Chapter 16

Light-Scattering Studies of Polyelectrolyte Complex Formation

Effect of Polymer Concentration

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Polyelectrolyte complex formation in diluted aqueous solutions was studied on the system Na-poly(styrenesulfonate)/poly(diallyl-dimethylammonium chloride), using static and dynamic light scattering. By variation of the polymer concentration of the component solutions the level of aggregation could be changed and polyelectrolyte complex homologues could be prepared, offering the possibility of a comprehensive structural characterization. The polyelectrolyte complex investigated exists as a highly polydisperse system of compact and nearly spherical particles.

Polyelectrolyte complex (PEC) formation represents an interesting principle of structure formation with extremely high variability, due to the great variety of polyelectrolyte components and the influence of the solvent and the external preparation conditions. In practice polyelectrolyte complexes are used, e.g. as membranes with special separation properties, coatings, flocculants or for microencapsulation (1), in more or less concentrated systems. Under such conditions it is difficult to assess the influence of the different parameters which control the structure of PEC. The investigation of PEC formation in highly diluted aqueous solutions offers the possibility to study these effects by methods, normally used in polymer characterization (1-5). While the characteristics of the polyelectrolyte components (molecular weight, nature of ionic groups, charge density, branching) and the solvent (ionic strength, pH-value) primarily determine the internal structure of the PEC particles, the level of aggregation is dominantly controlled by the polymer concentration of the component solutions (1).

Especially scattering methods seem to be a powerful tool to obtain comprehensive information about the structure of PEC particles. Since the PEC particles in highly diluted solutions are stable for some hours, but change their structure in long times
(6), small-angle X-ray and neutron scattering experiments are difficult to realize. Therefore, light scattering should be the appropriate method, particularly the combination of static and dynamic light scattering. However, light scattering data suffer from the disadvantage that only a limited section of the scattering curves can be measured, leading to a loss of structural information for small particles and problems in a reliable extrapolation to the scattering angle zero for large ones (7). The handicap may be overcome, if we are successful in preparation of PEC homologues, which would additionally allow to determine the mass-size relation. Main objectives of this paper are the preparation of such PEC homologues and the determination of the structure type, structural parameters of the particles as well as the polydispersity of the systems investigated by light scattering experiments. The effectiveness of such investigations is demonstrated on the system Na-poly(styrenesulfonate) (NaPSS)/poly(diallyl-dimethyl-ammonium chloride) (PDADMAC).

Experimental

Materials. The samples employed were prepared under laboratory conditions, carefully purified by repeated dialysis, freeze-dried and characterized by osmometry and light scattering. The molecular weight $M_w$, polydispersity $M_w/M_n$ and the refractive index increment $dn/dc$ in water as well as the molecular weights $m_0$ of the monomer units are given in Table I.

All investigations were carried out in pure water, highly clarified by ion exchange and filtration.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$ g/mol</th>
<th>$M_w/M_n$</th>
<th>$dn/dc$ cm$^3$/g$^{-1}$</th>
<th>$m_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na-PSS</td>
<td>60 000</td>
<td>1.1</td>
<td>0.192</td>
<td>206</td>
</tr>
<tr>
<td>PDADMAC</td>
<td>140 000</td>
<td>2.0</td>
<td>0.193</td>
<td>161.5</td>
</tr>
</tbody>
</table>

Solvent: saltfree water, purified by repeated ion exchange and filtration

Static light scattering. For static light scattering a Sofica 42 000 (Wippler and Scheibling, Strasbourg, France) was used, which was equipped with a 5mW He-Ne-laser as light source and a PC for data record. The accuracy of measurements was better than 1%. PEC formations were carried out directly in the scattering cell by mixing the polyelectrolyte component solutions under gentle stirring.

8 mL of the polycation solutions were put into the scattering cell and the polyanion solutions of twice of the concentration of the polycation solutions were added slowly via an immersed capillary. The scattering intensity at fixed angle ($\theta=45^\circ$) was continuously registered. Solutions were made dust-free by filtration through 0.2 $\mu$m membrane filters. The success of filtration must be checked carefully, because
extremely low amounts of remaining aggregates or gel particles may influence the PEC formation to a great extent, leading to bad reproducibility. To include a large size range of the PEC particles we studied the complex formation in a concentration range of the polycation solutions \( c_c \) between \( 1 \cdot 10^{-5} \) and \( 1 \cdot 10^{-3} \) g mL\(^{-1}\) in seven steps:

\[
1 \cdot c_c = 1 \cdot 10^{-5}, \quad 2 \cdot 2 \cdot 10^{-5}, \quad 3 \cdot 5 \cdot 10^{-5}, \quad 4 \cdot 1 \cdot 10^{-4}, \quad 5 \cdot 2 \cdot 10^{-4}, \quad 6 \cdot 5 \cdot 10^{-4}, \quad 7 \cdot 1 \cdot 10^{-3} \text{ g mL}^{-1}.
\]

In all systems a clearly pronounced flocculation occurred at a composition, corresponding to a 1:1 charge stoichiometry. For the concentration \( c_c = 1 \cdot 10^{-4} \) g mL\(^{-1}\) the dosage was interrupted in steps of ten percent of conversion \( \chi \) and the complete angular dependence of the scattering intensity was measured. From all PEC solutions of different concentrations, given above, a sample was taken at a conversion of 50% and studied by static and dynamic light scattering. For higher concentrations the scattering intensity is very large, suggesting effects of multiple scattering. However, it could be proved that the systems can be diluted without disturbances of the PEC particles. Therefore the scattering intensity could be adjusted by subsequent dilution to an appropriate level.

**Dynamic light scattering.** Dynamic light scattering measurements were carried out with the instrument SIMULTAN (ALV, Langen; Germany), equipped with the correlator 3 000. As light source a 140 mW YAG Laser DPY 325c (Adlas GmbH, Luebeck, Germany), \( \lambda_0 = 532 \) nm, was used. All measurements were performed in linear sampling time mode. The correlation functions were measured in steps of 10° in the range between 30° and 150°.

**Data Analysis**

**Static light scattering.** For quantitative analysis of static light scattering the concentration and the refractive index increment of the PEC particles must be known. We calculated the concentration of the PEC under the assumption of a 1:1 stoichiometry, neglecting the contribution of the low molecular counterions. As refractive index increment the identical value of the two components was used.

For particle radii smaller than 50 nm the scattering curves can be analyzed by a Guinier plot, which allows a reliable extrapolation to the scattering angle zero and yields the weight average molecular mass \( M_w \) and the \( z \)-average of the square of the radius of gyration \( <S^2> \). However, no conclusions can be drawn from the scattering curves about the polydispersity of the particle systems and also no information about the structure type, the average polymer packing density and an unadulterated mass-size relation can be obtained. With increasing particle size the scattering curves become more instructive, but reveal a stronger curvature in the small-angle range, impeding a reliable extrapolation to the scattering angle zero and the determination of the correct structural parameters. Therefore, we used an algorithm based on a comparison of the experimental scattering curves with theoretically calculated ones for various basic structure types (7,8).

For highly diluted particle systems the Rayleigh ratio of the scattering intensity \( R(q) \) is given by the simple expression (9):
where $M_w$ is the weight average molecular mass of the scattering particle, $K$ - a contrast factor, containing the optical parameters of the system, $c$ - the mass concentration in g mL$^{-1}$ and $P(q)$ is the intraparticulate scattering function, $q = 4 \pi \lambda \sin(\theta/2)$, $\lambda$ - wavelength in the medium, $\theta$ - scattering angle between the incident and the scattered beam.

Describing the polydispersity of the system by a continuous normalized mass distribution function $p_w(M)$, we obtain:

$$M_w = \int_{0}^{\infty} M \, p_w(M) \, dM$$  \hspace{1cm} (2)

and

$$P(q) = \frac{1}{M_w} \int_{0}^{\infty} P(q;M) \, M \, p_w(M) \, dM$$  \hspace{1cm} (3)

In the framework of the Rayleigh-Debye-approximation (RDA) the relation

$$P(q) = 1 - \frac{1}{3} <S^2\tau> q^2 + ...$$  \hspace{1cm} (4)

was derived, whatever the shape and structure of the particles. However, $P(q)$ is known for a variety of structure types and in the RDA the argument of the scattering function is the product of the size parameter and $q$. Therefore, a double logarithmic plot $\log R(q)/(Kc)$ versus $\log q$ yields a scaled representation, where a change of $M_w$ corresponds to a shift along the ordinate and a change of the size parameter to a shift along the abscissa. Model calculations were carried out for spheres, Gaussian coils, branched chains and rods (8), assuming a logarithmic as well as a Schulz-Zimm distribution for $p_w(M)$. Results obtained show that the influence of the type of distribution function on the shape of the scattering function may be neglected, but the structure type can be discussed, if an appropriate section of the scattering curve is known. In the following we restrict the considerations to the model of polydisperse systems of homogeneous spheres, which has been proved quite well in describing the scattering curves of the PEC solutions investigated. As distribution function we used the special logarithmic distribution of radii:

$$p_w(a) = \frac{a^{-3n} \exp[-(\ln a - \ln a_w)^2 / 2 \, \sigma^2]}{\sqrt{2\pi} \, \sigma \, a_w^{-3n} \exp[9 \, \sigma^2/8]}$$  \hspace{1cm} (5)

For the distribution function (equation 5) the following integration rule is valid:
\[ \int_0^\theta a^i p_w(a) \, da = a_m^i \exp[(-5i + i^2 + 2i) \sigma^2/2] \]  

(6)

The parameter \( a_m \) is then related to \( M_w \) by the expression

\[ M_w = \frac{4\pi}{3} \rho N_A a_m^3 \]  

(7)

\( <S^2>_z^{1/2} \) is given by:

\[ <S^2>_z^{1/2} = \left( \frac{3}{5} \right)^{1/2} a_m \sigma e^{2 \sigma^2} \]  

(8)

where \( N_A \) is the Avogadro's number and \( \rho \) is the average polymer density in the particles. The parameter \( \sigma \) corresponds for low polydispersities to the relative standard deviation. For the scattering function of spheres following equation was derived:

\[ P(q) = [3 \sin aq - aq \cos aq] a^3 q^3 ]^2 \]  

(9)

The scattering curves of polydisperse systems of spheres are given in Figure 1a. With increasing polydispersity the curves become more flat, so that the polydispersity may be estimated by the assignment of an experimental scattering curve to the appropriate theoretical one, if a sufficient section is known. The dashed lines in Figure 1 mark the available range of typical light scattering experiments (30° ≤ \( \theta \) ≤ 150°, \( \lambda = 633 \text{ nm}, n = 1.333 \)) for \( a_m = 200 \text{ nm} \). However, it must be emphasized that the interpretation can not be unambiguous, because deviations from the spherical shape and internal density gradients are largely equivalent to an additional polydispersity.

**Dynamic light scattering.** Dynamic light scattering measurements yield the electric field correlation function \( g(q,t) \), which corresponds to the Fourier transform of the fluctuating number density of scattering particles. Considering the center of mass motion of a monodisperse system of particles, the simple expression is valid:

\[ g(q,t) = \exp[-\Gamma t] \]  

(10)

where \( \Gamma = D q^2 \), \( \Gamma \) is the decay constant or line width (reciprocal of decay time \( \tau \)) and \( D \) is the translational diffusion constant (for details see (10,11)). For a polydisperse system \( g(q,t) \) is given by an integral equation

\[ g(q,t) = \int_0^\infty G(q,\Gamma) \, e^{-\Gamma t} \, d\Gamma \]  

(11)
Figure 1. Scaled representation of the q-dependence of the static particle scattering factor $P(q)$ (a) and the apparent hydrodynamic radius $R_h(q)$ (b) in a double logarithmic plot ($a_m = 1 \mu m$, $q$ in $\mu m^{-1}$).
where \( G(q, \Gamma) \) is the normalized characteristic line width distribution. In principle \( G(q, \Gamma) \) can be calculated from equation (11) by an inverse Laplace transform, but the mathematical problem is ill-conditioned. A corresponding procedure was derived by Provencher (12), yielding \( G(q, \Gamma) \) and the moments \( m_i \) up to \( m_3 \) of \( G(q, \Gamma) \), where

\[
m_i = \int_0^\Gamma \Gamma^i G(q, \Gamma) \, d\Gamma
\]

(12)

To obtain the polydispersity in molecular weight of a particle system from \( G(q, \Gamma) \), the contribution of a particle must be weighted by its scattering intensity, leading to

\[
m_i = \frac{1}{M_w P(q)} \int_0^\infty M \, P(q, M) \, (q^2 \, D)^i \, p_w(M) \, dM
\]

(13)

For \( q \to 0 \) the first moment yields the \( z \)-average of the diffusion coefficient.

From each \( D \) value the hydrodynamic radius \( R_h \) can be calculated by the Einstein-Stokes-equation

\[
R_h = \frac{kT}{6\pi \eta D}
\]

(14)

where \( k \) is Boltzmann's constant, \( T \) is the absolute temperature and \( \eta \) is the viscosity of the solvent. For spheres the hydrodynamic radius is equal to the radius \( a \). Changing from the mass distribution function \( p_w(M) \) to the distribution of radii (equation 5), also the parameter of polydispersity \( \sigma \) can be calculated from the ratio of different moments.

We used for the inverse Laplace transform a version of the Provencher program, installed by ALV (Langen, Germany).

However, all correlation functions were also analyzed by a third order cumulant fit, corresponding to the expression:

\[
\ln g(q,t) = -\bar{\Gamma} \, t + \frac{\mu_2}{2} \, t^2 - \ldots
\]

(15)

where \( \bar{\Gamma} = m_1 \), \( \mu_2 = m_2 - m_1^2 \).

For systems of large particles (> 50 nm) and higher polydispersity the angular dependence of the apparent diffusion coefficient must be taken into account and an extrapolation to the scattering angle zero is necessary to determine \( D_\perp \) and the hydrodynamic radius \( R_h \). Assuming that no interparticle interactions and internal motions contribute to the angular dependence of the apparent diffusion coefficient, \( D_{\text{app}}(q) \) may be calculated by the equation:
\[
D_{app}(q) = \frac{\int D(M) P(q,M) M p_w(M) \, dM}{\int P(q,M) M p_w(M) \, dM}
\]

or expressed in radii:

\[
R_{h}^{app}(q) = \frac{\int a^3 P(aq) p_w(a) \, da}{\int a^2 P(aq) p_w(a) \, da}
\]

Using the logarithmic distribution (equation 5), we obtain:

\[
R_h(0) = a_m e^{\sigma^2}
\]

Corresponding to \( P(q) \) also \( R_h(q) \) can be calculated. The results obtained are given in Figure 1b in the scaled double logarithmic representation, showing the inverse behavior in comparison to the particle scattering function. While for monodisperse systems no angular dependence occurs, the curves decrease steeper with increasing polydispersity. Therefore, the combination of static and dynamic light scattering should provide a reliable information about the polydispersity of the systems investigated. Additionally, the polydispersity can be calculated by the inverse Laplace transform, if the structural model is known.

**Results and Discussion**

**Degree of conversion.** First we checked our previous findings (1) that for strong and highly charged polyelectrolytes the size and structure of PEC particles depend only slightly on the degree of conversion. The scattering curves of PEC solutions at a polycation concentration of \( c_c = 1 \cdot 10^{-4} \, \text{g mL}^{-1} \) are given in Figure 2 for a degree of conversion from 10 to nearly 100 % in steps of 10 %. All scattering curves are very similar and could be fitted quite well by polydisperse systems of spheres with \( \sigma = 0.6 \). The polydispersity obtained is very high and corresponds to a \( M_w/M_a \) - ratio of 25. Therefore it must be absolutely taken into account in the estimation of the average polymer density of the particles. The structural parameters, obtained by a quantitative analysis of the scattering curves are represented in Figure 3. With increasing conversion we find a decrease of the particle mass \( M_w \) and the size parameter \( a_m \), while the polymer density \( \rho \) increases slightly. The results confirm our previous findings (1) that the generation of new particles is the dominating process with increasing conversion and no further particle growth.
Figure 2. Scattering curves of the PEC NaPSS/PDADMAC in dependence on the degree of conversion \( (c_c = 1 \cdot 10^{-4} \text{ g cm}^{-3}) \)

Figure 3. Structural parameters of the PEC NaPSS/PDADMAC in dependence on the degree of conversion \( (c_c = 1 \cdot 10^{-4} \text{ g cm}^{-3}) \)
occurs. The decrease of the aggregation level may be explained by the diminishing concentration of free polycations in the system with increasing conversion.

Concentration dependence. Very interesting findings result from the investigation of the influence of polymer concentration on PEC formation. Figure 4 depicts the scattering curves obtained at different concentrations in a range of two orders of magnitude at a degree of conversion of 50%. Again all curves could be fitted quite well by the scattering functions of polydisperse systems of spheres with the \( \sigma \)-values given in Figure 4. It must be noticed here that no conclusions about the polydispersity could be drawn from the slight angular dependence of the curves 1 and 2. Therefore we analyzed these curves with \( \sigma \) suggested from the other curves. Figure 4 shows that the scattering curves become steeper with increasing polymer concentration, indicating the increase of the level of aggregation. This effect may be understood by the existence of two competitive processes of charge compensation, by conformational changes of the chains and by incorporation of other polyelectrolyte molecules, where the latter is favored in more concentrated systems. Figure 5 demonstrates that simple power laws were found for the concentration dependence of the particle mass and size, resulting in a mass-size-relation \( a_m \sim M^{1/3} \) and confirming the compact structure of the PEC particles (Figure 6). In the whole range of concentration we found a polymer density in the particles of \( \rho = 0.43 \pm 0.03 \text{ g mL}^{-1} \).

Since all scattering curves could be fitted by the same structural model, it should be expected that the superposition of the normalized experimental curves yield a common scattering curve in a wide range of the argument \( a_m q \). This is illustrated in an excellent manner by Figure 7. The composed scattering curve extends from the initial range up to the asymptotic one, which gives the expected \( q^{-4} \) dependence of spheres.

The findings confirm that for the PEC NaPSS/PDADMAC the objective to prepare PEC homologues could be realized, offering the possibility of reliable assessing of the structure type and determination of the structural parameters. The PEC solutions of different concentration levels were additionally studied by dynamic light scattering. Figure 8 shows the angular dependence of the apparent hydrodynamic radius, determined from the third order cumulant fit.

Therefore, an extrapolation to the scattering angle zero is absolutely necessary when conclusions about the structure type should be drawn via the ratio of the radius of gyration to the hydrodynamic one and again the polydispersity must be taken into account. Using the structural parameters, obtained by static light scattering, we calculated the angular dependence of \( R_g(q) \) corresponding to equation 17. The results are given as full lines in Figure 8. While for the curves 1 to 5 a sufficient agreement could be observed, remarkable deviations occur for the last two systems with the largest particles. The reason for this is not quite clear, but the calculations contain a lot of assumptions (structure type, distribution function, monomodality, no interparticular interactions). Moreover, the cumulant method is correct only for low polydispersities (10) and gives in our case reliable results with respect to the first cumulant, while the second cumulant reveals too low polydispersities.

Despite of the deviating shape of the experimental and theoretical \( R_g(q) \) curves,
Figure 4. Scattering curves of PEC systems NaPSS/PDADMAC at different polymer concentrations ($X = 50\%$)
Figure 5. Structural parameters $M_w$ and $a_m$ of PEC systems NaPSS/PDADMAC in dependence on the polycation concentration

Figure 6. $a_m - M_w$ - relation of NaPSS/PDADMAC - PEC "homologues"
Figure 7. Superposition of the normalized scattering curves of the NaPSS/PDADMAC - PEC solutions of different polymer concentrations x - experimental points, full line - scattering curve of polydisperse systems of spheres (σ = 0.6)

Figure 8. Angular dependence of the apparent hydrodynamic radius of NaPSS/PDADMAC - PEC solutions of different polymer concentrations symbols - experimental points, full lines - theoretical curves
Figure 9. Inverse Laplace transform of the correlation function of the PEC NaPSS/PDADMAC ($c_C = 1 \cdot 10^{-4}$ g cm$^{-3}$) at 50% conversion, scattering angle $\theta = 90^\circ$

they yield nearly the same $R_h(0)$-values, which correspond for all systems to a ratio of the radius of gyration to the hydrodynamic one of about 0.78, when the polydispersity is taken into account. This value is characteristic for spheres (13).

The correlation functions were partly analyzed by inverse Laplace transform too. A typical result is given in Figure 9, showing a broad distribution of the decay constant $\Gamma$ and also confirming that the logarithmic distribution function is a good approximation for the systems investigated. From the different moments of the distribution function $R_h(q)$ and $\sigma$ were calculated. $R_h(q)$ is in good agreement with the value obtained by the cumulant fit and also the polydispersity parameter $\sigma$ is nearly the same as it was determined by static light scattering. Normally, the $\sigma$-values must be extrapolated to the scattering angle zero, but this can be neglected due to the slight angular dependence for the given example.

Conclusions

Static and dynamic light scattering investigations on PEC solutions of NaPSS / PDADMAC, prepared at different polymer concentrations of the component solutions, show that for this system PEC homologues could be obtained. This makes it possible to study the structure type in detail and to determine the structural parameters of the PEC particles in a reliable way. All results obtained are consistent and lead to the following picture:
The NaPSS/PDADMAC complex exists in diluted solutions as a highly polydisperse system of compact and nearly spherical particles.

The level of aggregation increases proportional to $c^*$, where $c$ is the polymer concentration of the component solutions. The exponent $\nu$ was found to be 1.7 and the size parameter $a_m$ is proportional to $M_w^{1/3}$ in the whole concentration range. The average polymer density of the PEC particles does not change with the level of aggregation.

The consideration of the high polydispersity is a necessary precondition to get correct structural information.

Although the experimental work was consciously restricted to one system, the methodical progress achieved by the combination of SLS and DLS opens the way for systematic and comprehensive studies of the influence of the molecular and solvent parameters as well as of the preparation conditions, on the structure of PECs.

Literature cited


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