# Experimental report

08/08/2021

**Proposal:** 9-12-607 **Council:** 4/2020

**Title:** Dynamics of coacervate phase formed by comb polyelectrolyte and oppositely charged ionic surfactant

**Research area:** Soft condensed matter

**This proposal is a resubmission of 9-12-582**


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**Experimental team:**

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**Samples:** poly(methacrylate-co-polyethylene glycol methyl ether methacrylate) (PMAA-PEGMA), 1 mg/mL in 50 mM Na2B4O7/D2O + dodecylpyridinium chloride (DPCl), charge ratio, Z=1
poly(methacrylate-co-polyethylene glycol methyl ether methacrylate) (PMAA-PEGMA), 1 mg/mL in 50 mM Na2B4O7/D2O + dodecylpyridinium chloride (DPCl), charge ratio, Z=0.5

| Instrument | Requested days | Allocated days | From | To |
|---|---|---|---|---|
| IN15 | 2 | 3 | 14/09/2020 | 17/09/2020 |


**Abstract:**

We propose a series of NSE measurements to study dynamics of comb polyelectrolyte chains poly(methacrylate-co-polyethylene glycol methyl ether methacrylate) (PMAA-PEGMA) and cationic surfactant dodecylpyridinium chloride (DPCl) micelles confined in micrometer-sized coacervate droplets of the PMAA-PEGMA/DPCl polyelectrolyte-surfactant complex.

In this experiment, dynamics of anionic comb polyelectrolyte poly[methacrylic acid-*stat*-poly(ethylene glycol) methyl ether methacrylate] (PMAA-PEGMA) and cationic surfactant *N*-dodecylpyridinium chloride (DPCl) in coacervate emulsion formed by electrostatic complexation of PMAA-PEGMA and DPCl in alkaline aqueous solution (pH 9) was followed by neutron spin echo spectroscopy at two molar ratios between DPCl cations and PMAA monomeric units, $Z$=0.5 and $Z$=1.0.

NSE measurements at Z=1.0 revealed that apparent diffusion coefficients, $D_{app}(q)$, in the high $q$ region, 1.1 – 2.0 $nm^{-1}$, dominated by scattering from densely packed DPCl micelles were much lower ($R_H$ of ~$10^2$ nm) than those in the low $q$ region, 0.2 – 1.1 $nm^{-1}$, dominated by scattering from collapsed PMAA-PEGMA chains ($R_H$ of ca. 5 nm). NSE measurements thus confirmed that DPCl micelles were present in the coacervate phase, while the scattering contribution in 0.2 – 1.1 $nm^{-1}$ was mainly from PMAA-PEGMA chains in the bulk solution.

In 2021, the investigation of the PMAA-PEGMA/DPCl system by NSE was further supplemented by DOSY NMR measurements, conducted for various charge ratios $Z$. NMR measurements confirmed partitioning of both PMAA-PEGMA and DPCl between the bulk aqueous phase and micrometer-sized coacervate droplets formed at $Z > 0.7$. While diffusion coefficients assigned to protons in the aqueous phase corresponded to those of PMAA-PEGMA chains (effective hydrodynamic radius, $R_H$ = ~5 nm) or DPCl ions ($R_H$ = ~0.7 nm) in water, the diffusion coefficients of both polymer and surfactant in the coacervate phase were decreased substantially, corresponding to $R_H$ of ca. $10^2$ nm. The DOSY NMR data thus supported the results obtained from NSE measurements.

Currently, a manuscript summarizing the results of both NSE and DOSY NMR study of PMAA-PEGMA/DPCl coacervate emulsion is under preparation. We expect its publication by the end of 2021.