POLY(ACRYLIC ACID) NANOGELS: LOADING-RELEASE BEHAVIOUR WITH OLIGOTHIOPHENE-LABELLED BOVINE SERUM ALBUMIN.

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In this work we report on loading and release experiments of labelled protein systems with polyacrylic acid (PAA) nanogels, demonstrating that they are suitable pH-sensitive carriers for biomedical applications. The nanogels were synthesized by emulsion polymerization of methylacrylate and subsequent acidic hydrolysis. It was observed by light scattering measurements that the more basic the pH solution, the larger the nanogel diameter was (Fig. 1). In the swollen state the nanogel shows an increased permeability, which favours the pH-controlled loading or release of small molecules or proteins through the nanometer-sized meshes of the polymer network. As prototype systems we used an oligothiophene fluorophore (OTF) and its bovine serum albumin conjugated (BSA-OTF). The first is hydrophobic and pH-insensitive, while its conjugate with BSA is pH-sensitive due to its proteic moiety. The loading experiments were performed at two different pH values (4.5 and 7.0). Our results demonstrate that the loading and release processes are driven by electrostatic and/or hydrophobic interactions depending on the chemical nature of the solutes and on the pH of the external solution. Indeed, with OTF loading occurs in a quite pHinsensitive way, while with BSA-OTF loading seems to be strictly pH-dependent (Fig. 2). As oligothiophenes present remarkable photostability, fluorescence intensity and colour tunability, the possibility to encapsulate them or proteins labelled with them could be interesting in bio-imaging, and in particular for multicolour experiments and simultaneous tracking of different cell events.



Figure 1. Plot of the hydrodynamic diameter of nanogel versus the pH of the surrounding solution. **Inset.** Schematic representation of PAA nanogels swelling as a function of the pH.



Figure 2. Plot of the uptake data into nanogels (mg fluorophore/mg nanogel) concerning the loading experiments run with OTF and BSA-OTF.