SORBONNE UNIVERSITÉ

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Thesis proposal

Title of the research project: **New materials from a simple and fast separation and characterisation of polyelectrolytes**

Keywords: polymer chemistry, analytical chemistry, separation science

Joint supervision: no

Joint PhD (cotutelle): no

Thesis supervisor: Patrice Castignolles

Email address of the thesis supervisor: patrice.castignolles@sorbonne-universite.fr

Institution: Sorbonne Université

Doctoral school (N°+name): ED 397 Physique et Chimie des Matériaux

Research laboratory: IPCM (UMR8232)

Address of the laboratory: 4 place Jussieu, 75252 Paris cedex 05, France

Name of the laboratory director: L. Fensterbank

Email address of the laboratory director: louis.fensterbank@sorbonne-universite.fr

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AVIS et VALIDATION de l'ECOLE DOCTORALE :

Avis favorable

Ecole Doctorale Physique et Chimie des Matériaux
ED
Directrice
Nadine WITKOWSKI

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Subject description:

1) Study context

Polyelectrolyte are key ingredients in cosmetics, biomedical systems, superabsorbents, paints or coatings. They can be artificial, such as chitosan obtained from crab or prawn shell, or synthetic such as poly(acrylic acid)/poly(sodium acrylate). Due to their charge and often their acid-base properties, polyelectrolytes react to stimuli from the environment. They are thus sometimes named "smart" polymers and this is also the reason for the sustained interest in research and development. However, these very sensitive polymers proved also challenging to separation and characterise. For example, round-robin tests on the chromatography (SEC) of poly(acrylic acid) showed the determination of the molar mass of this polymer suffers from poor accuracy.[1] This may be due to the limited solubility of poly(acrylic acid) in the solvents commonly used for its dissolution.[2] In the case of chitosan, full solubility is only obtained at the expense of chemical degradation.[3]

DNA and proteins are two types of polyelectrolytes which form their own field of research. Capillary electrophoresis is a major separation and characterization methods for these two polymers. It is not the case for all other polyelectrolytes, natural, artificial or synthetic.

2) Details of the proposal

The dissolution of polyelectrolytes will be monitored online using time-resolved NMR spectroscopy[3] (Figure) and capillary electrophoresis[4]. Solubility will be quantified by fast and quantitative NMR spectroscopy.[3,5] One aim is to map which polyelectrolytes from single-chain nanoparticles simply upon dissolution (Figure 1).

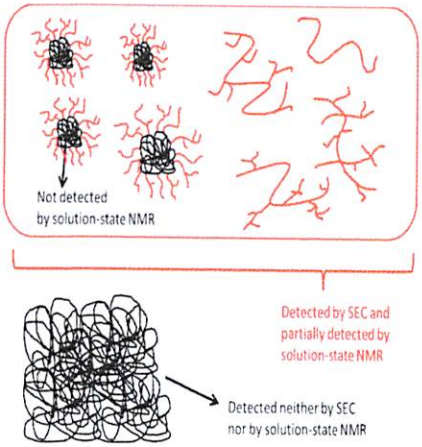

Figure 1. Polymer chains in solvent (poly(acrylic acid)[2])

The molecular size of the polyelectrolytes will be determined by standard SEC but also by comprehensive multiple detection SEC and fast Taylor Dispersion Analysis. The distribution of chemical composition will be determined by capillary electrophoresis.[6]

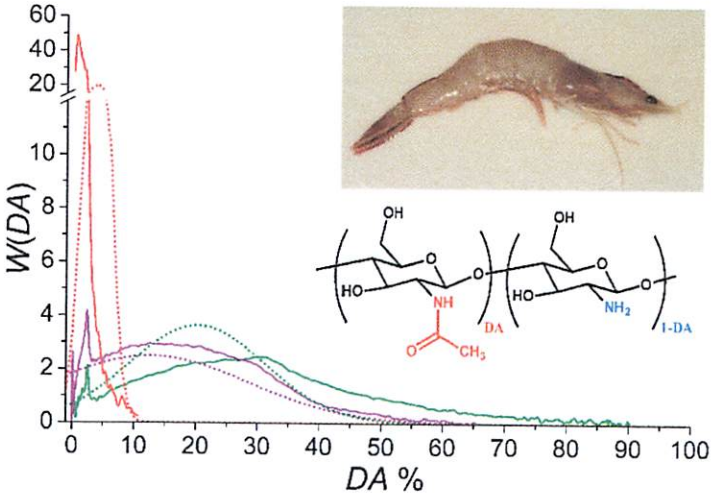

Figure 2. Distributions of composition (degree of acetylation, DA, in this case). Example of chitosan. The distibutions are experimental (full line) with the corresponding theoretical one (dotted line).

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3) References

[1] Lacík, I., Stach, M., Kasák, P., Semak, V., Uhelská, L., Chovancová, A., . . . Buback, M. (2015). SEC Analysis of Poly(Acrylic Acid) and Poly(Methacrylic Acid). *Macromol. Chem. Phys.*, **2015**, 216, 23-37.

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[3] Thevarajah, J. J., Bulanadi, J. C., Wagner, M., Gaborieau, M., & Castignolles, P. Towards a less biased dissolution of chitosan. Analytica Chimica Acta,**2016**, 935, 258-268.

[4] Sutton, A. T., Arrua, R. D., Gaborieau, M., Castignolles, P., & Hilder, E. F. Characterization of oligo(acrylic acid)s and their block co-oligomers. Analytica Chimica Acta, **2018**, 1032, 163-177.

[5] Van Leeuwen, M. P., Toutounji, M. R., Mata, J., Ward, R., Gilbert, E. P., Castignolles, P., & Gaborieau, M. Assessment of starch branching and lamellar structure in rice flours. Food Structure, **2021**, 29, 100201.

[6] Thevarajah, J. J., Van Leeuwen, M. P., Cottet, H., Castignolles, P., & Gaborieau, M.. Determination of the Distributions of Degrees of Acetylation of Chitosan. *Int. J. Biol. Macromol.*, **2017**, 95, 40-48.

4°) Profile of the Applicant (skills/diploma...)

We are looking for a motivated candidate with practical experience in polymer science or analytical chemistry.

Contacts:

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