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The Stability of Polyelectrolyte Complex Systems of Poly(diallydimethyl-ammonium chloride) with Different Polyanions

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Summary: Polyelectrolyte complex (PEC) dispersions formed by fast ionic exchange reaction between polyelectrolytes (PELs) bearing oppositely charged groups have been characterized by turbidity and dynamic light scattering. The stability of the formed PEC dispersions, the average hydrodynamic particle size d_h and the also determined polydispersity index PI of the PEC particles were of special interest. In this study poly(diallyldimethylammonium chloride) (PD) of different molar mass is used in combination with copolymers of maleic acid and α-methylstyrene (P(MS-αMeSty)) as well as propene (P(MS-P)), with a copolymer of acrylamide and sodium acrylate ($PR2540^{UD}$) and poly(styrene-p-sodium sulfonate) (NaPSS).
A strong dependence of the PEC stability on the molar charge ratio n_-/n_+, the mixing conditions and especially on the chemical structures of the used polyanions was found. If the employed polyanion (PA) have a π-system (phenyl-) in the polymer chain a higher tendency to instability results. The average hydrodynamic particle sizes d_h and the polydispersity indices PIs of the formed stable PEC dispersions determined by dynamic light scattering were strongly influenced by the mixing conditions of the PECs. If we are able to prepare stable complexes where the isoelectric point is exceeded during complex formation which is possible for PD/P(MS-P) and $PD/PR2540^{UD}$ systems a distinct increase of d_h and decrease of PI is observed. The polymer concentration C_P and the chain length L of the used PELs have a minor effect on d_h and PI.

Keywords: dispersions; dispersion stability; dynamic light scattering; polyelectrolyte complex; polyelectrolytes

Introduction

It is well known that oppositely charged polyions (polycation, PC and polyanion, PA) dissolved in aqueous solution form polyelectrolyte complexes (PEC).[1-3] The following three different types can be distinguished[1]: (i) The so-called soluble complexes, which contain small PEC aggregates and therefore they form macroscopically homogeneous systems. (ii) Turbid

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colloidal systems with suspended complex particles in the transition range to phase separation. (iii) Phase separation by precipitation of PEC-polysalt.

It depends on several parameters, such as the chain length L of the employed polyions, their chemical structures as well as the type and distribution of the charged groups along the polymer chains of what type ((i), (ii) or (iii)) a PEC is. Beside these structural influences polymer concentration C_P, molar ratio of mixed anionic to cationic charges n_-/n_+, ionic strength I, pH of the medium etc. play an important role.

It is a well-established fact that stable PECs with no phase separation during complexation can be formed under certain conditions, i.e. polyelectrolytes with weak ionic groups and significant different molecular weights at non-stoichiometric mixing ratios.[4-8] These PECs consist of a long host molecule and shorter sequentially attached guest polyions of opposite charge as comprehensively studied by the groups of Tsuchida and Kabanov.[9,10] In dependence on the ionic sites at the polyelectrolyte chains and the mixing conditions the formed stable PECs contain single stranded hydrophilic and double stranded hydrophobic sections. PECs of high hydrophobicity result in supermolecular structures and precipitate.

As shown and discussed in different studies the formed PEC particles consist of a neutralized, hydrophobic core and a shell of the excess component which stabilizes the particles against further coagulation.[11-13]

In connection with the use of the PEC particles as flocculating agent[14, 15] or as carrier for dyes or solved organic molecules from the waste water,[16] we investigated the stability and the behavior of PECs in more detail.[17]

In this study we want to compare the properties of four PEC systems, such as turbidity, particle size and their distribution, in dependence on the molar charge ratio n_-/n_+, the polymer concentration C_P and the initial polycation concentration C_0^{PC}, respectively, the chain length L of the PELs and the types of the functional groups of the polyanions. Additional the chemical structures of the employed polyions and the mixing conditions (starting solution) were of special interest.

Experimental part

Materials

The used cationic poly(diallyldimethylammonium chloride) (PD) has two different molecular weights, $M_W = 5 \cdot 10^3\ g/mol$ and $M_W = 2.9 \cdot 10^5\ g/mol$. The first one was purchased from Aldrich and used without further purification. The second one was synthesized by free radical polymerization in aqueous solution, purified by ultrafiltration and characterized as described in.[18]

Poly(styrene-p-sodium sulfonate)s (NaPSS) with molecular weights of $7 \cdot 10^4\,\mathrm{g/mol}$ and $10^6\,\mathrm{g/mol}$ were also purchased from Aldrich and used as obtained.

Poly(acrylamid-co-sodium acrylate) (PR2540^{UD}), a commercial product (PRAESTOL®) was obtained by Degussa.Stockhausen GmbH & Co. KG (Krefeld, Germany). The molecular weight was about $M_W = 14 \cdot 10^6\,\mathrm{g/mol}$ and the charge density was 40 wt.-% (according to the manufacturer). By means of ultrasonic degradation the molecular weight of the polymer has been decreased to $5 \cdot 10^5\,\mathrm{g/mol}$.[17, 19] The effective charge density determined by PEL-titration was 28 mol-% (33 wt.-%) before as well as after ultrasonic degradation.

Poly(maleic acid-co-propene) (P(MS-P)) and poly(maleic acid-co-α-methylstyrene) (P(MS-αMeSty)) were prepared by hydrolysis of the corresponding anhydrides. The pH-values of the solutions were adjusted to 6. These anhydrides were obtained from Leuna GmbH (Germany) with $M_W = 5 \cdot 10^4\,\mathrm{g/mol}$ for the propene-copolymer and $M_W = 2.5 \cdot 10^4\,\mathrm{g/mol}$ for the α-methylstyrene-copolymer. More characteristic parameters of the used PELs are summarized in Table 1 where P_W is the degree of polymerization, L is the contour length of the polymer chain and b is the average distance of charges along the polymer chain.

Table 1. Characteristic parameters of used PELs

PEL	M_W g/mol	P_W	L nm	b nm
PD	5 000 290 000	31 1800	15.5 900	0.5
PR2540^{UD}	500 000	6400	1970	1.1[a)]
NaPSS	70 000 10^6	340 4850	85 1212	0.25
P(MS-P)	50 000[c)]	357	178	0.5[d)]
P(MS-αMeSty)	25 000[c)]	116	58	0.5[d)]

[a)] calculated concerning 28 mol-% acrylate
[b)] before ultrasonic degradation (UD) M_W was ca. 14×10^6 g/mol
[c)] is correlated to the anhydride
[d)] approximately the half of the functional groups of the copolymers are available as salt at pH ≈ 6

Preparation of Polyelectrolyte Complexes

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, $C_{PD} = 1.62\,g/l$, $C_{NaPSS} = 2.06\,g/l$, $C_{PR2540} = 1\,g/l$, $C_{P(MS-\alpha MeSty)} = 2.2\,g/l$ and $C_{P(MS-P)} = 1.4\,g/l$ in Millipore water. Concerning the charge contents all PEL solutions were characterized by PEL titration carried out by means of a PCD 02 particle charge detector (Mütek GmbH, Germany).

The initial concentration of polycation solution (C_0^{PC}) was kept constant for all prepared PECs within a complex series, while the amount of anionic charges corresponds to the desired n_-/n_+-ratio. n_-/n_+ is the calculated ratio of charges. Under continuous stirring one PEL solution was added to the used starting PEL solution with a flow rate of 0.2 l/h. In the experiments PC solutions as well as PA solutions were used as starting solution. Detailed information is given in Table 2. It should be mentioned that C_0^{PC} is the concentration of the polycation solution at the beginning of complex fomation ($v_0^{PC} = 50\,ml$). At the end of the complex formation the volume of the formed complex dispersion is twice the volume of the separate initial solutions. The polymer concentration C_P is relatd to the end state of the complex formation. Hence the value of C_P can be lower than C_0^{PC} in spite of that the amount of polycation as well as the amount of polyanion is included in C_P.

Table 2. Concentrations and molar ratios of formed PECs

PEC system		M_W^{PC} g/mol	M_W^{PA} g/mol	C_0^{PC} mmol/l	n_-/n_+	C_P mmol/l
PD/NaPSS-I	a	5 000	10^6	4	0.4-2.0	2.8-6.0
PD/NaPSS-II	a b	290 000	70 000	4	0.4-2.0	2.8-6.0
PD/NaPSS-III	a b	5 000	70 000	4	0.4-2.0	2.8-6.0
PD/NaPSS-IV	a b	5 000	70 000	1	0.4-2.0	0.7-1.5
PD/PR2540^{UD}	a b	290 000	500 000	1.5	0.4-2.0	1.0-2.2
PD/P(MS-P)	a b	290 000	50 000	1.5	0.5-1.2	1.125-1.65
PD/P(MS-αMeSty)	a b	290 000	25 000	1.5	0.5-1.2	1.125-1.65

a...starting solution: PC (polycation)
b...starting solution: PA (polyanion)

After complete addition the mixtures were still stirred for 10 minutes. Two hours later and after a storage time of 2 days the PEC dispersions were characterized.

Characterization of the Complex Dispersions

Measurements of optical density (OD) were used to characterize the stability of the PECs. The values of OD were obtained with a Lambda 900 UV/VIS/NIR spectrometer (Perkin-Elmer, UK). All measurements were made at $\lambda = 500$ nm. Deionized water was used as reference.

Dynamic light scattering measurements were performed by Zetasizer 3000 (Malvern Instruments, UK). 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°. The analysis of the autocorrelation function $g^{(2)}(\tau)$ was done automatically to yield the mean diffusion coefficient D_T. Thereafter z-average hydrodynamic diameter d_h of PEC particles was calculated by the Stokes-Einstein equation.

To get information about size distribution of PEC particles the polydispersity index (PI) was also included in the interpretation. PI is defined as

$$PI = \frac{2c}{b^2} \qquad (1)$$

where b and c are the coefficients of an infinite series in powers of the delay time as which the logarithm of the autocorrelation function can be expressed. This is a dimensionless measure of the broadness of the distribution.

In addition all PECs were characterized by PEL titration (PCD 02, Mütek GmbH, Germany) in order to determine the isoelectric points $(n_-/n_+)_{IP}$ within a complex series.

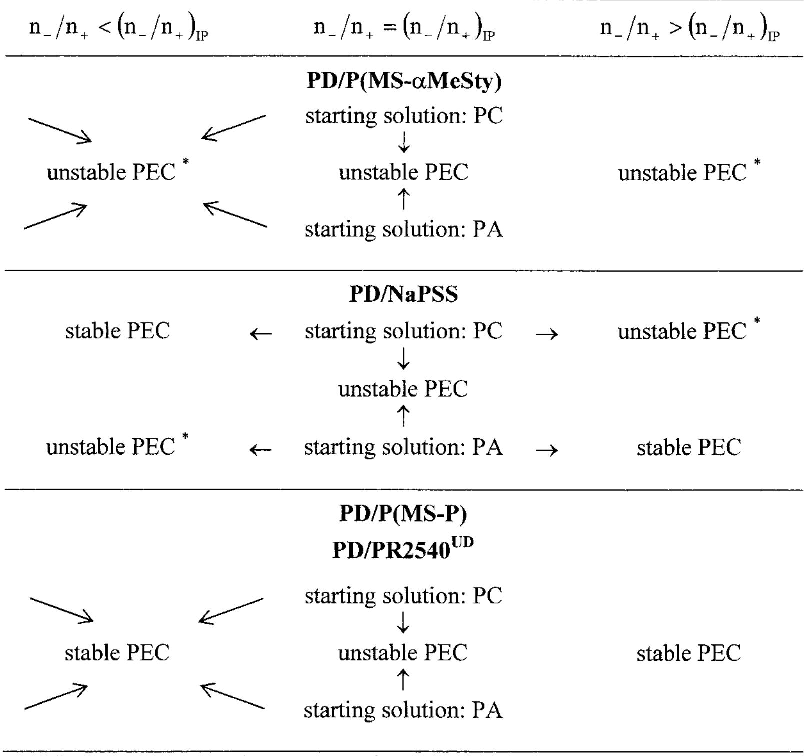
Discussion

All investigated PECs were characterized by their charge excess. The determined isoelectric points of the PEC series are in the range of $0.85 \leq (n_-/n_+)_{IP} \leq 0.95$. The difference to $n_-/n_+ = (n_-/n_+)_{IP} = 1$ can be explained by the adsorption of the PC at the reaction vessel wall. We used glass vessels in order to observe the PEC formation visual. At the isoelectric point complete precipitation of all these formed PECs is observed. In Scheme 1 we summarize the general observations and in the next part we will discuss them in conjunction with the turbidity (OD_{500}).

At first let us look for the system PD/P(MS-αMeSty). In spite of low polymer concentrations ($C_0^{PC} = 1.5\,\mathrm{mmol/l}$) non of the complexes within the series is absolute stable. Also at molar mixing ratios of charges, which guarantees a high charge excess, we found partial flocculation of the PECs. That means that precipitation occurs besides the formation of turbid supernatants and stable dispersions, respectively, which were stable for few weeks.

For the next PEC system PD/NaPSS stable complexes were found as long as the starting solution is in excess, independent if PC or PA is the starting solution, independent on the initial polymer concentration of the PC C_0^{PC} and independent on the chain length L of the employed PELs. If the starting solution is deficient at the end of complex formation, that means that we exceed the isoelectric point $(n_-/n_+)_{IP}$ during complex formation, partial precipitation is observed and the supernatants form dispersions as in the case of PD/P(MS-αMeSty) mentioned above.

Scheme 1. Stability of formed PECs



* Additional to flocculation the supernatants form dispersions.

At the higher polymer concentrations the stability/instability is reflected by the values of turbidity (OD_{500}) in some degree as expected. But for the interpretation of the OD_{500} it should be taken into consideration, that the optical density is influenced by different parameters of the light scattered complex particles such as shape, number, size and polydispersity.

Figure 1a and b show the turbidity of the PEC system PD/NaPSS at $C_0^{PC} = 4\,\text{mmol/l}$ in dependence on the molar mixing ratio of the charges n_-/n_+ and the chain length L of the PELs. Moreover the starting solution was varied. In figure 1a PA was added to PC and the order of addition was changed in figure 1b.

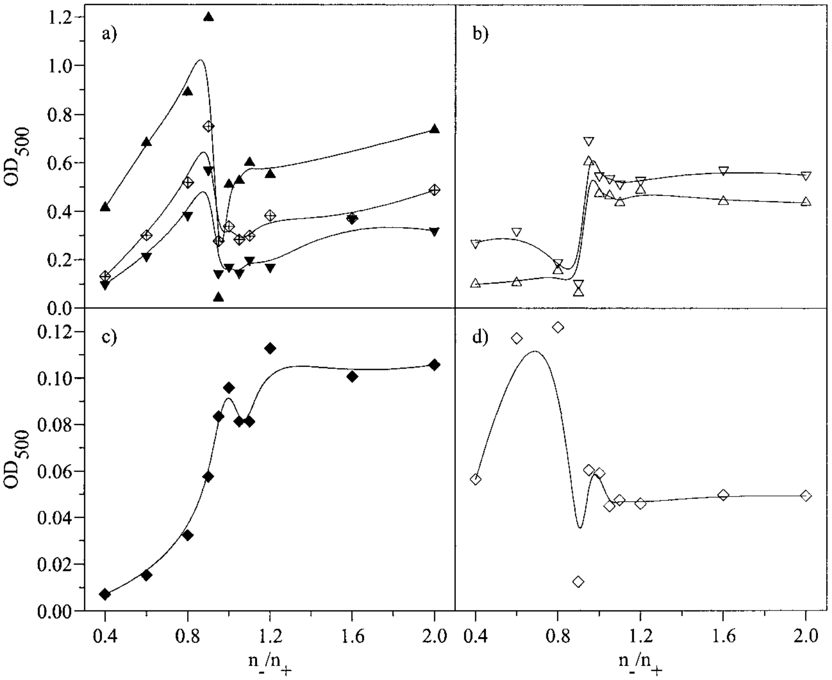


Figure 1. Optical density (OD_{500}) of PD/NaPSS complexes as a function of the molar charge ratio n_-/n_+; a) PC is starting solution, $C_0^{PC} = 4\,\text{mmol/l}$, ◈ = PD/NaPSS-Ia, ▲ = PD/NaPSS-IIa, ▼ = PD/NaPSS-IIIa; b) PA is starting solution, $C_0^{PC} = 4\,\text{mmol/l}$, △ = PD/NaPSS-IIb, ▽ = PD/NaPSS-IIIb; c) PC is starting solution, $C_0^{PC} = 1\,\text{mmol/l}$, ◆ = PD/NaPSS-IVa; d) PA is starting solution, $C_0^{PC} = 1\,\text{mmol/l}$, ◇ = PD/NaPSS-IVb.

As presented in figure 1a the optical density increased in the range of $n_-/n_+ < (n_-/n_+)_{IP}$ with increasing n_-/n_+ for all the stable complexes. Near the isoelectric point a maximum is reached. Beyond the isoelectric point we found partial flocculation of the formed PECs. The OD_{500}-values of these dispersions are lower than for complete stable PECs normally. In our case the values are of the same magnitude as the OD_{500}-values for the stable complexes with $n_-/n_+ << (n_-/n_+)_{IP}$ of the same complex series because the polymer concentration C_P increases within the complex series. With increasing of n_-/n_+ in the range of $n_-/n_+ > (n_-/n_+)_{IP}$ the turbidity only slightly increases in contrast to the range of $n_-/n_+ < (n_-/n_+)_{IP}$.

If we compare complexes with the same n_-/n_+-ratio we could see that the turbidity rises with increasing chain length of the employed PELs. The PEL used as starting solution (PC) has a stronger effect on the magnitude of the turbidity as the added component (PA).

The behavior of the turbidity of the PD/NaPSS PECs at $C_0^{PC} = 4\,\mathrm{mmol/l}$ with the polyanion as starting solution is shown in Figure 1b. Here we have a clear difference of the OD_{500}-values between the complete stable PEC dispersions and supernatants of unstable PEC. We did not found a pronounced maximum near $(n_-/n_+)_{IP}$.

The complexes of the series PD/NaPSS-IV presented in Figure 1c and d were prepared at $C_0^{PC} = 1\,\mathrm{mmol/l}$. Hence the turbidity of the PECs is essentially lower than the turbidity at higher polymer concentrations. Surprisingly the OD_{500}-values of the supernatants of unstable PECs with $n_-/n_+ \neq (n_-/n_+)_{IP}$ are distinctly higher than the values of the stable PECs in most cases. This cannot be explained in each case by the increase of C_P within the complex series. But the OD_{500}-values increase over time slowly for the same n_-/n_+ in contrast to the stable PECs, which is admittedly not shown in the Figure. This behavior indicates aggregation and consequently instability.

The next two PEC systems, PD/P(MS-P) and PD/PR2540^{UD}, form at $C_0^{PC} = 1.5\,\mathrm{mmol/l}$ stable PECs in the ranges where the starting solution is in excess as well as in deficient. Only at $n_-/n_+ = (n_-/n_+)_{IP}$ complete unstable PECs are observed because of the absence of charge excess.

As long as the starting solution is in excess OD_{500}-values are approximately constant and in a range of magnitude as stable PD/NaPSS PECs at $C_0^{PC} = 1\,\mathrm{mmol/l}$ as seen in Figure 2. Only near the isoelectric point a raising is observed. If the isoelectric point is exceeded during complex formation a pronounced increase of the OD_{500}-values take place within a complex series. This increase correlates with particle size measurements which we will discuss later.

It should be noticed that the OD_{500}-values decrease with an increase of the charge excess if isoelectric point is exceeded during complex formation, that means with decrease of n_-/n_+ for the used PC in excess and with increase of n_-/n_+ for the employed PAs in excess. Whereas the decrease of the turbidity is pronounced for the increased excess of the PC as for the used PAs which could be an effect of the polymer concentration C_P. The polymer concentration increases with n_-/n_+ within a complex series.

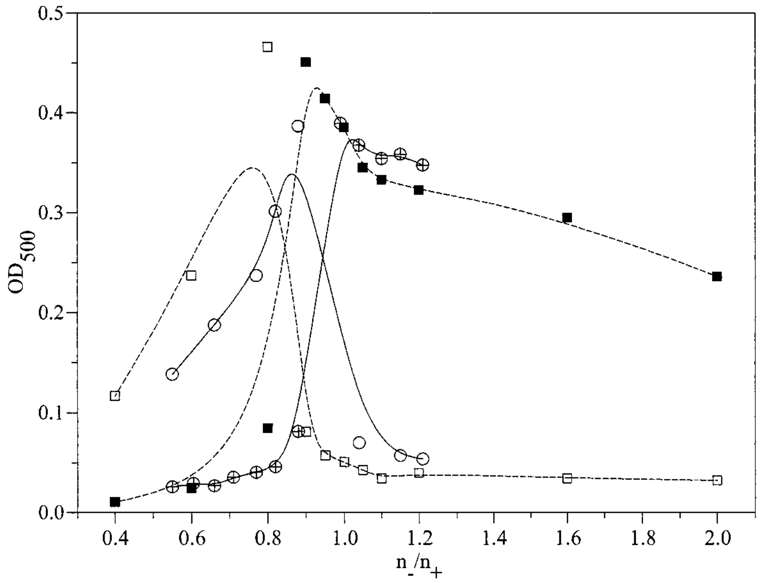


Figure 2. Optical density (OD_{500}) of the PEC systems which were stable at all n_-/n_+-ratios (except PECs at $(n_-/n_+)_{IP}$) as a function of the molar charge ratio n_-/n_+; ■ = PD/PR2540^{UD}-a; □ = PD/PR2540^{UD}-b; ⊕ = PD/P(MS-P)-a; ○ = PD/P(MS-P)-b; $C_0^{PC} = 1.5\,\text{mmol/l}$ for PD/PR2540^{UD} and $C_0^{PC} = 1\,\text{mmol/l}$ for PD/P(MS-P).

If we compare the OD_{500}-values of complexes with the same n_-/n_+ und hence the same C_p in dependence of the starting solution so we found higher turbidity if the $(n_-/n_+)_{IP}$ is exceeded during complex formation.

In the next discussion part we will study the average hydrodynamic particle sizes d_h and their distributions of all formed stable PECs. Figure 3a and Figure 3b show the measured particle sizes of all stable PECs of PD/NaPSS, PD/P(MS-P) and PD/PR2540^{UD} systems in dependence on n_-/n_+, the polymer concentration C_P and the initial concentration of the PC C_0^{PC}, respectively, and in dependence on the PEL chain length L. In order to interpret the value d_h better we also take into account in our analyses the so-called polydispersity index PI, presented in Figure 3c and Figure 3d, as a measure of the size distribution. From mathematical point of view the PI describes the deviation between the determined autocorrelation function in photon correlation spectroscopy and the adjusted correlation function. In practice dispersions with PI-values between 0.03 and 0.06 are called as monodisperse. A narrow distribution is available at values between 0.1 and 0.2. If the polydispersity index is in the range of $0.25 \leq PI \leq 0.5$ the distribution is broad and at values above 0.5 the measured result is not analyzable and indicates a broad distribution of indefinite particle shapes.[20]

Let us look at the d_h-values of the stable PD/NaPSS PECs. The average hydrodynamic particle sizes d_h are approximately constant within a complex series independent on the molar charge ratio n_-/n_+. Above all it is found for PA as starting solution. If PC is the starting solution a very low increase is observed like for OD_{500} too. The influence of the chain length L of the used PELs on d_h is not fairly clear. The most significant effect of the measured average hydrodynamic size d_h has the initial concentration of PC C_0^{PC}. The d_h-values for PECs at $C_0^{PC} = 1\,\mathrm{mmol/l}$ are distinctly lower than that at $C_0^{PC} = 4\,\mathrm{mmol/l}$. The behavior of the accompanying PIs is analogous. Essentially by decreasing the initial concentration C_0^{PC} the PIs decreased also.

In the range of $n_-/n_+ < (n_-/n_+)_{IP}$, if PC is the starting solution, the PIs decreased within a complex series with increasing n_-/n_+ normally. If PA is the starting solution ($n_-/n_+ > (n_-/n_+)_{IP}$) the change of the PIs within a complex series is less pronounced. Only near $(n_-/n_+)_{IP}$ the PIs decreased more distinctly with decrease of n_-/n_+. However the PIs of all PD/NaPSS PECs are high.

A comparison of the d_h of the PEC systems which form stable PECs at all molar charge ratios n_-/n_+ within a complex series, except of PEC with $n_-/n_+ = (n_-/n_+)_{IP}$, is shown in Figure 3b and the belonging at PIs in Figure 3d.

For both systems, PD/PR2540^{UD} and PD/P(MS-P), we found distinct higher d_h-values (ca. 250 – 300 nm) if isoelectric point is exceeded during complex formation. It is the case in the range of $n_-/n_+ < (n_-/n_+)_{IP}$ if PA is starting solution and in the range of $n_-/n_+ > (n_-/n_+)_{IP}$ if PC is starting solution. Simultaneously we observe very low PIs of such complexes. They are all in the range of monodisperse dispersions.

In contrast to this the average particle size d_h of PECs formed without exceeding the isoelectric point are about 100 – 150 nm lower at the same n_-/n_+ and in the range of stable PD/NaPSS PECs for the same C_0^{PC} $(= 1\,\mathrm{mmol/l})$. In the range of starting solution excess the PIs of stable PD/NaPSS PECs decrease in direction to isoelectric point, that means for PC as starting solution with increase of n_-/n_+ and for PA as starting solution with decrease of n_-/n_+ up to $(n_-/n_+)_{IP}$.

Now we will give an explanation for the behavior of the average particle size d_h connected with polydispersity index PI. As long as the PEC formation stops if the starting solution is in excess the determined average particle size of the PEC particles and the PI belongs to it are definite by electrostatic interactions and kinetic. Because of the large size of the polyions in contrast to the small counterions, the polyions will react preferentially with the oppositely charged polyions in the neighborhood. So that bigger particles are formed initially beside smaller particles and hence a higher polydispersity is observed. The stabilization of the PEC particles is caused by the excess PEL. If n_-/n_+-ratio approaches $(n_-/n_+)_{IP}$ electrostatic interaction will decrease and hydrophobic interaction will increase. Hence the probability of aggregation of PEC particles formed before will rise and the number of smaller PEC aggregates will decrease. Lower PIs result even though a drastic change in average

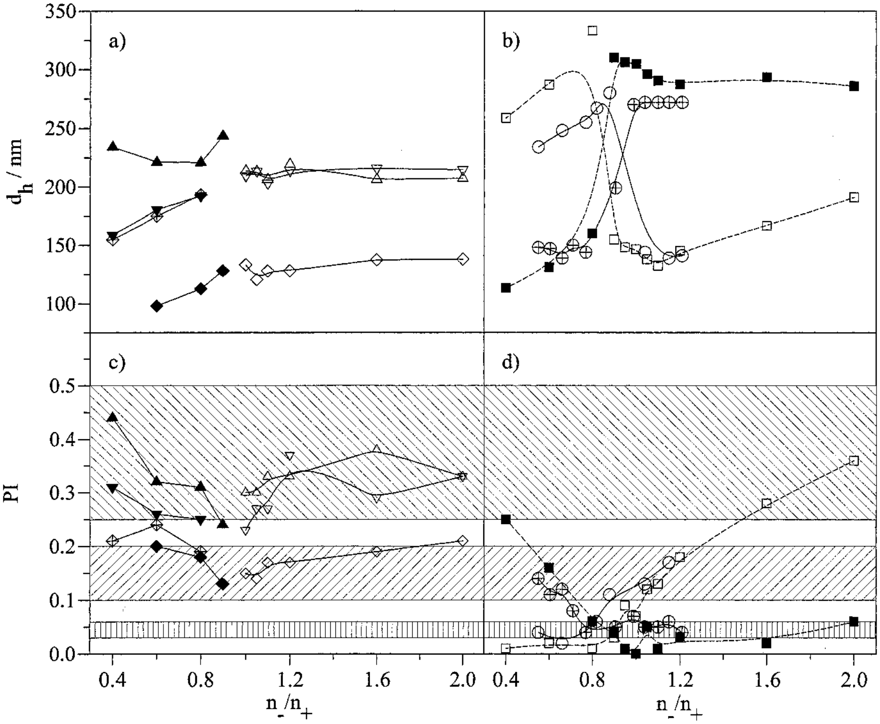


Figure 3. Average hydrodynamic particle size d_h and polydispersity index (PI) of the studied stable PEC dispersions in dependence of the molar charge ratio n_-/n_+; a) and c) PD/NaPSS systems, b) and d) PD/PR2540^{UD} and PD/P(MS-P) systems; the symbols are the same as in Figure 1 and Figure 3; the marked fields for PI means \\\\\ broad distribution, ///// narrow distribution and IIIII monodisperse distribution.[19]

hydrodynamic particle size d_h is not observed. In this moment where $(n_-/n_+)_{IP}$ is exceeded during PEC formation and hence starting solution is deficient in the mixture the PEC aggregates formed earlier were stabilized by adsorption of the excess PEL again. A further aggregation is prevented. But caused by the formed shell of the excess PEL onto the surface of the PEC aggregates formed before we determine a distinct higher average hydrodynamic particle size d_h and no change of PI.

The ability of PEC systems to form stable PECs is closely connected with hydrophobic interactions. If hydrophobic interactions play a dominant role a tendency to instability results. We studied two PEC systems (PD/P(MS-αMeSty) and PD/NaPSS) in which one of the used PELs contains a π-system. This π-system causes stronger hydrophobic interactions which means a stronger addiction to aggregation. But as in the case of NaPSS a functional group is bound at the π-system hydrophobic interactions play a dominant role only beyond the isoelectric point (and at $(n_-/n_+)_{IP}$) caused by the structure of the formed PECs. In contrast to this partially flocculation is found for all n_-/n_+-ratios in the case of P(MS-αMeSty) ($n_-/n_+ = (n_-/n_+)_{IP}$: complete flocculation) because of the absence of functional groups at the π-system. We observed no distinct effect on complex formation by weak or strong functional groups of the employed PELs.

Conclusion

Dynamic light scattering and turbidity have been used to study the effects of polyanion chain length L, initial polymer concentration of the polycation C_0^{PC}, molar charge ratio n_-/n_+, mixing conditions and chemical structure of the used polyanions on the stability of PEC dispersions and on properties of formed PEC particles such as average hydrodynamic particle size d_h and polydispersity index PI as a measure of particle size distribution.

It has been found that PEC systems which include a PA with a π-system (phenyl-) at the polymer chain (PD/P(MS-αMeSty) and PD/NaPSS) show a higher tendency towards instability. PD/P(MS-αMeSty) are not able to form complete stable PEC dispersions. The system PD/NaPSS forms stable PEC dispersions as long as the starting solution is in excess, that means stable PECs for PC as starting solution as long as $n_-/n_+ < (n_-/n_+)_{IP}$. If PA is employed as starting solution PECs with $n_-/n_+ > (n_-/n_+)_{IP}$ are stable. The determined average hydrodynamic particle sizes of the stable PD/NaPSS PECs are all in the range of about 150 – 250 nm if $C_0^{PC} = 4\,\mathrm{mmol/l}$. It seems that the average d_h-value is determined by the chain length L of PEL which is in excess in the mixture. All of them have a very high polydispersity indices (PIs). If C_0^{PC} is reduced to 1 mmol/l the d_h-values are lower than 150 nm. Simultaneously the determined PI decreased also to the range of narrow distribution.

In contrast to the PEC systems mentioned above two of the studied systems, (PD/P(MS-P) and PD/PR2540^{UD}), form stable dispersions even if the starting solution is deficient in the mixture. That means that during complex formation the isoelectric point is exceeded. It is remarkable that the d_h increases by about 80 – 125 nm in contrast to these PECs which were formed at the same n_-/n_+ but under the condition that the starting solution is in excess in the mixture. The PI values of all these dispersions are very low and in the range of monodisperse distributions, respectively.

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