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ABSTRACT HABILITATION THESIS

Title: BIOINSPIRED CRYSTAL GROWTH THROUGH POLYMERIC ADDITIVES AND TEMPLATES. FROM BASIC RESEARCH TO APPLICATION

***Fundamental domain*:** CHEMISTRY

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Thesis developed to obtain habilitation certificate in order to manage doctoral theses in the domain CHEMISTRY

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Abstract

The abilitation thesis entitled BIOINSPIRED CRYSTAL GROWTH THROUGH POLYMERIC ADDITIVES AND TEMPLATES. FROM BASIC RESEARCH TO APPLICATION presents the most important research and contributions of the author and her activities in the "Petru Poni" Institute of Macromolecular Chemistry (PPIMC) in Iasi since obtaining the PhD title (2009).

The thesis begins with a section dedicated to the scientific and professional activity of the author, activity developed after the defense of the doctoral thesis. Since 2011, the author began studies in a new field, not previously addressed by researchers in PPIMC. These studies had the overall objective of obtaining porous composite microspheres based on pH-sensitive polyelectrolytes. They were inspired by the idea that ionic polymers are able to control the nucleation of calcium carbonate polymorphs and they may tune their growth in ordered structures by controlling their complex hierarchical structure, shape, size, and orientation.

In this context, the habilitation thesis contains in Section II – SCIENTIFIC ACHIEVEMENTS – nine chapters that follow the influence of some experimental parameters in the formation of composite materials based on calcium carbonate as well as on their properties, as given by polymorphs nature, namely:

Synthesis and characteristics of calcium carbonate microparticles obtained under different conditions of supersaturation in inorganic precursor compounds – **Chapter 2**.

Chapters 3-9 discuss the influence of different parameters in the synthesis of $CaCO_3$ / polymer composite materials, namely:

Chapter 3 - The influence of polymer structure. Various synthetic polymers [sodium poly (2-acrylamido-2-methylpropanesulfonate-co-acrylic acid), PAMPSAA, poly (p-hydroxystyrene-b-methacrylic acid), PHOS-b-PMMA, a polymer-drug conjugate based on poly (N-vinylpyrrolidone-co-maleic anhydride) and 2-amino-5- (4-methoxy-phenyl) -1,3,4-oxadiazole], P (NVP-MA-Ox)] and natural polymers (chondroitin A sulfate, CSA) were used.

Chapter 4 - The influence of polymer functional groups. Most of the used polymers contain carboxylic groups in the macromolecular structure, and these groups are known as being responsible for nucleation and / or stabilization of $CaCO_3$ polymorphs. The investigations also demonstrated that the polymers functionalized with primary amine groups may show strong interactions and therefore represent an efficient class of additives for $CaCO_3$ crystallization.

Chapters 5 and **6** are related to the relationship between organic and inorganic precursors and its influence on the characteristics of the final composite material. The organic/inorganic ratio was adjusted either by changing polymer concentration (**Chapter 5**), or by changing the concentration of calcium carbonate precursors (**Chapter 6**).

Chapter 7 - Influence of solutions pH. This parameter can significantly influence the characteristics of the composite materials, by adjusting the nature of the active ionic species in the reaction system, namely the charge density of the pH sensitive polymers or ionic species such as HCO_3^- sau CO_3^{2-}.

Chapter 8 - Influence of the crystallization time. Since calcium carbonate polymorphs have different solubility constants, increasing crystallization duration can lead to a re-crystallization of the polymorphs with high solubility constants (vaterite, aragonite) and their stabilization in calcite.

Chapter 9 follows the effects of polyanionic / polycation complex systems on $CaCO_3$ crystallization. Two simple, not previously used methods were tested to introduce the polycation in the crystallization of $CaCO_3$, namely the non-stoichiometric polyelectrolyte complex approach or the *in-situ* introduction of the mixture of polyelectrolytes.

Section II – SCIENTIFIC ACHIEVEMENTS – ends with **Chapter 10** that includes original results on the properties and application of calcium carbonate / polymer composite materials as sorbents for different materials - cationic dyes (methylene blue) or metal ion (copper, nickel).

In conclusion, the studies summarized in this habilitation thesis focused on *in vitro* chemical approach of mineralization using different polymeric materials, such as: soluble polymers, colloidal dispersion based on complementary polyions and some ionic insoluble matrix.

Given the present state of knowledge, the prospects for finding simple, tough explanations for different effects of biomineralization mechanisms represent challenges for further investigations. Moreover, bioinspired mineralization can transfer biomineralization principles to the synthesis of organic-inorganic materials, offering a large playground to develop future materials.

Section III – FUTURE SCIENTIFIC, PROFESSIONAL AND ACADEMIC DEVELOPMENT PLAN – presents, based on a synthesis of scientific achievements, a set of principles underlying the future work directions and professional development as well as some specific elements that will contribute to author future development. Plans related to international cooperation and accessing national and international funding programs are also highlighted.

Section IV – REFERENCES – includes a list of references used in the habilitation thesis.