Experimental report

22/09/2022

Proposal:	**9-11-2032**	**Council:**	10/2020
Title:	Formation of nanogels from alginate-block-dextran copolymer and Ca2+ ions under equilibrium conditions		
Research area:	Soft condensed matter		

This proposal is a new proposal

Main proposer:	**Martin FAUQUIGNON**
Experimental team:	Amalie SOLBERG Christophe SCHATZ Martin FAUQUIGNON
Local contacts:	Lionel PORCAR

Samples: Oligoguluronate-block-dextran

Instrument	Requested days	Allocated days	From	To
D22	3	2	26/06/2021	28/06/2021

Abstract:

Alginates are well-known for their capacity to form strong gels in presence of calcium ions. Here, we propose to study the behaviour of hydrophilic diblock copolymers containing alginate and dextran blocks. These copolymers form nanogels with Ca2+ as shown through preliminary experiments by ligh scattering. We will take advantage of the dialysis cell developed by the D22 team to perform the gelation of the copolymers close-to-equilibrium conditions. This will enable us: i) to highlight the mechanism of formation of nanogels, from unimers to final aggregates, ii) to better understand the role of key parameters on the size and morphology of nanogels : the molar mass and composition of BCs, the type of cations (Ca2+, Ba2+, Sr2+) and the dialysis kinetics that can be varied by modifying the pore size of the membrane.

Impact of added salt (NaCl) on the local structure of a complex coacervate phase

The effect of salt addition on the behavior of a coacervate phase is well known and documented in the litterature. The salt will screen and then weaken the strength of the electrostatic interaction between the oppositely charged PEs until a concentration where the complexation disappears.[1-3] However, structural evidence for this effect is not well documented in the literature. Here we present some key SANS evidence showing the change in complexation intensity leading to a change in newtork mesh size in a coacervate phase with the addition of NaCl.

The static SANS signatures of the salt effect on the local network structure of a coacervate phase generated from the PDAMAC/PANa system at charge stoichiometry is presented in **Figure 1**.

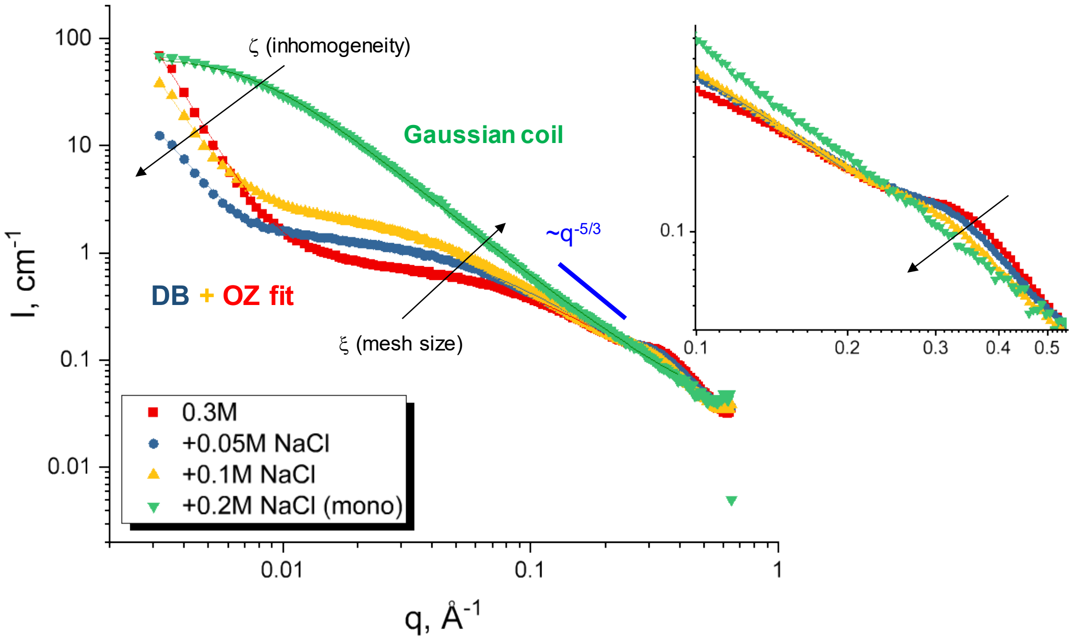

Figure 1. Small angle neutron scattering (SANS) signature of PDADMAC/PANa 0.3M coacervate phases as a function of added NaCl concentration. The measurements were performed at ILL on D22 in D_2O. The solid lines correspond to an *Ornstein-Zernike (OZ)-Debye-Buche (DB)* fit of the data, except when 0.2M NaCl is added, where a Guassian coil-type fit applies. The insert is a high-q zoom (>0.2 Å^{-1}) of the different formulations where the correlation peak (q*) are more easily seen.

In this case, the semi-dilute polymer solution at equilibrium follows the Ornstein-Zernike (OZ) structure factor accounting for the concentration fluctuations at high q [4]

$$S_{OZ}(q) = \frac{S_{OZ}(0)}{1+(q\xi)^m}$$

with S(0) the structure factor extrapolated to q=0 (and related to the entanglement density and longitudinal osmotic modulus of the network) and ξ the correlation length or mesh size of the entangled network. The exponent m characterizes the polymer/solvent interaction and thus the underlying thermodynamics (m=2 for theta solvent or m=5/3 for good solvent). In addition, an excess of diffusion at low q is always present in PE solutions. This upturn has been attributed to local inhomogeneities several times larger than the radius of gyration of PEs in the solutions[5]. We believe that these inhomogeneities actually originate from transient aggregates arising from dipole-dipole interactions and highlighted by Muthukumar in the dynamics of charged macromolecule solutions [6]. It turns out that if the spatial scale of the concentration fluctuations due to the presence of these large transient inhomogeneities is large relative to the correlation length, then the two contributions can be summed and treated separately [7]. The overall structure factor becomes

$$S_{total}(q) = S_{OZ}(q) + \frac{S_{DB}(0)}{1+(q^2\zeta^2)^2}$$

where the second term is the Debye–Bueche (DB) structure factor $S_{DB}(q)$[8] which accounts for the scattering by an inhomogeneous solid. $S_{DB}(0)$ is the extrapolated structure factor at q=0 and ζ represents the size of the inhomogeneities in the system. At low q, the DB contribution $S_{DB}(q) \sim 1/q^4$ dominates over that of the OZ, while at high q, where the DB scales as $S_{OZ}(q) \sim 1/q^2$ it is the reverse. The DB fit, however, should be taken with caution as a trend only because it is based on only a few low q data points and large errors are then possible. Indeed, **Figure 1** shows that the OZ-DB structure factor model accounts for the SANS data particularly well. As expected, the static correlation length ξ and the size of the transient aggregates ζ increase and decrease respectively with the ionic strength very well in line with dynamic data as shwon in **Figure 2.** It should be noted, however, that when 0.2M NacL is added to the coacervate phase a single phase appears where the oppositely charged chains no longer interact due to complete electrostatic screening. In this case, a Gaussian coil form factor perfectly fits the scattered intensity with an Rg~19nm in full agreement with the PDADMAC chain size. Note also that the upturn at low q disappears in this single phase in complete agreement with DLS data (not shwon) where the slow mode is effectively absent when 0.2M NaCl is added.

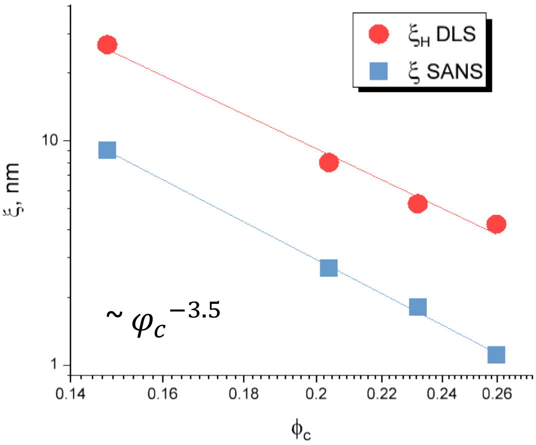

Figure 2. SANS and DLS correlation lengths ξ as a function of the polymer mass fraction φ_m.The solid lines are a power law fit to the data.

Moreover, we can clearly see on the insert of Figure 1 that the correlation peak (q*) seen at high q tends to move towards low q values with the increase of the complexation strength. It then disappears in the single-phase region where the chains do not interact anymore.

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