Experimental report

14/03/2016

Proposal:	**9-11-1765**	**Council:**	4/2015
Title:	Early events in the electrostatic complexation of oppositely charged polyelectrolytes		
Research area:	Soft condensed matter		

This proposal is a new proposal

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Samples:
Sodium polyacrylate
polydiallyldimethylammonium chloride

Instrument	Requested days	Allocated days	From	To
D22	3	3	27/11/2015	30/11/2015

Abstract:

We would like to shed some light on the complexation mechanism and morphological signature at the nm scale of the very early stage assembly of oppositely charged polyelectrolytes (PEs) by combining the unique characterization potential of neutron scattering with the extremely fast mixing time (< 10 ms) of the stopped-flow method. The evolution of the inner structure of the well-known PDADMAC/PANa PEs couple will be investigate as a function of the molar charge ratio in pure and buffered solutions.

Polyelectrolyte complexes (PECs) are formed through electrostatic interaction between oppositely charged polyelectrolytes. The kinetics of complexation is so fast, in the range of the millisecond, that the complexation pathway has never been put in evidence. It is speculated that transient primary complexes are formed at short times before undergoing intra- and intermolecular rearrangements towards final structures. The consequence of such fast complexation kinetics is the high sensitivity to the formulation pathway used to prepare the complexes. Especially it has been shown that the mixing time exerts a strong influence on the final morphology of the complexes. Here, the goal of the study was twofold. At first, we would like to gain insight into the kinetics of complexation of oppositely charged polyelectrolytes using the stopped flow technique under beam illumination. Second, we aim at analyzing the structure of a large library of polyelectrolyte complexes including colloidal particles and coacervates prepared in a stopped flow instrument that enables a very short mixing time of components.

1) Early stage complexation *kinetics* using SF conditions under beam illumination

The system under investigation was composed of polyacrylic acid (PAA, M = 2kDa) and poly(diallyldimethylammonium chloride) (PDADMAC, M = 32kDa) at pH 10 with or without added salt. Two concentrations of polymer, 1 and 10 g/L have been studied. The molar charge ratio (Z = +/-) was varied between 0.2 and 1.0. The overall conditions have been previously tested with a stopped flow instrument using a light scattering detection at 90°. The goal of the study was to reproduce the complexation using the stopped flow (SF) conditions under the beam in a large range of q. Three configurations have been tested (6 Å – 5.6 m / 6 Å – 8 m / 6 Å – 17.6 m). Some typical results obtained during this study are shown in figure 1.

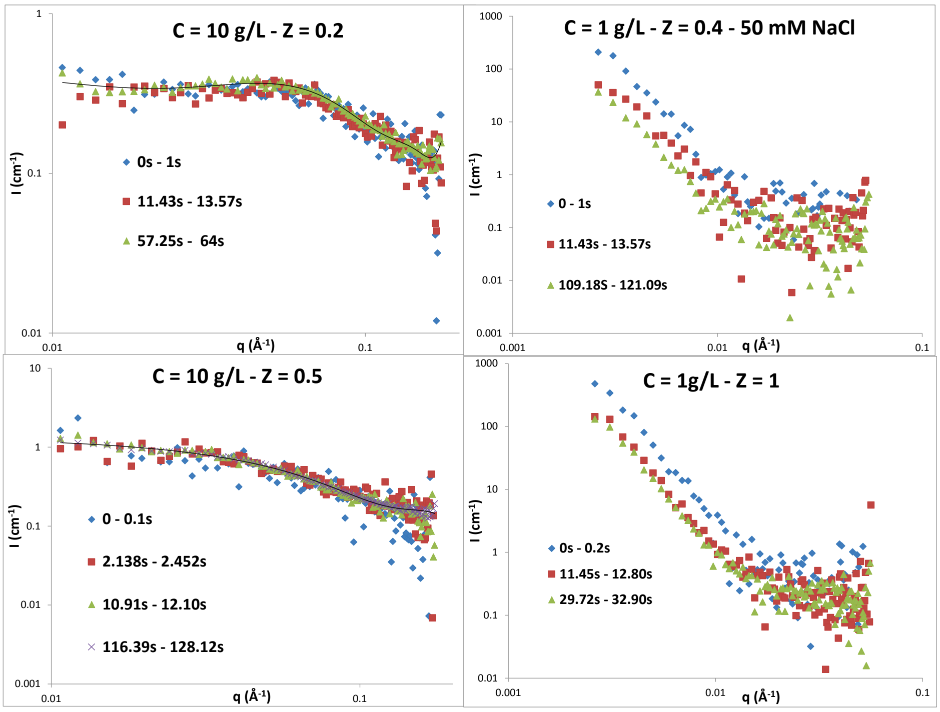

Figure 1. Typical SANS curves of PAA/PDADMAC complexes at various Z ratios prepared by SF under the beam. Two detector distances are investigated here: 5.6 m (left) and 17.6 m (right). λ= 6Å in both cases.

The main conclusions drawn from the PE complexation in SF conditions are the following:

- The complexation kinetics is extremely fast whatever the conditions (Z, salt, concentration); in most cases the complexation was over one second after the mixing as seen from scattering curves at low and high q.

- The low contrast of PECs made of PAA and PDADMAC even at relatively high concentration did not permit to record kinetics at short times (< 200 ms) especially in the low q range.
- Increasing the Z ratio or the salt concentration accounts for a better contrast, then enabling to record faster kinetics.
- Increasing the Z ratio also increases the kinetics of complexation as a consequence of the charge neutralization.

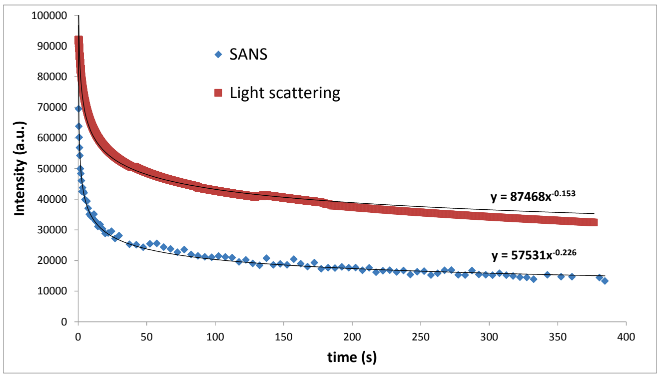

Figure 2. PAA/PDADMAC coacervates (Z=1) prepared by SF under beam illumination. Comparison of light scattering vs neutron scattering detection (λ=6Å-d=17m).

It is worth noting too that the variation of the count number versus time in the low q range is very similar to the trends observed in light scattering. Both data could be well fitted with a similar power law (Figure 2).

2) Later stage *static* morphologies of PE complexes using SF mixing conditions

PDADMAC/PAA complexes at different z ratio and ionic strength and Mw (PAA_{2k} &PAA_{60k} were made within the SF set-up and then transferred in regular quartz cells to analyze their quasi-static morphologies (long time).

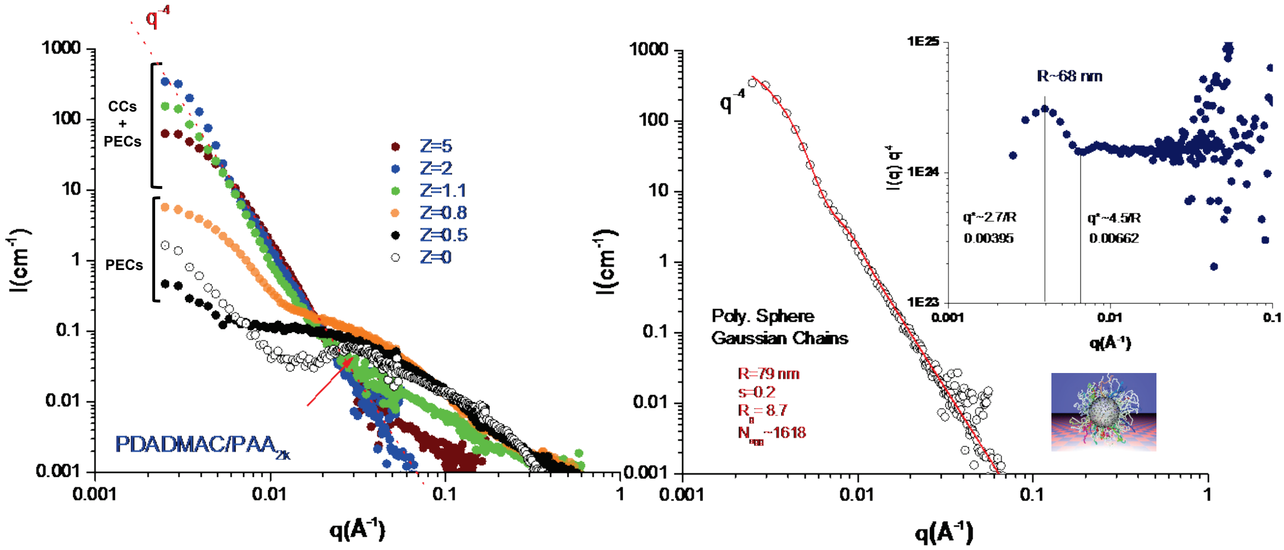

Figure 3. Typical SANS curves of PDADMAC/PAA2k complexes with no added salt (0=M) on the full q range. (left) at various molar charge ratio Z. the red arrow indicate the polyelectrolyte peak seen for pure PDADMAC(Z=0) (right) at Z=2. The data are fitted (red line) with a *Polydisperse Sphere with attached Gaussian Chains* model (SASFIT software). The ***Porod*** representation (insert) highlights the presence of spherical objects around 70 nm in radius as well.

For all investigated systems with no added salt ~~(=0)~~ the PDADMAC polyelectrolyte peak is always seen (Z=0) and disappears with increasing Z or when salt is added as expected. In Fig. 3 (left) one can distinguish two different zones. Z<=0.8 where the scattered intensity varies from pure polyelectrolyte chains to small complexes keeping the overall features of the large PDADMAC SANS signature. Above Z=0.8, where we do have the coexistence of coacervate droplets and PECs we observe a similar variation in q^{-4} suggesting the presence of objects with sharp interfaces. A typical *Porod* representation (Z=2) is pointing out the presence of spherical objects (insert) that can be fitted using *Polydisperse Spheres with attached Gaussian Chains.* The sizes and polydispersity are in agreement with dynamic light scattering measurements. The rather large polydispersity seems to be a feature of (highly frozen) complexes produced with the very fast mixing occurring in the SF set-up. Furthermore, working with higher ionic strength solutions (and then with a screened electrostatic interaction) will tend to broaden the coacervation zone where PECs and neutral droplets coexist leading to a faster coarsening stage; with a scattering signature in line with leftover PECs in equilibrium with the coalesced (and sedimented) coacervate phase. Finally, working with a higher PAA (60k) M_w tends to broaden the coexistence zone as well: *larger and denser (polydisperse) spheres (scattering well as* q^{-4}*) seem to form more rapidly as in the case of lower PAA* M_w.

3) Pure coacervate phase SANS signature

The coacervate phase remains nowadays a concept not entirely well defined yet. We filled regular quartz cells with the pure phase obtained for both PAA M_w through manual fast *injection* mixing pathway (in order to increase the formulation yield). Parallel dry extract and NMR characterizations have shown a very dense polymer phase with Z ratio slightly above 1 as foreseen.

	Coacervate phase		Supernatant	
	Content (%/w)	Z-/+(NMR)	Content (%/w)	Z-/+(NMR)
PADAMAC/PAA$_{2k}$	23	1.15	0.7	0.78
PADAMAC/PAA$_{60k}$	30	1.12	0.68	0 (PDADMAC)

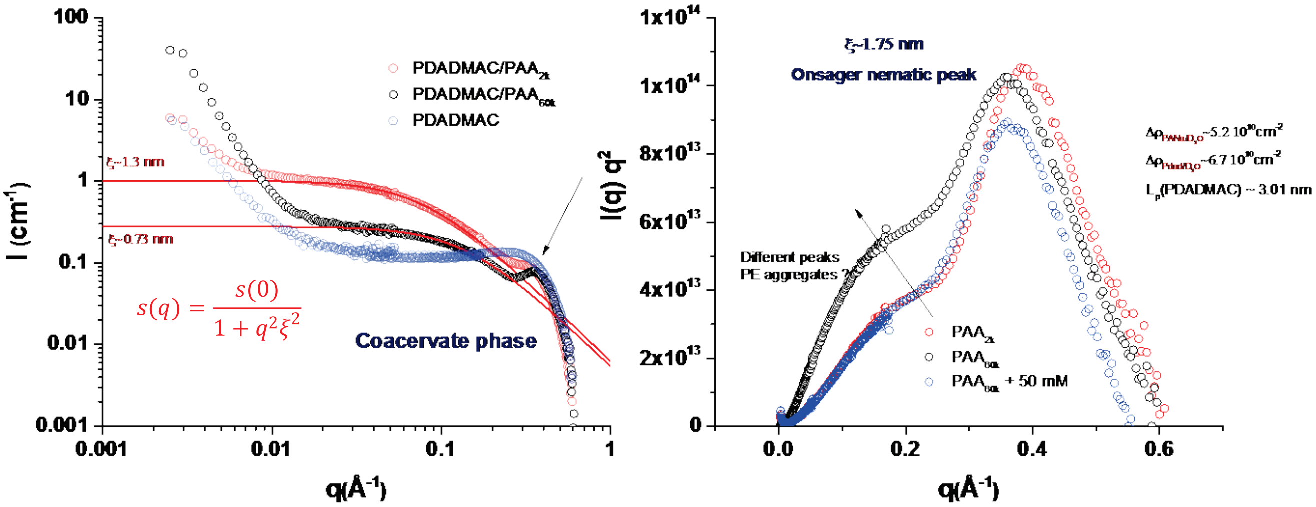

Figure 4. SANS signature for both dense coacervate phases obtained for PAA$_{2k}$ and PAA$_{60k}$. (left) I(q) *vs.* q representation. The red lines are a fit to the data using the Orstein-Zernike static form factor model for semi-dilute polymer enabling to determine the correlation length ζ. (Right) ***Krakty*** plot I(q)q^2 *vs.* q highlighting the presence of a strong correlation peak at very high q beyond 1/persistence length of PDADMAC.

The PE peak is not present at low q as expected in such concentrated regime. Both mesh size ζ are smaller than the PDADMAC R_g indicating that the polymer chains are indeed overlapping (φ>φ*) and scale with the coacervate polymer content. The ***Krakty*** representation shown in Fig.4 (Right) presents an astonishing correlation peak at very high q (d~1.75 nm^{-1}) well beyond the PDADMAC persistence length L_p (3 nm). We might ascribe this peak seen in the ionomer region as correlated PDADMAC cylinders from excluded volume effects: we coin them *Onsager nematic peaks*. Some others convoluted peaks are also visible at slightly lower q; Are they due to correlation of PE small aggregates? It should be noted that the presence of 50mM of NaCl does not change the observations…