Poly(vinyl alcohol)-based microgels prepared through salting out: rationalising the aggregation process

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Poly(vinyl alcohol) (PVA) is a biocompatible water-soluble polymer of great interest thanks to its large-scale applications as a material for drug-delivery systems or for building sensors and membranes with selective permittivity. The cryogenic route is one of the most studied and widely employed techniques for the preparation of PVA physical hydrogels [1]: the advantages of such gels is the absence of toxic chemicals for their preparation and the consequent possibility to obtain a completely eco-friendly product [2].
In this work we propose a new route for the preparation of PVA-based microgels through the salting-out effect: after a screening of different salts belonging to the Hofmeister series, sodium chloride represented the best cosmotropic species to use in order to favour the polymer aggregation over a reasonable time-scale. The thermodynamic properties and the kinetics of the aggregation process were deeply studied through a combined Dynamic Light Scattering (DLS), Static Light Scattering (SLS) and Small Angle Neutron Scattering (SANS) study, which allowed rationalising how such process is influenced by different parameters like salt molality, polymer concentration and time from the preparation (fig. 1).
Moreover, we were able to shed light on the structural and morphological properties of PVA particles, showing the role of the salt in the aggregation process and its effect on the supramolecular organization. In particular, we determined the molecular weight and the radius of gyration of the aggregates and we estimated the packing degree of polymer chains within the aggregates, strongly influenced by the time and the salt concentration.

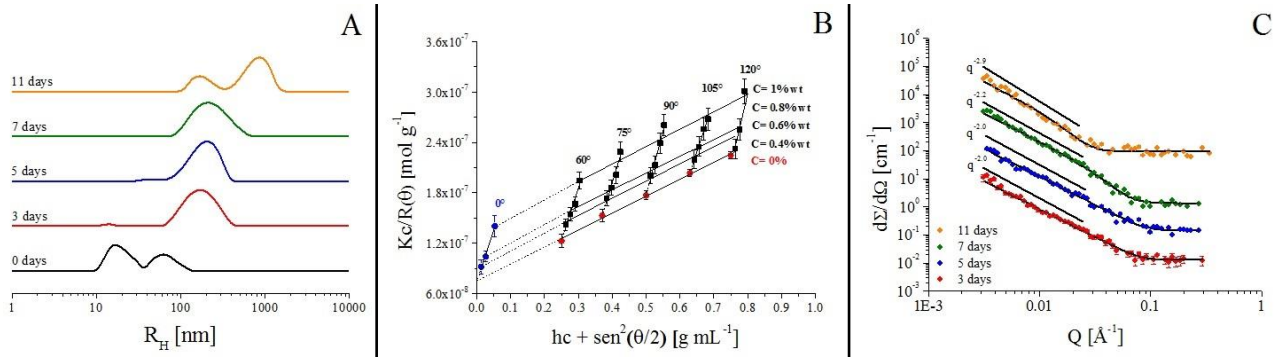

Figure 1 – PVA 1% wt, NaCl 2 mol kg^{-1}: study of the evolution of hydrodynamic radii over time by DLS (panel A); Zimm plot obtained from SLS measurements (panel B); SANS results at different times from the preparation (panel C).

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[2] Nayak, S., Lyon, A., *Angewandte Chemie,* 2005, **44**, 7686.