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Formation of Soft Nanoparticles via Polyelectrolyte Complexation: A Viscometric Study

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Résumé — Formation de nanoparticules molles par complexation de polyelectrolytes : une étude viscosimétrique — Cet article décrit la formation de nanoparticules par complexation de polyelectrolytes de charge opposée. Le système est constitué d’un polyanion fort (PolyStyrene Sulfonate, PSS) et d’un polycation faible (Hydrochlorure de Poly(Allylamine), PAH) en large excès. Les nanoparticules ont été obtenues en incorporant progressivement une solution de PSS dans une solution de PAH sous agitation. Les Polyelectrolytes Complexés (PEC) ont été caractérisés par viscosimétrie, diffusion dynamique de la lumière, zéttamétrie et turbidimétrie. Les suspensions de PEC ont été centrifugées et après avoir mesuré la viscosité du surnageant, il a été possible d’estimer la concentration du polycation libre et le pourcentage de polycation complexé. Nous avons aussi mesuré la viscosité relative des suspensions; la fraction volumique des particules a pu être estimée en faisant l’hypothèse que la contribution des particules et du polycation en excès sont indépendantes. Nous avons pu établir l’évolution de la stœchiométrie des PEC et de leur fraction volumique en fonction du ratio PAH/PSS dans le mélange initial et du pH. Nos résultats montrent que l’accessibilité des charges (conformation des chaines) détermine à la fois la stœchiométrie et le niveau de compaction des complexes.

Abstract — Formation of Soft Nanoparticles via Polyelectrolyte Complexation: A Viscometric Study — This paper describes the formation of soft nanoparticles resulting from electrostatically driven complexation of oppositely charged polyelectrolytes. The system was composed of a strong polyanion (PolyStyrene Sulfonate, PSS) and a weak polycation (Poly(Allylamine) Hydrochloride, PAH) in large excess. Soft nanoparticles were obtained by pouring a PSS solution into a PAH one under constant stirring. The Polyelectrolyte Complexes (PEC) were characterized through a viscometric study complemented by Dynamic Light Scattering (DLS), electrophoretic mobility and suspension turbidity measurements. PEC suspensions were centrifuged and by measuring the viscosity of the supernatant, we were able to estimate the free polycation concentration and hence the percentage of complexed polycation. We also measured the relative viscosity of the suspensions; from the estimated contribution of the PEC particles and of the polycation in excess, the average particle volume fraction was estimated. From all viscometric data, we could derive the evolution of the binding stoichiometry in PEC and of the effective particle volume fraction as a function of the mixing ratio (ratio of the cationic to anionic groups) and of the pH. Our results emphasize the importance of charge accessibility in controlling both the stoichiometry and packing density of the complexes.
INTRODUCTION

When solutions of two oppositely charged polymer chains are mixed, PolyElectrolyte Complexes (PEC) are formed spontaneously. They result from an electrostatic binding between oppositely charged chains, with counterions release (Michaels et al., 1965; Sukhorukov et al., 1998; Petrov et al., 2003; Dautzenberg and Kriz, 2003; Schatz et al., 2004; Gårdlund et al., 2007; Saether et al., 2008). PEC can be composed of natural and/or synthetic polyions, charged surfactants, etc. They are widely used in various fields such as water treatments, coatings, paper industry, drug delivery and gene therapy.

Two different types of polyelectrolyte complexes are usually obtained by appropriate choice of experimental conditions, i.e., water-soluble PEC forming stable, optically transparent solutions and water-insoluble PEC, which either precipitate in water or exist as homogeneous turbid colloid systems without phase separation. Water-soluble polyelectrolyte complexes are formed with polyelectrolytes having a weak charge density and large differences in molecular dimensions when they are mixed in non-stoichiometric ratios (Dautzenberg and Karibyants, 1999; Kabanov and Zezin, 1984). Alternatively, polyions having a high charge density and/or similar high molar masses lead to insoluble and highly aggregated complexes, according to the scrambled-egg model, by the incorporation of several polyelectrolyte chains (Dautzenberg et al., 1996; Thünemann et al., 2004). Colloidal dispersions in the submicrometer range can be obtained by polyelectrolyte complexation, provided polymer concentrations remain low.

The aggregates of PEC formed in aqueous solutions upon mixing solutions of polycations and polyanions are usually amorphous in structure and do not reveal any order in spatial disposition of polymeric chains. Two decades ago, a new type of PEC systems was developed in which a regularity of spatial arrangement of polycations and polyanions was achieved at least in one direction. An alternative Layer-by-Layer (LbL) technology of sequential deposition of oppositely charged polyelectrolytes onto flat macrosubstrates, developed by Decher et al. (1992), has resulted in a burst of studies on the designing, structure, and properties of multilayered polyelectrolyte films (Hammond, 1999; Bharadwaj et al., 2006) which can be considered as a special kind of PEC with ordered architecture.

The formation of PEC raises many questions regarding the impact of the primary polyelectrolyte properties on the average binding stoichiometry and packing density. Depending on the molar mixing ratio, acidity/basicity, chain length or accessibility of the charged centre and chain flexibility of the polyelectrolytes, stoichiometric as well as non-stoichiometric PEC can be obtained (Ström et al., 1985; Michaels and Miekka, 1961; Buchhammer et al., 2003; Pergushov et al., 1999; Ström and Stenius, 1981; Zhang and Huang, 2000; Brand and Dautzenberg, 1997; Reihs et al., 2003; Thünemann et al., 2000; Dautzenberg, 1997; Pogodina and Tsvetkov, 1997; Zintchenko et al., 2002). Chain conformation in polyelectrolytes is strongly dependent on both the intensity and spatial extent of the repulsive electrostatic force between neighboring segments. For instance, chains adopt an elongated conformation if the charge density is rather elevated and/or the ionic strength is low (Dobrynin and Rubinstein, 2005). The stretched conformation actually enhances charge accessibility for electrostatic binding with chains of opposite charge. As a result, the obtained PEC may exhibit large packing densities (Kudlay et al., 2004). Conversely, at low charge density and/or high ionic strength, a coiled conformation is favored and, because of the steric hindrance, charge accessibility is considerably reduced resulting in lower PEC packing densities. Of course, the solution conditions during PEC formation (mainly the ionic strength and the pH value) and the preparation method (stirring intensity, order of mixing, one shot or progressive incorporation) used are very important determinants of the physicochemical properties of the PEC.

To contribute to a better understanding of the mechanism of PEC formation, particularly of the influence of charge density on PEC formation, we studied in the present work the structural changes during complex formation between Poly(StyreneSulfonate) (PSS) and Poly(Allylamine) Hydrochloride (PAH). Following the pioneering work of Michaels and Miekka (1961) and Brand and Dautzenberg (1997), we explored the viscosity behavior of PEC as a function of the polycation/polyanion molar ratio. Under the experimental conditions that were probed, PAH was always in excess.

The viscosity data were analyzed in conjunction with nanoparticle size, electrophoretic mobility and turbidity measurements. Particles were obtained by mixing the two oppositely charged polyelectrolyte solutions under vigorous stirring. We measured both the overall viscosity of the PEC suspensions and that of the supernatant phase containing PAH in excess (collected after centrifugation). From the viscosity data, we were able to characterize the binding stoichiometry, i.e. the polyanion/polycation molecular ratio within the soft particles and to derive generic rules concerning the complexation process. The charge density in PAH chains was pH-dependent. The experiments were carried out at two different pH values, corresponding to two distinct situations in terms of charge accessibility.
1 MATERIALS AND METHODS

1.1 Materials

The polyanion used is Sodium Poly(styrene sulfonate), with Mw = 70 000 g.mol⁻¹, referred to as PSS₇₀k, with a sulfonation degree equal to x = 0.51; the polycation is Poly(allylamine Hydrochloride), Mw = 70 000 g.mol⁻¹, referred to as PAH₇₀k (Fig. 1). Being a strong polyeon, PSS is fully dissociated whatever the pH from 1 to 14 (Petrov et al., 2003). Conversely, PAH is a weak polyelectrolyte whose charge density is pH-dependant: it is fully charged for pH < 5.5, and for higher pH values the protonation degree decreases and becomes almost zero at pH = 11 (Petrov et al., 2003). Both polyelectrolytes were purchased from Aldrich and were used without further purification. Sodium chloride, sodium hydroxide and hydrochloric acid were from VWR. MilliQ water was used for the preparation of all the solutions.

Polyelectrolyte solutions were prepared by adding the polymer in powder form in the aqueous phase at the desired pH under magnetic stirring until complete dissolution. Various PEC suspensions were then prepared at different weight concentration ratios (Cₚₛₛ/Cₚ₉₅ₐ₉), namely 0.12, 0.17, 0.2, 0.25 and 0.3. The pH of the polyelectrolyte solutions to be mixed was adjusted at either 5.5 or 10 using 0.1 M HCl or NaOH solutions (at 0.1 mol.L⁻¹ and 0.01 mol.L⁻¹ respectively) and the ionic strength was fixed by dissolving NaCl at 0.1 mol.L⁻¹. The polycation concentration, Cₚ₉₅ₐ₉, was kept constant at 1 wt% in all samples. For each ratio, PEC suspensions were obtained by drop wise addition of 25 mL of PSS₇₀k solution into 25 mL of PAH₇₀k solution (at 2 wt%) under intense magnetic stirring (1 800 rpm) with a cylindrical bar (length = 3 cm, diameter = 0.5 cm, vial diameter = 5 cm). The PSS solutions were introduced into the PAH ones at a rate of 1 mL/min. Magnetic stirring was maintained at least 15 h.

All solutions and suspensions were prepared at room temperature (22±1°C).

1.2 Particle Size

Particles size and polydispersity were measured at 25°C by Photon Correlation Spectroscopy (PCS) at a detection angle of 173°, using a Zetasizer Nano ZS (Malvern Instrument) equipped with a He-Ne laser. The particle size range accessible to the apparatus is 1 nm-5 µm. The detection angle of 173° is large enough to ensure that the signal is not pertubated neither by multiple scattering nor by the presence of dust particles. The hydrodynamic diameters were calculated from diffusion coefficients using Stokes-Einstein equation. Each value reported on the graphs was an average over 12 repetitions. All analyses were performed with the software supplied by the manufacturer. The PolyDisperity Index (PDI) was derived from the cumulant analysis method.

1.3 Electrophoretic Mobility

Electrophoretic mobility measurements were carried out at 25°C using a Zetasizer Nano ZS (same as for size measurements), after allowing the mixture to equilibrate for 10 min. This technique is based on the comparative phase analysis of the light scattered from the colloidal dispersion and a well-known frequency reference beam. The phase difference rate of change is related to the particle velocity and, therefore, to the electrophoretic mobility. Each value results from 15 measurements.

1.4 Turbidity

The two primary solutions containing PSS and PAH were optically transparent. However, after mixing them, the obtained suspensions became turbid because of the relatively large size of PEC (diameter comparable to visible light wavelength) and polymer compaction within the cores. We characterized the evolution of turbidity by measuring the transmittance, i.e. the percentage of transmitted light through the samples. Measurements were carried out using a Turbiscan MA2000® (Formulaction, France) at a wavelength of 880 nm.

1.5 Viscosity

The relative viscosity of polymer solutions and PEC suspensions was measured at 25°C using a high-precision Low Shear 30® viscometer with a Couette-Mooney geometry and a 500 µm gap (Contraves LS 30).

![Figure 1](attachment:image.png)

Figure 1

a) PSS and b) PAH molecules.
This viscometer allows measuring absolute viscosities of the order of 1 mPa.s with 5% precision. The error bars reported on the graphs are mean standard deviations from 3 repetitions.

2 RESULTS AND DISCUSSION

2.1 Nanoparticles Characterization

Figure 2 shows the evolution of the hydrodynamic diameter, \( D_H \), and of the electrophoretic mobility, \( \mu_E \), of the PEC particles as a function of the concentration ratio, \( R_c = C_{\text{PSS}}/C_{\text{PAH}} \), at constant PAH concentration of 1 wt% and in presence of NaCl 0.1 M. At pH = 10 (Fig. 2a), both \( D_H \) and \( \mu_E \) keep almost the same value (around 300 nm and \( 1.3 \times 10^{-8} \) m\(^2\)/V/s, respectively) whatever the concentration ratio \( R_c \). However, at pH = 5.5 (Fig. 2b), the behavior is markedly different: \( D_H \) is strongly increasing with \( R_c \), and \( \mu_E \) remains almost invariant (close to \( 2.3 \times 10^{-8} \) m\(^2\)/V/s).

As indicated above, to fabricate PEC particles, the amount of PAH remained constant (1 wt%) and each value of the concentration ratio \( R_c \) corresponds to a different PSS content. Since PAH macromolecules are in large excess, it is likely that only a fraction of them is involved in the complexation process. It can also be hypothesized that PSS is entirely used up and that the effective volume fraction of PEC particles increases with \( R_c \). This is reflected in Figure 3, where we report the evolution of the suspensions transmittance. Irrespective of the pH value, the transmittance tends to decrease with \( R_c \). At pH = 10, since \( D_H \) remains almost constant (Fig. 2a), complexation necessarily leads to an increasing number of PEC particles as \( R_c \) is augmented. However, at pH = 5.5, \( D_H \) undergoes a 3-fold increment (corresponding to a 3\(^3\) = 27-fold increment in volume) within the same \( R_c \) range. In this case, it is probable that the number of microgels either remains constant or even decreases with \( R_c \).

It is well known that the electrophoretic mobility of soft particles like microgels swollen by water depends strongly on their volume charge density (Ohshima, 1994; Sierra-Martin et al., 2006). In our case, it is not possible to state whether the electrophoretic mobility is mainly due to volume or surface charges. Interestingly, the zeta potential of the microgels is always positive, reflecting the excess of positive charges originating from cationic PAH segments. Assuming that the mobility is reflecting volume properties, the invariance of the electrophoretic mobility with \( R_c \) (at both pH values, Fig. 2) can only be interpreted considering that the bulk composition of the microgels, and especially the volume charge density is independent of the composition ratio \( R_c \). Alternatively, considering that the electrophoretic mobility is due to surface charges leads to the conclusion that the surface composition is independent of \( R_c \).

Our experiments were performed at a relatively high ionic strength. In general, polyelectrolyte chains adopt

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**Figure 2**

Evolution of PEC hydrodynamic diameter and of the electrophoretic mobility as a function of the concentration ratio, \( C_{\text{PSS}}/C_{\text{PAH}} \), at a) pH = 10 and b) pH = 5.5. In both cases, \( C_{\text{PAH}} = 1 \) wt% and \( C_{\text{NaCl}} = 0.1 \) mol.L\(^{-1}\).
less stiff and more coiled structures at large salt concentrations. The fact that the complexation process is pH-sensitive, as revealed by the data of Figure 2, suggests that the charge density along the PAH chains (which impacts chain conformation) is playing an important role despite the screening effect of the salt. Further studies as a function of the ionic strength (not described here) show that ionic strength needs to be much higher to screen completely the electrostatic interactions.

The formation of PEC particles results from a process involving ionic complexation, shear-induced rupturing and recombination of the polymeric aggregates. At pH = 5.5, the protonation degree of PAH segments is close to unity (full protonation) and so the polymeric chains adopt a stretched conformation to minimize the electrostatic repulsion between neighboring segments (Dobrynin and Rubinstein, 2005). Owing to this elongated structure, the cationic sites are relatively accessible for binding with PSS chains. The resulting aggregates are thus rather cohesive and the applied shear only produces a limited number of fragments. This would explain why at pH = 5.5, the average diameter of PEC is continuously increasing with PSS content (equivalently with $R_c$). At pH = 10, the protonation degree is considerably lowered, namely to 0.35 (Petrov et al., 2003). Thus, PAH chains adopt a coiled conformation, where only the outermost charges are available for binding. In this limit, the aggregates should be less cohesive than those formed at pH = 10, and consequently more prone to shear fragmentation. Because of the lability of the aggregates, the final size of PEC particles is mainly determined by the applied shear and is almost insensitive to the PSS content.

### 2.2 Viscosity of Polyelectrolytes Solutions

We measured the viscosity of the polyelectrolytes solutions of PAH and PSS separately, at the same concentration as in the mixture, and of the PEC suspensions. Measurements were carried out at shear rates ranging from 37 to 127 s$^{-1}$. For instance, Figure 4 shows the results corresponding to pH = 5.5 and $R_c = 0.3$. Within experimental uncertainty, it can be stated that both the primary polyelectrolytes solutions and the PEC suspension exhibit Newtonian behavior in the explored range of shear rates. This was expected for the polyelectrolytes solutions due to the moderate concentration (<1.3 wt%) and to the relatively low molecular weight (70 kDa). Similar results were obtained regardless of the pH and of the concentration ratio $R_c$.

The systems were characterized at 25°C in terms of their Newtonian viscosity, $\eta$, or of their relative viscosity, $\eta_r$, defined as $\eta_r = \eta/\eta_s$, $\eta_s$ being the solvent viscosity (0.99 mPa.s and 1.02 mPa.s at pH = 5.5 and 10, respectively). The values obtained at $R_c = 0.12$, 0.2 and 0.3 for pH = 10 and at $R_c = 0.3$ for pH = 5.5 are given in Table 1. We report the data relative to PEC suspensions and of solutions containing only one polyelectrolyte at the same concentration as in the mixture.

The viscosity of the PSS solutions at 0.3 wt% is only slightly larger than that of the solvent and is almost identical for the two pH values. This result is not surprising considering that sodium sulfonate is a strong polyelectrolyte which is fully dissociated whatever the pH.
Consequently, PSS does not undergo pH-induced conformational changes. Despite the data are not available, we expect the same statement to be valid over the whole explored PSS concentration range. On the contrary, the behavior of PAH solutions is pH-dependent as revealed by the viscosity of PAH solution which is larger in acidic conditions. At pH = 5.5, the higher ionization degree enhances the repulsive electrostatic interactions between neighboring segments which in turn favors chain stretching. The elongated state of the chains induces larger viscosities.

Figure 5 shows the evolution of the viscosity of PAH solutions with concentration at pH = 5.5 and pH = 10. The obtained plots were used as calibration curves for determining the amount of free PAH in the continuous phase of PEC suspensions. The viscosity evolution with concentration is well fitted in our low concentration regime by a 2-degree polynomial function.

### 2.3 Determination of the Amount of Complexed PAH

We used a “depletion” method based on viscosity measurements of the supernatant to determine the amount of complexed PAH. The depletion method relies on the measurement of the amount of remaining polyelectrolyte in the supernatant, leading to the amount of polymer effectively involved in the complex. For that purpose, PEC suspensions were submitted to intense centrifugation (17,300 g, where g is the earth gravity constant, for 1 h at 17°C, Sorvall RC5C centrifuge). At the end of this step, all the particles were present in the sediment at the bottom of the tube, as confirmed by light scattering/transmission measurements. Indeed, the supernatant was optically clear (transmittance close to 100%) and the average particle size measured by PCS was close to 25 nm, reflecting the presence of single primary (i.e. non complexed) polyelectrolyte coils. Considering the relative polyelectrolyte amounts in the blend (C\(_{PAH} >> C_{PSS}\)), it can be assumed that all PSS chains have been complexed and that the supernatant only contains free excess PAH chains. The concentration of free PAH can thus be deduced from viscosity measurements, considering the calibration curves of Figure 5. The fraction of PAH involved in PEC particles is then straightforwardly obtained.

Figure 6 shows the evolution of the fraction of bound PAH (i.e. in the complexed state) as a function of \(R_c\) (for a constant PAH concentration at 1 wt%). It is worth noticing that for both pH values, the percentage of complexed PAH increases linearly with \(R_c\), and therefore with PSS concentration, since PAH concentration is constant. The slope of the linear plots is pH-dependent, being higher at pH = 10 than at pH = 5.5. Again, this behavior can be
rationalized considering the evolution of PAH chain conformation as a function of the protonation degree. At pH = 10, PAH functions undergo partial ionization, and the chains are likely to adopt a relatively compact coiled conformation, with most of the charges located in the core of the coil and thus inaccessible for binding. As a consequence, the charge compensation causes the inclusion of a higher number of PAH chains. On the other hand, at pH = 5.5, PAH is almost fully protonated, the polycation chains are more elongated and charges along the backbone become more accessible. As a result, a smaller amount of PAH is necessary to neutralize PSS charges.

We now address the stoichiometry of the complexation process. A 1:1 stoichiometry is generally found for mixtures of strong polyelectrolytes. The stoichiometry depends on polymer flexibility. Rigid polymers with uneven charge distribution, due to their inability to reconfigure, are more likely to form non-stoichiometric PEC. The presence of salt makes the polyelectrolytes form denser structures, which can lead to deviations from 1:1 stoichiometry (Vanerek and van de Ven, 2006). However, since the main driving force is the release of countercations, real deviations from 1:1 stoichiometry occur when the Debye length starts to be of the same order of magnitude as the distance between two charges along the chain of the polyelectrolyte with the lowest charge density. Deviations from unit stoichiometry in the presence of salts have been interpreted as due to conformational changes in the polyelectrolytes (Cundall et al., 1979).

With the aim of estimating the average charge stoichiometry within PEC particles, the data of Figure 6 based on mass concentrations were recast considering charge concentrations. In Figure 7, we plot the number of cationic PAH charges involved in the complexes as a function of the number of anionic PSS charges, normalized by the sample volume (they are thus expressed as concentrations). The amounts were calculated assuming that PSS functions are fully dissociated whatever the pH, while the ionization rate of PAH is equal to 0.35 and to 1 at pH = 10 and 5.5, respectively (Petrov et al., 2003). The curves obtained at both pH values clearly overlap. This result indicates that the average charge stoichiometry within the particles does not depend on pH and consequently on PAH chain conformation. From the slope of the curve, we deduce that the average positive-to-negative charge ratio in the particles is close to 3. Thus, on average, 1 out of every 3 PAH charges is actually involved in the binding process, reflecting the reduced availability of the charged sites. The excess of positive charges is consistent with the sign of the zeta potential reported in Figure 2. Moreover, assuming that the electrophoretic mobility is controlled by volume properties, the invariance of $\mu_E$ can be interpreted considering that the polyelectrolyte chain (and charge) density within the particle cores remains almost constant with $R_c$.

We also estimated the average molar chain stoichiometry, i.e. the PAH-to-PSS chain molar ratio in PEC particles. In Figure 8, we report the number of moles of PAH trapped within the particles as a function of the total number of moles of PSS chains introduced in the blend (normalized by sample volume). The number of moles being simply proportional to mass concentrations, linear plots are obtained like in Figure 6. Again assuming full incorporation of PSS chains in the particles, we deduce from the slope that the PAH-to-PSS molar ratio is equal to 2 at pH = 10 and to 0.7 at pH = 5.5.
2.4 Estimation of PEC Volume Fraction

From the viscometric data, it is possible to estimate the effective volume fraction of PEC particles as well as the polymer fraction within the particle cores.

As a first approximation, the interactions between the PEC and the polyelectrolyte are neglected. The specific viscosity of PEC suspensions, $\eta_{sp}(R_c)$, is thus additively composed of the contributions of the free (noncomplexed) polyelectrolytes, $\eta_{sp,free}(R_c)$, and of the PEC particles, $\eta_{sp,PEC}(R_c)$ (Brand and Dautzenberg, 1997):

$$\eta_{sp}(R_c) = \eta/\eta_s - 1 = \eta_{sp,free}(R_c) + \eta_{sp,PEC}(R_c) \quad (1)$$

Due to the compact structure of the PEC, the contribution of the complexes to the relative viscosity of the reacting mixture can be described by the Krieger-Dougherty equation, assuming spherical complexes:

$$\eta_{sp,PEC}(R_c) \left[1 - \frac{\phi}{\phi_m}\right]^{-2.5\phi_w} - 1 \quad (2)$$

where $\phi$ is the effective volume fraction of PEC particles and $\phi_m$ is the random close packing fraction equal to 0.64. By combining Equations (1) and (2), we obtain:

$$\phi = \phi_m \left[1 - \left(\frac{\eta_{sp}(R_c) - \eta_{sp,free}(R_c) + 1}{\eta_{sp,free}(R_c)}\right)^{-2.5\phi_w}\right] \quad (3)$$

The term $\eta_{sp,free}(R_c)$ is deduced from viscosity measurements of the supernatant phase containing free PAH chains, as described in the previous section. The effective PEC volume fraction, $\phi$, is then straightforwardly obtained from Equation (3). The data are reported in Table 2. As expected, the effective volume fraction increases with the composition ratio $R_c$.

We are aware that such calculations provide only rough estimates of the volume fractions because of the simplifying assumptions. PEC particles were assumed to behave as non-attractive hard spheres. This is certainly questionable considering that:

- van der Waals forces may produce particle aggregation at the ionic strength that was adopted in the experiments;
- free PAA chains in the continuous phase may induce attractive depletion forces (Asakura and Oosawa, 1958);
- attractive interactions would tend to increase the viscosity, leading to an overestimation of $\phi$, especially at the highest polymer fractions (equivalently, largest $R_c$ values).

We also tried to calculate the average content of polymer in PEC cores assuming that PSS is fully incorporated in the particles and taking into account the percentage of complexed PAH reported in Figure 6. The results are rather scattered (data not shown) probably because of the above-mentioned limitations in the estimation of $\phi$. The most reliable result is certainly the one deriving from the lowest fraction, namely $R_c = 0.12$. The obtained value for the polymer concentration inside the particles at pH = 10 is close to 0.3 g/mL, reflecting a very compact structure within the particle cores.

### CONCLUSION

In this paper, we examined the complexation process occurring when two polyelectrolytes of opposite charges are mixed under intense stirring, one polyelectrolyte being in large excess with respect to the other one. Our experimental approach based on viscosity measurements lead to quantitative information about the complexed fraction of the polyon introduced in excess, the average molar stoechiometry and polymer fraction within the particle cores, etc. The study was carried out at 2 different pH values corresponding to 2 different situations in terms of charge accessibility for binding. Our data indicate that higher degree of polymer compaction within the formed PEC particles is achieved when charge accessibility is enhanced. Interestingly, at a given pH and at constant concentration of the polyon in excess, the same binding stoichiometry (and thus same composition) is obtained in PEC particles whatever the overall mass ratio of the polymer blend initially introduced.

Particles dissociation occurs upon salt addition and further work is ongoing to characterize the dissociation kinetics using the same viscometric approach.

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