

# Experimental report

27/10/2023

**Proposal:** 9-11-2116

**Council:** 4/2023

**Title:** Characterization of the structure and dynamics of the hydrophobic domains in InterPolyElectrolyte Complexes

**Research area:** Soft condensed matter

**This proposal is a new proposal**

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**Samples:** H3COCOCHCH3 - (CH2CCH3COOC12H25)25 - (CH2CCH3COOCH2CH2N(CH3)2)225 - Br  
H3C (OCH2CH2)45 - OCOC(CH3)2 - (CH2CCH3COOH)100 - Br  
C17H38N Br  
(C8H18CINO2) n

Instrument	Requested days	Allocated days	From	To
D22	1	1	26/08/2023	27/08/2023
IN15	5	5	24/08/2023	29/08/2023
D33	1	0		

## Abstract:

Advances in polymer science allow to create evermore complex self-assembled polymeric structures which can be interesting e.g. in the field of drug delivery. Interpolyelectrolyte complexes (IPECs) are promising systems owing to their possibility to form hydrophobic domains, which allows incorporating hydrophobic molecules that are otherwise not soluble in water. This competition between hydrophobic and hydrophilic domains have been also observed in polyelectrolyte surfactant complexes (PESCs).

The proposed experiment aims to compare the structure and dynamics of the hydrophobic domains in PESCs and IPECs. In IPECs, the hydrophobic moieties are attached to a polymer backbone, which acts as a constraint on the space they can explore and it competes with their tendency to aggregate. Such constraint does not appear in PESCs with non HM-PEs, since the polar heads of the surfactants are free.

To characterise the structure of the systems we request 5 days of Neutron Spin Echo measurements on IN15 and 1 day of Small Angle Neutron Scattering on either D22 or D33.

# Characterization of the inner dynamics of InterPolyElectrolyte Complexes

## 1 SCIENTIFIC BACKGROUND:

The system we are investigating are InterPolyelectrolyte Complexes (IPECs) given by two polymers synthesised in the Physikalische Chemie lab in TU Berlin. These polymers are a double hydrophilic blockcopolymer, with a tail of poly(ethylene glycol) and one of poly(methacrylic acid) (PEG-PMAA) and the counter polycation is an hydrophobically modified poly(2-(Dimethylamino)ethyl methacrylate) (PDMAEMA). These polyelectrolyte mixtures are forming self assemble structures of a size  $\simeq 1000\text{\AA}$  when the mixing ratio  $z^* = [-]/([+] + [-]) \in [1/3, 2/3]$ . This aggregates are interesting in many fields, such as drug delivery or water treatment and they present an internal dynamics which affects the mobility of a possible active agents. Such dynamics can be explored with Neutron Spin Echo (NSE) at IN15. This investigation tackled a q-range that reflects the inner structure of IPECs through SANS as depicted in fig. 2. The dynamics investigation has been performed at concentration  $c = 1.0\%$  by weight, while stock solution has been prepared at 1.7%.

## 2 Outcomes

### 2.1 D22:

Concerning Small Angle Neutron Scattering (SANS), we already explored the spectra of such IPECs during an investigation at ANSTO, so in this example we focused in testing the reproducibility of such data and expand the investigation testing a reference polymer without hydrophobic modifications attached. We also performed dilution series to see how the polymeric network structure is composed, such dilutions series will be also important to test a computational model that we are developing.

Concerning the reproducibility, we see that for most of the values of  $z^*$ , the low-q behavior is preserved. At high-q, we see the shoulder of the upturn between the low-q scattering and the polymeric contribution at high q to vary for the pure polycation. We also see the background of the polyanion to be higher.

Since we observed precipitations at  $z^* = 0.5$ , we did not reproduce the measurements at D22.

The sample we tested at IN15 were prepared more than 24 h in advance: we wanted to ensure the sample to stabilize from the slow kinetics of formation.

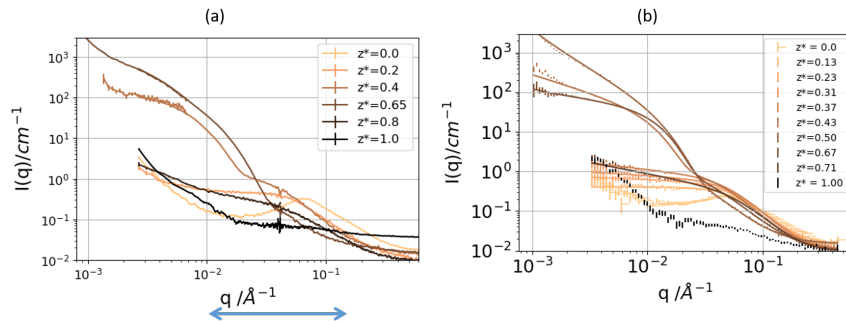


Figure 1: Comparison between data obtained at ILL at D22 instrument (a) and at ANSTO at BILBY (b). The blue arrow in (a) corresponds to the explored q-range at IN15.

We also have investigated a polymer which will be useful in an follow up experiment on IN15, to unravel the role of the hydrophobic modifications on IPECs, which is a commercial version of the PDMAEMA, without hydrophobic modifications (fig. 2.1-(a)).

Finally, we studied dilution series of both the polymers and the complexes (fig. 3): observing the spectra of the polymers, we see a correlation peak corresponding to the size of the polymers, which is in the case of  $c \simeq 1.7\%$ ,  $q = 0.068 \text{\AA}^{-1}$ ,  $r = 2\pi/q = 92.35\text{\AA}$  in the real space. Moreover, by studying this value for different concentrations, we will extract the power law of the dilution law, which is informative on the dimensionality of the systems. We also investigated how a diluted sample will look like (fig. 3 (b)): sample where prepared at the usual concentration (1%), and after the preparation we

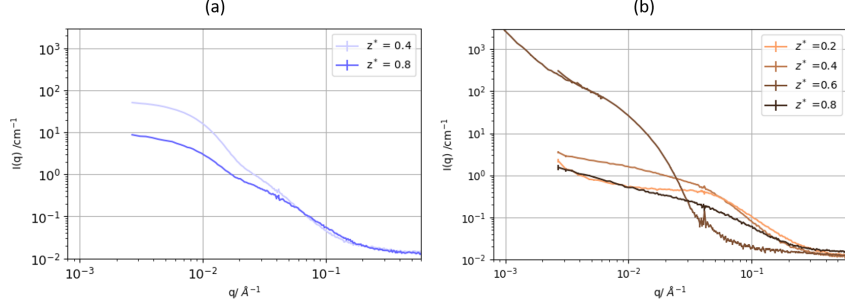


Figure 2: SANS spectra for the SANS data for different values of  $z^*$  of the IPECs composed by PDMAEMA and the double hydrophilic block-copolymer PEG-PMAA. (a) and for samples prepared right before testing (b) using the HM-PDMAEMA.

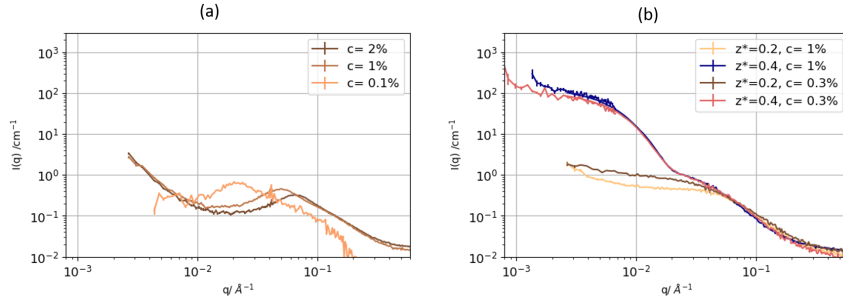


Figure 3: SANS spectra for different concentrations for the polycation (a) and for the IPECs at different  $z^*$  values (b).

diluted them by a factor of 3: renormalizing the curves with respect to the concentration ratio, we see that at  $z^* = 0.4$ , where we clearly see the low- $q$  shoulder of the aggregates, to dilute the sample does not change the structure. However, at  $z^* = 0.2$ , the spectrum shows a correlation peak with a low- $q$  upturn that could be assessed to a structure factor. This spectrum is similar to what we observed in pure polyelectrolyte solutions. This upturn and the correlation peak become a broad peak while diluting the samples. These 2 observations are showing that at  $z^* = 0.4$  IPECs are neutral colloids and diluting them does not change the structure of the aggregates, however at  $z^* = 0.2$ , the polymers are free and they will experience less electrostatic interactions in a more dilute conditions.

## 2.2 IN15:

Observing the Intermediate scattering functions  $I(q,t)/I(q,0)$  on NSE (fig. 4), we can see there is a visible single exponential decay for most of the samples: thus we assumed to have particle following a Fickian diffusion. In this theoretical framework, we extracted the characteristic time  $\tau$  and the diffusion coefficient  $D(q)$ :

$$I(q,t)/I(q,0) = Ae^{-t/\Gamma} \quad (1)$$

$$\Gamma(q) = Dq^2 \quad (2)$$

Where  $\Gamma(q) = 1/\tau(q)$ .

By observing  $\Gamma(q)$  in fig. 5, its dependency of  $q^2$  is linear at low  $q$ , meaning that we can assume a Brownian diffusion in this range. Under such condition, we extracted the diffusion coefficient  $D$  and the hydrodynamic radius  $R_H$  defined as:

$$R_H = \frac{k_B T}{6\pi\eta D} \quad (3)$$

Where  $k_B$  is the Boltzmann constant,  $T$  is the temperature and  $\eta$  is the viscosity of D2O.

Intermediate scattering functions

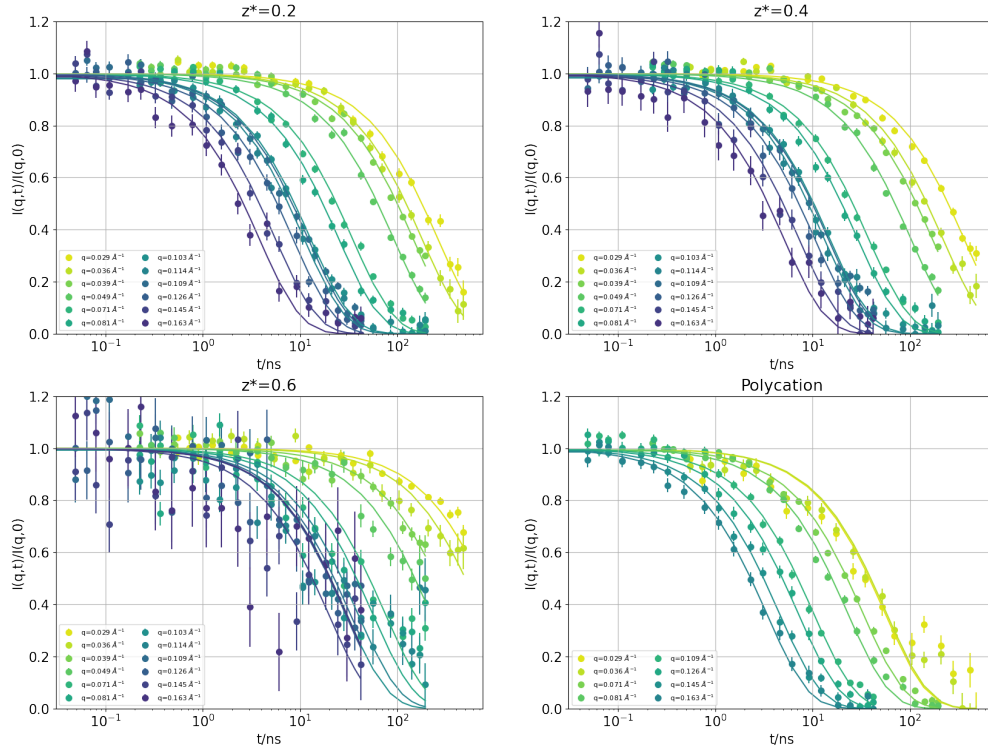


Figure 4: Intermediate scattering functions obtained at IN15 for different values of  $q$  and  $z^*$ .

and  $D$  is the diffusion coefficient. In a further modelization on the ANSTO data, we have found that such aggregates are very hydrate, with a volume fraction of water inside the aggregates  $v_{D_2O} \simeq 90\%$ , which also agrees with the hydrophilic nature of these polymers. With this level of hydration, the polymers inside the aggregates are freely diffusing, thus it is plausible to assume Stokes-Einstein diffusion. After a certain  $q$ -value ( $\simeq 0.02\text{\AA}^{-1}$ ), the dynamics is not free, but we observed the polymer dynamics.

While increasing  $z^*$ , the hydrodynamic radius increase, due to the formations of the aggregates. We see a huge jump between  $z^* = 0.4$  and  $z^* = 0.6$ : we address this jump to the fact that this structure are becoming denser ( as observed on previous investigations on SANS spectra).

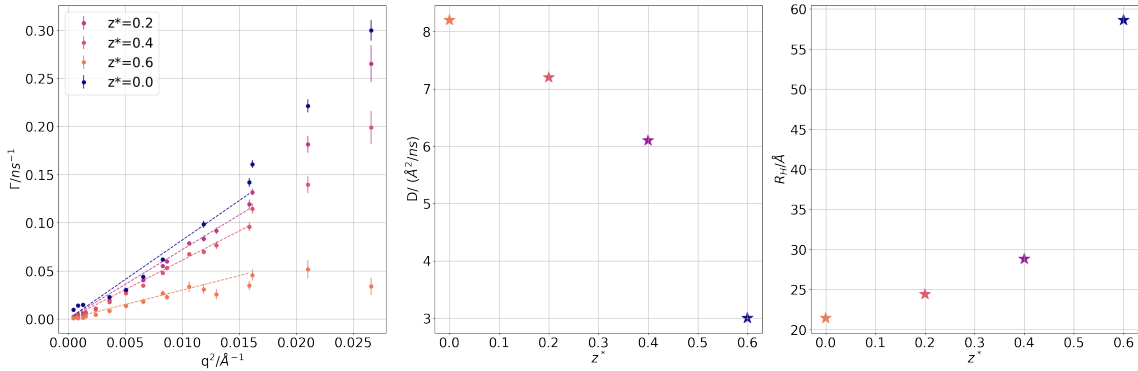


Figure 5: Outcome from Spin-Echo analysis.