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ORIGINAL CONTRIBUTION

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Polyelectrolyte complex formation between poly(diallyldimethyl-ammonium chloride) and copolymers of acrylamide and sodium-acrylate

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Abstract The interaction between oppositely charged polyelectrolytes, in this study poly(diallyldimethyl-ammonium chloride) (PDADMAC) and copolymers of acrylamide and sodium-acrylate differing in their chain length and charge density parameter (ξ) was investigated in relation to the molar charge ratio of anionic to cationic charges (n_-/n_+). The molecular weights of the polyelectrolytes used were $2.9 \cdot 10^5$ g/mol for PDADMAC and for the polyacrylamide copolymers $14 \cdot 10^6$ g/mol as well as $5 \cdot 10^5$ g/mol obtained by ultrasonic degradation of the high molecular weight copolymers. The charge density parameters of the polyanions used (ξ^{PR}) varied between 0.14 and 0.64. Complexation between PDADMAC and high molecular weight polyanions leads mainly to macroscopic phase separation whereas the degraded polyanions and PDADMAC formed soluble complexes as well as stable dispersions, if charge excess was available. Precipitates and dispersions were characterized by several methods such as element analysis, thermogravimetry, pyrolysis-GC/MS, PEL titration, ζ-potential measurements, determination of turbidity, particle size measurements and determination of carbon content (TOC).

All precipitated complexes include about 20% water and are of 1:1 stoichiometry concerning ionic binding. Investigations of dispersions confirm 1:1 stoichiometry of complex particles stabilized by excess polyelectrolyte and soluble complexes. It was also found that the particle size can be varied via the charge density parameter of the polyanions used in the range of negative charge excess.

Keywords Polyelectrolyte complexes · Colloidal dispersions · Polyacrylamide copolymers · Poly(diallydimethylammonium chloride)

Introduction

The very large number of papers published in recent decades demonstrates the great interest of scientists in polyelectrolytes (PEL) and their ability to spontaneously form interpolyelectrolyte complexes (PEC) due to Coulombic interaction between the oppositely charged groups located along the polymer chains. Not only fundamental research [1–4] in the field of PEC formation is in center of science at the present time but also the various different possible practical applications such as for microencapsulation [5, 6] or as membranes with special separation properties [7, 8]. In our group the work was focused on the application of polyelectrolyte complexes as flocculants for colloidal dispersions [9, 10], on surface modification of silicate powders [11, 12] and on the sorption of organic molecules in wastewater cleaning [13].

As expressed by many authors a deeper understanding of the complex formation is very complicated due to the enormous number of parameters, influencing this formation process. Different states of such systems (soluble complexes, stable dispersions and precipitates) can be observed to be dependent on polymer chain length (degree of polymerization), type and distribution of charged groups along the polymer chain (charge density), polymer concentration, molar ratio of mixed anionic to cationic charges (n_-/n_+), ionic strength, pH of the medium etc.

Successful contributions to the study of the formation of polyelectrolyte complexes have been made by Kabanov and Zezin [14] as well as by Philipp et al. [15] and Dautzenberg et al. [16]. With the help of static light scattering, Dautzenberg was able to make deductions about the composition and structure of PEC particles being dependent on the mixing ratio of the components [17–19]. So he found that in highly diluted systems quasi-soluble PEC particles on a colloidal level are built, even between two oppositely charged polyelectrolytes of high molecular weight. Compactness and stability of PEC particles depend strongly on the charge density of polyions.

In this study the interaction between two polyelectrolytes, usually used for dual-flocculation for dispersions of fine particles, was investigated. The strong polycation poly(diallyldimethylammonium chloride) was applied in combination with copolymers of acrylamide and sodium acrylate as weak polyanions. Normally the short polycation is added to the suspension prior to the extremely high molecular weight polyanion preferential of lower charge density, because the polyanion has to briged the particles in the dual flocculation process. However, another way could be to use pre-formed complexes from the same polymers. For that reason it is necessary to obtain stable and well characterized dispersions of such complexes. So special attention was given to the influence of the molecular weight of the polyanions used and the ratio of the contour lengths between polyanion and polycation (L^{PR}/L^{PD}), respectively. The ratio of charge distances of the polyanion to the polycation (b^{PR}/b^{PD}) and the molar charge ratio (n_-/n_+) were also of interest. In contrast to Dautzenberg [19] the molecular weight of the polyanions used was extremely high (about 14×10^6 g/mol). With the help of ultrasonic degradation [20] we were able to reduce the molecular weight of the polyanions from 14×10^6 g/mol to 5×10^5 g/mol. In this way we obtained polymers of different molecular weight (chain length) on the same structure but with constant charge density. The charge density parameters (ξ^{PR}) of the polyanions used varied between 0.14 and 0.64. The Manning parameter ξ [21] is defined by the following equation:

$$\xi = \frac{e^2}{4\pi\varepsilon_0\varepsilon kTb} \tag{1}$$

where e is the charge of the electron, ε the dielectric constant, b the average distance between charges along the contour length of the polymer chain and kT the Boltzmann term.

Experimental part

Materials

Polycation

The cationic poly(diallyldimethylammonium chloride) (PDADMAC, PD) has a molecular weight of 2.9×10^5 g/mol and was synthesized and characterized by W. Jaeger, IAP Golm (Germany). Because of the quaternary ammonium groups, PDADMAC is a strong PEL of the pendant type (Fig. 1a) and the charge density along the polymer chain is nearly independent of pH.

Polyanion

The anionic poly(acrylamide-co-sodium acrylate)s used ($M_w = 14 \times 10^6$ g/mol, Fig. 1b) were commercial products with the name PRAESTOL (PR, Table 1). They were obtained from Stockhausen (Krefeld, Germany) and differ in their charge densities.

For complex formation we used the same polymers degraded in an ultrasonic bath [20]. The molecular weights decreased from 14×10^6 g/mol to about 5×10^5 g/mol with narrow weight distributions of $M_w/M_n = 1.14 - 1.16$. The degraded polymers were characterized by GPC. Polysaccharides were used as standards for calibration. The parameters of the polymers used are summarized in Table 1.

Methods

Ultrasonic degradation of the poly(acrylamide-co-sodium acrylate)s

The degradation of 300 ml of 1 g/l polymer solutions was carried out with a Branson Ultrasonic Desintegrator "Sonifer W-450" with

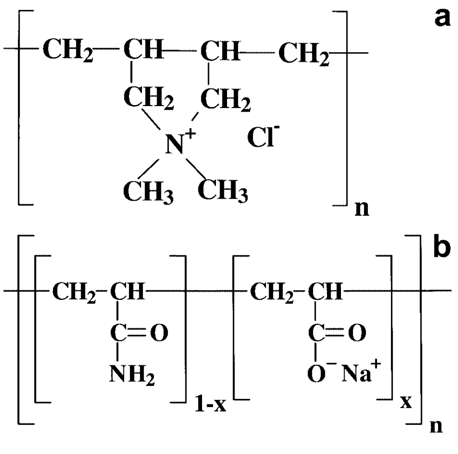

Fig. 1 Structure of monomer units of the polyelectrolytes used **a** PDADMAC; **b** Poly(acrylamide-*co*-sodium acrylate)s: x = 0.06, 0.11, 0.2, 0.28

Table 1 Characteristic parameters of the poly(acrylamide-co-sodium acrylate)s used

PRAESTOL	charge density			M_0 (g/mol)	P_w^{PR}		L^{PR} (nm)		L^{PR}/L^{PD}		b^{PR} (nm)	b^{PR}/b^{PD}	ξ^{PR}
	manufacturer	PEL-Titration			for M_w^{PR}		for M_w^{PR}		for M_w^{PR}				
	(w%)	(mol%)	(w%)		$14 \cdot 10^6 \cdot$ (g/mol)	$5 \cdot 10^5 \cdot$ (g/mol)	$14 \cdot 10^6 \cdot$ (g/mol)	$5 \cdot 10^5 \cdot$ (g/mol)	$14 \cdot 10^6 \cdot$ (g/mol)	$5 \cdot 10^5 \cdot$ (g/mol)			
2510	10	6.2	8.1	72.38	193400	6900	59567	2125	66	2.36	5.13	10.26	0.14
2515	15	11.2	14.3	73.53	189800	6800	58458	2094	65	2.33	2.8	5.6	0.25
2530	30	20.3	25.2	75.60	185200	6600	57041	2032	63	2.26	1.54	3.08	0.45
2540	40	28.1	34.1	77.44	180800	6400	55686	1971	62	2.19	1.1	2.2	0.64

$L_{mon}^{PR} = 0.308$ nm for all PRAESTOLs (calculated by means of C-C-distance of 0.154 nm)

3/4″ Titan resonator, operating at a frequency of 20 kHz. The power output was about 40 W for all samples. During ultrasonic treatments temperature was maintained at about 25 °C by cooling in a water bath. In order to obtain good heat drainage, samples were treated in special glass vessels.

Preparation of PEC

Figure 2 shows the procedure of complex formation. The PECs were prepared by combination of equal amounts (50 ml) of aqueous solutions of oppositely charged PELs. These solutions were obtained by dilution of definite amounts of stock PEL solutions, PDADMAC 1.617 g/l and PRAESTOL solutions 1 g/l, in Millipore water. Within a complex series the set amounts of cationic charges was kept constant (Table 2). Under continuous stirring, a definite amount of anionic charges corresponding to the desired n_-/n_+ ratio was added with a flow rate of 0.2 l/h. The calculated ratio of charges is n_-/n_+. After complete addition the mixtures were stirred for a further 10 minutes and characterized 2 hours after preparation.

PEL titration

PEL titration was used to determine the charge of stock PEL solutions and also the net charges of the formed complexes. The device used was the Particle Charge Detector, PCD 02 from Mütek GmbH (Herrsching, Germany). The method is based on the generation of a streaming potential.

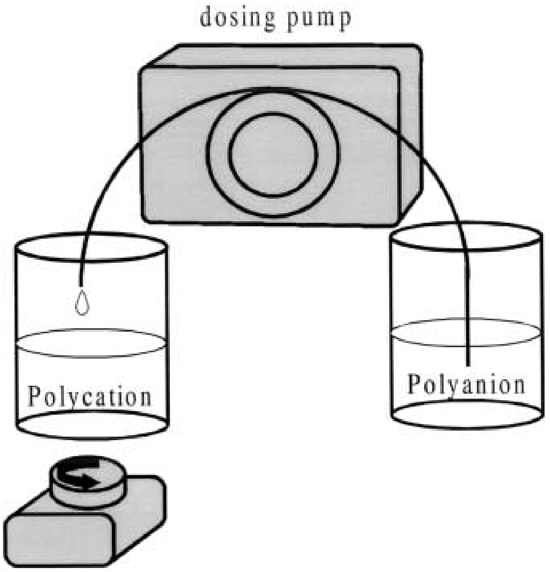

Fig. 2 Procedure of polyelectrolyte complex formation

Table 2 Initial concentration of positive charges for complex formation

complex series	C_0^{PD} (mmol/l)
PD/PR 2510	0.32
PD/PR 2510^{UD}	
PD/PR 2515	0.63
PD/PR 2515^{UD}	
PD/PR 2530	1.00
PD/PR 2530^{UD}	
PD/PR 2540	1.48
PD/PR 2540^{UD}	

PD, PDADMAC; PR, PRAESTOL; UD, ultrasonic degradation

Electrophoretic measurements

To measure the electrophoretic potential(ζ-potential), Zetamaster from Malvern Instruments (U.K.) was used. The electrophoretic mobility can be measured in an incorporated microelectrophoresis cell by application of laser doppler anemometry. The optical unit has a 5 mW Helium Neon laser with $\lambda = 633$ nm. All measured samples were diluted in 10^{-3} mol/l KCl.

Particle size measurements

By means of photon correlation spectroscopy the average particle diameter (d_h) and information on size distribution (polydispersity index) were obtained. The measurements were carried out with a commercial apparatus, the Zetasizer 3000 (Malvern, U.K.) equipped with a monochromatic coherent 10 mW Helium Neon laser ($\lambda = 633$ nm) as light source. The light scattered by particles was recorded at an angle of 90°.

Turbidity

The stability of dispersions was characterized by optical density (OD) with the UV/VIS/NIR-Spectrometer Lambda 900 from Perkin Elmer. Measurements were made at $\lambda = 500$ nm. Deionized water was used as reference.

Determination of carbon content

Complex dispersions were centrifuged (11,000 rpm for 20 min) and then the carbon concentration (C_c) was determined in the supernatants by means of the TOC-5000 (Total Organic Carbon

Analyzer, Shimadzu). In order to estimate if the large complex particles were removed completely from the dispersion we also measured the turbidity of the visually clear solutions. Usually the values of turbidity were nearly zero. Carbon concentration was also determined in some whole PEC dispersions.

Element analysis

The very hard and colourless precipitates were analyzed by element analysis (carbon, nitrogen and hydrogen) carried out by means of vario EL of elementar analysis systems GmbH, Hanau, Germany.

Thermogravimetry

Thermogravimetric analysis of precipitated complexes was carried out using a Perkin Elmer TGA 7 with Pyris-Software Version 3.51 at temperatures from 30 °C to 700 °C. The heating rate was 10 K/min and the carrier gas was nitrogen.

Pyrolysis-GC/MS

The precipitated PECs were degraded by pyrolysis at different temperatures (150 °C, 300 °C, 430 °C and partly 500 °C and 550 °C) with the device Pyroprobe 2000 (Fa. CDS) and analysed by gas chromatography (GC 5890, Hewlett Packard) and mass spectrometry (MSD 5971, Hewlett Packard).

Results and discussion

Interpolyelectrolyte complex formation is influenced by an enormous number of parameters as mentioned above. We focused our studies on the following parameters: polymer chain length (L^{PR}) and charge density parameter (ξ^{PR}) of the polyanions used and the variation of the molar charge ratio of mixed anionic to cationic charges (n_-/n_+).

For the polycation used , PDADMAC (PD) with a molecular weight of 2.9×10^5 g/mol, the degree of polymerisation ($P^{PD}{}_W = 1800$) and the contour length ($L^{PD} = 900$ nm) were calculated. The charge density parameter $\xi^{PD} = 1.4$ under the condition that the distance between charges along the polymer chain $b^{PD} = 0.5$ nm [15]. According to Manning's counterion condensation theory, ξ should be reduced to below the critical value 1. Even considering this fact it should be accepted that in our experiments ξ^{PD} is higher than that of the polyacrylamide copolymers used (Table 1). For the anionic copolymers (PRAESTOLs, PR) the distance between charges b^{PR} was calculated using the distance between carbon atoms in the polymer chain as 0.154 nm. From this follows a change in the charge density parameter of the polyanions ξ^{PR} from 0.14 to 0.64. The ratio of distances between charges on polyanions to that on the polycation b^{PR}/b^{PD} varied between about 10 and 2.

The results of the examinations confirm our expectation that the chain length of the polyanion has an essential influence on the stability of complex dispersions. Figure 3 shows the influence of the polymerization degree of the polyanions on the complex formation and stability at the same concentration. The range marked dark gray denotes macroscopic phase separation, ranges marked light gray are those of stable dispersions and the intermediate gray denotes soluble complexes. Soluble complexes are solutions of a complex with turbidity values of lower than 0.02. These are visually clear solutions. Stable dispersions are dispersed aggregates of complexes.

It was found that the desired stability of dispersions depends not only on the degree of polymerization of the polyanions but also that the excess charge of PEL is a very important parameter. For a complex series the molar charge ratio n_-/n_+ was in the range 0.4–2.0. For the complexes of individual complex series on lowest χ of the polymers and highest χ_{H_2O}, respectively, $n_-/n_+ = 0.4$ and on highest χ of polymers and lowest χ_{H_2O}, $n_-/n_+ = 2.0$. The other n_-/n_+ ratios are situated between them. The mass fraction of the polyanion, polycation or the solvent (water) is represented by χ.

As illustrated in Figure 3a the interaction between the ultra high molecular weight polyanions and the polycation results in a macroscopic phase separation even on relatively low polymer concentration ($C_{polymer}$). Exceptions are complexes with the acrylamide copolymers of the lowest charge density parameter (ξ^{PR}). Under these conditions soluble complexes as well as stable dispersions are formed at $n_-/n_+ < (n_-/n_+)_{ip}$ (index ip is the isoelectric point).

In Figure 3b complexes prepared with polyanions of lower molecular weight are shown. We could obtain stable dispersions having cationic as well as anionic charge excess. Polyelectrolyte complexes became unstable only near the molar charge ratio $n_-/n_+ = (n_-/n_+)_{ip} \cong 0.93$ because the charge excess is missing.

Isoelectric points of PEC dispersions

In Table 3 isoelectric points of PECs with low molecular weight polyanions are summarized. We do not observe distinct differences between the values determined from PEL titration and electrophoretic measurements nor dependence on the charge density parameter of the polyanion. Both polycation and polyanion are polyelectrolytes of pendant type and so a good arrangement of oppositely charged sites is possible. That should be one of the reasons that the isoelectric points of PECs are near to the molar mixing ratio of $n_-/n_+ = 1$. To obtain stable complex dispersions we work with relative low concentrations.

Figure 4 shows the results of PEL titrations and ζ-potential measurements for PD/PR2540^{UD}. Curve 1 shows the change of charge excess is dependent on the mixing ratio n_-/n_+. Curve 2 shows that the theoretical course of the charge excess changed also in dependence on the molar charge ratio if we assume 1:1 stoichiometry

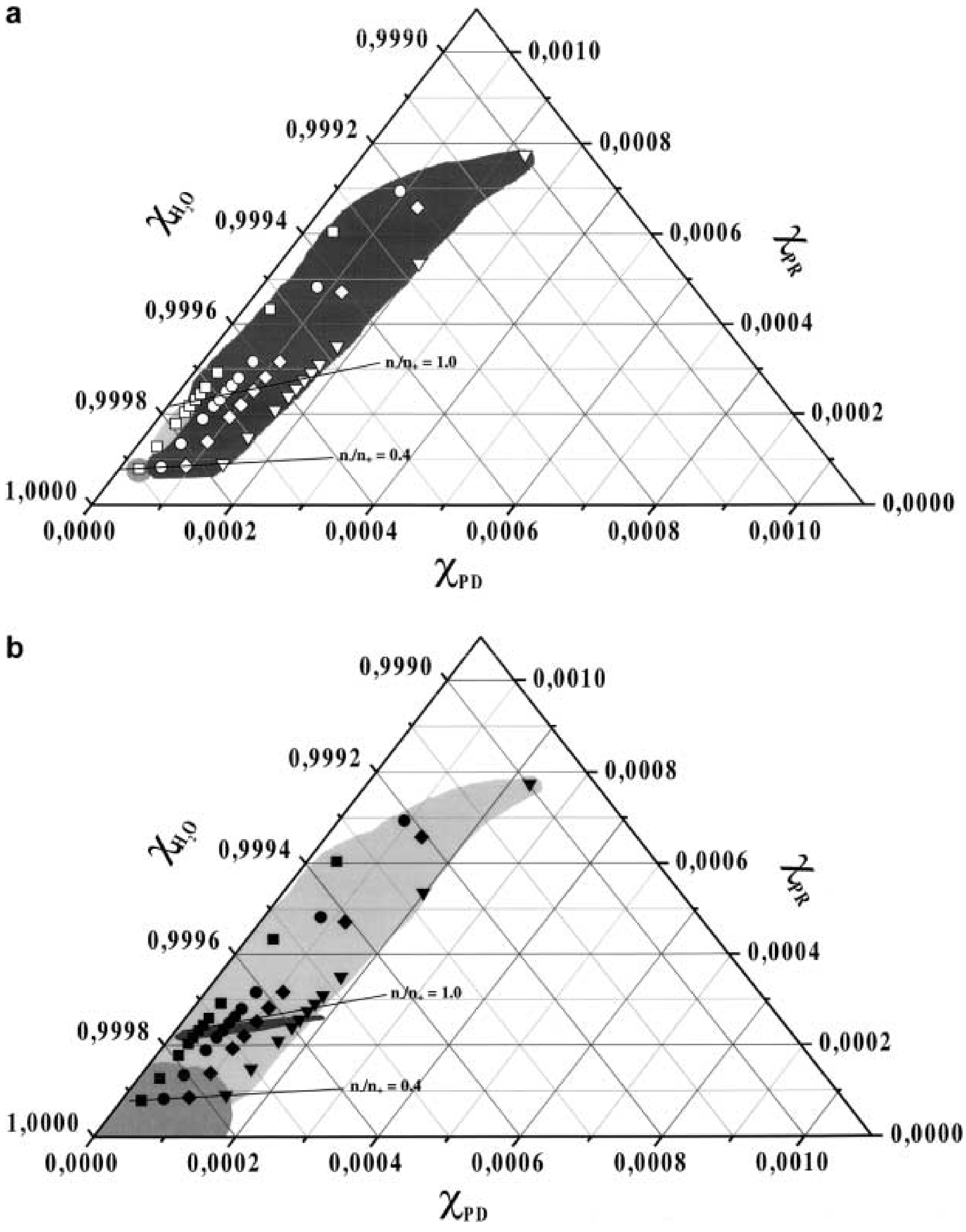

Fig. 3 States of formed PECs versus mass fraction χ of the polycation, polyanion and water (solvent) *Intermediate gray range*, soluble complexes; *light gray range*, stable dispersions; *dark gray range*, precipitates. (a) $P_w^{PR} \approx 1.8 \times 10^5$–$1.9 \times 10^5$: □ PD/PR2510, ○ PD/PR2515, ◇ PD/PR2530, ▽ PD/PR2540 (b) $P_w^{PR} \approx 6.4 \times 10^3$–$6.9 \times 10^3$: ■ PD/PR2510^{UD}, ● PD/PR2515^{UD}, ◆ PD/PR2530^{UD}, ▼ PD/PR2540^{UD}

Table 3 Isoelectric points of PEC formed with degraded polyacrylamides

PEC	$(n_-/n_+)_{\text{isoelectric point}}$ from	
	PEL titration	ζ-potential
PD/PR2510^{UD}	0.91	0.91
PD/PR2515^{UD}	0.94	0.94
PD/PR2530^{UD}	0.90	0.94
PD/PR2540^{UD}	0.93	0.95

PD, PDADMAC; PR, PRAESTOL; UD, ultrasonic degradation

of ionic binding. The range marked gray represents the detection limit of PEL titration method. Curve 3 shows the ζ-potentials of the PECs formed.

The curves 1 and 2 are parallel and are in relative good agreement. So we can conclude that complexes were formed with 1:1 stoichiometry concerning the ionic bindings, independent of the molar charge mixing ratio. This was found for all investigated dispersions, not only for this example. These results confirm the proposed structure model of PEC particles (aggregates) of Dautzenberg [18]. Polyelectrolyte complex particles

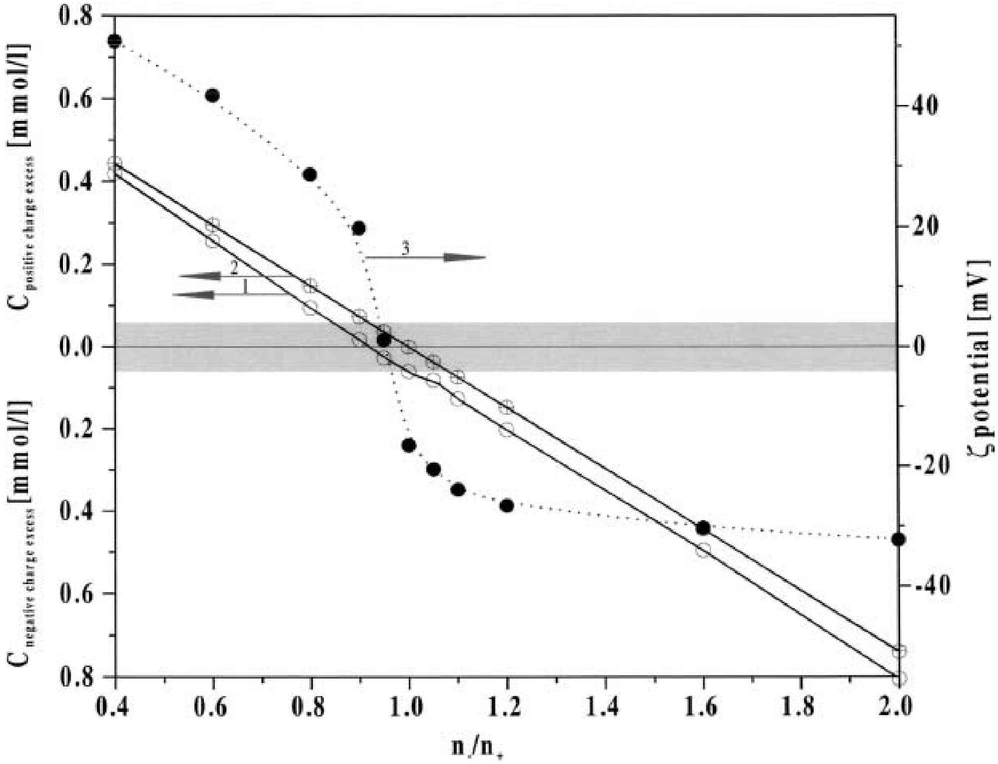

Fig. 4 Charge excess and ζ-potential of PD/PR2540^{UD} versus molar charge ratio n_-/n_+ ○ curve 1: measured charge excess ⊕ curve 2: calculated charge excess by assumption of 1:1 stoichiometry of ionic binding ● curve 3: ζ-potential measurements

consist of a neutralized core and were stabilized by a surrounding shell of the excess component.

Stability of the complex dispersions

The turbidity (OD_{500}) is a simple tool to check the stability of complex dispersions. Optical density depends on different parameters of the light scattering particles such as shape, number (concentration), size and polydispersity.

Figure 5a demonstrates the typical behavior of the optical density for complexes prepared with the whole series of degraded acrylamide copolymers ($L^{PR}/L^{PD} \approx 2$). In the first part of the curves [$n_-/n_+ < (n_-/n_+)_{ip}$] optical density increases only a little bit up to the isoelectric point. From particle size measurements (Fig. 6a) it was found that in this range the average hydrodynamic particle diameter (d_h) is approximately constant. Therefore we are able to conclude that an increased number of particles (aggregates) should be responsible for increased optical density.

Near the isoelectric point, dispersions became unstable and the optical density shows a strong time-dependent behavior. A short time after the preparation of PECs at $(n_-/n_+)_{ip} \cong 0.93$ an extremely turbid dispersion is observed. About 24 hours later the precipitation is complete.

Beyond the isoelectric point complexes are stable again. The values of optical density are higher than that in the region of positive charge excess. The maximum number of aggregates formed up to the isoelectric point were here stabilized by the excess of polyanion which is adsorbed onto the surface of the earlier-formed positive aggregates. This was reflected by increasing of the optical density and also the particle size (Fig. 5a and 6a). In contrast to particle size measurements which show clear dependence of particle size on charge density parameter of polyanion (ξ^{PR}) for $n_-/n_+ > (n_-/n_+)_{ip}$, no significant dependence of OD_{500} is found.

The time dependence of the OD_{500}-values for the complex series of PD/PR 2540^{UD} and PD/PR 2515^{UD} is shown in Figure 5b. It is interesting to note that the complex dispersions with charge excess were stable over a few days, independent of n_-/n_+.

Particle size

Figure 6a depicts the dependence of average hydrodynamic diameter (d_h) of particles on a definite molar ratio (n_-/n_+) and the charge density parameter of the polyanions used (ξ^{PR}). As long as positive charges are available in excess, n_-/n_+ as well as ξ^{PR} show no significant influence on average d_h. However, the polydispersity shown in Figure 6b is relatively high at first

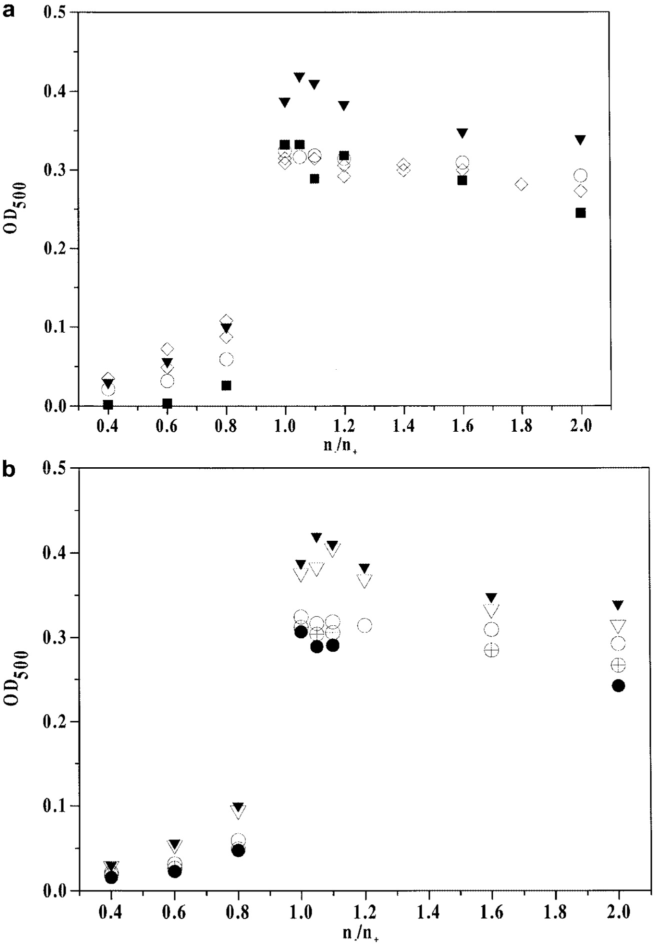

Fig. 5 Optical density OD_{500} versus n_-/n_+ of the formed PECs (a) influence of charge density parameter of polyanion ξ^{PR}: ■ PD/PR2510^{UD}, ○ PD/PR2515^{UD}, ◇ PD/PR2530^{UD}, ▼ PD/PR2540^{UD}; (b) influence of time on stability of PECs: PD/PR2515^{UD}: ○ 2 hours after formation, ⊕ 5 days after formation, ● 20 days after formation; PD/PR2540^{UD}: ▼ 2 hours after formation, ▽ 10 days after formation

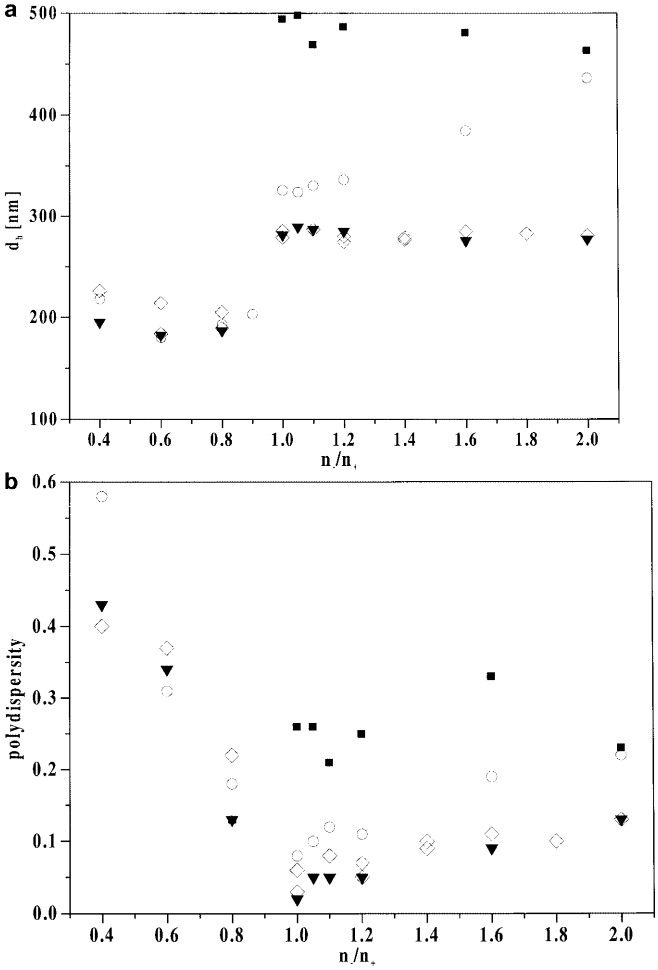

Fig. 6 Particle size and polydispersity of formed PEC dispersions versus molar charge ratio n_-/n_+ **a** particle size: ■ PD/PR2510^{UD}, ○ PD/PR2515^{UD}, ◇ PD/PR2530^{UD}, ▼ PD/PR2540^{UD} **b** polydispersity: symbols are the same as for (**a**)

and decreases with increasing n_-/n_+ for $n_-/n_+ < (n_-/n_+)_{ip}$. It should be mentioned that the particle sizes of PD/PR2510^{UD} for $n_-/n_+ < (n_-/n_+)_{ip}$ are not measurable.

For $n_-/n_+ > (n_-/n_+)_{ip}$ there is a strong increase in d_h by decreasing the charge density parameter ξ^{PR} whereas the molar ratio n_-/n_+ shows an influence on the particle size only for PD/PR2515^{UD} complex series. In this case the earlier-formed complex aggregates were bridged by the lowly charged polyanion excess. This process is more pronounced by PR2510^{UD} than by PR2515^{UD} because of the different charge densities.

Simultaneously polydispersity increases again whereas the rise is pronounced for lower charge density parameter ξ^{PR}.

Our explanation is that with higher ξ^{PR} parameter of the polyanion, the average distance b^{PR} between charges along the polyanion chain becomes closer to that of the polycation chain. The ratio b^{PR}/b^{PD} decreases from about 10 to 2 if ξ^{PR} increases from 0.14 to 0.64 (Table 1). Therefore the coil dimensions of the polyanions used should increase with increasing ξ, as recognizable from the change in relative viscosity η_{rel} from 1.22 to 2.89 of the 1 g/l stock PEL solutions of the degraded polyanions, their ξ^{PR} increases from 0.14 to 0.45. Consequently, the arrangement of the oppositely charged polyelectrolyte chains to one another should be different for $b^{PR}/b^{PD} \approx 2$ and for $b^{PR}/b^{PD} \approx 10$ as schematically illustrated in Figure 7. By means of these models of PECs we are able to demonstrate that polymers with good fitting properties such as average distance between charges, similar rigidity of polymer chains and geometric position of charged sites (both PELs are of pendant-type) can obviously form PEC particles having a higher structure density. With an

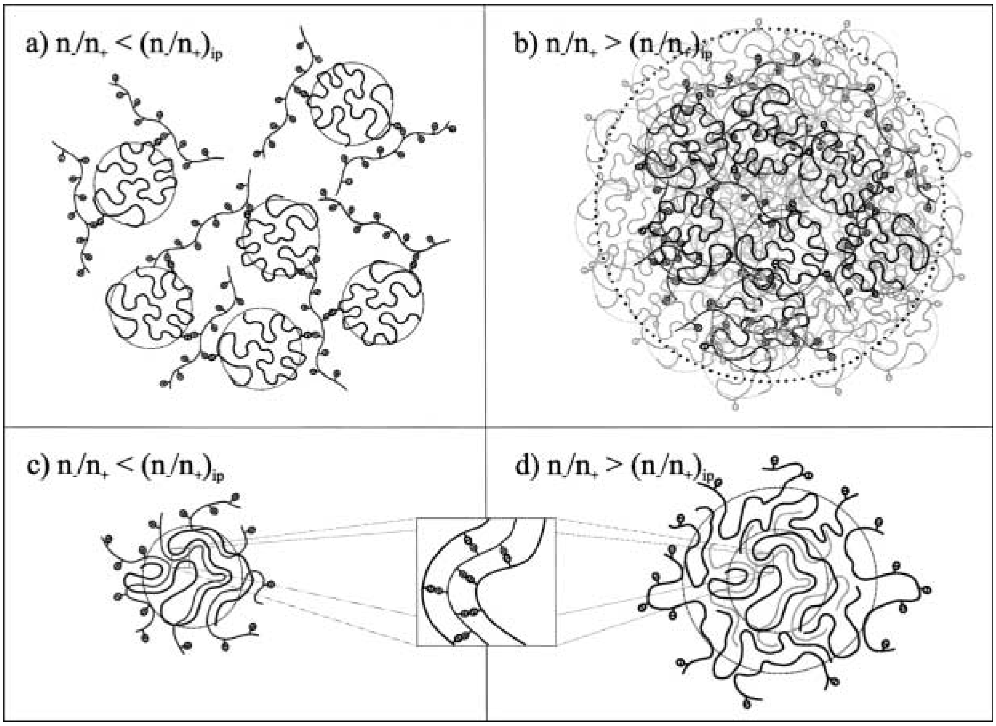

Fig. 7 Model of structure of formed PEC aggregates for $L^{PR}/L^{PD} \approx 2$ **a** and **b** $b^{PR}/b^{PD} \approx 10$; **c** and **d** $b^{PR}/b^{PD} \approx 2$

increase of b^{PR}/b^{PD} we assume that higher swollen aggregates were formed. Already Dautzenberg reported that the compactness of the core of PEC particles can be varied via charge density of the components [17].

In the following section we want to give some explanation of the models in Figure 7.

We compare two cases in PEC formation. On the one hand PD/PR2510^{UD} (Figure 7a and 7b) and on the other hand PD/PR2540^{UD} (Figure 7c and 7d).

Figure 7a is a speculation, because we are not able to measure the particle size. We cannot compare the particle size between the two examples for $n_-/n_+ < (n_-/n_+)_{ip}$. However, we think that it is right to assume that PR2510^{UD} is higher coiled than PR2540^{UD} caused by the different charge densities. So in the case of Figure 7a the coiled macromolecules of PR2510^{UD} were bridged by the shorter and higher charged molecules of the polycation. In contrast to PR2510^{UD}, the higher charged PR2540^{UD} can form more extended coils caused by the repulsive forces. The average charge distance b^{PR} on PR2540^{UD} is only twice the distance of the used polycation b^{PD}. So we deduce in Figure 7c that a good arrangement like a ladder between the polyelectrolytes is possible. Therefore we think that in this case a higher structure density could be reached than at the formed particles shown in Figure 7a.

Figures 7b and 7d show our ideas concerning the particles on polyanion charge excess. In Figure 7b it is shown that small complex aggregates were bridged by the coils of the polyanion in excess forming very large and swollen complex aggregates. Figure 7d demonstrates, that the size of the particles increases by changing the molar ratio from $n_-/n_+ < (n_-/n_+)_{ip}$ to $n_-/n_+ > (n_-/n_+)_{ip}$. In this case the higher charged polyanions in excess can adsorb and stabilize the complex aggregates and therefore a further increase of the particle size was prevented. This is also reflected by the smaller values of polydispersity for PD/PR2540^{UD} compared with PD/PR2510^{UD} in the range of $n_-/n_+ > (n_-/n_+)_{ip}$ (Figure 6b).

PEL excess in dispersions

With regard to the model of polyelectrolyte complex particles given by Dautzenberg we want to check if it is possible to estimate the part of excess polyelectrolyte by TOC measurements. For the experiments, the larger PEC particles were separated from the complex dispersion by centrifugation. The supernatants obtained were clear. Because PEL titration indicates the same charge concentration for supernatants as for dispersions, we conclude that polymer excess which carried charges was separated from PEC particles by centrifugation and also that the polymer excess adsorbed on neutralized particle core. Consequently we should measure the portion of carbon content which results from monomers of the excess PEL.

In Figure 8 the results obtained with complex series PD/PR2540^{UD} are shown. Range I corresponds to the amount of C_c from monomers which carry charges. The measured C_c in the supernatant is significantly higher (the sum of range I and II). A good correlation between calculated C_c and measured C_c was found only for PECs near $(n_-/n_+)_{ip}$. This was observed for all complex series.

The higher C_c measured means that we have soluble complexes or/and small aggregates in combination with free polyelectrolytes in the supernatants, especially in ranges of $n_-/n_+ \ll (n_-/n_+)_{ip}$ and $n_-/n_+ \gg (n_-/n_+)_{ip}$. Near the isoelectric point we assume that no really free polyelectrolyte is available. Here the stabilization is not only an electrostatic effect. Hydrophobic interaction between the soluble complexes (small aggregates) and the larger PEC particles should be possible.

Range III corresponds to the amount of PEC which was sedimentated before the measurements. The lower stability of PECs is clearly recognized near the isoelectric point.

Stoichiometry and water content of precipitated complexes

In addition, the precipitated PECs were analyzed by element analysis. We could show that the composition of the PECs is the same within a complex series. In Table 4 are summarized the theoretical and measured values for the content of carbon C, nitrogen N, hydrogen H and oxygen O, but oxygen could not be measured. The theoretical values were calculated using the following assumptions: acrylate content of PR2515 10%, for PR2530 20%, for PR 2540 30% and 1:1 stoichiometry concerning charges of polyelectrolytes.

A significant difference between calculated and measured values was found. Noteworthy is the smaller C:H ratio of the measured values. Compared to this the calculated and measured C:N ratios are in relatively good agreement. One possible interpretation could be that precipitates contain a considerable part of water. In column 15 of Table 4 the calculated content of water $X_{calc}^{H_2O}$ is summarized.

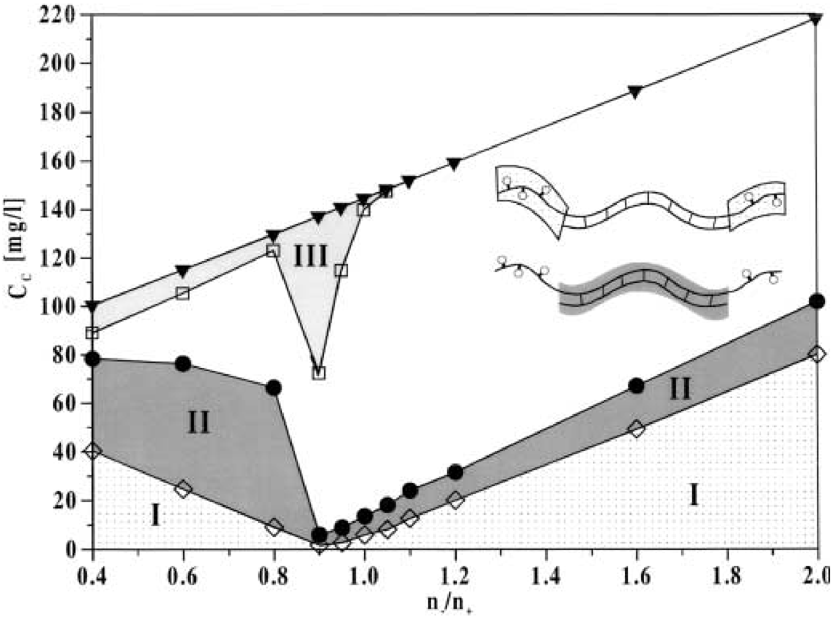

Fig. 8 Carbon concentration C_c versus molar charge ratio n_-/n_+ for PD/PR2540^{UD}: ▼ calculated C_c for whole dispersions (mixed amounts of polymers) □ measured C_c in PEC dispersions 3 days after formation (range III: amount C_c of sedimentated PEC before the measurement) ● measured C_c in the supernatants of centrifugated PECs (range I + II) ◇ calculated C_c concerning the titrated charge concentration from PEL titration

Table 4 Elemental analysis of precipitated complexes from complexation of PDADMAC with high molecular weight polyacrylamides

complex series	calculated content (%)				calculated ratios			measured content (%)				meas. ratios		$X_{calc}^{H_2O}$	$X_{meas}^{H_2O\,a}$
	C	N	H	O	C:N	C:H	C:O	C	N	H	O	C:N	C:H	(%)	(%)
PD/PR2515	54.53	16.73	7.71	21.03	3.26	7.07	2.59	44.84	13.19	8.514	–	3.40	5.27	18.32	20.7
PD/PR2530	57.36	14.54	8.16	19.93	3.94	7.03	2.88	46.02	10.93	8.585	–	4.21	5.36	20.52	21.5
PD/PR2540	59.54	12.86	8.51	19.09	4.63	7.00	3.12	46.27	9.66	9.26	–	4.79	5.00	22.63	23.0

[a] from thermogravimetry

Table 5 Thermogravimetric analysis of precipitated complexes

PEC series	T (°C)	mass loss (%)
PD/PR2515	254 ± 1	20.7 ± 1
	392 ± 1	46 ± 1
	465 ± 1	85 ± 0
PD/PR2530	253.5 ± 2.5	21.5 ± 0.5
	388 ± 10	43 ± 2
	470 ± 2	85 ± 1
PD/PR2540	248 ± 1	23 ± 0.3
	387 ± 7	44 ± 0
	472 ± 1.5	86.5 ± 0.5

In order to confirm this speculation, PECs were analyzed by thermogravimetry and pyrolysis in combination with gas chromatography and mass spectrometry. For all investigated complexes, three stages of mass loss were found by thermogravimetry which are summarized in Table 5. By means of the combination of pyrolysis with gas chromatography and mass spectrometry we proved that the first degradation stage of thermogravimetry at a temperature of about 250 °C for all complexes contains only the release of water. On second stage other molecules can be observed. By comparing the percentage of mass loss up to the first degradation stage in thermogravimetric analysis ($X^{H_2O}_{meas}$, see Table 4, column 16) with the calculated percentage part of water from elemental analysis ($X^{H_2O}_{calc}$, Table 4, column 15) a good agreement is found. So we can conclude that our PECs contain about 20% water and the ionic binding of the PECs is of 1:1 stoichiometry.

Summary

The complexation between the PDADMAC empolyed and the high molecular weight polyacrylamides ($M_w = 14{\cdot}10^6$ g/mol) leads mainly to phase separation. The precipitated complexes contain about 20% water and are of 1:1 stoichiometry.

Using degraded polyacrylamides ($M_w = 5{\cdot}10^5$ g/mol) for complex formation we obtained mainly stable complex dispersions. These dispersions are stable over a few days. Only on the isoelectric point ($n_-/n_+ \cong 0.93$) did the complexes become unstable because charge excess is missing. The investigation of the dispersions by several methods proved the structure model of polyelectrolyte complexes represented by Dautzenberg [18]. But we can conclude from our results that PEC particles were also stabilized by soluble complexes. It was also found that the size and structure of PEC particles can be varied via the ratio of the distances of charge sites of the polyacrylamides used to the PDADMAC used, b^{PR}/b^{PD} for $n_-/n_+ > (n_-/n_+)_{ip}$. For a low ratio ($b^{PR}/b^{PD} \approx 2$) it seems that the compactness of particles is higher than that for a higher ratio ($b^{PR}/b^{PD} \approx 10$).

References

1. Schindler T, Nordmeier E (1994) Polym J 26 (10):1124
2. Webster L, Huglin MB, Robb ID (1997) Polymer 38 (6):1373
3. Argüelles-Monal W, Pérez-Gramatges A, Peniche-Covas C, Desbrieres J, Rinaudo M (1998) Eur Polym J 34 (5/6):809
4. Argüelles-Monal W, Cabrera G, Peniche C, Rinaudo M (2000) Polymer 41 (7):2373
5. Lee KY, Park WH, Ha WS (1997) J Appl Polym Sci 63 (4):425
6. Radtchenko IL, Sukhorukov GB, Leporatti S, Khomutov GB, Donath E, Möhwald H (2000) J Colloid Interface Sci 230 (2):272
7. Lee SH, (2000) Polym J 32 (9):716
8. Zhumadilova GT, Gazizov AD, Bimendina LA, Kudaibergenov SE (2001) Polymer 42 (7):2985
9. Petzold G, Lunkwitz K (1995) Colloids Surf A 98:225
10. Petzold G, Nebel A, Buchhammer HM, Lunkwitz K (1998) Colloid Polym Sci 276:125
11. Kramer G, Buchhammer HM, Lunkwitz K (1997) J Appl Polym Sci 65:41
12. Buchhammer HM, Lunkwitz K (1996) Ber Bunsenges Phys Chem 100:1039
13. Buchhammer HM, Petzold G, Lunkwitz K (2000) Colloid Polym Sci 278:841
14. Kabanov VA, Zezin AB (1984) Makromol Chem, Suppl 6:259
15. Philipp B, Dautzenberg H, Linow KJ, Koetz J, Dawydoff W (1989) Prog Polym Sci 14:91
16. Dautzenberg H, Jaeger W, Kötz J, Philipp B, Seidel C, Stscherbina D (1994) Polyelectrolytes – Formation, characterization and application. Hanser, Munich, pp 253–262
17. Dautzenberg H (2000) Macromol Chem Phys 201:1765
18. Dautzenberg H (2000) Macromol Symp 162:1
19. Dautzenberg H, Koetz J, Linow KJ, Philipp B, Rother G (1994) Static light scattering of polyelectrolyte complex solutions. In: Dubin PL (ed) Macromolecular complexes in chemistry and biology. Springer, Berlin Heidelberg, pp 119–134
20. Kulicke WM, Otto M, Baar A (1993) Makromol Chem 194:751
21. Manning GS (1969) J Chem Phys 51 (3):924