

# Destabilization of Model Silica Dispersions by Polyelectrolyte Complex Particles with Different Charge Excess, Hydrophobicity, and Particle Size

Mandy Mende,<sup>1</sup> Simona Schwarz,<sup>1</sup> Gudrun Petzold,<sup>1</sup> W. Jaeger<sup>2</sup>

<sup>1</sup>Leibniz-Institute of Polymer Research Dresden e.V., Hohe Strasse 6, 01069 Dresden, Germany

<sup>2</sup>Fraunhofer Institute of Applied Polymer Research, Geiselbergstr. 69, 14476 Golm, Germany

Received 19 May 2006; accepted 5 October 2006

DOI 10.1002/app.25573

Published online in Wiley InterScience (www.interscience.wiley.com).

**ABSTRACT:** Nonstoichiometric polyelectrolyte complex dispersions (PECs) with different charge excess and hydrophobicity as well as different average hydrodynamic particle size were used to induce flocculation of oppositely charged silica dispersions. PECs were formed with poly(diallyldimethylammonium chloride) (PD) as polycation and poly(styrene-*p*-sodium sulfonate) (NaPSS) and poly(acrylamide-*co*-sodium acrylate) (PR2540) as polyanions. PD was used as single polymer flocculant too. Flocculation process was characterized by optical densities of supernatants OD<sub>500</sub>, by UV/VIS spectrometry, and determination of average floc sizes  $D(v; 0.5)$  as well as volume distribution of floc sizes by laser diffraction and determination of sedimentation velocity  $s$  by means of LUMiFuge<sup>TM</sup> 114. It was found that the reaction process between silica and the used floccu-

lants could be divided into three intervals (destabilization, flocculation optimum, and restabilization) as it is known for all other polymer flocculants. For an effective flocculation of a charged substrate, both electrostatic as well as hydrophobic interactions play an important role. The interval up to the beginning of the flocculation optimum is mainly ascertained by electrostatic interactions (the charge density of the flocculant) but the broadness of flocculation optimum depends largely on hydrophobic interactions. Hydrophobic interactions also play an important role for shear stability of the formed flocs. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 3776–3784, 2007

**Key words:** polyelectrolyte complex; flocculation; silica; polyelectrolyte; hydrophobicity

## INTRODUCTION

Flocculation is a very important process in many fields of our daily life, as purification of drinking and wastewater, paper manufacturing, pharmaceutical manufacturing, soil conditioning, and food processing. In former times, inorganic agents such as alum and ferric chloride were used as flocculants. But with the discovery of high flocculation efficiency of charged polymers, the polymers have largely replaced the traditional agents. Since that time, many investigations were done about mechanisms of polymer-induced flocculation process and whose manipulation by molecular mass and charge density of the flocculant. But also, the influence of salt was investigated. Compact overviews about the most important aspects of flocculation can be found in Refs. 1 and 2.

As a rule, the flocculation is induced by one polymer alone.<sup>3–5</sup> But in the last decades, the advantages of combinations of polymers was recognized. In such systems of two (or more) components, oppositely charged polymers, polycation and polyanion, can be added step by step<sup>6–11</sup> or as preformed polyelectro-

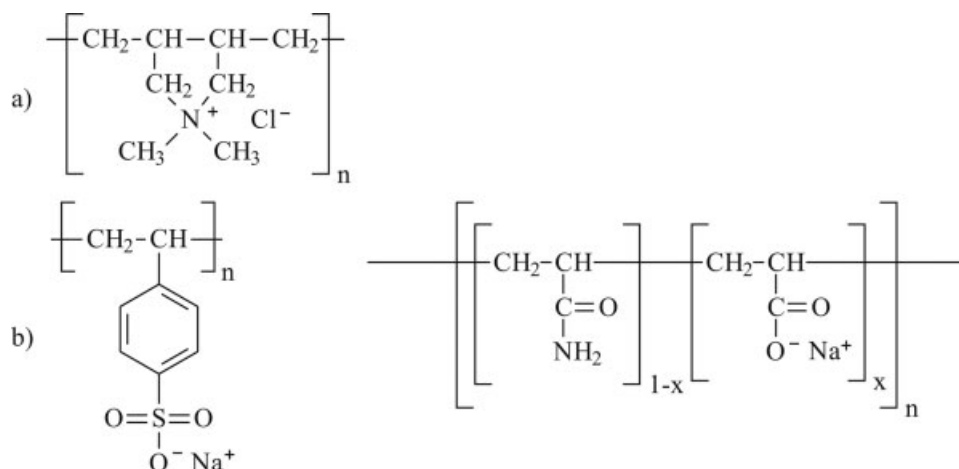
lyte complexes (PEC).<sup>7,12–15</sup> In the first case, known as dual flocculation, the effectiveness of flocculation is influenced in a large extent by the application of suitable composition of the two components. The advantages and disadvantages in the second case are not intensively investigated.

Our report deals with the flocculation of a charged model substrate induced by PECs of different charge excess and hydrophobicity. The balance of electrostatic/hydrophilic and hydrophobic properties of the flocculant and their influence on the flocculation process were in the focus of our study. A further minor aspect was the question to what extent the flocculant hydrodynamic particle size  $d_h$  has an influence on flocculation.

Silica particles (200 nm) served as negative charged model substrate, which were dispersed in water. Preformed polyelectrolyte (PEL) complex particles were used as flocculants because of the possibility to vary easily their hydrophobicity by the chemical structure of the polyanion as well as by the change of the portion of the polyanion inside the PEC.

All PECs were made of the same polycation, poly(diallyldimethylammonium chloride) (PD), that was used as single polymer flocculant too. The oppositely charged polyanions were poly(styrene-*p*-sodium sulfonate) (NaPSS) and a poly(acrylamide-*co*-sodium

Correspondence to: M. Mende (mende@ipfdd.de).



**Figure 1** PELs used in the formation of PECs; (a) polycation: PD; (b) polyanions: NaPSS and poly(acrylamide-*co*-sodium acrylate) (PR2540) with  $x = 0.28$  determined by colloid titration.

acrylate) (PR2540). Results from colloid titration, optical density measurements, dynamic light scattering, and laser diffraction were compared and analyzed.

## EXPERIMENTAL

### Materials

#### Polyelectrolytes

The cationic poly(diallyldimethylammonium chloride) (PD) had a molecular weight of  $M_w = 2.9 \times 10^5$  g/mol and was synthesized by free radical polymerization in aqueous solution.<sup>16</sup>

Poly(styrene-*p*-sodium sulfonate) (NaPSS) with a molecular weight of  $7 \times 10^4$  g/mol was purchased from Aldrich and used as obtained.

Poly(acrylamide-*co*-sodium acrylate) was a commercial product made by Stockhausen (Krefeld, Germany) with the name PRAESTOL<sup>®</sup> 2540. The molecular weight and the charge density were  $1.4 \times 10^7$  g/mol and 40% (according to the producer). By means of ultrasonic degradation, the molecular weight of this polymer has been decreased to  $5 \times 10^5$  g/mol (PR2540). Compared to the information of the producer, we determined a charge density of 28% by colloid titration before as well as after ultrasonic degradation.

All polyelectrolytes (PELs) are of pendent type with structure of monomer units shown in Figure 1.

#### Substrate

Silica powder from Geltech was used as model substrate for fine particles. In good accordance with the producer, which give a particle size of 200 nm, we determined hydrodynamic average particle size by cumulant analyses from dynamic light scattering,  $d_{h,z,av} = 180$  nm, and the median of volume distribution

from laser diffraction,  $D(v, 0.5) = 300$  nm. The specific amount of charge of silica was determined to be  $-0.29$  C/g.

To obtain a very stable model dispersion of fine particles for flocculation experiments, we suspended the silica powder (10 g/L) in Millipore-water for 15 min by means of Branson Ultrasonic Disintegrator "Sonifier W-450" with 3/4" Titan resonator. The power output was 65 W. After 24 h, in which the suspensions stand to let heavy particles and aggregates settle out, the suspensions were decanted and the solid concentration of silica was determined by gravimetry to be 6 g/L. After this procedure, we obtained silica dispersions that were stable for a few weeks.

### Methods and measurements

#### Preparation of PEC

The PECs were prepared by combination of same amounts (50 mL) of aqueous solutions of oppositely charged PELs. These solutions were obtained by dilution of definite amounts of stock PEL solutions, PD 1.617 g/L, NaPSS 2.062 g/L, and PR2540 1 g/L in Millipore water. PD solution was the starting solution (except PEC PD/PR2540-b) and their initial concentration was constant for all prepared PECs ( $C_0^{PD} = 4$  mmol/L). Under continuous stirring, a definite amount of anionic charges, which corresponds to the desired  $n_-/n_+$  ratio, was added with a flow rate of 0.2 L/h.  $n_-/n_+$  is the calculated ratio of molar charges. After complete addition, the mixtures were still stirred for 10 min and characterized 2 h after preparation.

#### Flocculation experiments

A defined amount of PEL or PEC was given to 50 mL of silica dispersions under stirring. Twenty milliliter were taken from the samples for sedimentation analy-

**TABLE I**  
**Molar Charge Ratio of Oppositely Charged Polymers  $n_-/n_+$ , Optical Density  $OD_{500}$ ,  $z$  Average Hydrodynamic Particle Size (Diameter;  $d_{h, z\text{ av}}$ ), and Polydispersity Index (PI), Charge Concentration ( $C_+$ ), and Polymer Concentration ( $C_p$ ) of the Flocculants**

Flocculant	$n_-/n_+$	$OD_{500}$	$d_{h, z\text{ av}}$ (nm)	PI	$C_+$ (mmol/L)	$C_p$ (mmol/L)
PD	0.0	–	–	–	12.60	12.60
PD/NaPSS	0.4	0.415	234	0.44	1.17	2.8
	0.6	0.683	221	0.32	0.63	3.2
	0.8	0.890	220	0.31	0.29	3.6
PD/PR2540-a	0.6	0.080	152	0.16	0.65	3.2
PD/PR2540-b	0.6	0.815	440	0.10	0.66	3.2

ses with LUMiFuge™ 114 15 min later. After that time, the stirring was finished and 1 h later, 10 mL of the supernatants were taken from the samples to determine the optical density  $OD_{500}$ . The residue was used to determine the average floc size  $D(v; 0.5)$  and volume distribution of floc sizes by laser diffraction.

#### Optical density

Determination of optical density ( $OD_{500}$ ) was used to characterize the PECs as well as the supernatants in flocculation experiments. The values of  $OD_{500}$  were obtained with a Lambda 900 UV/VIS/NIR spectrometer (Perkin–Elmer, UK). The measurements were made at  $\lambda = 500$  nm. Deionized water was used as reference.

#### PEC particle size

Dynamic light scattering measurements were made by a Zetasizer 3000 (Malvern Instr., UK) to determine  $z$  average diffusion coefficient of PEC particles and to calculate their  $z$  average hydrodynamic diameter by the Stokes-Einstein-equation. The instrument was equipped with a monochromatic coherent 10 mW Helium Neon laser ( $\lambda = 633$  nm) as light source. The light scattered by particles is recorded at an angle of  $90^\circ$ .

#### Floc size

The sizes of flocs in flocculation experiments were determined by means of laser diffractometry. The used device (Mastersizer Microplus, Malvern Instr., UK) was equipped with a 2 mW Helium Neon laser. Samples were stirred at 2000 rpm during measurements.

#### Colloid titration

The concentrations of the charged groups of the used PELs in their stock solutions as well as the charge concentration of the silica dispersions and the charge excess of PECs were determined by colloid titration

carried out by means of a PCD 02 particle charge detector (Mütek, Germany).

#### Separation behavior under acceleration of gravity

To characterize the separation behavior of silica dispersion alone as well as under the influence of the used flocculants, we used a microprocessor controlled analytical centrifuge, the LUMiFuge 114 from LUM, Germany. It processes up to eight samples simultaneously. Transmission is measured along the whole samples. The measurements were made on 690 rpm, which corresponds to a relative centrifugal force of  $60 \times g$  at the bottom of the measuring cell.

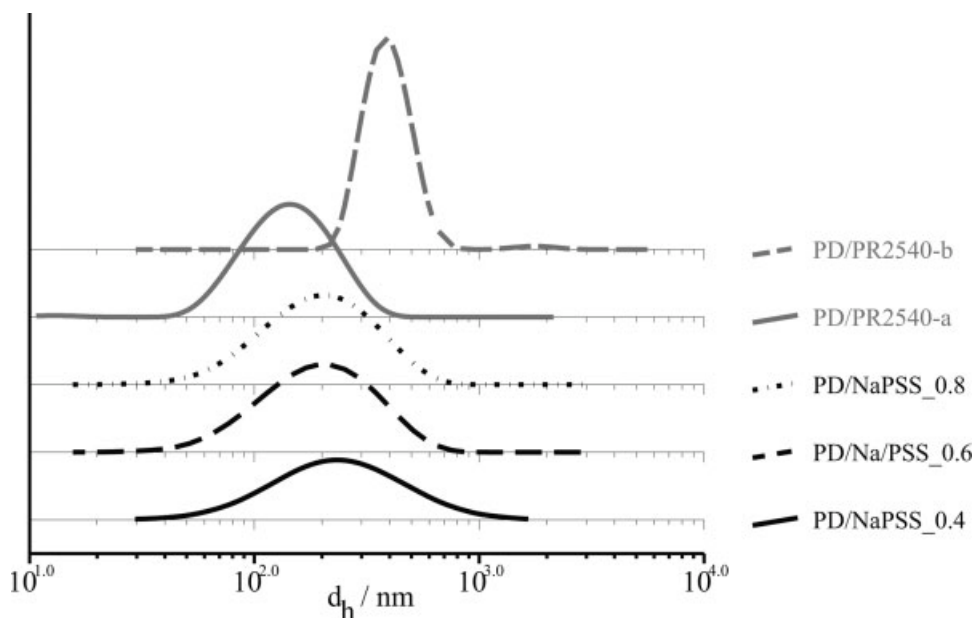
## RESULTS AND DISCUSSION

### Characterization of flocculants

Used flocculants in this study were first PD alone, second PEC dispersions from PD and NaPSS, and third PEC dispersions from PD and poly(acrylamide-co-sodium acrylate) (PR2540). In all cases, the same PD was used. Detailed description of complex preparation and characterization can be found in Refs. 17 and 18.

Table I shows all essential information about the employed flocculants. The calculated molar charge ratio of the oppositely charged polymers is  $n_-/n_+$ . PI and  $d_{h, z\text{ av}}$  indicates polydispersity index and  $z$  average hydrodynamic particle size (diameter), which were obtained from cumulant analyses in dynamic light scattering.  $C_+$  is positive charge excess concentration of the flocculant determined by colloid titration. As the concentration of polycation was kept constant in complex formation and the concentration of polyanion was varied with desired  $n_-/n_+$ -ratio, the charge excess of the PECs decreases with increase of  $n_-/n_+$ . But, the polymer concentration  $C_p$ , which is the sum of mol monomers of polycation and polyanion in PEC dispersion, increases with increase of  $n_-/n_+$ . In the following we used the denotation PEC for PEC dispersions.

$Z$  average hydrodynamic particle size  $d_{h, z\text{ av}}$  of PD/NaPSS PECs is independent on  $n_-/n_+$ -ratio and



**Figure 2** Hydrodynamic particle size distributions obtained from dynamic light scattering of PECs formed from PD with first poly(acrylamide-*co*-sodium acrylate) (PR2540) with  $n_-/n_+ = 0.6$  at different PEC formation conditions: (a) PD starting solution, (b) PR2540 starting solution and second NaPSS with different  $n_-/n_+$ -ratios, which are the digits in the labels.

nearly constant. The polydispersity indices are very high for all these PECs. It can be seen also from particle size distribution analysis in dynamic light scattering presented in Figure 2.

Statements about the influence of flocculant hydrophobicity should be possible as the hydrophobic parts inside the PEC increase with increasing amount of polyanion and consequently with increasing  $n_-/n_+$ -ratio.

PD/PR2540-a and PD/PR2540-b differ neither in  $n_-/n_+$ -ratio nor in  $C_+$  (see Table I). But on the strength of different PEC formation conditions<sup>16,17</sup> we are able to vary the  $z$  average hydrodynamic particle size distinctly. Appendix a in the PEC name means polycation was starting solution in PEC formation and b means polyanion was starting solution. As isoelectric point is exceeded during PD/PR2540-b formation, we obtain a distinct increase in particle size depicted in Figure 2 too. So, we are able to investigate the influence of flocculant particle size on flocculation process.

Also, statements about the influence of flocculant hydrophobicity caused by the chemical structure of PELs (here polyanion) on flocculation process should be possible if we compare the data from flocculation with PD/NaPSS and PD/PR2540 for the same  $n_-/n_+$ -ratio (0.6).

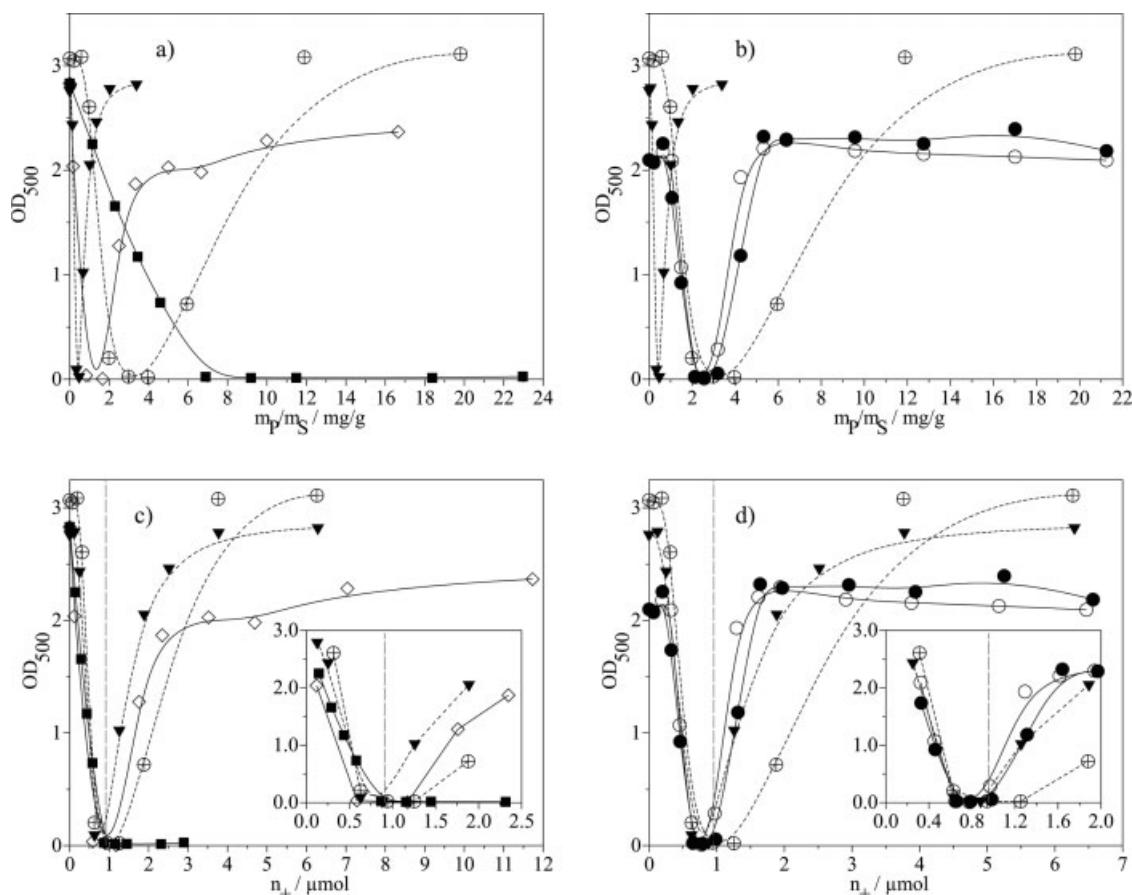
However, in our experience, a nonstoichiometric PEC dispersion contains beside free excess PEL (here polycation) a relative broad size distribution of colloid nanoparticles. These particles differ not only in their size but also in their charge excess and consequently in their hydrophobicity.

### Flocculation of silica dispersion

A common method to estimate the efficiency of a flocculation process is to determine the supernatants optical density  $OD_{500}$  after a desired sedimentation time. The flocculation process efficiency is defined first by the amount of flocculant required to reach the flocculation optimum and second by the broadness of flocculation optimum, which is dedicated to the smallest supernatant optical density values in our study. Figures 3(a) and 3(b) show supernatants' optical density values of the silica flocculation induced by PD and PECs of PD/NaPSS in dependence on the mass ratio of polymer and solid substrate,  $m_P/m_S$ . In the case of PEC flocculant polymer mass  $m_P$  is the sum of the mass of polycation and polyanion. The solid concentration was 6 g/L and constant in all samples. Flocculation curve of silica with PD is incorporated in the diagrams for comparison.

First fundamental conclusions are the following. The amount of flocculant required reaching flocculation optimum as well as broadness of flocculation optimum increase with decrease of flocculant charge density. As we assume that the decrease of flocculant charge density is coupled with increase of hydrophobic parts in our used flocculants, we can attribute the broadness of flocculation optimum to the flocculant hydrophobicity caused by the higher amount of polyanion inside the PEC [Fig. 3(a)]. From Figure 3(b), we observe the influence of flocculant hydrophobicity caused by the structure of polyanion used in PEC formation. As all PEC flocculants in Figure 3(b) have the same  $n_-/n_+$ -ratio and  $C_P$ , the charge excess is also





**Figure 3** Optical densities of supernatants  $OD_{500}$  of silica dispersions after a sedimentation time of 1 h in dependence on mass ratio between polymer and substrate  $m_p/m_s$  (a and b) and in dependence on the flocculant charge added to silica dispersions  $n_+$ . PD:  $\blacktriangledown$ ; PD/NaPSS:  $\diamond$ ,  $n_-/n_+ = 0.4$ ,  $\oplus$ ,  $n_-/n_+ = 0.6$ ,  $\blacksquare$ ,  $n_-/n_+ = 0.8$ ; PD/PR2540 with  $n_-/n_+ = 0.6$ :  $\circ$ , (a),  $\bullet$ , (b). Dashed gray line in (c) and (d) denotes 100% of charge neutralization between flocculant and substrate.

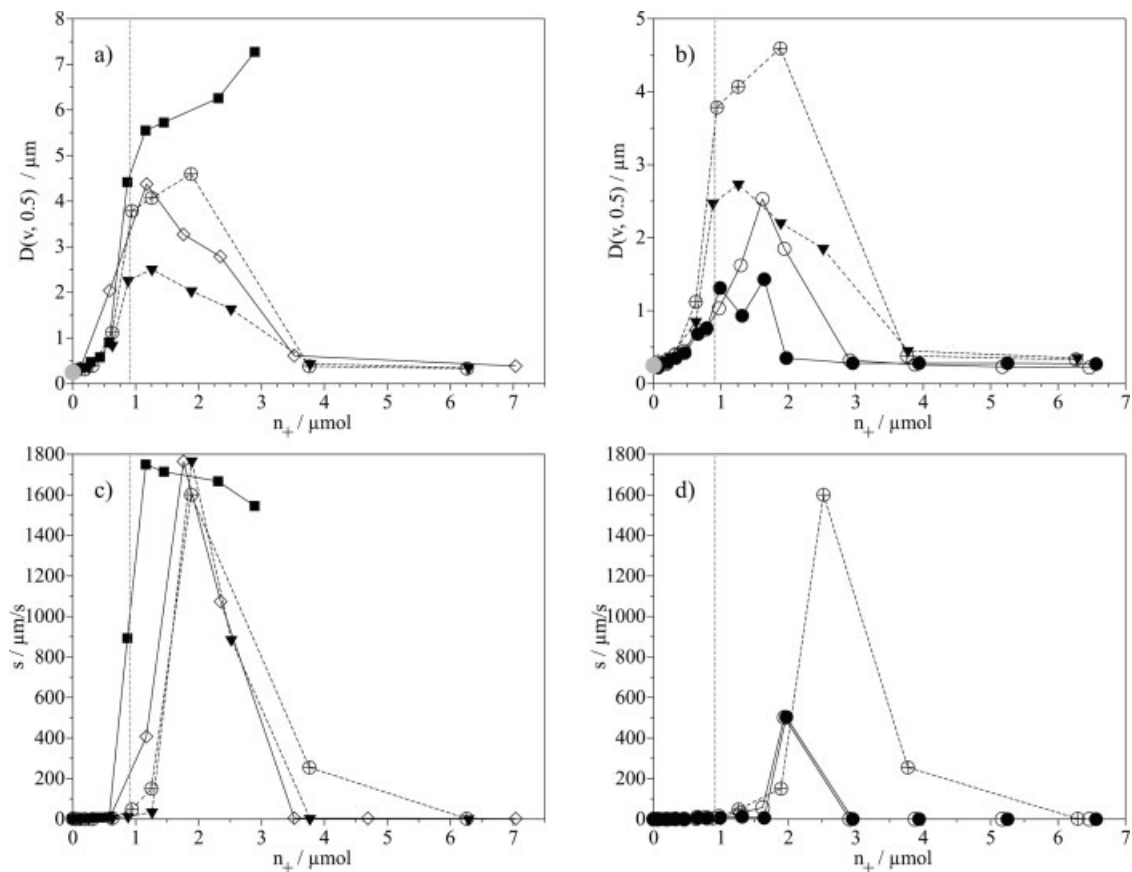
nearly the same for all these PECs. Hence, we reach the flocculation optimum at nearly the same  $m_p/m_s$ -ratio. Only the broadness of the flocculation optimum is different for different type of polyanion inside the PEC flocculant. Hydrophobicity of NaPSS is higher than of PR2540. The higher the hydrophobicity of the polyanion, the broader is the flocculation optimum.

These facts are shown more distinct in diagrams such as in Figures 3(c) and 3(d). Here optical density values are represented in dependence on the amount of molar charge of the flocculant  $n_+$ , which is added to the silica dispersion. The dashed gray line shows the point of charge neutralization between the substrate and the flocculant. So, additional from these diagrams we found that for all used flocculants exempted PEC PD/NaPSS with  $n_-/n_+ = 0.8$  the flocculation optimum is reached at about 65% charge neutralization. For the PEC flocculant with  $n_-/n_+ = 0.8$ , the flocculation optimum begins at nearly 100% charge neutralization. Moreover, the restabilization of the silica dispersions takes place at more higher molar charge excess of the flocculant  $n_+$  for flocculants of higher hydrophobicity. And it is indicated by Figure

3(d) that hydrophobicity of PD seems to be like that of PD/PR2540 PECs.

Another some unexpected result from Figures 3(b) and 3(d) is the independence of the flocculation process on the particle size of the PEC (PD/PR2540-a and -b). Maybe it is associated not only to the particle size but rather to the number of the particles, which are formed during PEC formation. As we have the same  $C_p$  in PEC formation and only the formation conditions are different, we obtain very different particle size. But this means also that the number of particles should be lower in the case of PD/PR2540-b than for PD/PR2540-a.

Similar results were obtained from floc size analysis by laser diffraction ( $D(v; 0.5)$ ) and transmission measurements during centrifugation by a microprocessor controlled analytical centrifuge, the LUMiFuge 114. From the last method we obtain sedimentation velocity  $s$ . These parameters are depicted in Figure 4 in dependence on the molar charge of flocculant  $n_+$ , which is added to the silica dispersion. The light gray point in Figures 4(a) and 4(b) represents the particle size  $D(v; 0.5) = 300$  nm of the silica particles without floc-



**Figure 4** (a) and (b): Average floc size of volume distribution ( $D(v, 0.5)$ ) named as median from laser diffraction in dependence on flocculant charge added to silica dispersions  $n_+$ . Symbols and dashed gray line are the same as in Figure 3. Light gray point in (a) and (b) means the  $D(v, 0.5)$  of silica dispersion without flocculant. (c) and (d): Sedimentation velocity  $s$  in dependence on  $n_+$ . Symbols and dashed gray line are the same as in Figure 3.

culant. This average size value has its source in volume distribution and means that 50% of the total volume of the silica particles has a size lower than 300 nm and the other 50% have a size higher than 300 nm.

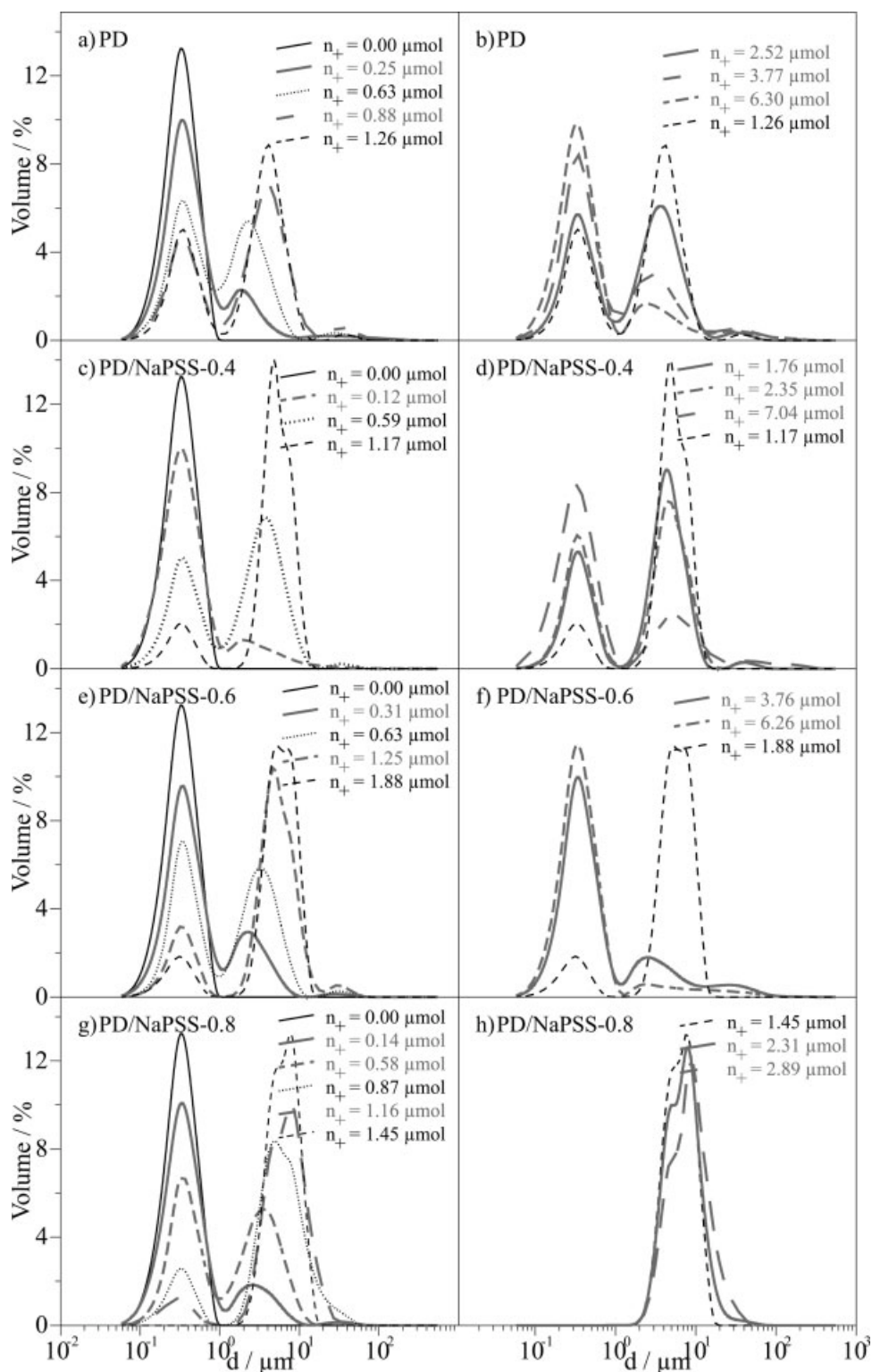
Figure 4(a) shows that the floc size  $D(v; 0.5)$  increases rapidly at the point of charge neutralization between flocculant and substrate. After this point, floc size rises hardly exempted flocculation with PD/NaPSS with  $n_-/n_+ = 0.8$ . Here, floc size increases in the whole investigated area. That we do not find a maximum in  $D(v; 0.5)$  for PD/NaPSS flocculant with  $n_-/n_+ = 0.8$  does not mean inevitably that restabilization could not occur at still higher  $n_+$ .

For all flocculants, the maximum floc size inside the flocculation optimum depends on the charge density of the flocculant and hydrophobicity, respectively. As hydrophobicity increases, the size of formed flocs also increases in spite of the same charge excess of the flocculant added to silica dispersion.

From Figure 4(b) we can conclude once again that the amount of hydrophobic parts inside the PEC flocculant formed by PEC formation has an influence on flocculation process. The average floc size is also

influenced by the choice of PELs for PEC formation. Flocculation of silica with PD/PR2540, independent on the formation conditions of these PECs, leads to distinct lower  $D(v; 0.5)$  values in the flocculation optimum when compared to flocculation of silica with PD/NaPSS with the same molar charge ratio  $n_-/n_+$  ( $=0.6$ ) and polymer concentration  $C_P$  ( $=3.2$  mM). Even PD alone is better suited as flocculant for silica.

If we compare the position and broadness of the flocculation optima defined by  $OD_{500}$  and  $D(v; 0.5)$  a discrepancy is observed. At one side the beginning of flocculation optima defined by  $D(v; 0.5)$  shape to a little bit higher molar charges of the flocculant  $n_+$  and the broadness seems to be higher. To explain the difference, we need the volume distributions of particles/flocs depicted in Figure 5 because  $D(v; 0.5)$  is an average value and consequently suitable to show tendencies only. In Figure 5 is shown the change of silica particle size volume distribution under the influence of PD and PD/NaPSS PEC flocculants in dependence on molar charge of added flocculant to the substrate  $n_+$ . Volume distribution of silica dispersion without flocculant ( $n_+ = 0.00$   $\mu\text{mol}$ ) is monomodal. Diagrams on the left side [Figs. 5(a), 5(c), 5(e),



**Figure 5** Volume distribution of silica dispersions without flocculant ( $n_+ = 0.00 \mu\text{mol}$ ) and treated with PD and PD/NaPSS with different  $n_-/n_+$ -ratios in dependence on the flocculant charge added to silica dispersions  $n_+$ .

and 5(g)] show that monomodal mode changes to bimodal and multimodal mode, respectively, under the influence of anything of the used flocculants. With increase of molar charge of flocculant  $n_+$ , the volume proportion of single silica particles decreases and vol-

ume proportion of bigger aggregates increases. If both volume proportions are all about the same (dotted black lines), we found the beginning of flocculation optimum determined by  $\text{OD}_{500}$ . Only the flocculation with PD/NaPSS with  $n_-/n_+ = 0.8$  seems to

differ from the rule. But the reason could be the increment of the flocculation measurements. However, in the case of such bi/multimodal volume distributions, we obtain  $D(v; 0.5)$  values that are still closer to the  $D(v; 0.5)$  of the single silica particles despite the presence of big silica aggregates, but their number is low. This low number of bigger silica aggregates is enough to give best clarification observed by  $OD_{500}$  but it is not enough to give maximum  $D(v; 0.5)$ . We should take into account that the silica particles are not only bridged by bigger PEC particles. They could fast adsorb also smaller PEC particles and free excess PEL. Then, they aggregate by patch-mechanism and settle down if no shear force affects this process. This is the case before samples are taken from flocculated silica dispersion to determine supernatants optical density  $OD_{500}$ . During the determination of volume distribution and  $D(v; 0.5)$ , respectively, samples were stirred and consequently aggregates formed only by patch-mechanism can be destroyed easily when compared to aggregates formed by bridging with bigger PEC particles. Consequently, flocculation optima are shifted to higher amount of flocculant. Flocculation optima are situated above the point of 100% of neutralization between substrate and flocculant.

At a defined amount of flocculant added to the substrate, we observe volume distribution with very high proportion of the bigger aggregates and only very low amount of single silica particles or no single silica particles as for flocculation with PD/NaPSS with  $n_-/n_+ = 0.8$ . A reason could be that due to the kind of PEC formation, more PEC particles are build with higher  $n_-/n_+$ -ratio. Hence in flocculation with PEC of  $n_-/n_+ = 0.8$  more silica particles could be bridged by bigger PEC particles.

At further addition of flocculant aggregation process returns and restabilization occurs expected of course flocculation with PD/NaPSS with  $n_-/n_+ = 0.8$  again. This is expressed by the decrease of volume proportion of the bigger silica aggregates and the increase of volume proportion of single silica particles, which is shown in Figures 5(b), 5(d), 5(f), and 5(h).

During the determination of sedimentation velocity  $s$  by LUMiFuge 114, we obtained analogical observations to the shift of flocculation optima due to shear force. The shift of flocculation optima to higher  $n_+$  is demonstrated in Figures 4(c) and 4(d). The flocculation optima seem to be a little bit closer than in the case of  $D(v; 0.5)$ . Here, the advantages of hydrophobic flocculants are shown again. Mainly for PD/NaPSS with  $n_-/n_+ = 0.8$  formed flocs are very stable against shear force and consequently sedimentation velocity is high.

If we compare Figures 4(c) and 4(d), we see that the hydrophobicity of the flocculant, which comes from PEC formation only, is not enough to give good flocculation result. Flocculation with the PD/PR2540

PECs results in distinct lower sedimentation velocities  $s$  compared to flocculation with PD/NaPSS PECs and even with PD. In these cases, sedimentation velocity is about 3.5 times higher in the flocculation optimum than for flocculation with PD/PR2540 PECs. Hydrophobicity that comes from chemical structure of the flocculant is obviously more important.

## SUMMARY

In this study the interaction between a polyelectrolyte (PD) or PECs and an oppositely charged substrate (silica, 200 nm) was investigated. Two different polyanions (NaPSS, PR2540) and PD as polycation were used for complex formation. The PECs differ in their charge excess ( $n_-/n_+$ ), and in their average hydrodynamic particle size  $d_{h, z, av}$ , and their hydrophobicity. Flocculation process was characterized by optical density  $OD_{500}$ , average floc size  $D(v; 0.5)$ , and sedimentation velocity  $s$ .

Following things were observed:

1. The reaction process between silica and the used flocculants can be divided into three intervals that are known for all other polymer flocculants too. First, we observed destabilization up to the beginning of the flocculation optimum followed by the restabilization.
2. From determination of supernatant, optical density can be concluded that in the destabilization interval electrostatic interactions play a dominant role. As lower the charge density of the flocculant as broader is this interval.
3. The broadness of the flocculation optimum determined by optical density depends on the hydrophobicity of the flocculant. As hydrophobicity increases, flocculation optimum becomes broader.
4. Flocculation optima determined by average floc size  $D(v; 0.5)$  and sedimentation velocity  $s$  are shifted to higher amount of flocculant because of the influence of shear force.
5. Average floc size  $D(v; 0.5)$  inside the flocculation optimum is higher with higher flocculant hydrophobicity.
6. The broadness of flocculation optimum observed by sedimentation velocity  $s$  as well as the magnitude of sedimentation velocity  $s$  are predominantly influenced by flocculant hydrophobicity, which comes from chemical structure of the flocculants.

## References

1. Smith-Palmer, T.; Pelton, R. In *Encyclopaedia of Surface and Colloid Science*; Marcel Dekker: New York, 2002; p 2207.



2. Somasundaran, P.; Das, K. K. In *Innovations in Mineral and Coal Processing*; Atak, S., Önal, G., Celik, M. S., Eds.; Balkema, A. A.: Rotterdam, Brookfield, 1998; p 81. ISBN 90 5809 0132.
3. Bratskaya, S.; Schwarz, S.; Liebert, T.; Heinze, T. *Colloids Surf A* 2005, 254, 75.
4. Lu, C.; Pelton, R. *Langmuir* 2001, 17, 7770.
5. Bajdur, W. M.; Sulkowski, W. W. *Macromol Symp* 2003, 202, 325.
6. Nyström, R.; Backfolk, K.; Rosenholm, J. B.; Nurmi, K. *J Colloid Interface Sci* 2003, 262, 48.
7. Nyström, R.; Rosenholm, J. B. *Colloids Surf A* 2005, 252, 135.
8. Fan, A.; Turro, N. J.; Somasundaran, P. *Colloids Surf A* 2000, 162, 141.
9. Yu, X.; Somasundaran, P. *Colloids Surf A* 1993, 81, 17.
10. Petzold, G.; Mende, M.; Lunkwitz, K.; Schwarz, S.; Buchhammer, H.-M. *Colloids Surf A* 2003, 218, 47.
11. Petzold, G. In *Colloid-Polymer Interactions: From Fundamentals to Practice*; Farinato, R. S., Dubin P., Eds.; Wiley: New York, 1999; p 83.
12. Petzold, G.; Nebel, A.; Buchhammer, H.-M.; Lunkwitz, K. *Colloid Polym Sci* 1998, 276, 125.
13. Schwarz, S.; Dragan, S. *Macromol Symp* 2004, 210, 185.
14. Nyström, R.; Rosenholm, J. B.; Nurmi, K. *Langmuir* 2003, 19, 3981.
15. Nyström, R.; Hedström, G.; Gustafsson, J.; Rosenholm, J. B. *Colloids Surf A* 2004, 234, 85.
16. Hahn, W.; Jaeger, W. *Angew Makromol Chem* 1992, 198, 165.
17. Mende, M.; Petzold, G.; Buchhammer, H.-M. *Colloid Polym Sci* 2002, 280, 342.
18. Mende, M.; Buchhammer, H.-M.; Schwarz, S.; Petzold, G.; Jaeger, W. *Macromol Symp* 2004, 211, 121.