} leads to aggregation of the particles. The only reported R_h value drops below the plateau value observed at intermediate pH values. This arises mostly due to the fact that apart from the PAA brushes, sulfate groups ($-\text{OSO}_3^-$) coming from the persulfate initiator are also present, which can be protonated at such a low pH value. This leads to further decrease in the inter- and intra-chain electrostatic repulsion, as well as the osmotic pressure of the counterions present in the brush, consequently, to further collapse of the brushes.

For P2 latex, the low pH-responsiveness of its R_h value does not allow us to perform the same type of analysis. It is therefore unsafe to speculate about the difference in the absolute thickness or surface grafting density of the PE brushes between P2 and P3. Moreover, since the particles were synthesized through emulsion copolymerization, the acrylic acid content along the chains is unknown and can differ from P2 to P3.

Stability of P1 latex

Among the three latexes, P1 is the simplest one possessing only fixed sulfate charges on the particle surface, without the PAA brushes. The corresponding measured W value at $\phi = 5\%$ and low pH are shown in Fig. 5a as a function of the concentration of both NaCl and H_2SO_4 , while the corresponding measured pH values are shown in Fig. 5b.

As expected, the W value decreases as the NaCl or H_2SO_4 concentration increases. However, the W curve for H_2SO_4 is located at substantially lower C_s region with respect to that for NaCl. Note that this difference is not due to the fact that H_2SO_4 is a bivalent salt. At such low pH, H_2SO_4 is only singly deprotonated, and acts as a symmetrical monovalent electrolyte. To understand the difference in the W values measured above in the presence of NaCl and H_2SO_4 , one has instead to consider the difference in the association of Na^+ and H^+ to the surface fixed charge groups, $-\text{OSO}_3^-$. In particular, the association of H^+ with sulfate groups is stronger than that of Na^+ [29]. This leads to a much stronger reduction of the surface charge density in the presence of H^+ than in the presence of equal amount of Na^+ , thus making H_2SO_4 much more effective in destabilizing the P1 latex than NaCl.

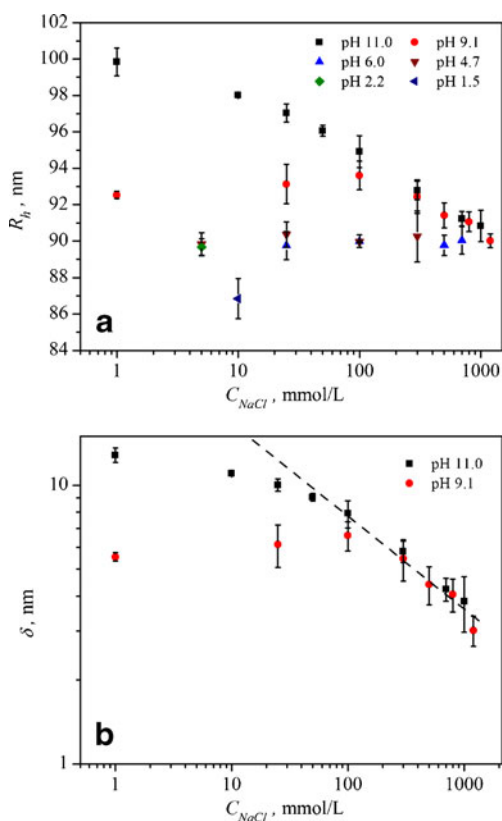


Fig. 4 Mean hydrodynamic radius (R_h) (a) and the estimated brush thickness (δ) in the salted-brush regime (b) as a function of NaCl concentration at various pH values for P3 latex. The broken line represents the theoretically predicted relationship, $\delta \propto C_{\text{NaCl}}^{-1/3}$ [17]

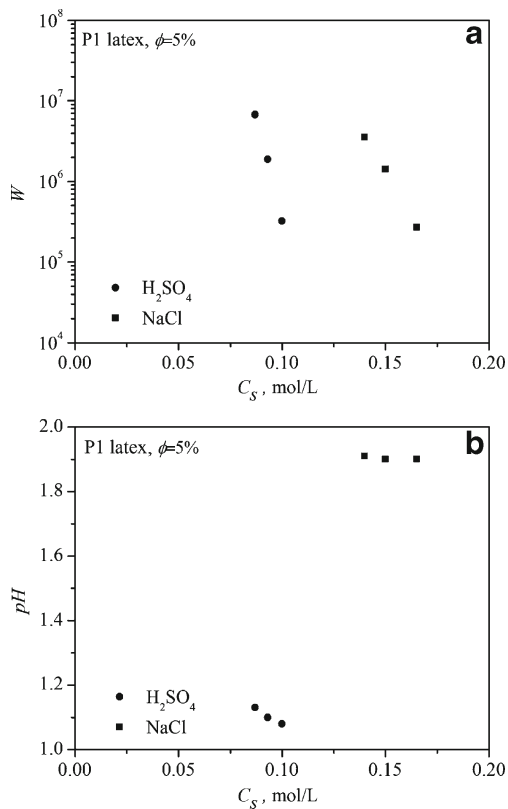


Fig. 5 Fuchs stability ratio W (a) and the corresponding pH (b) for P1 latex as a function of the electrolyte concentration

The above results clearly demonstrate the importance in accounting for the counterion association with the surface ionizable groups when studying colloidal stability, as also demonstrated in other related systems [30–32].

Contributions of PAA brushes to colloidal stability

The particles of P2 and P3 latexes, apart from the fixed sulfate charge groups, contain 1 % and 2 % AA monomers, respectively, which, as discussed in the previous section, are in the form of PAA brushes on the particle surface. Clearly, their carboxylic groups, when deprotonated, *i.e.*, $-\text{COO}^-$, contribute to the surface charges. Fig. 6a compares the W values for latexes, P1, P2 and P3, as a function of the NaCl concentration at $\text{pH} \in [1.8, 9.0]$, and the corresponding measured pH values are reported in Fig. 6b.

It can be observed that the stability of P1, in the absence of the PAA brushes, depends weakly on pH. In fact, even at $\text{pH} 9.1$ the W values of P1 are only comparable to those of P2 and P3 at $\text{pH} < 3$, *i.e.*, under protonated conditions. This weak dependency clearly reflects the low pK_a value of the sulfate groups, which ensures full ionization of the sulfate groups for $\text{pH} > 3$. In this case, the charge density is practically independent of pH. Note that for $\text{pH} < 2.5$ in Fig. 6a, the W values of P1 are slightly smaller than those of P2 and P3. To explain this behavior, we need to consider that the

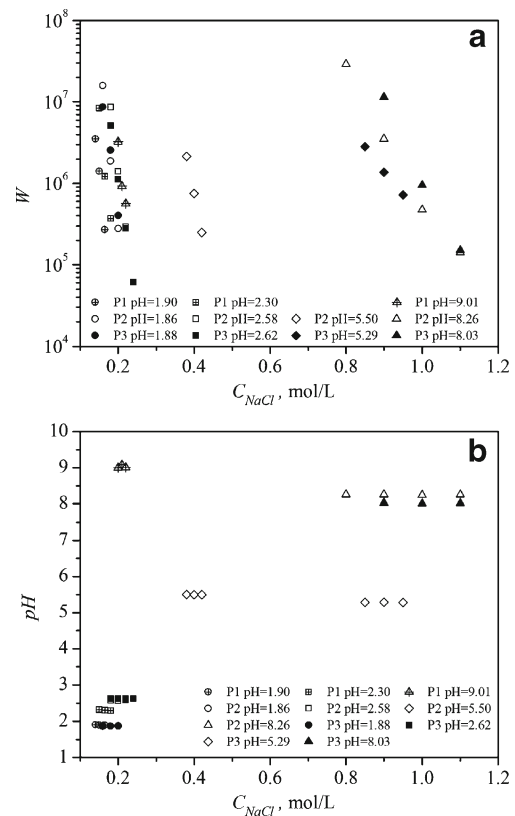


Fig. 6 Fuchs stability ratio W (a) for P1, P2 and P3 latexes as a function of the NaCl concentration, at various pH values as reported in (b).

polarity of the AA groups, even protonated in this low pH range, is higher than that of MMA or BA, leading to certain surface hydrophilicity, thus contributing partially to the particle stability in the case of P2 and P3. For P1, since this additional hydrophilicity is missing, its stability is certainly lower. For the same reason, slightly more hydrophilicity generated by protonated 2 % AA than 1 % AA leads to the W curves of P3 moving slightly towards higher salt concentration with respect to that of P2. This becomes more evident in Fig. 7, where the W curves of P1, P2 and P3 latexes are compared at extremely low pH, obtained using H_2SO_4 as the destabilizers.

The situation however changes at higher pH values for P2 and P3. At pH around 5.5, the W curves in Fig. 6a for both P2 and P3 move towards larger NaCl concentrations, indicating that the stability of the latexes increases with respect to that at $\text{pH} < 3$. It is therefore evident that now a significant amount of carboxylic groups have been deprotonated and contribute to the colloidal stability. In the case of P3 latex, the W values shift much more towards larger NaCl concentrations than those in the case of P2 latex. This is understandable when one considers that P3 carries 2 % AA while P2 only 1 %. In addition, it should be mentioned that in this intermediate pH range, close to the pK_a of PAA,

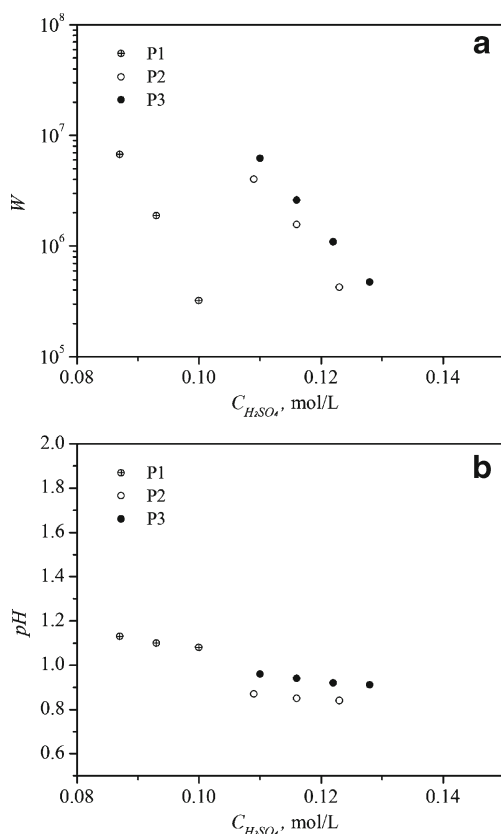


Fig. 7 Comparison of the Fuchs stability ratio W for P1, P2 and P3 latexes as a function of H_2SO_4 concentration (a), and the corresponding pH (b)

small difference in the composition of the brushes would lead to significant variations in the colloidal stability (e.g. the effective pKa value might be slightly different between P2 and P3, leading to difference in AA ionization).

Finally, as shown again in Fig. 6a, at pH~8, i.e., under alkaline conditions, although the W values for both P2 and P3 continue to increase with respect to the case at pH=5.5, the difference between P2 and P3 is insignificant. This result is somewhat surprising if one considers that at pH=8 and such high salt concentrations, which ensure an ionization state in the brush close to that in the bulk [17], most of the carboxylic groups should be deprotonated, and the surface charge should be larger for particles with 2 % AA than with 1 % AA. On the other hand, it is well known from various modeling and simulations [16, 17] that for the weak PE brushes like PAA, the concentration of the mobile counterions in the brush-occupied region increases towards the particle surface, because of the strong electrostatic attraction between the mobile counterions and the opposite charges on the brushes. The consequence is that the effective charge of the groups (i.e., the AA groups in the present case) is substantially lower in the inner than in the outer region of the brush zone. In fact, scaling-type models [16, 18] proposed that the counterion concentration in the inner region is

approximately equal to that of the charged groups on the brushes, leading to the so-called local electroneutrality approximation (LEA).

On the other hand, it should be pointed out that the W curves of P2 and P3 at pH~8.0 are located in the substantially large NaCl concentrations, where the estimated Debye length is only $\kappa^{-1} \approx 3 \text{ \AA}$, and the measured stability cannot be explained purely by the electrostatic repulsion generated at the external surface of the particles, as noted for similar systems by Fritz et al. [33]. Instead, steric interactions have to be taken into account, which are related to both the brush thickness and the free energy of mixing among the brushes [34]. In particular, it can be seen from Fig. 4a that in the region of high salt concentrations, the R_h values (thus, the thickness of the brushes) at all the pH values are very similar. This implies that the only parameter, which changes with the salt concentration and affects the steric repulsion, is the mixing free energy of the brushes. This effect was investigated in semi-dilute polyelectrolyte solutions [35], and it was concluded that to explain the critical transition in polyelectrolyte chain structure, it is necessary to account for individual monomer-monomer electrostatic repulsion. The effective Flory interaction parameter estimated from this repulsion depends on the salt concentration and the ionization state of the polyelectrolytes. Therefore, the contribution of steric interactions to the observed colloidal stability results from both the hydrophilicity and charges of the PAA brushes, which make the brushes repel when overlapping, affected by the salt concentration. Again, since electroneutrality prevails in the inner region (LEA), such interactions are mainly generated by the outer region of the brushes, and consequently, the difference in the stability between P2 and P3 is small.

Concluding remarks

Poly-acrylic acid (PAA) chains are pH-sensitive polyelectrolytes, whose charging, hydrophobicity, polarity and conformation change with pH. In this work, we study experimentally the effect of pH on the stability of polymer colloids with surface-grafted PAA chains (brushes). In particular, we have prepared three acrylate copolymer colloids using the same recipe, but with 0 %, 1 % and 2%wt PAA brushes, respectively. The length of the brushes under the stretched state, measured from the dynamic light scattering, is about 2 and 8 nm for 1 % and 2 % PAA, respectively. In the case of 0 % PAA, the particles are stabilized only by the sulfate charges coming from the initiator, while in the latter two cases they are stabilized by both sulfate and carboxylic charges.

The colloidal stability of each latex has been characterized by measuring the corresponding Fuchs stability ratio

(W) as a function of electrolyte concentration and pH. It is found that at low pH values (<3), the W values of the particles with 1 % and 2 % PAA brushes are only marginally larger than those without PAA, indicating that in their protonated state, the carboxylic groups do not contribute significantly to the colloidal stability. The small increase in W for the latexes with 1 % and 2 % AA in this low pH range comes from slightly higher hydrophilicity generated by the protonated AA.

At intermediate pH (~ 5), the PAA brushes are partially deprotonated, and their contribution to the colloidal stability is substantial. Moreover, to reach the same W value, one has to use almost a doubled NaCl concentration in the case of 2 % PAA with respect to the case of 1 % PAA. This means that at the intermediate pH the ionization of the carboxylic groups (thus the particle charge) is directly linked to the total AA groups on the surface. Accordingly, higher particle charge leads to higher stability for P3 than for P2 latex.

Under alkaline conditions ($\text{pH} > 8$), one would expect all the carboxylic groups on the brushes to be fully ionized and participating to stability. On the contrary, we found that the W values are basically the same for particles with 1 % PAA and 2 % PAA, which implies that the contribution of the ionized AA in the two cases is practically the same. Such an experimental result confirms the local electroneutrality approximation (LEA) [16, 18] in the inner region of long brushes, which leads to the conclusion that only the ionized AA groups in the outer region of long brushes contribute to the particle stability. Accordingly, the P2 and P3 latexes that differ in the length of the brushes exhibit the same colloidal stability.

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