



ΠΡΟΣ

- 1) Όλα τα μέλη ΔΕΠ του Τμήματος Επιστήμης και Τεχνολογίας Υλικών
- 2) Την Επταμελή Εξεταστική Επιτροπή
- 3) Όλα τα μέλη της Πανεπιστημιακής Κοινότητας

Πρόσκληση σε Δημόσια Παρουσίαση της Διδακτορικής Διατριβής της

κ. Lucille Germaine Louise Chambon

(Σύμφωνα με το άρθρο 41 του Ν. 4485/2017)

Τη **Πέμπτη 25 Ιουλίου 2019** και ώρα **10:00** στην **αίθουσα τηλεεκπαίδευσης E130** στο κτήριο **Τμήματος Μαθηματικών και Εφαρμοσμένων Μαθηματικών**, Πανεπιστημίου Κρήτης, θα γίνει η δημόσια παρουσίαση και υποστήριξη της Διδακτορικής Διατριβής της υποψήφιας διδάκτωρ του Τμήματος Επιστήμης και Τεχνολογίας Υλικών κ. Lucille Germaine Louise Chambon με θέμα:

«Anisotropic Particles: Synthesis and Characterization of Responsive Rod-Like Colloids»

Abstract:

Rod-like particles have been shown to display a rich phase diagram, due to the additional degree of freedom induced by their orientation. They also assemble into percolated networks, at low loading fractions, which can be exploited for mechanical reinforcement or improved conductivity. The colloidal behaviour of rod-like systems is dependent on their aspect ratio and the interactions between the particles, and therefore it would be highly attractive to devise systems with tunable dimensions and/or interactions, for example by grafting responsive polymers onto the surface of rod-like colloids. The use of controlled radical polymerisation techniques allows the formation of well-defined layers of polymers end-tethered to the surface, whose conformations can be varied by parameters such as the grafting density or the size of polymer chain. Furthermore, additional properties are accessible from hollow rod-like particles, such as low density and the ability for encapsulation and release of molecules.

This thesis describes the development of model functional rod-like particles, based on silica microrods or fd-virus particles, for further study of their self-assembly behaviour in colloidal phases. Silica rods were first functionalised by grafting a pH- and temperature-responsive polymer, poly(2-(dimethylamino)ethyl methacrylate) (PDMA) onto their surface, using both “grafting from” and “grafting to” techniques in combination with atom transfer radical polymerisation (ATRP). The core-shell morphology, polymer content and responsiveness of the synthesised polymer-grafted silica rods were characterised. The “grafted from” rods were found to have a stronger response to temperature compared to their “grafted to” analogues. The stability of the “grafted from” polymer layer, when the particles are dispersed in water, was assessed. The polymer content was found to decrease after dispersion for a few days in water, which is detrimental for their further characterisation and use. This

phenomenon was attributed to the degrafting of the polymer chains, due to the hydrolysis of labile surface bonds, which was mechanically activated by the tension of the chains. The degrafting was delayed by first grafting a hydrophobic layer on the particles, that acts as a barrier for the penetration of water molecules, to the silica surface, followed by chain-extension with pH and temperature-responsive PDMA.

Next, the synthesis of hollow polymer rods from amphiphilic block copolymer brushes grafted onto the surface of the silica rods is discussed. Robust polymer microrods were obtained following the etching of the silica core, even in the absence of chemical cross-links within the polymer layer. The presence of the first hydrophobic block, and its size, was found to be crucial for the formation of the hollow polymer rod particles, whereas the flexibility of the rods was tuned by varying both the size of each block, and the copolymer composition. Fluorescently labelled particles were also obtained, which were characterised by optical and fluorescence microscopy, due to their large size. These non-cross-linked hollow polymer rods could be selectively dissolved in solvents compatible for both blocks, which is attractive for use in phase transformation studies or delivery applications, whereas chemical cross-linking of their hydrophobic polymer layer produced stable rods in all solvent media.

In the next part of this work, a TiO₂ layer was coated onto the surface of the silica rods, by a surfactant induced precipitation process. A uniform coating on the surface of the rods, without any side nucleation, was realised by balancing the kinetics of the hydrolysis and self-assembly processes between the surfactant and the TiO₂ species, which depend on the concentrations of the reactants. The coating mechanism was also optimised to yield a TiO₂ layer with tunable thickness. Finally, the silica cores were etched to obtain hollow amorphous TiO₂ rods, which caved in after drying, or robust crystalline TiO₂ tubes.

In the last part of this work, end-functional responsive polymers were synthesised to be “grafted to” fd-virus particles in aqueous media, utilising the amino groups present on the fd-virus surface. Fluorescent and non-fluorescent pH- and temperature-responsive PDMA, was synthesised by ATRP, however no grafting was achieved onto the fd-virus particle. The coupling reaction, between the end-functional PDMA and the amino groups, was shown to be only successful in organic media, while the coupling reaction between a small functional molecule and the amine moieties proceeded also in an aqueous buffer. This behaviour was attributed to the steric hindrance induced by the polymer chain to the functional chain-end, which reduced the accessibility of the surface functionalities to the polymer end-groups in water. In addition, well-defined end-functional PNIPAM polymers were synthesised by reversible addition-fractionation chain-transfer polymerisation (RAFT) and grafted onto fd-virus particles. Contrarily to their PDMA analogues, the coupling reaction between end-functional PNIPAM and the amino groups was successful, although its efficiency increased with the decrease of the polymer molecular weight, proving that the grafting reaction is indeed hindered by the long polymer chains. Finally, PEG-b-PNIPAM copolymers were also synthesised by RAFT to be “grafted to” fd-virus particles and obtain anisotropic colloids whose volume can be tuned without inducing any attractive interparticle interactions.