Experimental report

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Proposal: **9-13-715** **Council:** 4/2017

Title: Structure factor of DNA self-assembled hydrogels at the percolation threshold

Research area: Soft condensed matter

This proposal is a continuation of 9-13-559

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Samples: DNA H2O NaCl

Instrument	Requested days	Allocated days	From	To
D33	0	0		
D22	2	2	17/03/2018	19/03/2018

Abstract:

Recent SANS experiments have permitted the investigation of the structural properties of DNA Nanostars (NS), i.e. self-assembled DNA structures with a limited valence, f [1]. Both the F(Q) of DNA NS and the S(Q) of the resulting gels that these NS form on cooling were characterized thanks to the synergy between SANS studies and simulations [2].

Recent DLS measurements suggest that is possible to use DNA NS as a model-system for investigating in a controlled way the percolation transition and the cross-over from chemical to physical gelation, exploiting the strong T-dependence of the base-pair interaction free-energy. We have experimentally realized a system composed by a mixture of DNA chains (f=2) and DNA NS (f=4) in which the only relevant interaction is between particles with different valence thanks to the proper design of the sticky-ends. By tuning the A/B ratio, it is possible to bring the system at a well defined distance from percolation.

Complementing the DLS results, SANS measurements of the S(Q) will allow to characterize the fractal dimension associated to the percolating cluster providing important information about the gelation process of the DNA NS.

The present experiment was run at D22 during the allocated time of 2 days. We investigated the structural signatures of a binary mixture composed by tetrafunctional (Nanostars, NS) and bifunctional (chains, B) DNA nanosized structures. This system was designed to mimic colloidal patchy-particles with the ability to bond in a NS-B fashion, as shown in Fig. 1, while NS-NS and B-B bonds were prevented by the proper sequence design.

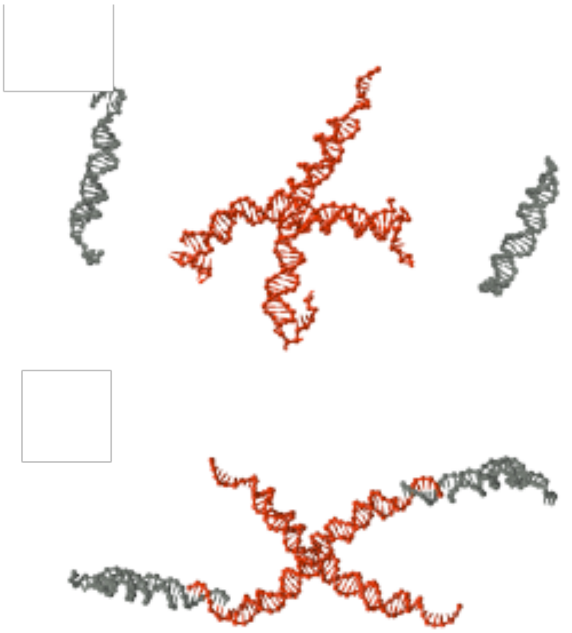

Fig. 1. The progressive self-assembling of the NS and B structures starts from complementary single-strands. In particular, four single strands are required to form NS structures (red) and two to form each B unit (grey). In the top panel we show NS (red) and B (grey) components already assembled while the bottom panel represents the binding via the presence of complementary sticky-ends, placed at the end of each NS and B arms, here exemplified by the formation of a NS-B compound.

Complementing our previous research that showed that both the form factor, F(Q), and the structure factor S(Q) of DNANS systems can be successfully studied with SANS experiments and supported by molecular dynamics simulations, as reported in more detail in a recent publication [1], in this occasion we investigated the structural signatures of the NS-B system, close to its percolation conditions, based on the Flory-Stockmayer polymerization models [2,3].

We extracted useful information about the fractal dimension of the formed DNA clusters from the characterization of the structure factor S(Q). SANS techniques were helpful in avoiding radiation damage of the samples while offering access to the region of Q of interest (0.003 – 1.5 Ang-1).
The information obtained from the D22 experiments was of great importance to understand the physical phenomena in the equilibrium sol-gel transition of branched

polymer systems as the one here discussed.

We measured by means of SANS techniques the structure factor S(Q) of a NS4-B2 system at 7 temperatures from 280 to 330 K to cover the sol-gel transition, from a fluid-like system (NS and B isolated) towards the formation of the percolating threshold in a buffer of H_2O at 200 mM NaCl.

The window of Q = 0.003 – 1.5 Ang-1 covered was consistent with our previous D22 experiments (Exp. 9-13-559, Exp. 9-13-695) by using the configuration of wavelength $\lambda = 6$ Ang, and detector distances D = 17 m, D = 5.6 m, D = 1.4 m.

The results are at the moment being treated in order to clarify their agreement with theoretical simulations with the aim of being published in a recent future.

References

[1] J. Fernandez-Castanon, F. Bomboi, L. Rovigatti, M. Zanatta, A. Paciaroni, L. Comez, L. Porcar, C. J. Jafta, G. C. Fadda, T. Bellini and F. Sciortino, J. Chem. Phys. 145 8 (2016).
[2] P. J. Flory, J. Am. Chem. Soc. 63 3091 (1941).
[3] W. H. Stockmayer, J. Chem. Phys. 12 125 (1944)