SYNTHESIS OF THERMO-RESPONSIVE NANOBIOPARTICLE-POLYMER CONJUGATES

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Proteins are well characterized nanoparticles and their stability in terms of shape and functionalities allows using them to build nano-objects or to introduce functionalities into polymer thin film and membranes. As a model protein, horse spleen ferritin is used to create thermo-responsive conjugates which can self-assemble at an interface to create a membrane [1,2]. Our approach is to transform first ferritin into a macro-initiator for Atom Transfer Radical Polymerization (ATRP) [3] by active ester chemistry and then to induce the polymerization as a grafting from the ferritin. We can then obtain monodisperse thermo-responsive ferritin-PNIPAAm conjugates.

Ferritin is an iron storage protein with a spherical diameter of 12 nm and a 6 nm central cavity. The protein shell is stable in a broad range of temperature and pH. It carries 24 chemically addressable amino end groups all around its capsid which allow bioconjugation.[4,5,6] The chosen polymer is PNIPAAm well known for its thermo-responsive properties, as it has a LCST of 32°C.[7]
The temperature-dependent characterization of the conjugates in solution was done by TEM, turbidity and dynamic light scattering measurements.
TEM allows visualizing the conjugates as shown in fig. 1, as ferritin is an iron storage protein, it has a high contrast compare to the polymer.
PNIPAAm in aqueous solution undergoes a transformation of its molecular dimension around 32°C, followed by an aggregation of individual polymer chains into globular particles yielding an optically detectable phase transition. At the non specific wavelength of 600nm, the absorption is measured. As seen in fig.2, the transition occurs at 31°C and is reversible, i.e. the conjugates are thermo-responsive.
Dynamic light scattering reveals that the behavior of the conjugates is not completely as expected. From 20 to 32°C the size of the conjugates decreases because of the shrinking of the polymer around the protein core. However, with further increasing temperature the conjugates show aggregation. Possibly, as the polymer becomes more hydrophobic upon collapse of the PNIPAAm it tends to reduce its interface with the aqueous solution, orienting the protein towards the interface.

In a further project the self-assembly behavior of these nanobioparticle-polymer conjugates within a polymer matrix will be demonstrated. Thus, these conjugates may serve as precursors for the generation of functional polymeric membranes with controlled pore sizes on the nanometer scale.

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Figures:

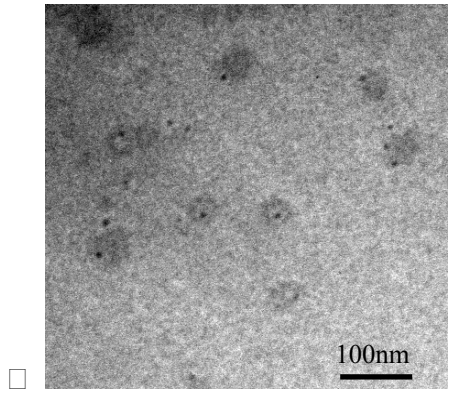

Fig.1 TEM image of the ferritin-PNIPAAm conjugates

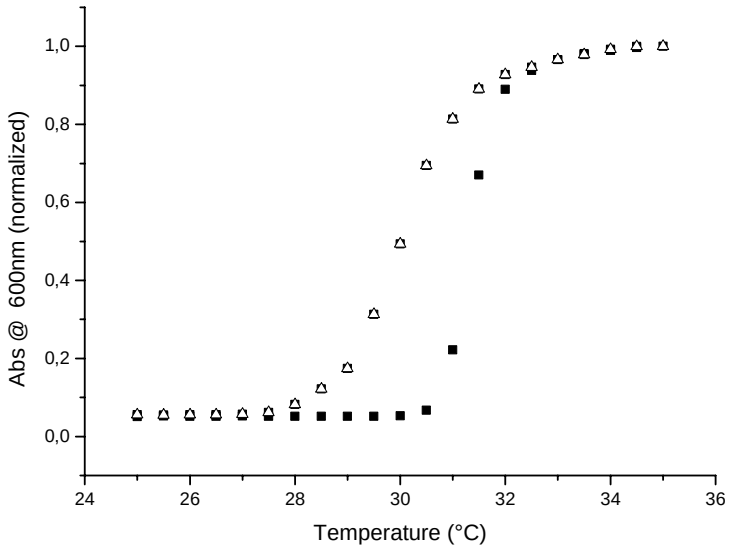

Fig.2 Turdibity measurement as a function of the temperature of the ferritin-PNIPAAm conjugates. (■ corresponds to the increase of temperature; Δ corresponds to the decrease of temperature)

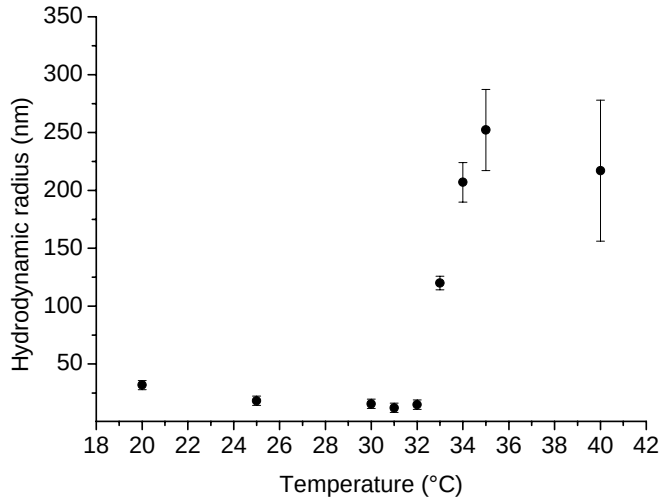

Fig.3. Dynamic light scattering measurement as a function of the temperature of the ferritin-PNIPAAm conjugates.