SANS and Molecular Dynamics structural study of gelling DNA nanostars

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Besides its undeniable biological relevance, DNA has been postulated as one of the most outstanding candidates to compose the next generation of nanomaterials [1]. We present the results of a series of small-angle neutron scattering (SANS) experiments (D22, ILL - V4, HZB *and* PACE, LLB) of one of the first DNA constructs designed and realized in the lab, the DNA nano-stars (NS) with controlled valence. Exploiting the base pairing specificity of DNA and via a cascade of self-assembly processes, bulk quantities of DNA tetramers were formed by mixing equimolar concentrations of *4* properly designed DNA single strands of 49 bases each. Self-complementary short sequences were intentionally placed at the end of each NS's arms, allowing bond formation between different NSs. Beyond the coexisting density of this DNA-NS physical gel, on cooling, the system moves continuously, i.e. without the interference of a transition of the first order, from a high-T state in which monomers only interact via their excluded volume repulsion to a fully bonded low temperature state (the equilibrium gel) [2,3]. The preparation of samples both at low and at high DNA-NS concentrations, permitted the investigation of the experimental form factor, P(q), and of the temperature evolution at a concentration where the system forms a tetravalent equilibrium gel. Molecular dynamics simulations, of one isolated tetramer were performed to evaluate P(q) theoretically [4]. The numerical P(q) was found in very good agreement with the experimental one, allowing us to estimate precisely the shape of the NS. These simulations offered the possibility to extract the effective structure factor S(q) and its evolution during the equilibrium gelation. We will discuss the realisation of this ideal biocompatible physical gel, and how the possibility to compare the neutron data with the accurate geometry provided by the simulations, was crucial for evaluating an effective gel S(q).

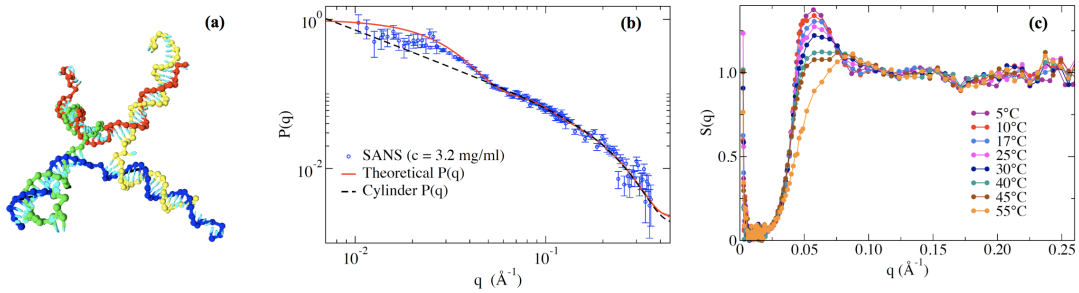

Figure 1. (a) Representation of the self-assembled NS, in which each base is modelled as a rigid body [4], **(b)** Normalized form factor P(q). Experimental SANS (blue dots) and simulated (red line) form factor at 50°C as a function of q in log-log scale. P(q) of an infinite long cylinder with cross section radius R_c = 8 Å (dashed black line), **(c)** Static structure factor S(q) at different temperatures (55-5°C).

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