Metallopolypeptide polymers : towards controlled helix to coil transition

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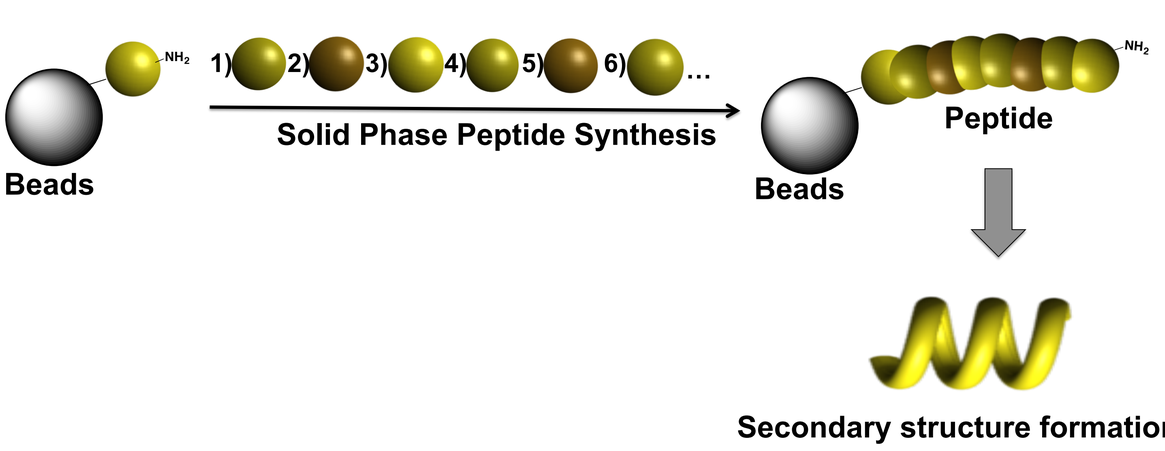
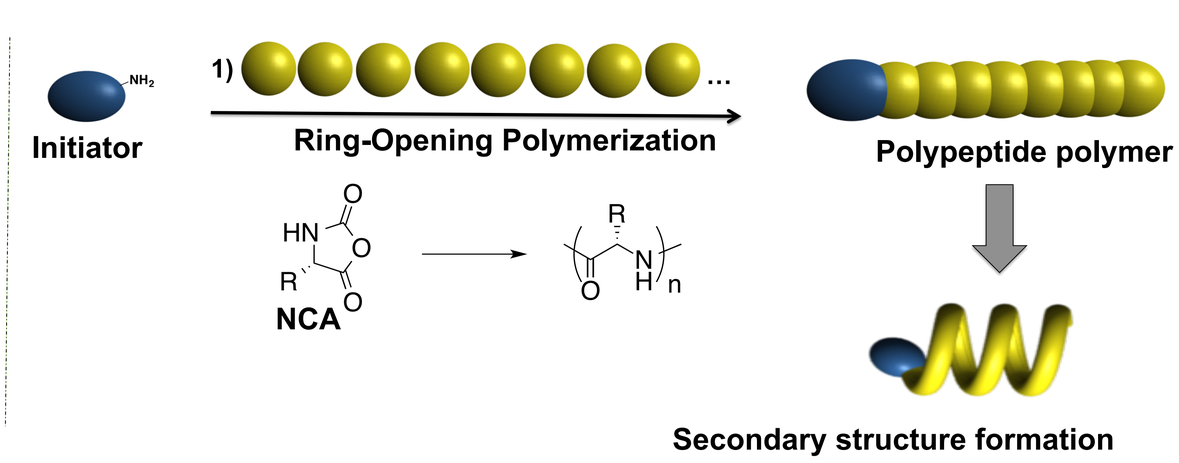
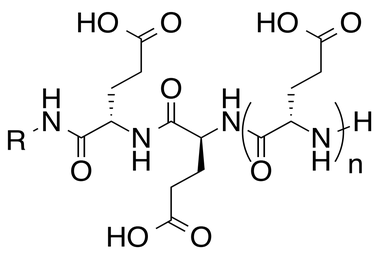
Context Proteins that interact with at least one metallic center are called **metalloproteins**. Their metallic centers are cations interacting with the amino-acids from the protein or with cofactors. The coordination with the metal is at the origin of 1) *the tridimensional shape of the macromolecules* or 2*) the biological function* (oxygen transport, catalytic activity) in the human body.

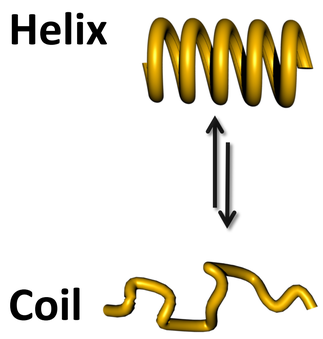




Chemical synthesis can be used to reproduce parts of the natural structures of metalloprotein by SPPS iterative coupling. Materials sciences offer an alternative approach to produce **simplified protein analogues through N-carboxyanhydride (NCA) polymerization.**[1]

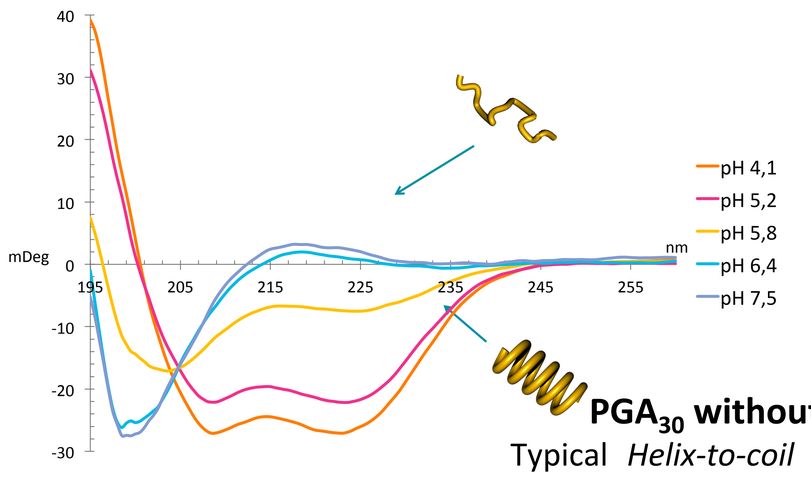
Polyglutamic acid (PGA)[2]



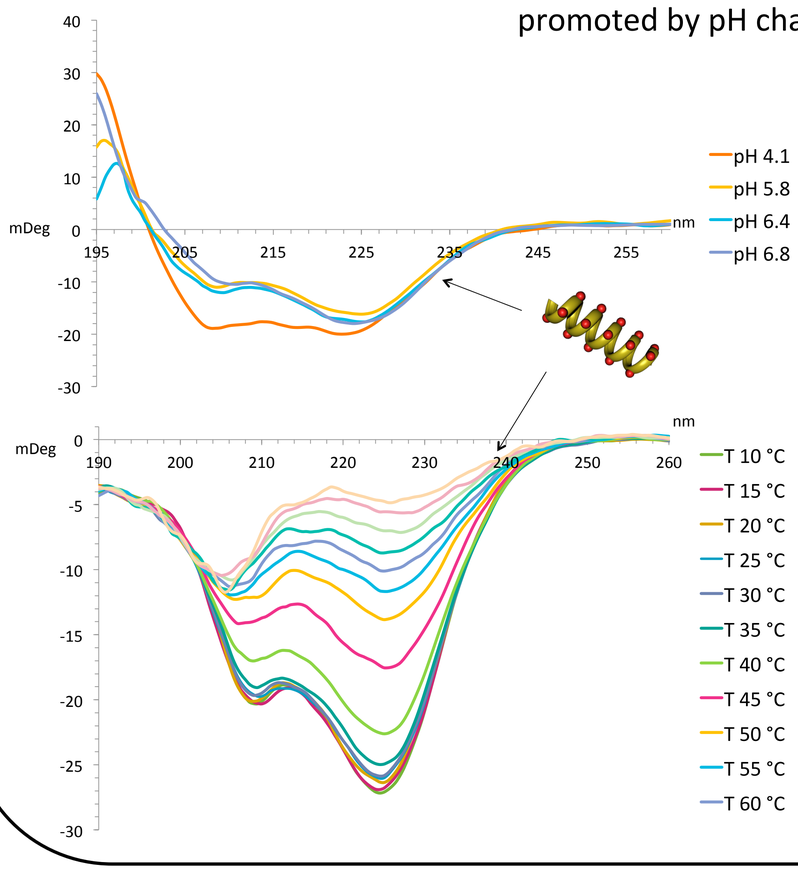


Several parameters can influence the PGA secondary structure and could lead us to find interesting applications at the interface between chemistry and biology. The **aim of this work** is to study the physico-chemical properties of the PGA in the presence of metal ions: *Could it be possible to control the secondary structure of PGA by means of this parameter?*

Circular Dichroism

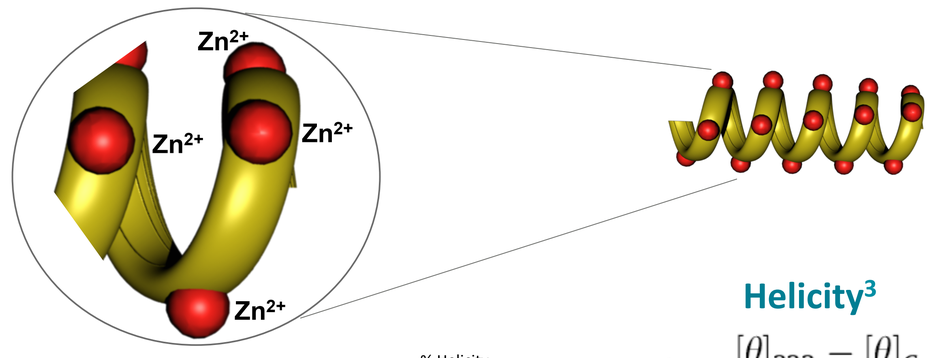


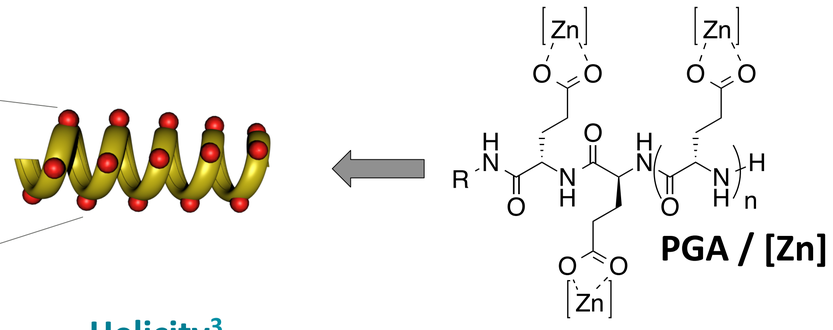
PGA_{30} without Zn
Typical *Helix-to-coil* transition promoted by pH changes.



PGA_{30} / $ZnSO_4$
In the presence of a metal the structure is controlled and the helix is maintained up to pH = 6,8.

PGA_{30} / $ZnSO_4$
The presence of the metal makes possible to maintain the helix even at high temperatures.





Helicity[3]

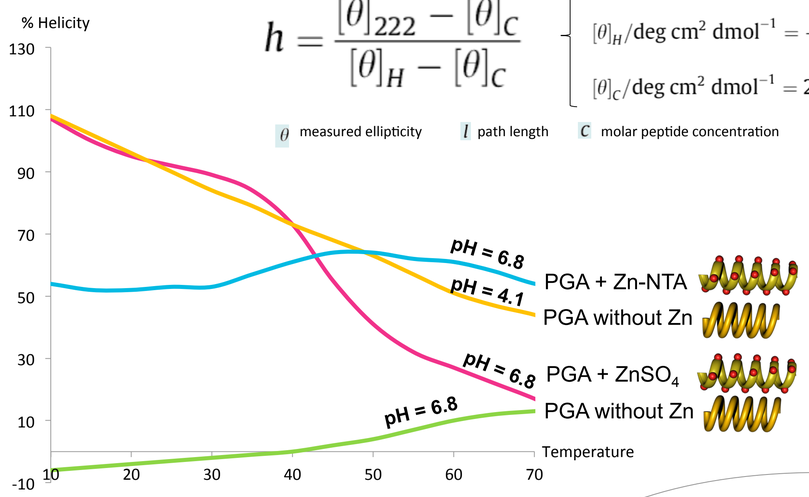
$$h = \frac{[\theta]_{222} - [\theta]_C}{[\theta]_H - [\theta]_C}$$

$$[\theta] = \theta/(10\ l\ c)$$

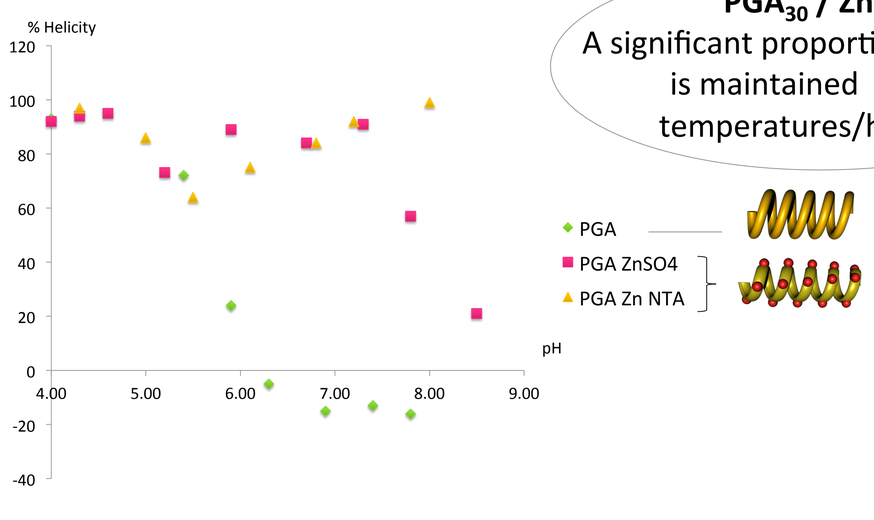
$$[\theta]_H/\mathrm{deg\ cm^2\ dmol^{-1}} = -(44,000 + 250\ T)(1 - 3/N_r)$$

$$[\theta]_C/\mathrm{deg\ cm^2\ dmol^{-1}} = 2220 - 53\ T$$

θ measured ellipticity l path length C molar peptide concentration T temperature N_r number of residues



PGA_{30} / $ZnSO_4$
A significant proportion of helicity is maintained at high temperatures/high pH.



References

[1] C. Bonduelle and S. Lecommandoux *Biomacromolecules* **2013**, *14*, 2973- 2983.
[2] M. Nagasawa and A. Holtzer *J. Am. Chem. Soc.* **1964**, *86*, 538-543.
[3] E. A. Gooding, S. Sharma, S. A. Petty, E. A. Fouts, C. J. Palmer, B. E. Nolan and M. Volk *Chemical Physics* **2013**, *422*, 115-123.