INFLUENCE OF THE MOLECULAR ARCHITECTURE ON THE SELF-ASSEMBLY OF PH- AND TEMPERATURE SENSITIVE ELASTIN-LIKE BLOCK-COPOLYMERS.

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Elastin-like polymers (ELPs) are a surprising kind of elastic biopolymers [1]. The best known model ELP is the polymer $(VPGVG)_n$ where V stands for L-Valine, G for Glycine, and P for L-Proline. This polymer exhibit some interesting features that make it an excellent candidate for some top nano(bio)tecnological applications. Among their main features are: their mechanical properties showing an almost ideal elasticity, although there are some derivatives can show a more thermoplastic behaviour; their extreme biocompatibility showing excellent results in all the tests made on these polymers; and an acute self-assembly and *smart* nature. This last feature is produced in a mechanism called the Inverse Temperature Transition (ITT), by which, in aqueous medium, there is a reversible phase transition when the temperature goes above a certain temperature (T_t). In this transition, the polymer changes from a soluble state to a segregated state with an acute increase in the solvent-polymer interaction parameter. Together with this phase transition there is dehydration and an increase in the conformational order adopting a regular non-random structure called β-spiral. With that conformational change there is a self-assemble of filaments of three β-spirals that finally gather to form nano- and micro-particles. The T_t depends on the polarity of the polymer chain so with the change of certain functional amino acids (with two states of polarity) in some of the monomers of the model polymer, different ELPs have been synthesized to exhibit a *smart* nature to different stimuli such as pH, electromagnetic waves, redox potential, etc [1].

Another characteristic of this kind of protein-based polymers is that, taking the advantage that they are made from amino acids, it is possible to produce then as recombinant proteins in genetically modified organisms such as bacteria, yeast or plants. This allows the synthesis and bioproduction of monodisperse and more complex polymers with an absolute control in the amino acid sequence and molecular weight, together with an increase in yield with respect to the chemically synthesized polymers. Another advantage of this method of production is that it is independent of petroleum, it uses water as solvent in all the process of production and the resultant polymer is completely biodegradable so they can be considered as environmentally friendly [2].

Two different ELPs have been designed and selected for the purpose of this work. The first one is $[(VPGVG)_2\text{-}(VPGEG)\text{-}(VPGVG)_2]_n$ where E stands for L-Glutamate. This polypeptide exhibits the same properties than the model polymer $(VPGVG)_n$ and in addition a pH-sensitive nature produced for the change in polarity in the protonation-deprotonation of the Glutamate-γ-carboxyl group under changes in the pH [3]. Together with this pH sensitive nature a self-assembly characteristic has been observed when this polymer is deposited on an hydrophobic substrate given rise to the formation of nanopores [4]; The second one is the more apolar polypentapeptide $(VPAVG)_m$ where A stands for L-Alanine. This polymer shows a dissimilar behaviour than the general ELPs. It shows, among other differences, different mechanical properties, or thermo-sensitive behaviour with a higher enthalpy of transition and a clear hysteresis in its heating-cooling cycle [5, 6].

Based in these two different ELPs a set of monodisperse ABA and AB block-copolymers have been synthesized with different precisely controlled block lengths, being A the Glutamate-containing aforementioned block and B the Alanine-containing block.

Depending on the temperature and the pH, different states of block-solvent interactions parameter will give rise to different states of aggregation and structures. Different series of measurements have been made for these di- and tri-block copolymers for different block lengths and different pHs. The results show the formation of different structures, with not-completely independent transitions between the different blocks transitions showing behaviour not only depending on the polarity of the bocks but also on the molecular architecture.

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Figures:

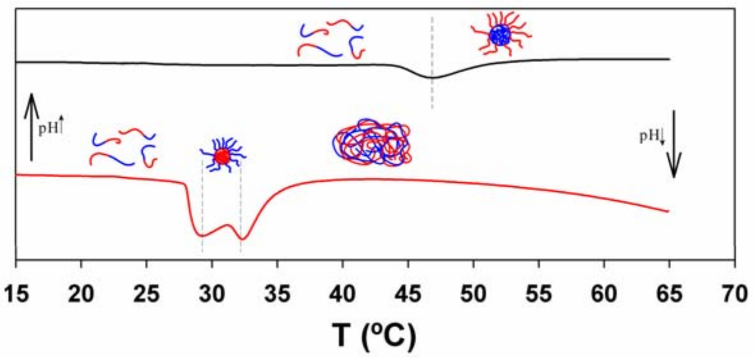

Figure 1: Scheme of the aggregation of the block-copolymers $\mathbf{[(VPGVG)_2\text{-}(VPGEG)\text{-}(VPGVG)_2]_{10}\text{-}[VPAVG]_{40}\text{-}[(VPGVG)_2\text{-}(VPGEG)\text{-}(VPGVG)_2]_{50}}$ on heating.