Defined Complexes of Negatively Charged Multisensitive Poly(*N*-isopropylacrylamide-*co*-methacrylic acid) Microgels and Poly(diallydimethylammonium chloride)

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ABSTRACT: The influence of poly(diallyldimethylammonium chloride) (PDADMAC) on pH- and temperature-sensitive negatively charged microgels was investigated with regards to different ratios between positive charges having their origin in PDADMAC and negative charges resulting from copolymerization of *N*-isopropylacrylamide (NiPAM) with methaacrylic acid (MAA). The concentration of the PDADMAC solution (regarding to monomeric units) was determined by argentometric and polyelectrolyte titration, the amount of MAA in the microgel was characterized with conductometric titration. The composition of the complexes between microgel and PDADMAC was available by centrifugation of the mixture and comparing the PDADMAC concentration in the supernatant with the initial concentration. Different from many other systems, we observed no flocculation at any microgel and PDADMAC ratio, but stable complexes were obtained. Because of the softness of a microgel in contrast to rigid particles, the microgel properties are strongly altered by the polyelectrolyte. Consequently, size, ζ-potential as well as the pH and temperature sensitivity of the microgel−polyelectrolyte complexes can be influenced by the adsorbed polyelectrolyte. Thus, polyelectrolyte adsorption allows tailoring the behavior of “smart” environmentally sensitive microgels.

Introduction

The adsorption of polyelectrolytes on oppositely charged colloidal systems has been widely investigated. Substrates can either be flat wafers (as, e.g., glass, silica, mica) or rigid particles (as, e.g., silica). The charge of the colloids and/or substrates is often influenced by the pH, and strong (pH-independent) as well as weak (pH-dependent) polyelectrolytes have been used.[1−3] While the combinations of polyelectrolytes and substrate cover a wide range, the methods to estimate the amount of adsorbed material are not so numerous. The established methods for flat substrates are quartz crystal microbalance (QCM)[4] and ellipsometry.[5] The amount of adsorbed material on rigid spheres is mainly measured by reflectometry.[6] However, rather little intention has been paid to the adsorption of polyelectrolytes on porous but rigid colloidal particles.[7]

In this work, we investigate the composition of complexes between polyelectrolyte and microgels as model systems for porous, nonrigid colloids.

Microgels are internally cross-linked spherical particles of colloidal dimensions and are used for different applications.[8] NiPAM has a lower critical solution temperature (LCST) of 32 °C in water, which means that the microgel transits from a hydrophilic and therefore swollen particle to a hydrophopic globule. The LCST of such microgels can be altered by copolymerization with other, temperature-sensitive monomers.[9] Besides the temperature, also the pH can be used to trigger the properties of microgels if pH-dependent monomers are incorporated in the microgel.[10−12] Microgels containing amines or carboxylic acids have different properties such as ζ-potential or the response to pH. Mixing of oppositely charged microgels leads to precipitation of the complex at stoichiometric charge neutralization.[13]

The behavior of these polyelectrolyte−microgel complexes is similar to complexes made of oppositely charged strong polyelectrolytes. Polyelectrolytes form water insoluble complexes over a wide ratio of polycation and polyanion.[14,15] The composition of these complexes is mainly influenced by the salt concentration and in the case of weak polyelectrolytes of course by the pH.[16]

Instead of investigating complexes made of either oppositely charged microgels or polyelectrolytes, our group studies complexes made of microgels and oppositely charged polyelectrolytes.[17] The microgel can be used as substrate to build up several layers by consecutive adsorption of polycations and polyanions.[18,19] In this work, we investigated complexes of a negatively charged PNiPAM-*co*-MAA-microgel and a strong polycation poly(diallyldimethylammonium chloride) (PDADMAC). Two different PDADMAC samples were used for adsorption experiments (i) low MW sample with MW of 10−20000 g mol^{-1} and (ii) high MW sample with MW 400−500000 g mol^{-1}. Polyelectrolyte titration[20] was used to determine the concentration of the PDADMAC solutions, titration with acid and base gave the number of titratable charges in the microgel. Solutions of microgel and PDADMAC were mixed in different ratios. This ratio is defined as initial charge ratio, icr. After centrifugation of the mixture the complex was investigated and the supernatant was analyzed by means of polyelectrolyte titration. If the supernatant still containes PDADMAC the composition of the complex does not correspond to the icr. By comparing the concentration of PDADMAC in the supernatant as well as in the stock solution and the amount of titratable charges in the microgel we were able to receive the nominal charge ratio ncr, which represents the true composition of the microgel−PDADMAC complex.

After the characterization of the microgel consisting of poly(*N*-isopropylacrylamide) and methacrylic acid, two sets of adsorption experiments will be presented. The first set of adsorption experiments was performed without adjusting the pH, the second one was conducted at basic pH and with two PDADMAC samples differing in the molecular weight. Size

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and ζ-potential are shown as a function of the nominal charge ratio ncr and the isoelectric point (IEP) of the complexes is also investigated. In the end, we summarize our results and compare them with the literature on complexes between polyelectrolytes and colloidal particles.

Experimental Section

Materials. *N,N′*-Methylenebis(acrylamide) (BIS) and potassium peroxodisulfate (KPS) were ordered from Merck. Methacrylic acid (MAA) was obtained by ABCR, and *N*-isopropylacrylamide (NiPAM) was purchased from Acros. Two different PDADMAC samples were used for adsorption experiments (i) low MW sample with MW of 10−20000 g mol^{-1} and (ii) high MW sample with MW 400−500000 g mol^{-1}. The low molecular weight PDADMAC was a gift by Katpol, Germany, the latter one was delivered by Aldrich, as well as Polystyrenesulfonate (PSS) with a molecular weight of 70−100000 g mol^{-1}. Tolidine O was purchased from Serva Chemicals.

All chemicals were used without further purification. All solutions were prepared with double distilled water.

Microgel Synthesis. A 1 L three-neck bottle, equipped with KPG stirrer, reflux condenser and nitrogen inlet was filled with 500 mL water and flushed with nitrogen at 75 °C. After 45 min, 7.545 g of NiPAM, 0.143 g of BIS, 0.735 g of MAA, and 0.230 g of KPS were added. After 6 h the reaction was allowed to cool over night. After passing the solution through glass wool, the solution was centrifuged in a Sorvall Discovery 90 ultracentrifuge for 45 min. Between each centrifugation the supernatant was removed and replaced by water to redisperse. After three cycles of centrifugation the solution was freeze-dried.

Conductometric Titration. Microgel solution was transferred to a tempered titration cell equipped with a nitrogen inlet and diluted to a volume of 50 mL. Then, 0.1 M HCl was added until solutions pH was around 3. After the solution was allowed to equilibrate for 30 min, portions of 2 μL 0.1 M NaOH were added by a Methrohm 665 autotitrator. Conductivity and pH were measured by electrodes. The titration was performed at 25 °C.

Dynamic Light Scattering. Dynamic light scattering measurements were done on an ALV goniometer with a programmable cyrostat to control the temperature of the sample. Laser wavelength was 633 nm, scattering angle was 60°. The samples were highly diluted to avoid multiple scattering. The samples were measured at different angles at room temperature prior to temperature-dependent runs.

Electrophoretic Mobility and ζ-Potential. Measurements of the electrophoretic mobility were performed on a NanoZS zetasizer (Malvern). All samples had the same concentration with respect to the microgel (see adsorption experiments). The point of zero charge of the complexes was measured by titration of aqueous solutions of the complexes. All solutions were titrated in a range of pH 3 to 10. Results were consistent if the titration was run from basic to acidic conditions. The ζ-potential was calculated from the electrophoretic mobility according to the Smoluchowski equation.

Polyelectrolyte Titration. The indication of a 1:1 complex between polycation and polyanion by a dye responding to an excess of one polyion was first described 1952.[21] We used a fototitrator, which was a gift by BASF and described by Horn.[22] A PSS solution was added by a autotitrator to a sample of PDADMAC which was diluted with approximately 100 mL of water. 20 μL of a 2 mM Tolidine O solution was added as indicator. Every PDADMAC solution was titrated a least three times to evaluate the concentration. The concentration of the PDADMAC stock solutions was estimated by polyelectrolyte and argentometric titration: Ag$^+$ was added to determine the concentration of the chloride counterions of the polycation.

Adsorption Experiments. Solutions of PDADMAC and microgels were mixed; water was added to give a total volume of 10 mL. After 3 days the mixture was centrifuged for 30 min at 50000 rpm in a Sorvall Discorery 90SE. The supernatant was removed carefully and kept for further experiments. A 5 mL aliquot of water was added to the precipitate in the centrifugation tube to redisperse the microgel−polyelectrolyte complex. After 2 days the redispersed complex was investigated by different techniques. Prior to use, samples of all polyelectrolyte solutions were centrifuged at 50000 rpm for 30 min. No precipitate was formed, and the supernatant had the same polyelectrolyte concentration as the starting solution.

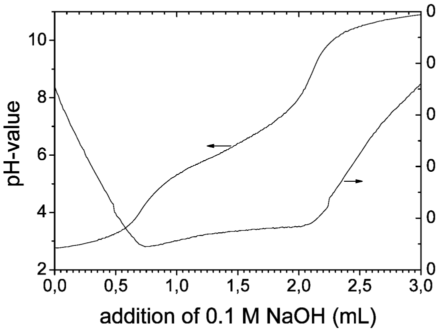

Figure 1. Results of the conductometric titration of the PNiPAM-*co*-MAA microgel. The change of pH and conductivity with added volume NaOH is shown. From this titration the degree of protonation as a function of pH was determined (compare Figure 3).

Table 1. Molar Masses, Used Amounts, and Theoretical Amounts of the Different Monomers in the Synthesized Microgel

monomer	molar mass [g mol^{-1}]	mass [g]	theor amount [wt %]
NiPAM	113.16	7.5447	87.20
BIS	154.17	0.1429	1.65
MAA	86.09	0.7345	8.49
KPS	270.33	0.2296	2.65

Results and Discussion

Characterization of the Polyelectrolyte Microgel. Figure 1 shows the result of the conductometric titration that was carried out at 25 °C. The microgel starts to deprotonate at pH 4 and is fully deprotonated at pH 9. The pKs of the microgel is 6.19, the pKs of pure poly(methacrylic acid) is 6.50.[23] The titration starts with an excess of HCl, adding of NaOH leads to a decrease due to removal of protons. From the weight of the titrated microgel and the buffering area, the amount of methacrylic acid was estimated to 11.5 wt %, though the amount in the feed was only 8.5 wt % (see Table 1). This indicates a preferred incorporation of MAA in the microgel because the yield of the reaction was only about 70%. Different copolymerization rates of MAA and NiPAM[24,25] as well as effects depending on the pH have to be taken into account. Table 1 shows the initial amounts used in the microgel synthesis. The big amount of MAA in the microgel has a large impact on the radius and the swelling properties of the microgel.

As seen in Figure 2, the size of the microgel depends on the pH because of the MAA but also on the temperature due to the NiPAM.

At high pH values, the microgel is highly swollen and shows only a weak temperature sensitivity. The lower the pH is, the smaller the radius of the microgel and the temperature sensitivity is more pronounced. The microgel can collapse strongly if the microgel is almost completely protonated.

The hysteresis in the size measurements may occur because of rearrangement of weakly cross-linked chains[26−28] and because of temperature-dependent equilibrium between microgels acid strength and the surrounding solution.[29] Not only the hydrodynamic radius but also the ζ-potential of the microgel is influenced by the pH as shown in Figure 3. The degree of deprotonation was derived from the titration data shown in Figure 1 and is also plotted in Figure 3. The higher the pH the

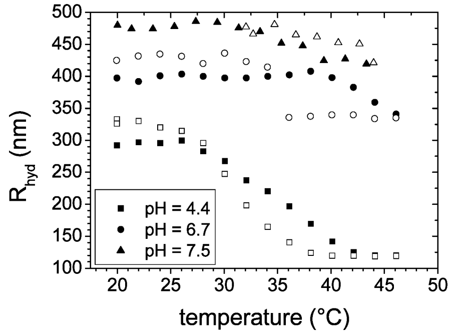

Figure 2. Hydrodynamic radii of the microgel at different pH values as a function of temperature. Filled symbols represent the heating curve; open symbols show the cooling cycle. The pH of the samples were adjusted by dilute HCl and NaOH respectively. The pH was determined at 20 °C after the DLS measurements.

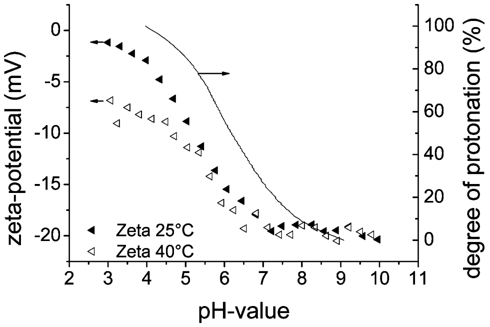

Figure 3. Degree of protonation and ζ-potential at 25 (filled symbols) and 40 °C (open symbols) in dependence of the pH.

more MAA units are deprotonated leading to a higher ζ-potential. If instead the microgel is fully protonated, the ζ-potential equals almost zero. The ζ-potential at 40 °C is different from the one at 25 °C for low pH values when the microgel is uncharged. At 40 °C and low pH, the microgel is collapsed but above pH 6 the influence of the MAA is so pronounced that it swells again and gives similar ζ-potentials as at 25 °C. ζ-Potential and the degree of protonation are not parallel to each other which could be due to different concentration during the individual measurements. In addition, titration reaches all titratable charges within the microgel, while the ζ-potential is influenced by the charges near the surface.[30−32]

Microgel—Polyelectrolyte Complexes. In the following, we discuss the complexes formed by the negatively charged microgel and PDADMC; two PDADMAC samples with different chain length were employed. We will term the ratio of positive charges originating from the PDADMAC and the number of tritratable negative charges of the microgel as *initial charge ratio,* icr. This ratio thus characterizes the initial microgel−PDADMAC mixture. The microgel−PDADMAC complexes will be characterized by the *nominal charge ratio,* ncr. The nominal charge ratio thus describes the ratio of PDADMAC to microgel charges *after* separation of excess polyelectrolyte.

Two series of experiments were done in order to investigate the adsorption of PDADMAC on the microgel. Microgel and PDADMAC were mixed at initial charge ratios of icr = 0, ..., 1.3. After 3 days, the pH was measured and the solution was centrifuged. The supernatant was investigated by means of polyelectrolyte titration to establish the amount of nonbound PDADMAC. The difference between the concentration of the supernatant and the initial concentration of PDADMAC represents the adsorbed amount of PDADMAC and allows calculating the nominal charge ratio.

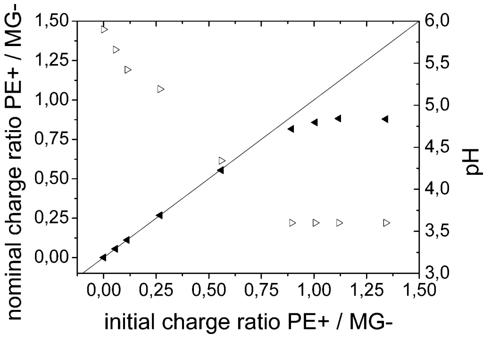

Figure 4. Adsorption of low MW PDADMAC on microgel without adjusting the pH of the solution. Experiments were done with the same amount of microgel but different amounts of PDADMAC. The drawn line equals one, the amount of MAA in the samples equals 13.02 μmol each (if the microgel is fully deprotonated). Filled symbols represent the nominal charge ratio at a given initial charge ratio. The pH values of the complexes are shown as open symbols.

The results of these experiments are shown in Figure 4. As soon as PDADMAC is added to the microgel solution, the pH decreases because PDADMAC replaces the protons bound to the MAA units in the microgel. The more PDADMAC is added the lower the pH becomes. Up to an icr of 0.7 the complete amount of PDADMAC is adsorbed, and the ncr matches the icr. The pH of the solution changed by two units from six to four.

At icr > 0.8, no complete adsorption was observed. The pH stays constant at around 3.6. Though the icr is increased up to 1.3, the ncr tends to a constant value of 0.9. The microgel is not able to bind extra polyelectrolyte as the microgel is less charged under acidic conditions.

In order to adsorb PDADMAC at constant conditions, the second set of experiments was conducted at constant temperature (room temperature), same amount of added sodium hydroxide, same total volume of sample but different amount of PDADMAC. The compositions as well as properties of the received complexes are listed in Table 2.

The initial ratio of PDAMAC to microgel was varied in a broad range up to an initial charge ratio of 10. The ratio icr of 0 represents the pure microgel at a pH of 9. As shown in Figure 5 the ncr equals the icr for icr < 1 for the low molecular weight PDADMAC. Adsorption of PDADMAC still takes places, also beyond the point of charge equality. Also the large molecular weight PDADMAC adsorbs completely if icr < 1. However, while the low molecular shows a clear breakpoint at an initial charge ratio of 1, the high molecular weight PDADMAC shows this breakpoint at a initial charge ratio of 1.2 which means that the interaction between the microgel and the PDADMAC with different size is not the same. Not only this breakpoint but also the amount of adsorbed PDADMAC beyond charge equality is different. While 13% of the low molecular weight PDADMAC is adsorbed, only 3% of the offered high molecular weight PDADMAC is adsorbed at initial charge ratio icr > 1. In the following, complexes are described by the nominal charge ratio ncr.

Figure 6 shows the hydrodynamic radii at 20 °C for the complexes made of microgel and different amounts of PDADMAC. The radii of the complexes decrease first. The influence of both molecular weights is more or less the same below a nominal charge ratio of 1. The 1:1 complex of microgel and the low molecular weight PDADMAC has the smallest particle size.

For bigger nominal charge ratios, the radius increases slightly. The complexes of the high molecular weight PDADMAC shows

Table 2. Composition and Properties of Complexes between Microgel and PDADMAC[a]

initial charge ratio PE$^+$/MG$^-$	added amount PDADMAC [μmol]	adsorbed amount PDADMAC [μmol]	nominal charge ratio PE$^+$/MG$^-$	R_h at 20 °C [nm]	R_h at 50 °C [nm]	ζ-potential at 20 °C [mV]	adsorbed amount PDADMAC [mg]/[mg microgel]
			Low Molecular Weight PDADMAC				
0.0	0	0	0	475	430	−24.2	0
0.2	1.35	1.35	0.208	333	128	−23.2	0.042
0.4	2.70	2.70	0.415	331	169	−24.3	0.085
0.6	4.04	4.04	0.623	235	170	−25.3	0.127
0.8	5.39	5.39	0.830	239	153	−16.2	0.169
1.0	6.74	6.56	1.011	218	165	2.0	0.205
2.0	13.48	7.54	1.161	220	172	43.9	0.251
3.0	20.21	8.12	1.250	238	150	47.3	0.266
4.0	26.95	8.96	1.380	236	148	53.5	0.283
4.3	27.99	9.08	1.399	239	170		0.308
5.0	33.69	10.30	1.587	243	153	50.8	0.323
			High Molecular Weight PDADMAC				
0.0	0	0	0	475	430	−24.2	0
0.2	1.29	1.29	0.198	287	135	−35.9	0.044
0.4	2.58	2.57	0.395	285	135	−39.3	0.089
0.6	3.87	3.86	0.593	255	135	−24.3	0.133
0.8	5.17	5.15	0.791	224	185	−20.3	0.177
1.0	6.46	6.25	0.960	238	208	26.0	0.215
1.5	9.76	7.65	1.176	216	168	41.0	0.247
2.0	12.92	8.11	1.246	218	145	50.6	0.266
4.0	25.83	8.62	1.323	219	146	60.5	0.294
6.6	43.05	9.37	1.439	288	251	67.7	0.298
11.0	71.75	9.84	1.511	395	173	70.1	0.338

[a] Each sample contained 5 mg of microgel (proportional to 6.51 μmol of titrable charges).

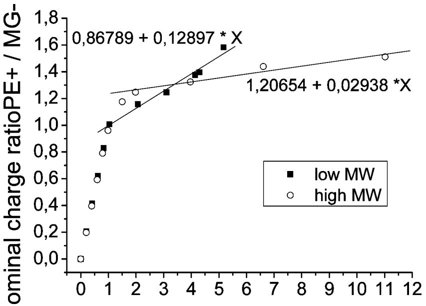

Figure 5. Stochiometry of the complexes as a function of the initial charge ratio of PDAMAC and microgel. The complexes made of microgel and low molecular weight PDADMAC are shown as filled squares; those of microgel and high molecular weight PDADMAC, as open circles. The lines are linear fits for initial charge ratios bigger than 1.

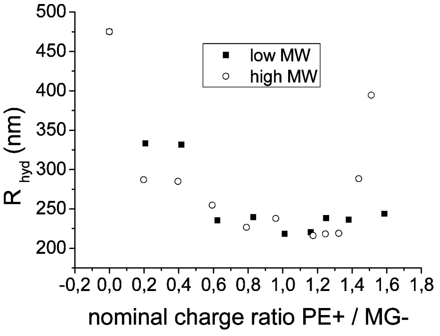

Figure 6. Hydrodynamic radii at 20 °C of the complexes obtained by mixing microgel and PDADMAC. Filled squares represent complexes between microgel and low MW PDADMAC open circles those made of high MW PDADMAC and microgel.

its minimum size at ncr ≈ 1.2. The radii of the complexes prepared with a big excess of the long chain PDADMAC grow again. The rise in size was not caused by flocculation as proven by angular dependent DLS measurements.

Figure 6 shows only the radii at 20 °C. All complexes were investigated at different temperatures to see whether the complexes maintain their temperature sensitivity. The samples were heated up to 50 °C and cooled down again to 20 °C. Temperature-dependent measurements of three different complexes are shown in Figure 7. The more PDADMAC is adsorbed, the lower the radius in the swollen state becomes (compare with Figure 6). However, at temperatures above the LCST the complexes can no longer collapse completely because the complex contains more material that furthermore acts as a type of physical cross-linker. The more PDADMAC is adsorbed the stiffer the complex becomes; in other words, the ratio of the radii in swollen and collapsed state becomes smaller.

However, the influence on the swelling ratio does not only depend on the adsorbed amount but also on the molecular weight of the adsorbed PDADMAC. Less adsorbed amount of the high molecular weight PDADMAC leads to a stiffer complex, for the complex is smaller in the swollen but bigger in the collapsed state (see circles in Figure 7). Apparently the large PDADMAC chains lead to more physical cross-links and alter the swelling properties more effectively.

The ζ-potentials of the complexes at 20 °C are shown in Figure 8. First the ζ-potential of the complexes stays constant or becomes even more negative by adding PDADMAC. Getting

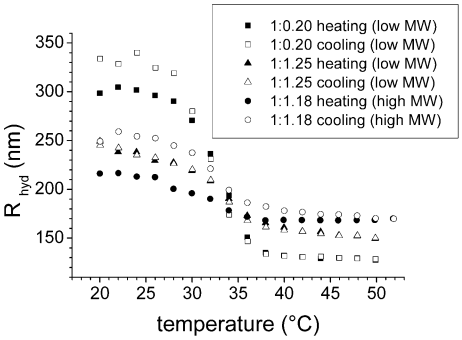

Figure 7. Results of DLS from different complexes. Filled symbols represent heating curves, open ones cooling curves respectively. (squares and triangles show complexes of low MW PDADMAC with ratios of 0.2 and 1.25 low MW PDADMAC; circles show a complex consisting of microgel and an excess of 1.18 of high MW PDADMAC).

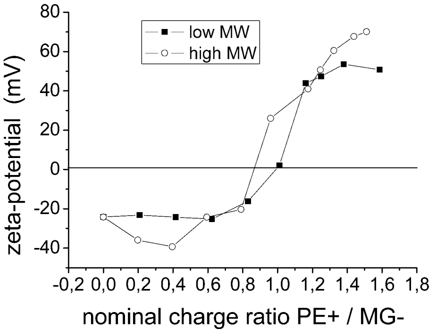

Figure 8. Measured ζ-potentials of the complexes at 20 °C. Filled squares represent complexes made of microgel and short chain PDADMAC, open circles those of microgel and long chain PDADMAC. Lines are a guide to the eye.

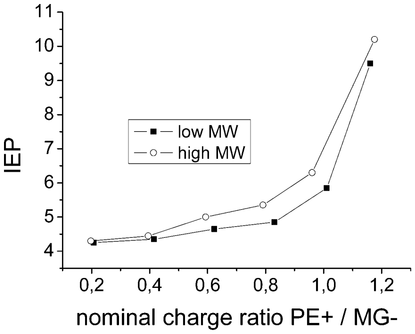

Figure 9. Isoelectic points of complexes made of low MW PDADMAC (filled squares) and high MW PDADMAC (open circles) at different ratios. Complexes of given ratio are negatively charged if pH of the solution is higher than the IEP.

closer to a nominal charge ratio of one the ζ-potential approaches toward zero and finally it turns positive with increasing adsorbed amount of PDADMAC. The ζ-potential for complexes of microgel and low MW PDADMAC equals zero for a nominal charge ratio of one as expected. The ζ-potential of the complexes made of microgel and the long chain PDADMAC equals zero already at a nominal charge ratio of around 1:0.865.

It was shown that the pH has an influence on the microgel as well as on the microgel−PDADMAC complex (compare Figure 4). The ζ-potentials of the complexes were measured at different pH in order to check that the measurements presented in Figure 8 are not affected by a pH effect.

Complexes of both PDADMAC samples with ncr < 1.15 changed the sign of the ζ-potential when the pH was varied between pH 3 and 10. With higher ncr the isoelectric point (IEP) was shifted to more basic pH. Since the complex with ncr $<$ 1.15 still have "unlocked" methacrylic acid functions, the complex can still adsorb and release protons. The number of negative charges can vary with pH while the number of positive charges stays constant.

Comparing the Results to the Literature. Most polyelectrolyte complexes with a one to one composition are insoluble in water. Also complexes made of polyelectrolytes and other colloidal systems show flocculation at ncr below one.[33−35] However, the complexes of microgel and polyelectrolyte investigated in this study did not precipitate. Only the high MW PDADMAC−microgel complex at a ncr $= 0.79$ and the complex made of low MW PDADMAC and microgel with a ncr $= 1.01$ precipitated but only above the LCST. In this case precipitation occurs due to the lack of electrostatic (compare Figure 8) and steric stabilization.

Charge reversal is achieved at high icr, similar to other colloidal particles.[1,36,37] The high MW PDADMAC-microgel-complexes revealed charge reversal at ncr < 1, indicating that not all ionic groups of the microgel are accessible for the linear polycation. On the other hand, the ζ-potential stays constant at negative values for ncr < 1 in contrast to nonporous rigid spheres.[4,38,39] Analogous behavior was observed by Kokufuta et al. for cationic microgels and polyanions.[40] Our results indicate that the polycation is able to partially penetrate the microgel. A similar observation was reported for the adsorption of poly(L-lysine) on micrometer-sized polyacrylic acid beads.[41]

Since polyelectrolytes can penetrate the microgel, one could argue that the term "absorption" describes the microgel-polyelectrolyte interaction better than the term "adsorption". The degree of penetration will depend on the ratio of polyelectrolyte chain length and mesh size of the microgel network. However, even the mesh size is not monodisperse, and the segment density inside the microgel is not homogeneous.[42]

Our results reveal different behaviors for the low and high MW PDADMAC samples used in this study. In addition, the observation of charge reversal and the possibility to form polyelectrolyte multilayers[17,18] demonstrate that the particle surface is covered by the polyelectrolyte. Therefore, we prefer the term "adsorption", however, keeping in mind that "absorption" also occurs.

The ζ-potentials of the complexes depend on the adsorbed polyelectrolyte amount as is known for other colloidal systems. However, due to the softness of a microgel in contrast to rigid particles, the microgel properties are altered by the polyelectrolyte. Thus, the microgel's swelling behavior, especially its sensitivity to pH and temperature, is strongly influenced. Obviously, polyelectrolyte adsorption provides a different means for tailoring the behavior of environmentally sensitive microgels.

Summary

The properties of complexes made of microgel containing negative charges and PDADMAC depend on the ratio of these two components. The ratio refers to the titratable MAA units in the microgel (determined by acid/base titration) and the positive charges of the PDADMAC (analyzed by polyelectrolyte and chloride titration).

Polyelectrolyte titration provides a sensitive and easy method to monitor the concentration of a polyelectrolyte solution. The titration allows determining not only the initial charge ratio of a solution of microgel and polyelectrolyte but also the nominal charge ratio of the obtained complexes.

The properties of the complexes like size and ζ-potential depend on the adsorbed amount and the molecular weight of the adsorbed polyelectrolyte.

As polyelectrolyte adsorption allows tailoring the behaviors of "smart" microgels, the microgel architecture will be relevant as well. The distribution of charges inside the microgel will also affect the swelling properties.[43] In particular, core−shell microgels are interesting[44,45] and will be investigated in the future.

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