MULTIFUNCTIONAL ORGANIC/INORGANIC HYBRIDS PREPARED THROUGH SOL-GEL AND/OR SELF-ASSEMBLY

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Multifunctional organic/inorganic hybrids prepared through sol-gel

and / or self-assembly

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Para os meus pais

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"Nada na vida é para ser temido, apenas sim para ser entendido."

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Abstract

This thesis is focused on the preparation of organic-inorganic hybrid systems with targeted properties.

In the first part of the work, the sol-gel process and self-assembly techniques were employed for the preparation of organic-inorganic hybrid materials. This combination is of great interest, not only from the fundamental point of view, but also because it allows the production of novel functional and hierarchically structured hybrid materials. Two families of materials were obtained, featuring two different types of cross links: urea and urethane. The influence of parameters such as the alkyl and alkylene chain length and the solvent on the nanostructure was analyzed.

In the second part of the work the sol-gel method was used to prepare organicinorganic hybrid electrolytes composed of novel di-urethane cross-linked poly(ε caprolactone)/siloxane biohybrids incorporating a wide range of potassium triflate concentration in one example and a mixture of lithium triflate and europium triflate in the other example. In both cases prototype ECDs have been constructed using a four layer-sandwich configuration comprising two outermost layers composed of transparent conducting oxide (TCO) films, an EC film of tungsten oxide (WO₃) and an IC active layer of selected ormolyte samples. The average optical transmittance, colour contrast, optical density and device response time associated with the colouring/bleaching processes have been determined. The colour change has been quantified in the prototype based on the Li/Eu mixture.

Calcium carbonate (CaCO₃) is an important biomineral in Nature, that can exist in six different polymorphic forms. Among them, the metastable amorphous CaCO₃ phase (ACC) is used in many organisms as a transient intermediate to form single crystals of calcite and aragonite with elaborate shapes. ACC has a tremendous potential in the orthopedic field. Herein we have employed poly(vinylpyrrolidone) to retard the crystallization of ACC. In addition, several ionic liquids and surfactants were employed to tune the morphology of calcite.

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Resumo

Esta tese centra-se na preparação de sistemas híbridos orgânicos-inorgânicos com propriedades específicas.

Na primeira parte do trabalho utilizaram-se o processo sol-gel e metodologias de auto-organização na preparação de materiais híbridos orgânicos-inorgânicos. Esta conjugação de métodos de síntese é particularmente interessante, não só do ponto de vista fundamental, mas também porque permite a produção de novos materiais híbridos, hierarquicamente estruturados e funcionalizáveis. Obtiveram-se duas famílias distintas de amostras, cuja principal diferença reside na natureza do nó de ligação entre os componentes orgânico e inorgânico: grupo ureia e grupo uretano. A influência exercida na estruturação dos materiais por parâmetros, tais como o comprimento da cadeia de tipo alquilo (pendente ou em ponte) e o tipo de solvente, foi analisada.

Na segunda parte do trabalho o método sol-gel foi usado na preparação de electrólitos híbridos orgânicos-inorgânicos inovadores. Foi preparada uma matriz biohíbrida de poly(ɛ-caprolactona)/siloxano, baseada em nós de ligação de uretano. A matriz foi dopada com uma gama de concentrações de triflato de potássio muito ampla, num caso, e com misturas de triflato de lítio/triflato de európio no segundo caso. Para ambos sistemas foram construídos protótipos de dispositivos electrocrómicos. Estes foram construídos usando-se uma configuração de tipo "sandwish" de quatro camadas, envolvendo duas camadas de filme de óxido condutor transparente, um filme de óxido de tungsténio (WO₃) e uma camada activa condutora iónica de um ormolito de composição optimizada. A transmitância óptica, o contraste de cor, a densidade óptica, e o tempo de resposta do dispositivo associado ao processo de coloração/descoloração foram determinados. A variação de cor foi quantificada para o protótipo cujo ormolito contém uma mistura de triflato de lítio/triflato de európio.

O carbonato de cálcio (CaCO₃) é um dos biominerais mais importantes na Natureza. Pode existir em seis formas polimórficas diferentes. De entre estas a fase metastável amorfa (carbonato de cálcio amorfo, CCA) é usada por muitos organismos

como uma fase intermediária transiente para a formação de cristais de calcite e aragonite exibindo formas elaboradas. Uma das potenciais aplicações do CCA encontra-se no domínio da ortopedia. Neste trabalho utilizou-se a poli(vinilpirrolidona) para retardar a cristalização do CCA. Foram ainda usados diferentes líquidos iónicos e tensioactivos para controlar a morfologia de calcite.

Résumé

Cette thèse décrit la préparation de matériaux hybrides organiques-inorganiques aux propriétés ciblées.

Dans la première partie de ce travail, le procédé sol-gel a été couplé aux techniques d'auto-assemblage pour la préparation de matériaux hybrides organiquesinorganiques. Cette combinaison est d'un grand intérêt, non seulement d'un point de vue fondamental, mais aussi parce qu'elle permet la production de nouveaux matériaux hybrides fonctionnels à structuration hiérarchique. Deux familles ont été étudiées, avec deux types de liens: urée ou uréthane. L'influence de paramètres tels que la longueur des chaînes alkyle et alkylène et le solvant sur la nanostructure a été analysée. Le comportement hystérétique d'une classe des matériaux à liens uréthane a été exploité.

Dans la seconde partie de ce manuscrit, le procédé sol-gel a été utilisé pour préparer des électrolytes hybrides organiques-inorganiques composés de biohybrides siloxane/poly(ɛ-caprolactone) à liens uréthane, contenant des proportions fortement variables de triflate de potassium dans un cas, et un mélange de triflates de lithium et d'europium dans l'autre exemple. Dans les deux cas, des prototypes de dispositifs électrochromes ont été construits, avec une structure sandwich constituée de quatre couches comprenant deux couches externes formées de films d'oxyde conducteur transparent, un film électrochrome d'oxyde de tungstène (WO₃) et une couche active conductrice d'ions constituée des échantillons d'ormolyte. Les transmittances optiques moyennes, les contrastes de couleur et les temps de réponse associés aux processus de coloration/décoloration ont été déterminés. Le changement de couleur a été quantifié dans le prototype à base du mélange Li/Eu.

Le carbonate de calcium (CaCO₃) est un composé minéral très important dans la Nature, qui peut exister sous six formes polymorphiques différentes. Parmi elles, la phase amorphe (ACC) métastable est utilisée par beaucoup d'organismes comme intermédiaire transitoire pour former des objets composés de monocristaux de calcite ou d'aragonite à morphologie élaborée. L'ACC a un potentiel inédit dans le domaine de l'orthopédie étant donnés sa vitesse de croissance, son caractère immunogène et les propriétés mécaniques des os qui en dérivent. Dans cette étude, nous avons utilisé une méthode de synthèse faisant appel à la poly(vinylpyrrolidone) pour retarder la cristallisation de l'ACC et à plusieurs liquides ioniques et tensio-actifs pour changer la morphologie de calcite.

Chapter 1

Introduction

Context and state of the art

Objectives and organization of the thesis

Communications resulting from this thesis

1. Introduction

1.1. Context and state of the art

Keywords

Materials science is located at the interface between chemistry, physics and biology. Chemical reactions allow producing new **materials** that are characterized by physical techniques. The inspiration from Nature is a constant [1-3]. Many ideas come from Nature giving origin to **bio-inspired materials**, also designated by **biomimetic materials**. Diatoms [4] and radiolariae [5], bones and crustacean carapaces [6], mollusk shells or nacre (also called mother of pearl) and wood are just a few examples of naturally occurring materials, inspiring materials' scientists.

Natural materials can serve as models to inspire and develop new concepts and new **biomimetic** approaches [2, 3]. The most famous example of biomimetic material is probably Velcro, the trend mark of a hook-and-loop fastener discovered in the 1940s by a Swiss Engineer. Other examples come from the lotus leaf and the gecko foot: their structures have provided inspiration for advanced functional materials such as superhydrophobic and superadhesives surfaces [7, and references therein].

Materials from Nature present a high degree of sophistication, miniaturization (i.e., they accommodate a maximum of elementary functions in a small volume) finding a compromise between different properties or functions [2]. They exhibit complexity and hierarchical structure from the nanometer, to the micrometer and millimeter scales. The properties of many materials are dependent on the **scale** [2] and on the **form** [8, 9]. The existence of a high degree of order across multiple length scales is of great importance since it can dictate the final application of the materials. Consequently, one of the major goals of materials science is to produce hierarchically structured materials that are ordered over all length scales. Nanostructured matter has become popular among industrials and academics. Nanomaterials characteristically exhibit physical and chemical properties different from the bulk as a consequence of having at least on spatial dimension in the size range of 1-1000 nm. Globally speaking, nanoscience and nanotechnology concern making, imaging, manipulating and using

really small things [10]. In the last decades Feynman's nanoworld ("on the head of a pin") has not ceased to inspire the scientific community. Nanoscale objects are crucial as components in the emergence of cellular life [11] and also as small-scale materials with advanced functions and properties that can be applied in numerous applications. Interestingly, science and art share in common the notion of form. Architecture is related with the **bottom-up** approach and sculpture is associated with the **top-down** approach. Nanomaterials fabrication usually applies bottom-up and top-down approaches [8, 12]. In architecture the building blocks (BBs) are integrated into a spatial structure [8] in order to build a new monument with specific shape, dimension and functionality. The bottom-up strategy employs chemical processes such as sol-gel, chemical vapour deposition (CVD), template synthesis or spray pyrolysis in the construction and growth through the use of precursors of organized materials from the nanometric level. In contrast, in sculpture the form is the result of the exclusion of matter(e.g., stone and wood). In the same way, **top-down** approaches essentially consist in the controlled nanostructuring of a bulk material by breaking it into smaller pieces or patterning it using diverse physical and/chemical tools. Top-down approaches are extensively employed in a wide range of well-known techniques such as photolithography, soft lithography, nanografting, electron beam lithography and focused ion beam lithography. In Figure 1.1 are indicated some representative keywords related with the main concepts behind this these: biomaterial (a), lotus leave showing an hydrophobic effect (b), botton up (c) and top down (d) approaches.



Figure 1.1. Representative examples of the keywords related with the main concepts discussed in thesis: a silica microskeleton a biomaterial, with a hierarchical structure (reproduced from reference [12] (a); a lotus leave displaying an hydrophobic effect (reproduced from reference [13]) (b) *Bottom up* represented by the architecture of a building (c) and *Top-down* represented by sculpture (d).

Organic-inorganic hybrid materials

In the last years a significant number of relevant books [14, 15] and reviews and/or feature articles [16-18] dealing with hybrid materials have appeared in the literature. The scope of such works spans from the strategies of synthesis, to the properties and applications [19-22], including biohybrids and related materials [1, 4].

By definition a hybrid material includes two moieties blended in the molecular scale. They can be defined as nanocomposites at the molecular scale, having at least one component (either organic or biological) with a characteristic length scale on the nanometer size [14, 23, 24].

The properties of the resulting materials are defined by the corresponding hybrid interface [14, 16]. The concept of organic-inorganic hybrids started to be used in the 1980s with the expansion of the soft inorganic chemistry, i.e. *Chimie Douce*, in which mild synthetic conditions open a versatile access to chemically designed organic-inorganic hybrid materials. Their potential applications have increased with the continuous development of novel physico-chemical characterization methods.

The organic-inorganic hybrids may be classified into two main classes, on the basis of the possible interactions connecting the inorganic and organic species.

In **Class I organic-inorganic hybrids** the organic-inorganic components additively exchange weak bonds (hydrogen, Van der Waals or ionic bonds). They may result from [14, 18] :

- (a) Organic dyes embedded in sol-gel matrices
- (b) Organic monomers embedded in sol-gel matrices
- (c) Inorganic polymers embedded in a polymer

One of the most popular examples of a class I hybrid material is the Maya blue (Figure 1.2). It is a very old and remarkable man-made hybrid material processed via soft chemical conditions [18]. Maya blue is a robust pigment, not only resisting biodegradation, but showing also unprecedented stability when exposed to acids, alkalis and organic solvents. In Maya blue molecules of the natural indigo are encapsulated within the channels of a clay mineral known as palygorskite. This material combines the color of the organic pigment and the resistance of the inorganic host, a synergic material with properties and performance well beyond those a simple mixture of components [18].



Figure 1.2. Computer enhanced Mayan Warrior from Bonampak –Mexico (reproduced from reference [18]).

In **Class II organic-inorganic hybrids** the two phases are totally or partly linked together through strong chemical bonds characterized by strong orbital overlap (covalent or iono-covalent bonds). The molecules used as starting building blocks for Class II hybrids possess at least two distinct functionalities: (1) Chloro- or alkoxy groups (M-OR bonds, where M represent metal) which can experience hydrolysis-condensation reactions in the presence of water and lead to an oxopolymer framework; (2) Metal-to-carbon (M-C) links which are hydrolytically stable. The nature of the stable M-C link depends on the nature of the metallic centre. Whereas the Si-C bond is inert towards hydrolysis, other M-C bonds are easily cleaved in the presence of water (e.g., M = Ti, Zr) [25, 26]. The existence of covalent chemical linkages between organic and mineral components present numerous advantages: (a) The potential to synthesize entirely new materials from functionalized alkoxides; (b) Minimization of phase separation; (c) Better definition of the organic-inorganic interface [24].

Many hybrid materials display both types of interactions and have the possibility to be classified either as Class I or Class II hybrids [24].

Strategies to produce organic-inorganic hybrids

General **bottom-up** strategies for the synthesis of sol-gel derived hybrid materials have been extensively discussed in several reviews [14, 16-18, 24]. These strategies are commonly designated by route A, route B and route C (Figure 1.3). In some cases a route D is also referred [16] (Figure 1.3).



Figure 1.3. Several strategies to produce organic-inorganic hybrids (reproduced from reference [17]).

Route A gathers the soft chemistry-based approaches including not only the conventional sol-gel chemistry from specific bridged and polyfunctional precursors, but also the hydrothermal processes [16].

Amorphous hybrid networks are obtained via conventional sol-gel pathways through hydrolysis-condensation of various metal species (alkoxydes /halide derivatives) which can be organically modified [16]. These strategies are simple, low cost and yield amorphous nanocomposite hybrid materials, easily shaped as films or bulks [17]. The materials are often polydisperse in size and locally heterogeneous in chemical composition.

A special group of materials obtained by this synthetic route are the bridged silsesquioxanes (BSs) [27, 28]. They are obtained from bridged organosilane precursors, represented by the notation X_3 -Si-R'-Si- X_3 , R' being an organic spacer and X = Cl, Br or OR. Upon chemically tailoring the bridge, materials with a high degree of organization where obtained, thanks to strong interactions between the organic fragments. Moreau *et al.* introduced for the first time a hybrid silica system with a

lamellar structure using self-assembly routes based on the strong hydrogen bonding association ability of the urea groups and van der Waals interactions taking place between the central alkylene chains [29-33]. In some recent works, these urea- BSs have been doped with europium ions, making them very promising materials field for the domain of optics [34, 35]. The study of these nanostructured silsesquioxanes will be the subject of an important part of the present thesis.

The last part of route A involves the hydrothermal synthesis of Metal Organic Frameworks (MOFs) [36]. MOFs constitute a very interesting class of hybrid materials with a high and tunable porosity, and a crystalline architecture. Applications of these materials [37] in the fields of gas sorption [38], separation or purification, luminescence [39], catalysis or nanomedicine [40] are being developed.

Route B corresponds to the assembling or dispersion of well-defined nanobuilding blocks (NBBs) [16]. These consist of perfectly calibrated preformed objects that keep their integrity in the final material, which means that the structural units that are present as sources for material formation can also be found in the final material. Examples of materials obtained with this technique are: clusters [41], organically pre- or post-functionalized nanoparticles, nano-core shells or layered compounds able to intercalate organic compounds[18]. These materials have commercial applications, such as nanofillers in the Green Tyres developed by Michelin through a collaboration with Rhodia [18]. The rolling bands are constituted by elastomers containing nanosilica particles fillers.

Route C corresponds to the well known self-assembly process [16]. Typically, selfassembled systems exhibit hierarchical structure and exhibit emergent properties. In practice, self-assembly may be carried out in the presence or absence of a structure directing agent (i.e., template), i.e., through template-directed self-assembly or selfdirected assembly, respectively. This particular issue will be discussed in further detail below. In the context of route C it consists in the organization or the texturation of growing inorganic or hybrid networks through the use of an external templates, such as micelles. These inorganic or hybrid phases can be generated from precursors previously described in route A or B [24], allowing a high control and tuning of the hybrids interfaces, and leads to a whole continuous range of nanocomposites, from ordered dispersions of inorganic bricks in a hybrid matrix to highly controlled nanosegregation of organic polymers within inorganic matrices [16].

In some reviews a route D is also mentioned [18, 24].

Route D corresponds to the so-called integrative synthesis [16]. The strategies reported above mainly offer the controlled design and assembling of hybrid materials in the 1 to 500 Å range. Micromolding methods have been developed, in which the use of controlled phase separation phenomena, emulsion droplets, latex beads, bacterial threads, colloidal templates or organogelators enable controlling the shapes of complex objects at the microscale [16, 18]. This strategy, when combined with routes A, B and C, allows the construction of hierarchically organized materials in terms of construction and functions.

Sol-gel process

The sol-gel process has been extensively employed and studied [42-45]. This process was developed in the 1930s using silicon alcoxides as precursors from which silica was produced. The reference book in this area [44] will be used as follows to describe the basic principles behind the method.

This chemistry is based on inorganic polymerization reactions in a solvent. The silicon based sol-gel process is probably the one that has been most investigated and is the base of this work: therefore the fundamental reaction principles are discussed using this process as a model system.

Two main reactions are involved in this process, namely *hydrolysis* and *condensation*.

In a hydrolysis reaction, an alcoxy group (-OR) is substituted by a hydroxyl group (-OH) at the silicon atom, with the concomitant formation of an alcohol (ROH):

$$Si(OR)_4 + H_2O \rightarrow HO-Si(OR)_3 + ROH$$
 (a)

According to the amount of water employed and the presence of catalyst the species can be partially hydrolyzed (as stated before) or totally hydrolyzed:

 $Si(OR)_4 + 4 H_2O \rightarrow Si(OR)_4 + 4 ROH$ (b)

In the condensation reactions two partially hydrolyzed species (or one partially hydrolyzed and other not reacted) react with each other to form a siloxane bridge (Si-O-Si), with the release of a water or alcohol molecule.

$$(RO)_3Si-OH + HO-Si(OR)_3 \rightarrow (RO)_3Si-O-Si(OR)_3 + H_2O$$
 (c)

$$(RO)_3Si-OR + HO-Si(OR)_3 \rightarrow (RO)_3Si-O-Si(OR)_3 + ROH$$
 (d)

The sol-gel process can also be described from the physical point of view, as transitions between a solution, a sol - composed of dispersed colloids - and a gel. At the beginning of the process (reaction (a)) of the initially homogeneous solution is transformed into a colloidal solution. A sol is by definition a fluid Colloidal system in which the dispersed phase is so small (\approx 1-1000 nm) that gravitational forces are considered to be negligible and interactions are dominated by short-range forces, such as van der Waals attraction and surface charges. As the process goes on, (reactions (c) or (d)) the dimensions of the molecules become bigger; the system transforms into a gel when the inorganic network reaches the macroscopic scale over the solution. The gelation point is attained when all the growing clusters connect with each other. During the aging process variations in the structure and properties of the materials take place. Another fundamental step is the drying process: (a) Under normal conditions, an important contraction of the gelified network results (5 to 10-fold decrease compared with the wet starting gel). The materials obtained under these conditions are called xerogels. Xerogels are interesting materials because of their porosity and high surface area, which make them useful for catalysis or sensing [45]. (b) Under supercritical conditions, there is a minimal contraction. The final product is denominated aerogel. Under certain conditions the destruction of the gel network can lead to the formation of powders instead of monoliths during materials formation. (c) Fibers or films may be produced by processing an aged sol (before the gelation point) thanks to a rapid evaporation of the solvent.

Figure 1.4 shows a schematic diagram representing the stages of the sol-gel process. In this scheme several techniques employed in the sol-gel field to obtain the final materials are also indicated: dip-coating, spin-coating, spray-coating, doctor blading, capillary or meniscus coating, flow-coating and roll-coating.



Figure 1.4. Processing routes to materials using sol-gel methods (reproduced from reference [17]).

Several aspects may influence the sol-gel process: H_2O/Si molar ratio, nature of the solvent, pH, type of catalyst, temperature, chemical additives.

Molar ratio H_2O/Si (R): Increasing the R value corresponds to a decrease in the hydrolysis reaction time. For R<<2 reaction (d) is favored. In contrast, reaction (a) is favored for R>>2.

Nature of solvent: The solvents are characterized by their protic or aprotic character, dielectric constant, dipolar moment and polarity index.

pH: The pH affects the mechanism of the overall process, and the microstructure of the materials. The effect of the pH is revealed in the gel time. The polymerization process was divided by Iller [46] into three main regions: pH < 2, 2 < pH < 7 and pH > 7. At the isoelectric point of silica (between 2.5 and 4.5, depending on different parameters) the reaction rate is minimal, but when the pH is changed the reaction rate also changes.

Catalyst: The process is catalyzed by acids, bases or nucleophiles (typically fluoride anions (F⁻)) resulting in different reaction mechanisms which depend on the relative rates between the hydrolysis and condensation reactions.

In Scheme 1.1 the mechanisms proposed for each situation are represented (the mechanism of the F⁻-assisted reaction is mostly similar to that of the base-catalyzed reaction).



Scheme 1.1. Representation of the mechanisms proposed according to the catalyst employed (adapted from reference [15]).

Considering all these aspects the sol-gel process presents several advantages, in particular the mild reaction conditions, the processing versatility, the possibility of mixing the inorganic precursor and organic components at the nanometer scale and the ability of tailoring the final properties of the material through the adequate choice of the organic and inorganic components.

Applications of organic-inorganic hybrids

Beyond the inherent fundamental knowledge, organic-inorganic hybrid materials obtained from the sol-gel process have found applications in a wide range of domains: from the fundamental studies to the market place [17, 18, 24, 47, 48]. A possible definition for "commercial product" could be that it is offered for sale and used in a regular production of a device or item in general commerce [47]. The commercial organic-inorganic hybrids have been part of the manufacturing technology since the 1950s.

It is possible to find applications is some different areas such as protective and decorative coating, energy applications, micro-optics, micro-electronics, photonics and optical sensors, ionics, catalysis, human care purposes or construction, automotive, sealant, textile and woods [17, 18, 24, 48]. Numerous examples are already commercially available, developed by trademarks (Schott, Toshiba, Variotropic, Essilor, Loreal), in a pre-industrial stage or in a prototyping step [17, and references therein]. Most of the commercial applications are protected as registered patents.

One of the first applications of hybrids that appeared in the market was in automotive coatings [47]. Another example comes from television screens by Toshiba, coated with a sol-gel material made of indigo dye embedded in a silicon/zirconia matrix. It is interesting to note that indigo was already used in the ancient Maya Blue [18, 48]. With the expansion of the market in flat panel devices the commercial applications of coated displays also extended. Indeed, coating is one of the most significant areas of application due to the low cost and the easy conditions to prepare quickly new products [17]. Another advantage is based on the fact that is possible to coat a variety of media such as glasses, metals or alloys, plastics, ceramics and papers employing the appropriate processing media, such as spray-, spin- or dip-coatings. These allow the development of different functionalities, protective and/or decorative. Another example often cited in the literature is the use of coating employed in art the conservation, namely on the long term protection of the 14th century "Last Judgement Mosaic" situated in St. Vitus Cathedral in Prague [18].

In the field of protection, examples can span from aeronautics to basic household articles. In the first case nanocomposite materials and surface films are being developed for corrosion resistance enhancement and improvement of the adhesion of organic matrix resins on aeronautical parts. In the second case nanocomposites are being employed to solve the long-term durability of the non-stick properties of cookware. One of the first and often referred examples is the glassware coated with dye-containing hybrids [17, 18, 24, 48]. This method has advantages from the visual point of view (increasing the possibility of colors and patterns) and environmental, since the bottles prepared in this way are easy to recycle as uncolored glass. The color of conventional glasses provided by transition metals is very difficult to remove upon remelting. Other example besides decorative coating can be in the field of optical coating, such as anti-reflective thin films or transparent hard-coats [17].

Nowadays due to critical environmental issues (nuclear waste and global warming associated with CO₂ emissions) the importance of developing new forms of

alternative green power energy are unquestionable. Research on the field of fuel cells, lithium batteries, electrochromic devices (ECD) and photovoltaic devices are mandatory, progressive replacement of classical forms of energy (gas, oil) by others environmental friendly. The use of the sol-gel process combined with the organic-inorganic hybrid concept allows potential applications in ECD. These important issues will be discussed in Chapter 3. In fuel cells, organic-inorganic materials which are protonic-based low temperature cell have found wide-spread in class as membranes, active layers or bipolar plates [17].

Hybrid materials have also been employed in several fields of human care such as dental applications, cancer therapy, drug delivery, implants, tissue engineering, body care and cosmetics [17, 18, 20, 21, 24]. The most spread application is on the dental care, where the organic-inorganic hybrid acts as filling composites. The advantage of these composites lies on their properties (appropriate hardness, elasticity, and thermal expansion behavior and non-toxicity) and in the fact that they penetrate easily into the cavity and harden quickly under the effect of blue light [18]. Another common example comes from the commercial sunscreens, where the encapsulation of the active organic UV filters in silica micro-capsules avoids the direct contact of these chemicals with the skin. The same concept was employed to incorporate anti-acne drugs (such as benzoyl peroxide) which are as effective as antibiotics but do not cause bacterial resistance or stomach upset [17].

Self-assembly

As stated above there are many references in the literature concerning selfassembly, in part because it has been used in numerous fields of research. For example in the materials research field self-assembly is related with the formation of liquid crystals, colloids, lipid bilayers and self-assembled monolayers [49].

Globally it is possible to define self-assembly as the result of the spontaneous organization of BBs giving origin to more complex structures, hierarchically organized in a more complex form. The properties obtained in that hierarchical structure may not be exactly the same as those of the starting components.

The self-assembly on the materials can be achieved by **bottom up** or **top-down** approaches, but in both cases is necessary to consider [9]:

- (a) Size, shape and structure of BBs (functional and structural roles).
- (b) Attractive and repulsive interactions between BBs and equilibrium separation (consist of interactions such as electrostatics or hydrophobic/ hydrophilic interactions).
- (c) Reversible association-dissociation of BBs during the organization and lowest energy structure (binding forces are noncovalent interactions that impart stability to the assembled structure and define the final structure)
- (d) Interaction between BBs and solvents, interfaces and molds (the environment is the medium in which the sub-unit, forces and assembled structures interact)
- (e) Dynamic, mass transport (random movement of the BBs which allow them to interact).

Reversibility of the system is achieved due to comparable magnitudes of binding and repulsives forces. A schematic representation of those principles is illustrated in Scheme 1.2



Scheme 1.2. Illustration of the principles of a self-assembled system. BBs (a); repulsive/attractive forces (b); binding forces (c); reaction medium (d); driving forces (e).

Two main situations may occur: (a) Molecular or supramolecular templates are present as directing agents in the synthesis solution; (b) The synthesis is spatially restricted by confining the reaction solutions within organized media [12]. In both cases the reaction chemistry, bonding and packing considerations are complemented by the chemical, spatial and structural properties of the template or enclosed reaction environment should complement the reaction chemistry, bonding and packing considerations of the incipient organic phase [12].

Four strategies may be considered to synthesize organized matter [12]:

 Transcritive synthesis is the formation of organized inorganic materials by direct templating using preformed self-assembled organic architectures. It can be described by the following sequence:

Self-assembly \rightarrow transcription \rightarrow replication

Some requisites must be fulfilled [12]:

- The organic template is in place prior to the formation of the inorganic phase.
- b) The organic template should be relatively stable throughout materials synthesis.
- c) Interactions of the organic surface should be competitive over analogous processes in bulk solution.
- d) Possibility to incorporate surface functional groups that direct interfacial events.

Some examples of the present strategy may be found from in the control of pore shape and size in the synthesis of zeolites and nanoamorphous silicas and also in the biomineralization field. Davis *et al.* [50] employed a bacterial superstructure consisting of coaligned multicellular fillaments of *Bacillus subtilis* as macroscale organic template. The bacterial superstructure that is formed resembles the arrangement of surfactant cylinders [50].

2) Synergistic synthesis implies the mechanistic process in which cooperative interactions between different molecular components give rise to the chemical construction of organized states of matter. It can be described by the following sequence:

Co-adaptation \rightarrow co-assembly \rightarrow replication

Considering an inorganic-organic with a structural and bonding complementarity in the first stage a co-adaptation will be observed. This co-adaptation is influenced by the balance between the thermodynamic and kinetic driving forces (it is sensitive to stoichiometry and relative chemical potentials of the reactants). Under certain conditions, the interfacial energy dominates and gives rise to changes in the spatial charge density and steric requirements at the head-group-silicate interface. Pattern replication then proceeds by further condensation and polymerization of silica within the interstitial spaces of the co-assembled template. The order structure could be achieved in a post-synthesis step with the removal of template.

3) Morphosynthesis is related with chemical transformations in spatially restricted reaction fields to produce materials with complex form. The complex and external morphologies of the final material are "molded" in *situ* by means of an organized and delineated chemical environment. The reactions field could be a static reaction, reconstructive or transitory.

In the case of a static reaction field the main idea is to impose an external spatial boundary which is not significantly changed by the chemical processes. The case of reconstructive reaction fields is represented by the sequence:

Reaction assembly \rightarrow replication \rightarrow metamorphism

and is better explained with an example. Bicontinuous micro-emulsions are a mixture of oil / water / surfactant. These microemulsions are structured as compartimentalized liquids in which the oil and water components are separated into a highly branched and interconnected nanoscale network. In the first stage the nucleation and initial growth of the inorganic phase appear to replicate the arrangement of the nanoscale water conduits. After that stage the growth is accompanied by reconstruction of localizes regions of the microemulsion structure. The last process results from the development of interactive coupling of the crystallization process and surrounding reaction environment. This is a time-dependent process such that morphological patterns at the micrometer scale evolve from the nanoscale replica through a series of intermediate structures facilitated by the reconstructive properties of organized media.

In the case of transitory reaction fields the formation of transient metastable phases is induced and is further employed to generate boundary surfaces and imprint for *in situ* sculpturing of inorganic materials. The onset of inorganic precipitation and formation of the transitional structures must be synchronized.

Reaction assembly \rightarrow transformation \rightarrow replication

4) Integrative synthesis results from a combination of the different techniques in order to prepare materials with hierarchical structure and morphology.

When self-assembly occurs without the presence of any template (self-direct assembly – **SDA**) giving origin to materials with ordered hierarchical architectures and well defined morphologies, the forces between the molecules must be weaker: hydrogen bonds, ionic, dipolar, van der Waals and hydrophobic interactions.

The importance of hydrogen bonds and the hydrophobic interactions in the structuring of materials will be discussed in the introduction of Chapter 2.

Biomineralization

Biomineralization encompasses a wide range of subjects from biology to chemistry and materials science. General definitions on biomineralization and specific aspects related with this subject can be found in textbooks [3] and reviews [51-54].

Biomineralization can be considered as a widespread phenomenon in Nature leading to the formation of a variety of solid inorganic structures by living organisms. In some cases the biominerals formed are so stable that they never precipitate under ambient conditions [55]. Many examples of living organisms employing biominerals have been reported: crustaceans [6, 54, 56], intracellular crystals in prokaryotes, exoskeletons in protozoa algae, and invertebrates, spicules [55, 57] and lenses [58], bone, teeth, statoliths and otoliths, eggshells, plant or mineral structures [59, 60]. These biologically-produced biominerals are organic-inorganic hybrid composites formed by self-assembling *bottom-up* approaches under mild conditions, exhibiting extraordinary properties and beauty, as well as controlled hierarchical structures.

Biominerals are typically organic-inorganic hybrids that are hierarchically organized from the nano- to the macroscopic length scale [3, 54]. The organic compounds of biominerals include proteins, glycoproteins, polysaccharides and other small organic biomolecules. The organic phase occluded in biominerals may or may not be directly involved in biomineralization [61]. The common ions involved in biomineralization are Mg, Ca, Sr, Ba, Si and Fe as their carbonates, oxalates, sulfates,

phosphates, hydroxides and oxides. Over 60 biominerals have been identified up to present. Around 50% of them are calcium-based minerals and half of these are calcium phosphates of variable composition. It is also noteworthy that biosilica can be found in diatoms, sponge spicules and in some plants. Biominerals can be amorphous or crystalline: curiously 25% of the biominerals are amorphous in Nature. Because amorphous minerals are isotropic under polarized light and do not diffract X-rays, their presence in biological tissue has often been overlooked. It is particularly difficult to identify and characterize them when a crystalline mineral is present [6]. As an amorphous mineral, it is isotropic and can thus sustain mechanical constraints from all directions and it may be shaped easily by the space in which it forms. Amorphous minerals are less stable and more soluble than crystalline ones [5, 56]. The stabilization of the amorphous phases can be attributed to the incorporation of macromolecules within their structures.

Biomaterials can generally be molded into specifically designed devices with well defined properties (structure, size, shape) [53]. The functionalities of biominerals range from gravity, support and sensing to navigation [5]. In table 1.1 some of the principal functions of the biominerals found in Nature are listed with the corresponding specific functions. This table is not however exhaustive; it only intends to illustrate the diversity of options. In some cases biominerals are also known and studied because of their contribution to diseases; for example calcium oxalate is found in kidney stones [54].

Biomineral formation may be understood from the standpoint of a classical crystallization pathway or in the light of a new approach based on the presence of an amorphous precursor [54]. The classical model of crystallization considers growth essentially as an amplification process in which stable nuclei are simply enlarged by unit cell replication without incurring structural changes in the bulk or at the surface [56]. In contrast, crystal growth by aggregation of preformed crystalline BBs is a mesoscale assembly process that results in single crystals with iso-oriented mosaic textures. This process can occur through the coalescence of primary nanoparticles into colloidal aggregates often to uniform size, and their subsequent internal restructuring to produce a crystallographically continuous particle. Alternatively, nanoparticle assemblies of aligned BBs produce chains of oriented nanocrystals. In Figure 1.5 a schematic diagram indicative of this process is represented.

Mineral	Formula	Organism	Location	Function
Calcite	CaCO ₃	Crustaceans	Crab cuticule	Mechanical
Amorphous	$CaCO_{3.}nH_2O$			Structural
Mg-calcite	Mg, $CaCO_3$	Octocorals	Spicules	support
Calcite	CaCO ₃	Birds	Eggshells	Protection
		Plants	Leaves	
Aragonite	CaCO ₃	Cephalopods	Shell	Buoyancy
Amorphous	$CaCO_{3.}nH_2O$	Plants	Leaves	Storage
Calcite	CaCO ₃	Tribolites	Eye lens	Optical sensors
Aragonite	CaCO ₃	Fish	Head	Grinding
Barite	BaSO ₄	Chara	Statoliths	
Gypsum	$CaSO_4.2H_2O$	Jellyfish	Statoconia	





Figure 1.5. Alternative mechanisms of growth for single crystals (adapted from reference [56]).

In 1983 Mann stated that "since amorphous phases are more soluble than crystalline phases at equilibrium, it seems possible that the formation of amorphous precursors could be widespread in Nature" [62]. This discussion is better understood with the help of the diagram of Figure 1.7 which demonstrates that the crystallization may occur by a sequential process involving structural and compositional modifications

of amorphous precursors and crystalline intermediates, rather than by a single-step pathway (pathway A). This process is predominantly based on the modification of the activation-energy barriers of nucleation, growth and phase separation. The stable intermediate phase depends on the solubilities of the minerals and on the free energies of activation of their interconversion, all of which being strongly influenced by additives. The corresponding changes in composition and structure usually occur by dissolution-renucleation processes closely associated with the surface and/or the interior of preformed particles [56]. The underlying basic concept is known as Ostwald-Lussac rules. If a solution is supersaturated with respect to more than one phase, the more soluble (least stable) phase is often the first phase to form. After some time and with the appropriate amount of energy the products should transform into the lower energy and more thermodynamically stable phase [62].



Figure 1.6. Crystallization pathways under thermodynamic and kinetic control (reproduced from reference [56]).
1.2. Objectives and organization of the thesis

The present thesis is composed of five chapters and one appendix. The first (present) chapter corresponds to the introduction and state of the art. The main results obtained throughout this thesis are presented in three main chapters: chapters 2, 3 and 4. Chapter 5 is devoted to conclusions and future perspectives of the work. In Appendix A the summary of the thesis is presented in French.

In **Chapter 2** typical sol-gel reactions and self-assembly routes have been combined to produce different hierarchically structured materials. This chapter begins with the study of the influence of the solvent on the materials morphology. The final morphology of the lamellar silsesquioxane produced from $(EtO)_3Si-(CH_2)_3-Y-(CH_2)_{12}-Y-(CH_2)_3-Si(OEt)_3$ (Y = urea group and Et = ethyl) using an acid catalyst and a large excess of water, was changed from rigid platelets (**L12**) [31] to micro-objects that resemble sea sponges (**L12D**) upon incorporation of dimethylsulfoxide (DMSO) in the reaction medium. The microstructural modifications observed were ascertained by several techniques. A mechanism for the morphology tuning based on the polarity of the solvent mixture is proposed.

The second section of Chapter 2 is related with di-urea alkylene-bridged silsesquioxanes. These materials were designated by the notation $C_{10}C_nC_{10}$ and are derived from organosilane precursors including decylene chains as side spacers and alkylene chains with variable length as central spacers (EtO)₃Si-(CH₂)₁₀-Y-(CH₂)_n-Y-(CH₂)₁₀-Si(OEt)₃ (n = 7, 9-12; Y = urea group and Et = ethyl). These materials are based on precursors similar to **P12** [31] which includes side spacers composed of propylene chains instead of decylene chains. The main goal of this work was to determine the influence of the side spacers S on the structuring and ultimately on the morphology of the **P12**-derived materials. These new family of hybrids has enabled us to conclude that the length of the side spacers plays a unique role in the structuring of alkylene-based bridged silsesquioxanes. All the samples obtained adopt a lamellar structure.

The same synthetic strategy (i.e., the combination of the sol-gel process with self-assembly techniques) was employed to prepare a novel class of hierarchically

structured hybrids. These new family of materials were prepared through the reaction of the series of alcohols C_YOH (where Y=14, 16 and 22) with (3-isocyanato)propyl triethoxysilane giving rise to a urethane linkages, followed by the sol-gel reactions. The samples were designated as mono-alkyl-urethanesils. The effect of the alkyl chain length and the nature of the cross-link on the the order/disorder phase transition have been analyzed and the influence of the solvent(s) has been explored to yield different morphologies.

Chapter 3 is dedicated to organic-inorganic biohybrids with potential applications in ECDs. The domain of ECDs is an exciting and rapidly-growing field of research. In view of their potential use as electrolytes in ECDs the sol-gel process was used to prepare two novel series of environmentally-friendly doped biohybrids composed of a di-urethane cross-linked siloxane-based host network incorporating short segments of the poly(ε-caprolactone) biopolymer, abbreviated as PCL(530).

A family of materials derived from such hybrid matrix doped with KCF₃SO₃ were been characterized and preliminary studies of the performance of prototype ECDs incorporating these xerogel materials as electrolytes were carried out.

With the primary goal of developing a new family of environmentally friendly multifunctional biohybrid materials displaying simultaneously high ionic conductivity and high luminescence the same host biohybrid matrix was doped with lithium triflate and europium triflate. The *mixed cation* approach, which basically involves the use of two guest salts instead of a single one, is an attractive procedure that usually results in a significant enhancement of the ionic conductivity of PEs and allows to obtain the luminescence properties. Preliminary tests performed with a prototype ECD was done.

In **Chapter 4** a biomimetic approach to control the growth of calcium carbonate (CaCO₃) systems was applied. CaCO₃ is one of the most important biominerals existing in Nature. It has six polymorphic forms: three anhydrous forms (calcite, vaterite and aragonite) and three hydrated forms. In the hydrated forms reference should be made to amorphous calcium carbonate (ACC) because it is one of the most instable forms, but at the same time, it is one of the most attractive ones due to its capacity as temporary storage site for calcium carbonate in many organisms.

ACC has a tremendous potential in the orthopedic field owing to its in-growth rate, immunogenicity and to the mechanical strength of the grown bones. Recently the use of macromolecules, such as phytic acid [63], DNA [64], poly(acrylic acid) [65] and poly(ethyleneimine) [66] has provided a biomimetic approach to ACC formation. In the present work we have used a synthetic method proposed by Lee *et al.* [67] and poly(vinyl)pyrrolidone (PVP) to inhibit the crystallization of ACC. The ACC crystallisation process was monitored in detail by means of several standard techniques during a timescale that ranged from one hour to one year after ACC synthesis.

Biomineralization in the presence of ionic liquids (ILs), which are molten salts at ambient temperature, is also a challenging field of research. Apart from offering unique characteristics, such as negligible vapor pressure, thermal and chemical stability, chemical tunability and recyclability, ILs have a bright future for inorganic materials synthesis, providing a means to produce materials that are not otherwise available [68]. ILs may act, not only as solvents, but also as reactants and templates. In the present work, we have adopted the synthetic method proposed by Lee *et al.* [67] and have used several commercial ILs to determine the structural and morphological changes produced on precipitated CaCO₃.

The surfactants are another class of compounds employed as templates in an attempt of mimicking the morphologies found in Nature. Lee's method reported [67] was applied using the commercial fatty alcohols C_YOH employed in Chapter 2 (section 2.3), because they may be classified as non-ionic surfactants.

The entire work was done both at the Chemistry Department of the University of Trás-os-Montes e Alto Douro (UTAD) and at the École Normale Supérieure de Chimie de Montpellier (ENSCM). A 3-month period was spent at Professor Kuroda's Group at Waseda University, Tokyo (Japan). The samples discussed in section 2.1 and 2.2 (Chapter 2) were synthesized at ENSCM. Some of the experimental techniques with the corresponding results were obtained in the framework of collaborations and projects.

For a full comprehension, the experimental techniques employed throughout the work, as well as the participating collaborators and institutions are listed in Table 1.2.

Characterization Technique	Department / University	Frame of Colaboration	Chapter
¹ H NMR	CACTI-University of Vigo	CQ-VR	2.3
¹³ C NMR	Institut Charles Gerhard-ENSCM	1	2.1/2.2/2.3
²⁹ Si MAS NMR	Chemistry Department - Aveiro University	Prof. João Rocha	2.3
²⁹ Si CP MAS NMR		Prof. Rute Sá Ferreira	
	Institut Charles Gerhard-ENSCM		2.1/2.2
¹³ C MAS NMR	Chemistry and Physics Departments /	Prof. João Rocha	2.3
¹³ C/ CP MAS NMR	Aveiro University	Prof. Rute Sá Ferreira	
	Institut Charles Gerhard-ENSCM	1	2.1/2.2
FT-IR	Chemistry Department – UTAD		2 / 3 / 4
Attenuated Total Reflectance	Chemistry Department – UTAD		2.3
FT-Raman Spectroscopy	Physics Department - Aveiro University	Prof. Rute Sá Ferreira	2.2/3.1
X-RAY diffraction	UME-UTAD	Lisete Fernandes	3.1
	Physics Department - Aveiro University	Prof. L. D. Carlos	2.2/2.3/3.2/4.3
		Prof. Rute Sá Ferreira	
	Chemistry Department - Aveiro University	Prof. Filipe Paz	4.1 / 4.2
		Dra. Rosário Soares	
			(cont.)

Table 1.2. Characterization techniques employed in the elaboration of the work.

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Introduction

Isotherms of Adsorption	Institut Charles Gerhard-ENSCM		2.1
MOd	Geology Departement- UTAD	Dr. Rui Teixeira	2.1 / 4.3
	Chemistry Department-UTAD	1	2.2 / 2.3 /
SEM	UTAD- UME	Prof. Pedro Tavares	2.2/2.3/3.1/3.2/4.3
		Lisete Fernandes	
	Institute European Membrans	Didier Cot	2.1 / 2.2
	University of Montpellier		
	CEMUP	Rui Rocha	4.1
HR-SEM	Waseda University	Prof. Kazayuki Kuroda's Group	2.3
	CEMUP	Rui Rocha	2.3/4.1/4.2/4.3
TEM	UTAD- UME	Prof. Pedro Tavares	2.1/2.2
		Lisete Fernandes	
	Physics Department	Franck Godiart	2.2
	University Montpellier		
AFM	Physics Department - Aveiro University	Dra. Andreia Macedo	2.2
	CEMUP	Rui Rocha	2
Chronoamperometry	Chemistry Department - UTAD	Prof. Rosa Rego	3.2
			(cont.)

Table 1.2 (cont.). Characterization techniques employed in the elaboration of the work.

Introduction

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Table 1.2 (cont.). Characterization techniques employed in the elaboration of the work.

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1.3. Communications resulting from this thesis

Publications

(1) <u>M. Fernandes</u>, X. Cattoën, V. de Zea Bermudez, M. Wong Chi Man
 "Solvent-controlled morphology of lamellar silsesquioxanes: from platelets to microsponges"
 CrystEngComm, 2011, 13, 1410-1415 (IF = 4,180, 2010)

DOI: 10.1039/c0ce00385a

(2) <u>M. Fernandes</u>, S. S. Nobre , L. C. Rodrigues, A. Gonçalves, R. Rego, M. C. Oliveira, R. A. S. Ferreira, M. M. Silva, E. Fortunato, L. D. Carlos, V. de Zea Bermudez

"Li^{*} and Eu³⁺-doped poly(ϵ -caprolactone)/siloxane biohybrid electrolytes for electrochromic devices"

ACS Applied Materials & Interfaces, **2011**, 3, 2953–2965 (IF = 2.925) DOI: 10.1021/am200391b

(3) <u>M. Fernandes</u>, S. S. Nobre, X. Qinghong, C. Carcel, J.-N. Cachia, X. Cattoën, J. Sousa, R. A. S. Ferreira, L. D. Carlos, C. V. Santilli, M. Wong Chi Man, V. de Zea Bermudez

"Self-structuring of lamellar bridged silsesquioxanes with long side spacers" Journal of Physical Chemistry B, **2011**, 115, 10877–10891 (IF = 3,603) DOI: 10.1021/jp2022902

(4) <u>M. Fernandes</u>, L. C. Rodrigues, R. A. Sá Ferreira, A. Gonçalves, E. Fortunato,
 M. M. Silva, M. J. Smith, L. D. Carlos, V. de Zea Bermudez

"K⁺-doped poly(ϵ -caprolactone)/siloxane biohybrid electrolytes for electrochromic devices"

Solid State Ionics, 2011, 204–205, Pages 129-139 (IF = 2,491, 2010)

(5) <u>M. Fernandes</u>, F. A. Almeida Paz, V. de Zea Bermudez

"Ionic Liquid-Assisted Morphology Tuning of Calcium Carbonate in Ethanolic Solution", European Journal of Inorganic Chemistry (IF = 2, 909, 2010)

Oral comunications

(1) M. Fernandes, X. Qinghong, J-C. Cachia, X. Cattoën, C. Carcel, R. A. S. Ferreira, L. D. Carlos, V. de Zea Bermudez, M. Wong Chi Man

"The Role of the Length of the Spacers on the Structuring of Self-Organized Di -Urea Akylene-Bridged Silsesquioxanes"

Hybrid Materials, March 2009, Tours, France

(2) <u>M. Fernandes</u>, X. Cattöen, R. A. S. Ferreira, L.D. Carlos, M. Wong Chi Man, V. de Zea Bermudez

"Synthesis of hierarchically structured mono-alkyl-urethanesil hybrid materials" e-MRS 2010 Spring Meeting, June 2010, Strasbourg, France

(3) M. Fernandes, S. S. Nobre, L. C. Rodrigues, R. A. S. Ferreira, A. Gonçalves, E. Fortunato, M. M. Silva, L. D. Carlos, <u>V. de Zea Bermudez</u>

"Conducting and luminescent sol-gel derived poly(ϵ -caprolactone)/siloxane hybrids"

XII International Symposium on Polymer Electrolytes, September 2010, Padova, Italy

(4) <u>M. Fernandes</u>, F. A. Paz, V. de Zea Bermudez

"Tuning the Morphology of Calcium Carbonate Through the Use of a Surfactant-Mediated Bioinspired Approach"

4th Iberian Meeting on Colloids and Interfaces Science, July 2011, Porto, Portugal

(5) <u>M. Fernandes</u>, X. Cattoën, R. A. S. Ferreira, L. D. Carlos, M. Wong Chi Man, V. de Zea Bermudez

"Tuning the morphology of mono-alkyl urethanesil through the use of DMSO as a solvent"

16th International Sol-Gel Conference, August 2011, Hangzhou, China

(6) <u>M. Fernandes</u>, D. Constante, V. de Zea Bermudez
 "Polymer-mediated precipitation of amorphous calcium carbonate"
 Euromat 2011, September 2011, Montpellier, France

(7) M. Fernandes, <u>V. de Zea Bermudez</u>
"Biomimetic growth of CaCO₃ mediated by ionic liquids"
Euromat 2011, September 2011, Montpellier, France

The work behind this thesis gives origin to 19 poster presentations in national and international conferences.

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Chapter 2

Organic-Inorganic hybrid materials obtained by sol-gel and self-assembly techniques

Solvent-controlled morphology of lamellar silsesquioxanes: from platelets to microsponges

Self-structuring of lamellar bridged silsesquioxanes with long side spacers

Synthesis of hierarchically structured mono-alkyl-urethanesil hybrid materials

2. Hybrids organic-Inorganic materials obtained by sol-gel andself-assembly techniques

In materials science, the structure and morphology are considered as key parameters that primarily dictate the features of the materials. Their control is thus of the utmost interest to tailor the properties of a single material depending on the required application.

In the past two decades growing attention has been devoted to organic/inorganic hybrid materials, in particular to the class of silsesquioxanes, owing to the attractive combined properties provided by the inorganic network (*e.g.*, thermal/chemical stability and rigidity) and the functional organic fragments [1-2].

Bridged silsesquioxanes (BSs) [3-6] constitute an important family of siliceous materials in which the intimate coexistence of inorganic domains and organic fragments endow them with very interesting perspectives for applications in extraction [7], optics [8-9], catalysis [10], microelectronics [11] or drug delivery [12]. Typically BSs are synthesized by means of the sol-gel process from bridged organosilanes. Although usually obtained as amorphous materials, BSs have also been produced in the form of periodic mesoporous organosilicas [13] *via* the addition of external templates, or as nanostructured materials *via* self-templating effects [14].

The particular case of the BSs obtained through a combination of self-directed assembly routes and sol-gel reactions offers a wide range of possibilities in terms of morphology fine-tuning. In these systems self-directed assembly [15] of bridged organosilane precursor molecules with general formula $(EtO)_3Si-S_2-Y-S_1-Y-S_2-Si(OEt)_3$ (where the central spacer S_1 is an alkylene chain with variable length (- $(CH_2)_n$ -), an arylene or a cyclohexylene group, the side spacers S_2 are short alkylene chains (- $(CH_2)_m$ -) (in general propylene chains, m = 3) and the cross-link Y is the urea (-NHC(=O)NH-) group) is governed by the growth of a supramolecular architecture that acts as internal structure directing agent [16-22]. The driving forces of the process are weak interactions (hydrogen bonds formed between Y groups and π - π and/or hydrophobic interactions established between S_1 moieties) which yield hierarchically

structured long-range ordered architectures with well defined morphologies at the macroscopic scale.

BS hybrids exhibiting chiral helical morphology were produced from (EtO)₃Si-S₂-Y-(C₆H₁₀)-Y-S₂-Si(OEt)₃ (where S₂ = -(CH₂)₃-) (*R*,*R*) and (*S*,*S*) enantiopure precursors [23]. Chirality transcription from the cyclohexyl-based enantiomers depends critically on the experimental conditions. Acid catalysis yielded right- or left-handed helical fibres, respectively, or a featureless granular solid from the racemic mixture. Basic catalysis led to the formation of hollow tubular or spherical organosilica from the enantiopure compounds or the racemic mixture, respectively [24, 25]. Interestingly, it was later shown that under acidic catalysis the length of the side spacer S₂ could also play an important role in the morphology of the resulting hybrids [26]. Materials incorporating propylene and butylene (S₂ = -(CH₂)₄-) side spacers consisted of fiber-like structures. Although chirality transcription prevailed, helicity was reversed, demonstrating an odd/even effect due to the odd or even number of carbon atoms in the S₂ chain. Platelike shapes were formed instead from the precursors containing pentylene (-(CH₂)₁₀-) and decylene (-(CH₂)₁₀-) side spacers. A lamellar structure was observed in the hybrid with the longest S₂ chain [26].

The case of the di-urea cross-linked alkyl-based silsesquioxane precursor $(EtO)_3Si(CH_2)_3NHC(=O)NH(CH_2)_{12}NHC(=O)NH(CH_2)_3Si(OEt)_3$ (**P12**) (Scheme 2.1). in section 2.1) is of particular interest, as it yields lamellar, long-range ordered materials under certain conditions. A more detailed presentation will be given in the next chapters.



Scheme 2.1. Representation of di-urea cross-linked alkyl-based silsesquioxane precursor (adapted from reference [15]).

The reports on silsesquioxanes derived from organosilanes with a pending chain are significantly less abundant. The basic concept behind this approach is that organoalkoxysilanes or organochlorosilanes containing hydrophobic tails become amphiphilic when silanol groups are formed by hydrolysis [27, 28]. The first example to appear involving the hydrolysis and condensation of alkyltriethoxysilanes $(C_nH_{2n+1}Si(OEt)_3 n = 12-18 [29]$ was reported by Shimojima *et. al* [29] (Scheme 2.2). The formation of layered structures through the polycondensation of *n*-alkyltrichlorosilanes was first reported by Parikh [30].



Scheme 2.2. Self-assembly of hydrolysed organosilanes into multilayered siloxane hybrids (adapted from reference [27]).

Later alkoxytrichlorosilanes ($n-C_nH_{2n+1}OSiCl_3$, n= 12, 14, 16, 18 and 20) were also used in the same context as single precursors [31]. A schematic representation is indicated in Scheme 2.3.



Scheme 2.3. Formation of layered silica-alcohol nanocomposites from alkoxytrichlorosilanes (adapted from reference [27]).

The strategy was further developed to produce a variety of nanostructured hybrids by keeping the hydrophobic chains and branching the trimethoxysilyl group $(C_nH_{2n+1}Si(OSi(OMe)_3)_3)$ yielding lamellar structures (n = 16) or two dimensional (2D) hexagonal hybrids depending on the alkyl chain length (n = 6-13) [32, 33]. Recently tridimensional (3D) mesostructured mesophases were obtained from a branched heptasiloxane precursor [34].

Recently a hierarchically-structured mono-amide cross-linked alkylene/siloxane hybrid (derived from the alkylsilane $(CH_3(CH_2)_{14}C(=O)NH(CH_2)_3Si-(OR)_3)$, where self-assembly is driven by hydrogen bonding between amide groups and tail-to-tail hydrophobic interactions between the alkyl chains, was reported [35]. This material is the first example of a photoluminescent bilayered suprastructure displaying a unique

nanoscopic sensitivity. The two self-assembling forces are determinant for the emergence of a thermally-actuated optical memory effect induced by a reversible order-disorder phase transition of the alkylene chains. Recovery of the emission energy is time-dependent [35].

$$O$$
 Si(CH₂)₃-N C-(CH₂)₁₄-CH₃

Scheme 2.4. Representation of the mono-amide cross-linked alkylene/siloxane hybrid (adapted from reference [35]).

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Solvent-controlled morphology of lamellar silsesquioxanes: from platelets to microsponges

This section is based on the following publication: *"Solvent-controlled morphology of lamellar silsesquioxanes: from platelets to microsponges"*M. Fernandes, X. Cattoën, V. de Zea Bermudez, M. Wong Chi Man *CrystEngComm*, 2011, **13**, 1410-1415



2.1. Solvent-controlled morphology of lamellar silsesquioxanes: from platelets to microsponges

2.1.1. Introduction

Well-defined morphology is a key parameter for the fine-tuning of the properties of silsesquioxane-type hybrids which are strongly dependent on the synthetic procedure.

The case of the di-urea cross-linked alkyl-based silsesquioxane precursor (EtO)₃Si(CH₂)₃NHC(=O)NH(CH₂)₁₂NHC(=O)NH(CH₂)₃Si(OEt)₃ (**P12**) (Scheme 2.1.1) is particularly interesting. This simple molecule may undergo, not only classical sol-gel reactions, but also self-directed assembly processes that rely on the establishment of van der Waals interactions between the hydrophobic bridging alkyl chains and intense hydrogen bonding between neighboring urea groups. In terms of morphology, it is extremely versatile.

Changes in the reaction medium induce dramatic alterations, not only in the degree of order, but especially in the dimension and design of the final material. While the hydrochloric acid (HCl)-catalyzed synthesis carried out in a large excess of water (molar ratio **P12**:H₂O:HCl=1:600:0.2) led to the formation of the crystalline lamellar structure **L12** (Figure 2.1.1 (a) and Scheme 2.1.1) [1-4], the use of the ammonium fluoride (NH₄F) catalyst in ethanol (EtOH) and a stoichiometric amount of water (molar ratio **P12**/H₂O/EtOH/NH₄F=1:6:60:0.01) yielded the amorphous material **A12** exhibiting a granular-like morphology [2] or an irregular microsphere shape with a rough surface composed of plates (Figure 2.1.1 (b)) [5].



Scheme 2.1.1. Syntheses of the L12 and L12D hybrids.



Figure 2.1.1. Different morphologies of the hybrids derived from the **P12** precursor: **L12** (a) (reproduced from reference [6]), **A12** (b) (reproduced from reference [5]), **Eu@A12-1** (c) (reproduced from reference [5]) and **Eu@A12-2** (d) (reproduced from reference [5]).

The structuring role played by lanthanide ions on the synthesis of the hybrids derived from the **P12** precursor under both types of reaction conditions has been reported more recently [5-7]. Upon adoption of the HCl-catalyzed-hydrolytic route and addition of Eu³⁺ ions (molar ratio **P12**:H₂O:HCl:EuCl₃=1:600:0.2:x, where x=0.05, 0.95 and 2.9) another family of highly organized photoluminescent silsesquioxanes (**Eu@L12**) displaying a lamellar morphology was introduced [6, 7]. In contrast, the combination of NH₄F-catalyzed sol-gel reactions and Eu³⁺ doping resulted in the production of a series of photoluminescent silsesquioxanes **Eu@A12** for which the morphology and size can be readily tuned through the control of the amount of Eu³⁺ incorporated: (1) Microfibers or twisted microbundles made of nanoplates assembled in a tile-to-tile arrangement are formed at low Eu³⁺ concentration (**Eu@A12-1**) (molar ratio **P12**/H₂O/EtOH/NH₄F/EuCl₃=1:6:60:0.01:0.74) (Figure 2.1.1 (c)), whereas dumbbell-like micro-objects result at high Eu³⁺ concentration (**Eu@A12-2**) (molar ratio **P12**/H₂O/EtOH/NH₄F/EuCl₃=1:6:60:0.01:1.42) (Figure 2.1.1 (d)) [5].

In this work we have been able to produce a silsesquioxane hybrid derived from the **P12** precursor with a completely different morphology. The new synthetic method adopted here is a modification of the route employed earlier to prepare **L12**, the only change introduced being the incorporation of a large excess of dimethyl sulfoxide (DMSO) to the reaction medium [8]. The presence of the latter solvent induced the formation of a material (henceforth designated as **L12D**) with a microsphere-like shape that closely resembles sea sponges. In an attempt to explain the independent roles played by water and DMSO in the production of the **L12** platelets and the **L12D** microsponges, respectively, both materials have been examined in depth using several techniques that provide rich structural information, specially X-ray diffraction (XRD), Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Atomic Force Microscopy (AFM), Polarized Optical Microscopy (POM), ¹³C and ²⁹Si Cross Polarization / Magic Angle Spinning (CP/MAS) Nuclear Magnetic Ressonance (NMR), nitrogen (N₂) adsorption-desorption measurements and Fourier Transform Infrared Spectroscopy (FT-IR).

2.1.2. Experimental part

Materials

Water was distilled prior to use. HCl solution and DMSO ($(CH_3)_2S=O$) were purchased from Carlo Erba and SDS (synthesis grade)), respectively.

Synthesis of L12D

P12 was obtained according to a procedure described elsewhere [2]. This compound (1.1 g, 1.6 mmol) was dissolved in DMSO (45 mL, 0.63 mol) at 80 °C. After cooling, water (12.6 mL, 0.70 mol) was added to the gelified mixture. The resulting mixture was heated up to 80 °C and 2.8 mL of 0.1 M HCl aqueous solution (0.28 mmol_{HCl} and 0.16 mol_{H2O}) was then added under vigorous stirring (final molar ratio **P12**/DMSO/H₂O/HCl=1:388:527:0.175). The reaction medium was kept under these conditions during 4 days. After this period, 657 mg of a white powder were recovered by filtration, washed successively with water, ethanol, acetone and water, and finally freeze-dried overnight.

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Characterization of the material

The sample for **Thermogravimetric Analysis** (TGA) was transferred to an open platinum pan and analysed using a TA Instruments Q50 thermobalance at a heating rate of 10 °C min⁻¹ using dry N_2 as purge gas (40 mL min⁻¹ balance and 60 mL min⁻¹ sample). Prior to measurement, the sample was vacuum-dried over phosphorus pentoxide for several days.

Solid state ¹³**C and** ²⁹**Si CP/MAS NMR** experiments were recorded on a Varian VNMRS 400 MHz spectrometer using a two channel probe with 7.5 mm diameter-size ZrO₂ rotors and TMS as reference for the chemical shifts.

The **SEM** images were obtained with a Hitachi S-4800 apparatus after platinum metallization.

TEM micrographs were obtained using a SEM/ESEM-FEI Quanta 400 scanning electron microscope at high-acceleration voltage (25 kV) and a LEO 906 E Leica microscope. The TEM images were printed as photographs using KODAK Electron film negatives.

AFM images were recorded using a Veeco Metrology Multimode/Nanoscope IVA equipment (CEMUP-Porto contract REEQ/1062/CTM/2005), in tapping mode using a super sharp silicon tip, curvature radius 10 nm, and frequency resonance equals to \approx 300 KHz. Flattening and elimination of line noise tools and a Lowpass filter provided by the WSXM software [9] were used to improve the quality of the images.

POM images were recorded with a Leitz Ortholux II Pol microscope. The images were obtained throught a digital camera Leica DC 100 and were analyzed with a software Leica IM50 (version 1.20).

N₂ adsorption-desorption experiments were performed on a Micromeritics ASAP2020 apparatus after outgassing the material for 30 hours at 55 °C.

XRD measurements of the dried powder samples were carried out in 1.5-mmdiameter glass capillaries in a transmission configuration. A copper rotating anode Xray source working at 4 kW with a multilayer focusing Osmic monochromator giving high flux and punctual collimation was employed. An image plate 2D detector was used.

FT-IR spectra were acquired using a Mattson Mod7000 spectrometer. The spectra were collected in the 4000-500 cm⁻¹ range by averaging 64 scans at a

resolution of 4 cm⁻¹. The solid samples (2 mg) were finely ground and mixed with approximately 175 mg of dried KBr (Merck, spectroscopic grade) and pressed into pellets. Prior to recording the spectra the pellets were stored under vacuum for about 24 hours at approximately 60 °C to reduce the levels of adsorbed water. To evaluate complex band FT-IR envelopes and to identify underlying spectral components, the iterative least-squares curve-fitting procedure in the PeakFit software [10] was used. The best fit of the experimental data was obtained using Gaussian shapes and by varying the frequency, bandwidth and intensity of the bands. A linear baseline correction with a tolerance of 0.2% was employed. The standard errors of the curve-fitting procedure were less than 0.03.

2.1.3. Results and discussion

L12D was synthesized from a mixture of **P12**, water, DMSO and HCl in a molar ratio **P12**:DMSO:H₂O:HCl = 1:388:527:0.175 at 80 °C (Scheme 2.1.1). It was obtained as a white powder after filtration, washing and freeze-drying.

The TGA curve of **L12D** (Figure 2.1.2) reveals that this hybrid sample is thermally stable up to 245 °C in a non-oxidizing atmosphere. Between this temperature and approximately 400 °C, a dramatic weight loss (*ca.* 60%) takes place. Between the latter temperature and 700 °C, the rate of thermal degradation is considerably lower. At the maximum temperature examined, about 20% of the mass of the sample still has not suffered thermal decomposition.



Figure 2.1.2.TGA curve of L12D.

The ²⁹Si CP/MAS NMR spectrum of **L12D** (Figure 2.1.3 (a)) exhibits signals peaking at -48, -57 and -67 ppm attributed to the T¹ (C-Si(OSi)(OR)₂), T² (C-Si(OSi)₂(OR)) and T³ (C-Si(OSi)₃) silicon environments, respectively, where R = H or Et. The condensation degree c (where c = 1/3 ($%T_1 + 2 %T_2 + 3 %T_3$)) was estimated to be *ca*. 71%. The similarity found between this value and those reported for the lamellar **L12** material [1, 2, 5, 6] and for lamellar alkylsiloxanes [11] suggests the occurrence of a two dimensional siloxane framework in the silsesquioxane **L12D** and consequently the formation of linear polymer siloxane linkages despite the significant steric hindrance associated with the alkyl groups. This explanation is corroborated by the existence of a major proportion of T₂ units in this material. We note, however, that the presence of T₁ and T₃ units is indicative of partial variation in the siloxane linkage. The absence of Q-type (SiO₄) environments (characteristic resonances expected at δ = -90 to -120 ppm) demonstrates the full preservation of the C-Si bonds in the final hybrid material.

The latter conclusion is further corroborated by the presence of a signal at 12 ppm typical of the CH₂-Si group in the ¹³C CP/MAS NMR spectrum of L12D (Figure 2.1.3 (b)). As expected, the C=O of the urea groups gives rise to a sharp signal at 160 ppm (full-width-at-half-maximum (fwhm) = 2.2 ppm). The ill-resolved and very weak peaks located at 58 ppm and 18 ppm, associated with the resonance of the ethoxy carbon atoms (CH_3CH_2-O and CH_3CH_2-O , respectively), demonstrate that the hydrolysis reaction was practically complete. The internal methylene carbon atoms of the alkylene chains appear between 30 and 35 ppm. The pair of prominent resonances distinguishable at 34 and 31 ppm in Figure 2.1.3) are ascribed to carbon atoms of ordered alkylene chains (i.e., densely packed all-trans chains) and amorphous domains (i.e., disordered chains that adopt essentially gauche conformations), respectively [12-14]. Although the all-trans/gauche conformational ratio - estimated through the calculation of the relative integrated areas via curve-fitting using Lorentzian functions practically coincides for L12D and L12, the fwhm is higher for L12D than for L12 (2.9 and 1.2 ppm, respectively), suggesting a higher chain conformational disorder in the former material.

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Figure 2.1.3. ²⁹Si CP/MAS (a) and ¹³C (b) CP/MAS NMR spectra of the L12D hybrid.

The SEM image depicted in Figure 2.1.4 (a) demonstrates that, unlike **L12** which is obtained as platelets, the **L12D** material is produced as micrometric spheres with a diameter of *ca*. 10-50 μ m. Higher magnification clearly reveals that the microspheres display a sponge-like morphology, which consists of very thin, folded films assembled along an edge-to-face fashion (Figures 2.1.4 (b-d)). The existence of very thin films that are subject to folding was confirmed by TEM (Figure 2.1.5).

Although **L12D** displays essentially void-like structure, only a low specific surface area of 35 m^2g^{-1} (a value similar to that reported for **L12** (42 m^2g^{-1}) [2]), was measured by N₂ adsorption-desorption analysis (Figure 2.1.6). The uptake at high p/p° results from the condensation of N₂ in the voids between the films.

Interestingly, the **L12D** material exhibits anisotropic character, as evidenced by the POM image recorded between crossed polarizers (Figure 2.1.7). The birefringence observed suggests submicrometric anisotropy.



Figure 2.1.4. SEM images of the **L12D** hybrid at different magnifications: (a) 30 μ m; (b) and (c) 6 μ m; (d) 3.75 μ m.



Figure 2.1.5. TEM image of the L12D hybrid.



Figure 2.1.6. Adsorption-desorption isotherm of the L12D hybrid.



Figure 2.1.7. POM image of the L12D hybrid.

The AFM images recorded upon scanning the surface of **L12D** in tapping mode indicate lamellar organization (Figure 2.1.8). The periodicity discerned in the amplified 2D phase image of Figure 2.1.8 (b) may also be inferred *grosso modo* from a derived profile plot (Figure 2.1.8 (c)).



Figure 2.1.8. AFM images of the L12D hybrid: (a) Plane; (b) Amplitude and (c) Phase.



Figure 2.1.9. 3D (a) and 2D (b) Phase AFM images of the L12D hybrid. Profile plot (c) corresponding to the line drawn in (b).

Comparison of the XRD patterns of L12D and L12 represented in Figure 2.1.10 allows concluding that the pattern produced by the hybrid synthesized in the present work is clearly less well resolved than that of **L12**. The peaks detected in the low q (where q is the wave vector) range at 2.17, 6.52 and 8.72 nm⁻¹ in the diffractogram of L12D correspond to the 1st, 3rd and 4th orders (see inset of Figure 2.1.10) of a lamellar structure with a characteristic interlamellar spacing / (where $l = n2\pi/q_n$ and n is the reflection order) of 2.85 nm. This value is slightly lower than the estimated length of the organic spacer (3.16 nm) [15]. In the high q range, the peak at 13.0 nm⁻¹ (d = 0.48nm) is associated with the separation between two neighbouring urea groups in the self-associated urea-urea hydrogen-bonded array [5, 6] and the prominent broad peak at 15.1 nm⁻¹ (d = 0.42 nm) (see inset of Figure 2.1.10) is attributed to ordering within the siloxane domains [5, 6]. Both the ill-defined peak at approximately 16.3 and the shoulder seen at approximately 17.0 nm⁻¹ (d = 0.39 and 0.37 nm, respectively) (see inset of Figure 2.1.10) provide information of chain packing density and in-plane chainchain ordering distances. The former peak is related with chains in gauche conformations and the latter to chains in all-trans conformations (highly packed and thus closer) [5, 6]. All the characteristic distances of L12D indicated above are in perfect agreement with those reported earlier for L12 [1].



Figure 2.1.10. XRD patterns of the **L12** (black line) (reproduced from reference [2]) and **L12D** (red line) hybrids.

To assess the influence of DMSO on the extent and strength of hydrogen bonding, we decided to examine the spectral signature of L12D in the 1800-1500 cm⁻¹ interval of the FT-IR spectrum and compare it with that of L12. This spectral region is of the utmost interest because it is where the amide I and amide II vibration modes absorb. The amide I mode (1800-1600 cm⁻¹), essentially due to the C=O stretching vibration, [16] is sensitive to the specificity and magnitude of hydrogen bonding. Usually the amide I band consists of several distinct components which correspond to different C=O environments or aggregates. As the absorption coefficients of C=O groups involved in different aggregates are likely to be different, it is not correct to compare the intensity of the different components. Consequently, only the changes undergone by each component are an adequate indication of concentration variations of each type of aggregate [16, 17]. The amide II mode (1600-1500 cm⁻¹), mainly associated with a N-H in-plane bending vibration, is sensitive to both chain conformation and intermolecular hydrogen bonding, providing valuable information about the distribution of hydrogen bond strengths [16]. In the case of urea-containing compounds, these modes have been designated as "amide I" and "amide II" modes, respectively.

The pair of broad bands centered at 1625 and 1583 cm⁻¹ in the spectrum of **L12D** depicted in Figure 2.1.11 are ascribed to the "amide I" and "amide II" modes, respectively.



Figure 2.1.11. Curve-fitting results of the FT-IR spectra of the **L12** (a) (reproduced from reference [6]) and **L12D** (b) hybrids in the "amide I" and "amide II" regions.

As the wavenumber difference ($\Delta v = 42 \text{ cm}^{-1}$) between the intensity maxima of these modes coincides for L12 [1] and L12D, one might be wrongly induced to conclude that the strength of the hydrogen-bonded array of urea-urea aggregates is independent of the nature of the solvent used in the synthetic procedure. Closer analysis of Figure 2.1.11 reveals that the band profiles of L12 and L12D are significantly different as a result of band redistribution. In fact the proportion of disordered aggregates responsible for the 1647 cm⁻¹ component [6] increases in L12D at the expense of the destruction of the ordered aggregates that give rise to the component at 1625 cm⁻¹ [6]. As a consequence, the integrated area of the "amide II" component at 1564 cm⁻¹ increases, whereas that of the 1583 cm⁻¹ feature decreases. These results give support to the explanation that the addition of a mixture of water/DMSO to P12 instead of only water leads to the formation of more disordered hydrogen-bonded urea-urea aggregates [6]. This conclusion is in perfect agreement with the increase of the *fwhm* of the urea signal in the ¹³C CP/MAS NMR spectra of **L12** and **L12D** from 1.5 to 2.2 ppm, respectively (Figure 2.1.3). Besides weakening the hydrogen-bonded ureaurea array, the incorporation of DMSO has no further spectral consequences. It is worth mentioning that the component characteristic of the absorption of "free" urea groups (i.e., urea groups devoid of any hydrogen bonding interactions), expected at 1751 cm⁻¹ [18] is not detected in the "amide I" region of either L12 or L12D (Figure 2.1.11).

To explain why the synthesis of the lamellar **L12** material in the presence of only water yields platelets, whereas the one carried out in a water/DMSO mixture gives rise to the formation of microsponges, we propose a mechanistic interpretation based on the physico-chemical properties of these two solvents. With respect to aprotic DMSO, water is a solvent with higher dielectric constant ($\varepsilon_{20} \circ_{C}$ = 46.68 and 80.10, respectively), but lower dipolar moment ($\mu_{25} \circ_{C}$ = 4.1 D and $\mu_{20} \circ_{C}$ = 1.87 D, respectively). Furthermore, both solvents have high polarity indexes (7.2 and 10.2, respectively). The dielectric constant of the water/DMSO mixture used in this study molar ratio DMSO:water = 527:328 was estimated to be 68 ± 6 [20]. We believe that the reason for the different morphologies of **L12** and **L12D** is likely to be found at an advanced stage of the synthetic mechanism (Figure 2.1.12). In the first step of the synthetic procedure the acidic hydrolysis of **P12** leads to the formation of a bis(silanetriol) amphiphilic precursor compound [18], soluble in water and in the

water/DMSO mixture. Strong intermolecular forces between neighbor molecules, such as hydrogen bonding between the urea groups or between the silanol functionalities [21], as well as van der Waals interactions between the alkylene chains, promote the formation of the siloxane network, leading ultimately to the formation and organization of thin lamellar ribbons (A) (Figure 2.1.12). Therefore the growing supramolecular architecture acts itself as an internal template directing the organization of the hybrid silica. Owing to the low pH of the reaction medium, the protonation of the silanol and urea groups of the growing structured objects (A) is expected to take place. The influence of the nature of the solvent on the structuring of P12 at the micrometer scale, which ends up with the formation of platelets in the case of L12 and microsponges in the case of L12D, might operate at this stage.



Figure 2.1.12. Proposed mechanism for the formation of the **L12** and **L12D** hybrids. For the sake of clarity the Cl⁻ ions have been omitted.

A plausible explanation for the different shapes of the two materials is the following. In water, the hydrophobic interactions between the alkylene chains promote face-to-face stacking of lamellar ribbons (**A**), leading ultimately to the formation of 3D platelets (**L12**) (Figure 2.1.12). Such a stacking is aided by the high charge mobility and the low charge repulsions that occur in water. In contrast, DMSO strongly interacts with the lipophilic alkylene chains, thus stabilizing the growing ribbons (**A**). Furthermore, the lower charge mobility in the water/DMSO mixture and the lower dielectric constant disfavor face-to-face stacking, privileging edge-to-face approach of the charged ribbons, which ultimately yields sponge-like micro-objects (**L12D**). Folding, enabled by the films' low thickness, contributes to the final morphology observed.

2.1.4. Conclusions

A novel type of morphology has been obtained for a hybrid silica prepared through acidic hydrolysis/condensation of the **P12** precursor using a water/DMSO mixture. The hydrogen bonds established between the urea groups, as well as the van der Waals forces between the long alkyl chains are the main driving forces that govern the ordering of the precursor molecule into a lamellar assembly. Although **L12** and **L12D** resemble closely both from the chemical and nanostructural standpoint, we show in this work that the nature of the solvent plays a major role on the shaping of the final material. We propose that the balance between attractive and repulsive interactions occurring at a late stage of the synthetic process is the key parameter that controls the final microstructure of **L12** and **L12D**.

The results reported here represent an important step forward in the comprehension of the processes governing the formation of self-organized hybrid siliceous materials.

2.1.5. References

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Self-structuring of lamellar bridged silsesquioxanes with long side spacers

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2.2. Self-structuring of lamellar bridged silsesquioxanes with long side spacers

2.2.1. Introduction

The most extensively investigated ordered BS structures have been undoubtedly the lamellar packed structures synthesized from the alkylene-based precursors $(EtO)_3Si-S_2-Y-S_1-Y-S_2-Si(OEt)_3$ (where the central spacer S_1 is an alkylene chain with variable length (- $(CH_2)_n$ and the side spacers S_2 are short alkylene chains (- $(CH_2)_m$ -) (in general propylene chains, m = 3) and the cross-link Y is the urea (-NHC(=O)NH-) group) (**Pn**) [1-7]. In this class of hybrids the degree of order of the hybrids increases with the length of the central spacer S_1 . Chains with less than 8 methylene groups lead to, however, to disordered materials regardless of the reaction conditions employed [2-4]. It was also demonstrated that the synthetic procedure adopted exerts a dramatic influence on the final morphology [1-12].

The case of the dodecylene (n=12)-based precursor **P12** is worth mentioning in this context, as it is an excellent example of easy-tuning of the degree of order, dimension and design of the final hybrid compound *via* judicious modification of the reaction conditions, such as the type of catalyst [1, 2-14], the **P12**:H₂O molar ratio [1,3-5] and the addition of Eu³⁺ ions [5, 6]. In the last section we demonstrated the crucial role played by the nature of the solvent(s) [7].

In the present section we will report on studies carried out with the goal of determining the influence of the side spacers S₂ on the structuring, morphology and ultimately on the optical properties of the P12-derived materials. We have investigated for this purpose a series of alkylene-based hybrid materials (henceforth designated as C₁₀C_nC₁₀) derived from silsesquioxane precursors similar to P12 including side spacers S₂ composed of decylene chains instead of propylene chains (EtO)₃Si- $(CH_2)_{10}$ -Y- $(CH_2)_n$ -Y- $(CH_2)_{10}$ -Si $(OEt)_3$ with n = 7, 9-12 (P10-n-10). Because of the higher proportion of organic component, the solubility of the precursor molecules in water is lower than that of the **Pn** precursor molecules. This problem was overcome through the use of а water/DMSO mixture. The molar ratio P10-n**10**:H₂O:DMSO:HCl=1:527:388:0.175 employed here coincides with that used in the previous section to prepare the sponge-like **L12D** material [7, 12].

2.2.2. Experimental part

Materials

The α, ω -diaminoalkanes were purchased from Aldrich (1,7-diaminoheptane, NH₂-C₇-NH₂, 97%), Acros (1,9-diaminononane, NH₂-C₉-NH₂, 98%, and 1,10-diaminodecane, NH₂-C₁₀-NH₂, 97%), ABCR (1,11-diaminoundecane, NH₂-C₁₁-NH₂, 97%) and Fluka (1,12-diaminododecane, NH₂-C₁₂-NH₂, 97%). 10-isocyanatodecyltriethoxysilane (ICDTES) was prepared according to a procedure described elsewhere [13]. Dichloromethane (CH₂Cl₂) and pentane were dried over CaH₂ and freshly distilled prior to use. Dimethylsulfoxide (DMSO, (CH₃)₂S=O, SDS, synthesis grade), ethanol and acetone were used as received.

Synthesis of the bridged organosilanes

The precursors P10-n-10 were synthesized in Schlenk tubes under anhydrous conditions (Scheme 2.2.1) and stored under a dry atmosphere of nitrogen (N_2). In a typical experiment, **ICDTES** (1.96 g, 5.6 mmol) was added to a CH₂Cl₂ solution (60 mL) of the diamine (2.6 mmol) at room temperature. A precipitate formed within a few minutes. After 24 hours, the solvent was removed under vacuum, and the residue was washed with pentane (40 mL). After drying, the bis(urea) compound was obtained as a white wax. **P10-7-10**: ¹H NMR (CDCl₃, 400 MHz): 0.60 (m, 4 H); 1.18-1.53 (m, 60 H); 3.09 (m, 8 H); 3.79 (q, 7.0 Hz, 12 H); 5.50 (br, 4 H). ¹³C NMR (CDCl₃, 100 MHz): 10.4; 18.3; 22.8; 26.4; 27.1; 28.6; 29.3; 29.48; 29.53; 29.7; 30.1; 30.5; 33.2; 40.0; 40.4; 58.3; 159.3. **P10-9-10**: ¹H NMR (CDCl₃, 400 MHz): 0.62 (m, 4 H); 1.20-1.53 (m, 64 H); 3.14 (m, 8 H); 3.81 (q, 7.0 Hz, 12 H); 4.74 (br, 4 H). ¹³C NMR (CDCl₃, 100 MHz): 10.4; 18.3; 22.8; 26.4; 27.0; 28.6; 28.9; 29.2; 29.4; 29.5; 29.6; 30.0; 30.3; 33.2; 40.2; 40.5; 58.3; 158.7. **P10-10-10**: ¹H NMR (CDCl₃, 400 MHz): 0.62 (m, 4 H); 1.18-1.34 (m, 66 H); 3.14 (m, 8 H); 3.81 (g, 7.0 Hz, 12 H); 4,52 (br, 4 H). ¹³C NMR (CDCl₃, 100 MHz): 10.4; 18.3; 22.8; 26.6; 26.9; 28.9; 29.0; 29.2; 29.4; 29.5; 29.6; 30.1; 30.3; 33.2; 40.5; 40.6; 58.3; 158.5. P10-11-**10**: ¹H NMR (CDCl₃, 400 MHz): 0.61 (m, 4 H); 1.15-1.51 (m, 68 H); 3.11 (m, 8 H); 3.80 (q, 7.0 Hz, 12 H); 5.04 (br, 4 H). ¹³C NMR (CDCl₃, 100 MHz): 10.4; 18.3; 22.8; 26.7; 27.0; 29.1; 29.2; 29.3 (2 C); 29.46; 29.52; 29.6; 30.3; 30.4; 33.2; 40.3; 40.4; 58.3; 158.9. P10-**12-10**: ¹H NMR (CDCl₃, 400 MHz): 0.61 (m, 4 H); 1.18-1.53 (m, 70 H); 3.14 (m, 8 H); 3.81 (q, 7.0 Hz, 12 H); 4.37 (br, 4 H). ¹³C NMR (CDCl₃, 100 MHz): 10.4; 18.3; 22.8; 26.7; 26.9; 29.1; 29.18; 29.23 (2 C); 29.4; 29.5; 29.6; 30.2; 30.3; 33.2; 40.6; 40.7; 58.3; 158.3.



P10-n-10 with n= 7, 9 and 11

Scheme 2.2.1. Synthetic scheme of the reaction.

Synthesis of the BSs

In a typical experiment a mass of **P10-n-10** (1.2 mmol) was heated in DMSO (33 mL, 464 mmol) until the solution got clear. While cooling to room temperature, the mixture gelified. After addition of water (9.3 mL, 517 mmol), the mixture was warmed up to 80 °C. To the resulting cloudy solution, a solution of HCl (0.1 N, 2.1 mL, 0.21 mmol_{HCl} and 117 mmol_{H2O}) was added. The molar ratio of **P10-n-10**:DMSO:H₂O:HCl was 1:388:527:0.175. The mixture was stirred for 1 hour at 80 °C, then kept under static conditions at the same temperature for 4 days. The resulting gel/precipitate was filtered off, washed successively with water, ethanol, acetone and water, and then freeze-dried overnight.

Characterization of the material

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²⁹Si and ¹³C solid state NMR spectra and SEM, AFM and POM images were recorded using the equipments and procedures described in section 2.1.

Some **TEM** micrographs were obtained using the equipment and procedure described in section 2.1. Some others were obtained using a JEOL 1200 EX2 apparatus equipped with a SIS Olympus Quemesa 11 Mpixel camera. These pictures were treated using the ImageJ software.

The **XRD** patterns were recorded at room temperature with a Rigaku Geigerflex D/max-c diffractometer system using monochromated CuK_{α} radiation (λ = 1.54 Å) over the 2 θ range of between 4 and 70° at a resolution of 0.05°. The samples were not subject to any thermal pre-treatment.

Small Angle X-ray Scattering (SAXS): The SAXS spectra were recorded at the National Synchrotron Light Laboratory (LNLS), Campinas (Brazil), using a SAXS beam line which provides a monochromatic (λ =1.608 Å) and horizontally focused beam. A vertical position-sensitive X-ray detector and a multichannel analyser were used to record the SAXS intensity, I(q), as a function of modulus of the scattering vector $q = 4\pi/\lambda \sin(\varepsilon/2)$, ε being the X-ray scattering angle. The parasitic scattering intensity from air, slits, and windows was subtracted from the total intensity. The scattering intensity was also normalized by taking into account the varying intensity of the direct X-ray beam, sample absorption and sample thickness.

Fourier Transform Raman (FT-Raman): The FT-Raman spectra were recorded at room temperature with a Bruker RFS 100/S spectrometer equipped with a near-infrared Nd:YAG laser with wavelength excitation (1064 nm at 400 mW). The spectra were collected over the 3200–300 cm⁻¹ range by averaging 200 scans at a maximum resolution of 4 cm⁻¹.

FT-IR spectra were recorded using the equipment and procedure described in section 2.1. Curve-fitting of complex FT-IR and FT-Raman band envelopes were carried out using the procedure described in detail in section 2.1.

Photoluminescence (PL): The PL spectra were recorded at room temperature and at 12 K with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Jobin Yvon-Spex Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were corrected for the spectral distribution of the lamp intensity using a photodiode reference detector. The lifetime measurements were acquired with the setup described for the luminescence spectra using a pulsed Xe-Hg lamp (6 μs pulse at half width and 20-30 μs tail). The absolute emission quantum yields were measured at room temperature using a quantum yield measurement system C9920-02 from Hamamatsu with a 150 W Xenon lamp coupled to a monochromator for wavelength discrimination, an integrating sphere as sample chamber and a multichannel analyzer for signal detection. Three measurements were made for each sample so that the average value is reported. The method is accurate to within 10%.

2.2.3. Results and discussion

The ²⁹Si MAS NMR spectra of the $C_{10}C_nC_{10}$ materials display three broad signals centered at -47, -58 and -68 ppm (Figure 2.2.1 and Table 2.2.1) ascribed to T^1 , T^2 and T^3 silicon sites, respectively. The condensation degrees deduced (Table 2.2.1) are of the same order of magnitude as those reported previously for the lamellar **L12** material [1, 2, 5] and more recently for the sponge-like **L12D** material (see section 2.1) [7]. These findings suggest that in the $C_{10}C_nC_{10}$ BSs the siloxane framework is a 2D network composed of linear polymer siloxane linkages.



Figure 2.2.1. ²⁹Si MAS NMR spectra of the $C_{10}C_nC_{10}$ bridged silsesquioxanes.

However, the spectra of Figure 2.2.1 demonstrate that, although the dominating silicon sites in the $C_{10}C_nC_{10}$ materials are T² units, T¹- and T³-type units are also present, revealing partial variation in the siloxane linkages. The absence of Q-type (SiO₄) resonances between -90 and -120 ppm in the ²⁹Si MAS NMR spectra (not shown) is a proof of the preservation of the C-Si bonds in the $C_{10}C_nC_{10}$ samples. The ¹³C CP/MAS NMR spectra of the hybrid samples (Figure 2.2.2) also provides evidence of the preservation of the Si-C bond (peak located at about 14 ppm) and also proves that no cleavage of the functional groups of the precursor molecule, *i.e.*, central spacer alkylene chains, side spacer decylene chains and urea cross-links, occurred during the synthesis of the C₁₀C_nC₁₀ BSs. The absence of the packs characteristic of ethoxyl carbon atoms at about 58 and 18 ppm demonstrate that the hydrolysis reaction was complete.

60



а



Figure 2.2.2. ¹³C CP/MAS NMR spectra of the $C_{10}C_nC_{10}$ bridged silsesquioxanes with even n (a) and odd n (b).

	Attribution	T ¹ -R-Si(OSi)(OH) ₂	T ² -R-Si(OSi) ₂ (OH)	T ³ -R-Si(OSi) ₃	C	Empirical Formula										
	n = 12	-48.9 (13%)	-57.6 (65%)	-67.8 (22%)	69	R[Si(OH) _{0.92} O _{1.04}]2										
tion) ²⁹ Si NMR	n = 11	47.4 (10%)	-57.0 (63%)	-67.7 (27%)	72	R[Si(OH) _{0.83} O _{1.08}] ₂										
δ (integral frac	n = 10	-48.4 (12%)	-57.5 (71%)	-67.4 (16%)	68	R[Si(OH) _{0.96} O _{1.02}]2		Attribution	NH C (=O)NH	Si-CH ₂ CH ₂ CH ₂ -N		<u>C</u> H ₂ trans		<u>C</u> H ₂ gauche	Si-CH ₂ CH ₂ CH ₂ -N	Si- <u>C</u> H ₂ CH ₂ CH ₂
	n = 9	-48.1 (13%)	-56.7 (66%)	-67.7 (21%)	69	R[Si(OH) _{0.92} O _{1.04}]2		n = 12	159	41		35	32	30	24	13
								n = 11	161	43	41	35	33	I	25	15
								n = 10	160	41	40	35	32	30	23	13
	7	-47.9 (10%)	-57.2 (64%)	-67.4 (26%)	72	R[Si(OH) _{0.84} O _{1.08}] ₂	/MAS	n = 9	161	42		35	32	I	24	14
	ш С						δ ¹³ C CI	n = 7	159	43		35	32	I	25	15

*c (polycondensation degree) = $1/3(\%T^{1} + 2\%T^{2} + 3\%T^{3}) \times 100$; Note: R = $-C_{10}H_{20}-(NHC(=O)NH)-(CH_{2})n-(CH_{2})n-(CH_{2})n-(C_{10}H_{2})n-($ **Table 2.2.1**. ²⁹Si MAS NMR and ¹³C CP/MAS data of the $C_{10}C_nC_{10}$ bridged silsesquioxanes (δ in ppm).

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Analysis of the SEM images reveals that the morphology of $C_{10}C_7C_{10}$ is rather irregular (Figures 2.2.3 (a-b)), whereas that of the $C_{10}C_9C_{10}$ and $C_{10}C_{10}C_{10}$ samples closely resembles that of L12D [see Figure 2.1.4, section 2.1] [7]. Both materials form micro-objects with a sponge-like morphology (Figures 2.2.3 (c, e), respectively), consisting of very thin, folded films assembled along an edge-to-face fashion (n = 9, Figure 2.2.3 (d) or entangled folded ribbons (n = 10, Figure 2.2.3 (f)). In $C_{10}C_{11}C_{10}$ the ribbons appear considerably more folded, forming less regular objects (Figures 2.2.3 (g, h)). The process ends up in $C_{10}C_{12}C_{10}$ with the production of 10 µm-diameter dense, homogeneous spheroïdal particles (Figure 2.2.3 (i)) which tend to link to each other (Figure 2.2.3 (j)).

The increasing contribution of the folding process to which the thin films are subject in these materials as the length of the central spacer increases is clearly recognized in the TEM images shown in Figure 2.2.4. The intrinsic ordered nanostructure of the films/ribbons is perfectly evident in the case of samples with n = 9 (Figure 2.2.5 (b)), n = 10 (Figures 2.2.4 (c, d)) and n = 12 (Figure 2.2.4 (h)).

Additional proofs of the organized texture of $C_{10}C_{12}C_{10}$ and in particular $C_{10}C_{10}C_{10}$ have been obtained by AFM upon scanning the surface of the samples in tapping mode (Figures 2.2.5 (c, b) respectively). The 3D topographic perspective of the BS with n = 10 is given in Figure 2.2.6. The organization fashion observed in both samples is, however, less well distinguishable in the case of the material with n = 9 (Figure 2.2.5 (a)).

The anisotropic nature of $C_{10}C_{10}C_{10}$ is demonstrated in the POM image recorded between crossed polarizers (Figure 2.2.7). The birefringence exhibited indicates submicrometric anisotropy.



Figure 2.2.3. SEM images of the $C_{10}C_nC_{10}$ bridged silsesquioxanes with n = 7 (scale bars = 6 µm (a) and 1.20 µm (b), n = 9 (scale bars = 12 µm (c) and 2 µm (d)), n = 10 (scale bars = 6 µm (e) and 1.20 µm (f)), n = 11 (scale bars = 20 µm (g) and 2 µm (h)) and n = 12 (scale bars = 30 µm (i) and 6 µm (j)).



Figure 2.2.4. TEM images of the $C_{10}C_nC_{10}$ bridged silsesquioxanes with n = 7 (a) scale bar = 173 nm; n = 9 (b) scale bar = 100 nm; n = 10 (c) scale bar = 100 nm and (d) Fast Fourier Transform image; n = 11 (e) scale bar = 435 nm; n = 12 (f) scale bar = 1 µm, (g) scale bar = 1 µm and (h) scale bar = 100 nm.

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Figure 2.2.6. 3D Topographic AFM image of the $C_{10}C_{10}C_{10}$ bridged silsesquioxane.



Figure 2.2.7. POM image of the $C_{10}C_{10}C_{10}$ bridged silsesquioxane recorded between crossed polarizers.

Figure 2.2.5. Plane AFM images of the $C_{10}C_nC_{10}$ bridged silsesquioxanes with n = 9 (a), n = 10 (b) and n = 12 (c).

The XRD patterns of selected samples exhibit completely different profiles in the high q range ($q > 10 \text{ nm}^{-1}$) (Figure 2.2.8). While the $C_{10}C_7C_{10}$ material produces a broad, ill-defined and asymmetric peak centered at about 15 nm⁻¹, the intensity maximum of the band is shifted to about 15.7 nm^{-1} for n = 9 and 11 and a shoulder is visible in the lower q side, especially in the pattern of the former hybrid. In the case of the BS with the longest central spacer S₁ (C₁₀C₁₂C₁₀) the band profile becomes better resolved and two peaks centered at 14.7 and 16.2 nm⁻¹ are discerned (Figure 2.2.8). Curve-fitting of the band envelopes performed between 12 and 19 nm⁻¹ by means of Gaussian shapes allowed us to identify four components in the XRD patterns of the samples with n = 7, 9, 11 and 12. The component at lowest q, centered at 13.54 nm⁻¹ ($d_1 = 0.464$ nm), is attributed to the separation between two neighboring urea groups of the urea-urea hydrogen-bonded array [5-7]. The characteristic component associated with ordering within the siloxane domains is centered at 14.65 nm⁻¹ ($d_2 = 0.429$ nm) [5-7]. The remaining two components, centered at 15.85 nm^{-1} (d_3 =0.392 nm) and 17.15 nm^{-1} $(d_4=0.366 \text{ nm})$, are ascribed to chain-chain spacings, indicating the occurrence of gauche and all-trans conformers in the alkylene chains, respectively [5-7].

In the low *q*-range ($q < 10 \text{ nm}^{-1}$) the XRD patterns of the $C_{10}C_nC_{10}$ BSs display narrow peaks which correspond presumably to the higher order (*i*) harmonics of the fundamental reflection located at q < 2 nm ⁻¹ (Figure 2.2.8).



Figure 2.2.8. XRD patterns of selected C₁₀C_nC₁₀ bridged silsesquioxanes.

This hypothesis is confirmed by the presence of a weak and ill-defined peak at q \approx 1.47-1.55 nm⁻¹ in the SAXS patterns of the $C_{10}C_nC_{10}$ hybrids with n = 9, 10 and 12 reproduced in Figure 2.2.9 (a). Unfortunately, this peak is masked by the intense scattering produced by the hybrid particles. In fact the linear dependency (slope close to -4) observed in the low q region of the log-log plot depicted in the inset of Figure 2.2.9 (a) is in agreement with the Porod power law decay expected for a two-phase system with a well-defined interface. Thus, the two peaks at q > 1 nm⁻¹ correspond to the reflections of inner particles crystalline structure. The position of the higher order Bragg peaks follow the sequence characteristic of a lamellar structure in which the interlamellar distance l is given by $l = 2\pi i/q_i$ (i = 1, 2, 3, ...). The l spacing values calculated on the basis of the SAXS data for the $C_{10}C_nC_{10}$ hybrids are 4.09±0.01 nm for n = 9, 4.13 ± 0.02 nm for n = 10 and 4.24 ± 0.02 nm for n = 12. The increase of / with n supports that the length of the alkylene chains of the central spacer is intimately correlated with the interlamellar distance. This result allows inferring that the hybrids have a lamellar structure composed of 2D siliceous domains separated by the alkylene chains. Assuming an average C-C distance of 0.13 nm, the addition of 3 CH₂ groups to a nonylene chain would be expected to result in an increment of I equal to 0.39 nm, which is considerably higher (it corresponds grosso modo to a threefold increase) than the value found experimentally (4.24-4.09 = 0.15 nm). In the graph of Figure 2.2.9 (b) the experimental I spacings are compared with those calculated if the alkylene chains of the central and side spacers (S₁ and S₂, respectively) adopted exclusively fully extended all-trans zigzag conformations. The trend observed allows inferring that alltrans and gauche conformers coexist in the three samples. We may further conclude from Figure 2.2.9 (b) that there is not a linear relationship between the increase of the length of the central spacer S₁ of C₁₀C₉C₁₀, C₁₀C₁₀C₁₀ and C₁₀C₁₂C₁₀ and the deviation of the experimental *I* values from those calculated for perfect all-*trans* alkylene chains (ΔI = 0.59, 0.68 and 0.83 nm for n = 9, 10 and 12, respectively). Therefore, it is clear that upon introduction of more methylene groups into the central spacer S_1 the proportion of gauche conformers increases and the alkylene chains become less well packed, a process that ultimately leads to the compression of the siliceous layers. Based on these data it is reasonable to propose that the alkylene chains of the $C_{10}C_nC_{10}$ samples with n = 9, 10 and 12 are very likely not perpendicularly oriented with respect to the 2D siliceous layers. To determine the average coherence length *L* of the lamellar order of the three hybrids examined by SAXS, the integral breadth of the second order diffraction peak observed in the SAXS patterns (*B*) was corrected from the instrumental broadening (*b*) by using a well crystallized poly(oxyethylene) [14] as standard reference of experimental aberrations. Assuming that the corrected integral breadth ($\beta^2 = B^2 - b^2$) [15] is essentially due to the size effects, the coherence length of the lamellar order, deduced by means of the Scherrer equation ($L = 4\pi/\beta$) [15], was 105±3 nm for **C**₁₀**C**₉**C**₁₀ and 33±2 nm for samples with n = 10 and 12, respectively, corresponding to *ca*. 25±1 and 8.0±0.7 lamellae, respectively.



Figure 2.2.9. SAXS patterns of selected $C_{10}C_nC_{10}$ bridged silsesquioxanes (a), chain length dependence of the characteristic interlamellar distance *I* (left axis) and of the deviation of a complete all-*trans* conformations situation (b). The lines drawn in (b) are just guides for the eyes.

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In spite of the conclusions retrieved from SAXS data, which suggest the presence of almost completely stretched chains, the absence of intramolecular cyclisation cannot be discarded. However, if present, it must be negligible and the result of a side reaction.

Valuable information regarding the conformational disorder of the alkylene chains may be retrieved from the intense, broad and ill-defined peak which dominates the ¹³C CP/MAS NMR spectra from 40 to 25 ppm (Figure 2.2.2). Two contributions at *ca.* 33 and 30 ppm are clearly discerned: the former resonance is due to the carbon atoms of ordered and densely packed alkylene chains in all-*trans* zigzag conformations, whereas the more shielded signal is produced by the carbon atoms of disordered chains adopting *gauche* conformations [16-18]. The shoulder visible at *ca.* 35 ppm (especially detected in the spectra of the C₁₀C₁₁C₁₀ material (Figure 2.2.3 (b)) suggests that crystalline alkylene chains with different packing structures coexist in these samples [16]. Attempts to calculate the all-*trans/gauche* conformational ratio through curve-fitting of this broad, prominent peak were not successful and thus any conclusions drawn from these data were considered to be highly speculative. Comparison of the peak profile of the C₁₀C_nC₁₀ materials studied suggests that the materials with even n appear to be more disordered than those with odd n, corroborating the conclusions drawn from SAXS data.

To gain complementary insight into the degree of chain packing and the *trans/gauche* conformational ratio in the $C_{10}C_nC_{10}$ hybrid samples we recorded the FT-IR and FT-Raman spectra and examined the following diagnostic modes of the alkylene chains: (1) The symmetric and asymmetric stretching CH₂ modes (v_sCH₂ and v_aCH₂, respectively). (2) The CH₂ bending (δ CH₂) mode.

The location and intensity of the v_sCH_2 mode is complicated due to Fermi resonance between the v_sCH_2 fundamental with the many overtones of the δCH_2 vibrations [18-22]. The v_aCH_2 mode is affected by coupling to the torsional and rotational motions of the chain [18-22]. In the Raman spectrum of ordered alkyl chains (all-*trans* conformations) the v_aCH_2 mode emerges as a strong band in the 2884-2878 cm⁻¹ interval, whereas the v_sCH_2 mode produces bands at 2930 cm⁻¹ (weak), 2900-2898 cm⁻¹ (medium) and 2850-2844 cm⁻¹ (strong) [18-22]. In the case of disordered alkylene chains (*gauche* conformations), the v_aCH_2 mode appears at 2897-2890 cm⁻¹

and the v_sCH_2 bands are typically seen at 2920 cm⁻¹ (medium), 2904 cm⁻¹ (medium) and 2858-2853 cm⁻¹ (strong) [18, 21, 22]. Up- shifting and band broadening are indicative of an increasing proportion of *gauche* conformers.

The inspection of the δ CH₂ region is of interest, since the frequency, intensity and band shape of the δ CH₂ mode are sensitive to interchain interaction and to packing arrangement of the chains [15, 23]. Higher frequency (~1472 cm⁻¹) in the IR spectra indicates ordering of the alkylene chains in all-*trans* conformations (crystalline state), whereas lower frequency (~1466 cm⁻¹), band broadening and decreasing intensity indicate an increase in chain motion (liquid-like state) and therefore a larger gauche/trans conformer ratio [23].

The FT-Raman spectra of the $C_{10}C_nC_{10}$ samples with even n and odd n in the vCH₂ region, depicted in Figures 2.2.10 (a, b), respectively, are dominated by two bands at 2885 cm⁻¹ (very strong, vS)/2857 cm⁻¹ (strong, S) and 2884 cm⁻¹ (vS)/2858 cm⁻¹ (S), respectively. In both cases an intense event, manifested as a shoulder and located at 2850 and 2848 cm⁻¹, respectively, is discerned (Figures 2.2.10 (a, b), respectively). The features at about 2885 and 2850 cm⁻¹ are attributed to the v_aCH_2 and v_sCH_2 modes of all-trans conformers of the alkylene chains [19-23]. The component at ca. 2858 cm⁻¹, also associated with the v_sCH_2 mode, is characteristic of gauche conformers [19, 22, 23]. The peak height ratio (r) of the v_aCH_2 and v_sCH_2 bands is a valuable tool to determine the conformational disorder of the alkylene chains and their packing arrangement [19]. High values (1.61-1.72) are produced by crystalline alkylene chains, whereas chains in the amorphous state give rise to values that range from 1.39 to 1.48 [19]. The dependence of the intensity ratio $r = I_{2885}/I_{2850}$ with the number of carbon atoms of the alkylene chains of the central spacer S₁ of the C₁₀C_nC₁₀ materials is represented in Figure 2.2.11 The trend observed suggests that all the alkylene chains of the $C_{10}C_7C_{10}$ sample (*i.e.*, the chains of the side spacers S₂ and that of the central spacer S₁) are completely disordered and consequently adopt gauche conformations. It may be further inferred from the plot of Figure 2.2.11 that in hybrids with a longer central spacer S_1 (n > 7) the proportion of fully stretched and densely packed alkylene chains (all-trans conformers) is enhanced considerably. In C10C9C10 the value attained for r practically coincides with the minimum value reported for solid n-alkanes, suggesting that the presence of two decylene side chains and one central nonylene chain promotes the highest degree of order and the tightest packing. In addition, these

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data also point out that the samples with n = 10, 11 and 12 contain more gauche conformers than $C_{10}C_9C_{10}$.







Figure 2.2.11. Dependence of the ratio r (with r = 2885 cm⁻¹/2850 cm⁻¹) with the length of the central spacer S₁ in the $C_{10}C_nC_{10}$ bridged silsesquioxanes.

The bands centered at about 1479 and 1466 cm⁻¹ in the δ CH₂ region of the FT-IR spectra of the **C**₁₀**C**_n**C**₁₀ hybrids (Figure 2.2.12) reveal the occurrence of ordered and disordered alkylene chains and thus the coexistence of all-*trans* and *gauche* conformers [23, 24]. The band at *ca*. 1440 cm⁻¹ discerned in the same spectra represents a further evidence of the existence of *gauche* arrangements [25, 26]. Interestingly, it may be inferred from the comparison between Figures 2.2.12 (a, b) that the δ CH₂ mode is sensitive to the parity of the number of carbon atoms of the alkylene chain of the central spacer. While the **C**₁₀**C**_n**C**₁₀ hybrids with odd n display a shoulder at about 1460 cm⁻¹ (Figure 2.2.12 (b)) such event is, however, absent in the case of the samples with even n (Figure 2.2.12 (a)). A similar effect was reported for the parent lamellar **L8-L12** materials [3].



Figure 2.2.12. Room temperature FT-IR spectra of the $C_{10}C_nC_{10}$ bridged silsesquioxanes with even n (a) and odd n (b) in the δCH_2 region.

The FT-IR spectroscopic data were also employed to get insight into the extent and strength of hydrogen bonding in the $C_{10}C_nC_{10}$ di-urea cross-linked BSs. This sort of information is fundamental to characterize this class of hybrids, since it has been extensively recognized [2,3, 27] that hydrogen bonding interactions between the urea groups play a key role, together with van der Waals interactions between the alkylene chains, in the self-assembly process and ultimately in the structuring of the materials. Recently, it was demonstrated that in **L12** all the urea groups present are involved in the formation of an array of strong urea-urea hydrogen-bonded associations that extends throughout the material [5]. This is not surprising considering that urea groups are known to produce impressive self-assembly effects (*e.g.*, excellent gelling properties [28, 29]). This unusual behavior is intimately associated with the particular geometry of the urea moiety. Indeed, the C=O group (hydrogen acceptor) of a urea group may form two hydrogen bonds with the pair of N-H groups (hydrogen donors) of a neighbor urea group, thus forming highly directional planar bifurcated hydrogen bonds [30]. For the reasons presented we decided to inspect the spectral signature of the **C**₁₀**C**_n**C**₁₀ silsesquioxanes in the "amide I" (1700-1600 cm⁻¹) and "amide II" (1600-1500 cm⁻¹) regions of the FT-IR spectra [31-33].]. Details concerning the "amide I" and "amide II" band can be found in section 2.1.

The "amide I" band of **L12** material had been previously decomposed into three components situated at 1668, 1645 and 1624 cm⁻¹, assigned to the absorption of C=O groups included in ordered hydrogen-bonded urea-urea aggregates of increasing strength [5]. These aggregates will be henceforth designated as aggregates **I**, **II** and **III**, respectively.

Close analysis of the "amide I" and "amide II" bands of the $C_{10}C_nC_{10}$ hybrids (Figure 2.2.13) allowed us to conclude that curve-fitting was not straightforward, due to the breadth of the band envelopes and the presence of multiple overlapped components. This problem induced us to perform a 2D Correlation FT-IR spectroscopic analysis on the "amide I" and "amide II" bands of the $C_{10}C_nC_{10}$ materials. To the best of our knowledge this is the first time that such sort of approach has been applied to BS hybrids [34]. 2D Correlation spectroscopic data pointed out that the replacement of the side propylene chains by decylene chains deeply influenced the strength and extent of the urea-urea hydrogen-bonded array. New highly ordered hydrogen-bonded aggregates (so-called aggregates IV) located at 1609 cm⁻¹, stronger than those found in L12 [5] (aggregates I, II and III) are formed. Moreover, in the $C_{10}C_nC_{10}$ series no

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aggregates II were detected [5]. The formation of aggregates IV occurs prior to that of aggregates III. Aggregates I are formed in last.



Figure 2.2.13. FT-IR spectra of the $C_{10}C_nC_{10}$ bridged silsesquioxanes in the 1750-1500 cm⁻¹ region. The spectra were scaled so that the height of the vSi-O-Si band was approximately the same. The wavenumbers indicated represent the intensity maxima of the band envelope of the $C_{10}C_9C_{10}$ sample.

In an attempt to elucidate the relationship between the photoluminescence features and the length of the side spacers in alkylene-based BSs, we decided to examine the emission and excitation spectra of the $C_{10}C_nC_{10}$ materials.

Figure 2.2.14 shows the emission spectra under UV excitation recorded for a selected sample, the amorphous $C_{10}C_7C_{10}$ hybrid. The spectra are formed of a large Gaussian-shaped broad band between 320 and 520 nm. Increasing the excitation wavelength from 280 to 320 nm induces an increase in the relative intensity of the high wavelength side of the spectra. The emission features are almost independent of the length of the central alkylene spacer S_1 (n = 7, 9-12) (Figure 2.2.15). Interestingly, these spectra are very similar to those reported for the P12-derived A12 [6] hybrid (inset of Figure 2.2.15), despite, not only the longer side spacers S_2 of $C_{10}C_nC_{10}$ BS, but also the different synthetic conditions used. Similar emission features were also observed and extensively detailed for amorphous analogous hybrids incorporating

propylene-based side spacers, such as the di-ureasils [35-36], the di-urethanesils [37], and the mono- [38] and di-[39] amidosils, being ascribed to the overlap of two distinct emissions mediated by donor–acceptor pair transitions that occur within the urea, urethane or amide cross-linkages, respectively, and within the siliceous skeleton, due to the presence of oxygen-related defects [35-36].



Figure 2.2.14. Room temperature emission spectra excited at (1) 280, (2) 300 and (3) 320 nm for the $C_{10}C_7C_{10}$ bridged silsesquioxane. The inset shows the room temperature excitation spectra monitored at (5) 312, (6) 330 and (7) 360 nm.



Figure 2.2.15. Room-temperature emission spectra of the $C_{10}C_nC_{10}$ bridged silsesquioxanes excited at 280 nm. The inset shows the emission spectra of A12 hybrid excited at 280 nm [16].

These two emission components were clearly identified through time-resolved spectroscopy. Figure 2.2.16 shows the emission spectra of $C_{10}C_{11}C_{10}$ acquired for distinct starting delay (SD) values under 365 nm excitation wavelength. For SD values smaller than 5.00 ms, the spectra unambiguously display two bands around 427 nm (marked with an arrow in Figure 2.2.16) and 500 nm, previously ascribed to electronhole recombination occurring in the siliceous domains and in the urea cross-linkages, respectively [35-36].

At higher SD values, only the long-lived urea-related component could be observed. In order to detail the time-scale behind each component, lifetime measurements were performed by monitoring the emission decay curves at 427 and 500 nm.



Figure 2.2.16. (a) Low-temperature (10 K) time-resolved emission spectra of the $C_{10}C_{11}C_{10}$ bridged silsesquioxane excited at 365 nm acquired under different starting delay values: (1) 0.05 ms, (2) 1.00 ms, (3) 5.00 ms and (4) 20.00 ms. The integration window was 20.00 ms. Emission decay curves monitored at (b) 427 nm and (c) 505 nm excited at 365 nm; the solid lines represent the data best fit using a single exponential function.

Both decay curves are modeled by a single exponential function yielding lifetime values of 3.4±0.2 ms and 42.7±4.0 ms for the siliceous and urea-related components, respectively. While the lifetime value of the siliceous-related component resembles

that acquired for the di-ureasils, the urea-related lifetime value is substantially smaller (3.5±0.2 ms and 160.0±8.0 ms, respectively [35]). Energy transfer between these two distinct emitting centers was quantitatively estimated for the di-ureasil host with the smallest number of polymer repeat units (d-U(600)) yielding rate values of 1.3×10^9 s⁻¹ (dipole-dipole mechanism) and 3.7×10^8 s⁻¹ (exchange process) [40]. As these energy transfer rates strongly depend on the distance between the two emitting centers, the similar lifetimes of the siliceous-related component in the long-chain analogue d-U(2000) and $C_{10}C_{11}C_{10}$ suggest a similar average distance between the siliceous domains and the urea cross-links, indicating that the side spacers in C₁₀C₁₁C₁₀ most probably adopt gauche conformations. Furthermore, the fourfold increase of the radiative transition decay rate (inverse of the lifetime at 10 K) in C₁₀C₁₁C₁₀, relatively to d-U(2000), is probably associated to the increasing of vibronic-spin-orbit interaction, [40] due to a distinct distribution of hydrogen bonds induced by the increase of the length of the side spacers. The latter result proves that the emission features of the urea-related component of di-urea-cross-linked BSs are sensitive to the length of the side spacers (we recall that there are only three methylene groups in the side spacers of the di-ureasils *versus* ten methylene groups in those of the C₁₀C_nC₁₀ hybrids).

The typical excitation spectra monitored within the emission band in Figure 2.2.14 shows a broad band peaking at 280 nm, whose peak position and full-width-at-half-maximum (fwhm) deviates towards the red as the monitoring wavelength increases (inset in Figure 2.2.14). Similarly to the situation found for the emission data, these excitation spectra are identical to those monitored for the **A12** [6] hybrid. The high- and low-energy side were attributed to the preferential excitation of the siliceous- and urea-related emission [35-36]. Apart from an increase in the relative intensity of the high- wavelength side of the emission spectra those acquired at 12 K (Figure 2.2.17) resemble those measured at room-temperature (Figure 2.2.14).

The absolute emission quantum yield was acquired under the excitation wavelength that maximises the emission features (*i.e.*, 280 nm). For higher excitation wavelengths (330-350 nm) the quantum yield values are below 0.01. The quantum yield values are poorly affected by changes in the alkylene chains length being 0.07±0.01 and 0.06±0.01 for the $C_{10}C_nC_{10}$ samples with n = 7 and 11, respectively. These are considerably smaller than those reported for the **P12**-derived hybrids,

namely the lamellar **L12** and for the amorphous **A12** with quantum yield values of 0.14±0.01 [5] and 0.24±0.02 [6], respectively, both excited at 290 nm, the latter being the maximum value measured for this type of materials. Nevertheless, it should be noted that the photoluminescence measurements and the quantum yield values of **A12** are time-dependent. Upon aging at ambient atmosphere the quantum yield value decreased approximately 2.5 times. The photoluminescence data and quantum yield values reported here for the **C**₁₀**C**_n**C**₁₀ BSs do not show any variation in the same period of time. We should also emphasize that the above mentioned quantum yield values resemble the maximum values measured for di-ureasil hybrids (0.07-0.09±0.01) under longer excitation wavelengths (360-400 nm) [35].



Figure 2.2.17. Low-temperature (12 K) emission spectra of the $C_{10}C_{11}C_{10}$ bridged silsesquioxane excited between 280 and 360 nm.

2.2.4. Conclusions

In this section, a novel series of hybrids, represented by the notation $C_{10}C_nC_{10}$, were prepared from silsesquioxane precursors including decylene chains as side spacers and alkylene chains containing 7, 9, 10, 11 or 12 methylene groups as central spacer. The main goal of the present study was to evaluate the influence of the length of the side spacers on the morphology and structure of alkylene-based BS hybrid materials.

The SEM images provided evidence that the morphology the $C_{10}C_nC_{10}$ samples, ranging from irregular micro-objects to dense spheroidal microparticles,

clearly differs from the platelet-like morphology of the L8-12 samples [1-8], but resembles closely that of the L12D material [section 2.1]. In particular, the characteristic L12D microsphere-like morphology mimicking sea sponges, in which thin folded films assemble along an edge-to face fashion, was especially recognized in $C_{10}C_9C_{10}$. Taking into account that the same synthetic procedure (HCI-catalyzed hydrolytic route in the presence of a large volume of DMSO) was employed to produce L12D and the $C_{10}C_nC_{10}$ hybrids, we believe that the morphological similarity found is a consequence of solvent polarity effects [section 2.1].

The lamellar structure of all the $C_{10}C_nC_{10}$ samples investigated was evidenced by XRD and SAXS. The lamellae are arranged along a structure composed of 2D siliceous domains separated by non perpendicularly oriented alkylene chains containing variable amounts of *trans* and *gauche* conformers. SAXS, ¹³C CP/MAS NMR, FT-IR and FT-Raman spectroscopic data demonstrated that, while the alkylene chains of the side and central spacers of $C_{10}C_7C_{10}$ are completely disordered, in samples with a longer central spacer S₁ the proportion of fully stretched and densely packed alkylene chains (all-*trans* conformers) is enhanced significantly. The highest degree of order and tightest packing are attained for n = 9. This structuring trend contrasts markedly with that observed in the case of the **Ln** family [6] for which the degree of order increases with the increase of the number of methylene groups in the central spacer, provided that at least 8 methylene groups are present in the alkylene chains.

The emission spectra of selected $C_{10}C_nC_{10}$ samples are practically independent of the length of the central alkylene spacer and similar to those reported for hybrid materials containing propylene side spacers, such as the non-structured BS **A12** [6], the di-ureasils [35,36], the di-urethanesils [37] and the di-amidosils [39] and the structured lamellar bilayer mono-amidosils [38]. The emission is ascribed to the overlap of two distinct components that occur within the urea, urethane and amide cross-linkages in the case of the di-ureasils, di-urethanesils, and amidosils, respectively, and within the siliceous nanodomains. Time-resolved spectroscopic data has enabled us to demonstrate for the first time that the emission features of the urea-related component of the emission of di-urea cross-linked BSs depend critically on the length of the alkylene-based side spacers. It also allowed us inferring that the average distance between the siliceous regions and the urea cross-links is practically the same in BSs including propylene- and decylene-based side chains, suggesting that the longer chains adopt *gauche* conformations.

The excitation spectra of the $C_{10}C_nC_{10}$ hybrids resemble that of A12 [6]. However, while the lifetime value of the siliceous-related component resembles that acquired for the di-ureasils, the urea-related lifetime value is substantially smaller, providing evidence of the crucial role played by the longer side spacers on the dynamics of the two distinct emissions.

The absolute emission quantum yield of $C_{10}C_{11}C_{10}$ is considerably smaller than the highest value reported for the **P12**-derived materials (**A12**), but, unlike the latter BS, it is time-independent.

2.2.5. References

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Synthesis of hierarchically structured mono-alkyl-urethanesil hybrid materials



2.3. Synthesis of hierarchically structured mono-alkylurethanesil hybrid materials

2.3.1. Brief introduction

The main goal of the work reported in the present section was to prepare a novel family of functional and hierarchically structured organic-inorganic hybrids by means of the sol-gel and self-assembly techniques.

This synthetic approach was successfully employed to produce a photoluminescent hierarchically structured lamellar bilayer mono-amide cross-linked alkyl/siloxane hybrid (mono-amidosil) [1]. In this white light emitter self-assembly is dictated by: (i) intermolecular hydrogen bonding between amide groups; (ii) van der Waals interactions between all-*trans* alkyl chains assuming a partially interdigitated packing mode; (iii) entropic term related to the phase separation between the alkyl chains and the siloxane nanodomains. These factors determine the emergence of a thermally-actuated photoluminescence memory effect, induced by the reversible order-disorder phase transition of the alkyl chains.

In sections 2.1 and 2.2 we demonstrated that the chemical structure of the bridged organosilane precursors (namely the length of the central and side spacers) and the choice of the experimental conditions (namely, water content, type of catalyst and nature of the solvents) determine the final structure and morphology of BS materials were emphasized.

In the present section we pursued our general investigation on the structuring of silsesquioxanes through the study of materials derived from organosilanes carrying pendant alkyl chains, thus structurally similar to the mono-amidosils [1]. The main goal of this work was to evaluate the consequences arising from the replacement of the **amidosil** linkage by the **urethane** linkage. In addition, we wanted to examine the influence of the chain length on the physical-chemical properties of these materials which were named *mono-alkyl-urethanesils*.

To prepare this new family of silsesquioxanes we used as organic precursors three fatty alcohols ($C_{\rm Y}OH$) (also called alkanols) of variable length. These compounds

are suitable because the reaction of the terminal OH group with the isocyanate group of ICPTES gives rise to the urethane linkage.

The notations used to represent the mono-alkyl urethanesils were **m-Ut(CY)-ac** and **m-Ut(CY)@a_x**. In both notations m stands for mono, Ut denotes urethanesil and Y corresponds to number of carbon atoms in the pendant alkyl chain of the alcohol precursor. In the former notation ac indicates that an acid catalyst was employed; in the latter notation $@a_x$ represents a set of three samples in which the effect of solvent was analyzed, x being the experience number.

2.3.2. Experimental part

Materials

1-Tetradecanol (C14OH, Aldrich, 97%, 214,39 g/mol), 1-hexadecanol (C16OH, Sigma-Aldrich, 99%, 242,45 g/mol), 1-docasanol (C22OH, Aldrich, 98%, 326,61 g/mol), (3-isocyanatopropyl)triethoxysilane (ICPTES, Fluka, 95%), hydrochloric acid (HCl, Panreac) and dimethylsulfoxide (DMSO), Merck, GC purity) were used as received. Ethanol (CH₃CH₂OH, Merck, PA grade) and tetrahydrofuran (THF, Merck, puriss. PA grade) were stored over molecular sieves. High purity distilled water was used in all experiments.

Synthesis and characterization

Synthesis of the m-UtPTES(Y) mono-alkyl-urethanesil precursors

To synthesize the mono-urethanepropyltriethoxysilane precursors, ICPTES was added to a solution (with the appropriate solvent) of fatty alcohol **CYOH**. The reaction was carried out at 60-70 °C under stirring, for several hours (Scheme 2.3.1). The progress of the reaction was monitored by infrared spectroscopy: the strong vibration due to the isocyanate group of ICPTES at 2274 cm⁻¹ decrease progressively, until it disappeared upon completion of the reaction. Simultaneously, a series of new bands, associated with the vibrations of the urethane group, grew in the 1800-1500 cm⁻¹ region. Their structure was confirmed by means of ¹H NMR (400 MHz, CDCl₃) and ¹³C NMR (100 MHz, CDCl₃).

C(14) ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.58-0.65 (m, 2H), 0.87 (t, *J* = 6,7 Hz, 3H), 1.18-1.37 (m, 31H), 1.50-1.67 (m, 4H), 3.10-3.20 (m, 2H), 3.80 (q, *J* = 7.0 Hz, 6H), 4.01 (t, *J* = 6,7 Hz, 2H), 4,90 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 7.6, 14.1, 18.2, 22.6, 23.3, 25.8, 29.29, 29.32, 29.4, 29.5, 29.57, 29.59, 29.62, 29.64, 29.7, 31.9, 43.1, 58.4, 64.8, 156.8.

C(16) ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0,59-0,63 (m, 2H), 0,86 (t, *J* = 6,8 Hz, 3H), 1,15-1,35 (m, 35H), 1,53-1,63 (m, 4H), 3,15-3,18 (m, 2H), 3,80 (q, *J* = 7,1 Hz, 6H), 4.00 (t, *J* = 6,6 Hz, 2H), 4.90 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 7.7, 14.2, 18.4, 22.8, 23.4, 26.0, 29.3, 29.4, 29.5, 29-7-29.8 (8 C), 32.0, 43.4, 58.5, 65.0, 156.9.

C(22) ¹H NMR (400 MHz, CDCl₃) δ (ppm): 0.58-0.65 (m, 2H), 0.87 (t, *J* = 6,8 Hz, 3H), 1.19-1.35 (m, 47H), 1.51-1.65 (m, 4H), 3.10-3.20 (m, 2H), 3.81 (q, *J* = 7.0 Hz, 6H); 4.01 (t, *J* = 6,6 Hz, 2H), 4.88 (br, 1H); ¹³C NMR (100 MHz, CDCl₃) δ (ppm): 7.6, 14.1, 18.2, 22.7, 23.3, 25.9, 29.0, 29.30, 29.33, 29.5, 29.58, 29.64, 29.7-29.8 (11 C), 31.9, 43.3, 58.4, 64.8, 156,8.

Synthesis of mono-alkyl-urethanesils *via* the acid-catalyzed hydrolytic route (m-Ut(CY)-ac).

An aqueous solution of HCl was added to the m-UtPTES(Y) precursor (molar ratio m-UtPTES(Y):H₂O:HCl = 1:600:0.2) (Table 2.3.1). The resulting mixture was stirred in a sealed flask at room temperature for 30 min and then cast onto a Teflon mold, which was covered with Parafilm (to ensure the slow evaporation of the solvent) and left in the fume cupboard for 24 hours.

Synthesis of mono-alkyl-urethanesils *via* the acid-catalized hydrolytic route in the presence of DMSO (m-Ut(C16)@a_x).

The present group of samples was derived solely from the 1-hexadecanol precursor with the variation of several conditions. Samples $@a_1$, $@a_2$ and $@a_3$ were prepared to observe the influence of DMSO (molar ratio CYOH: H₂O: DMSO = 1: 300: 300). The main difference between $@a_1$ and $@a_2$ is the absence of HCl (0,2 mol) in sample $@a_2$. Sample $@a_3$ was prepared in the absence of THF, meaning that DMSO was employed as solvent in the two stages of the synthetic procedure.



Scheme 2.3.1. Synthesis of the mono-alkyl-urethanesil.
	m-UtPT]	ES(y)		m-Ut	PTES(16)(<i>a</i> a _x
Materials	y = 14	y = 16	y = 22	a1	a ₂	a ₃
CYOH (g/mmol)	1.04/4.84	1.00/4.13	1.03/3.16	1.02/4.15	1.01/4.21	1.01/4.18
ICPTES (mL)	1.20	1.02	0.78	1.02	1.04	1.03
THF (mL)	10	10	10	10	10	0
DMSO (mL)	0	0	0	0	0	89.1
	m-Ut(C)	()-ac		m-	Ut(C16)@a	a _x
Materials	Y = 14	Y = 16	Y = 22	x = 1	x = 2	x = 3
H ₂ O (mL)	52.3	44.6	34.1	22.7	22.4	22.5
HCl (mL)	0.97	0.83	0.63	0.84	0	
DMSO (mL)	0	0	0	89.7	88.6	*
				*		

Table 2.3.1. Relevant details of the synthesis of the m-Ut(Y) and m-Ut(C16) a_x mono-alkyl urethanesils.

*no further volume was added

Characterization of the materials

TGA, XRD, AFM, SAXS, FT-IR and curve fitting deconvolutions were carried out using the equipment and procedures described in section 2.1.

²⁹Si NMR MAS/CP MAS and ¹³C MNR MAS / CP MAS: The samples were analyzed on a Bruker Avance 400 (9.4 T) spectrometer spinning at 5 kHz with ²⁹Si and ¹³C a frequencies of 100.62 MHz and 9 KHz, respectively.

Differential Scanning Calorimetry (DSC): A DSC131 Setaram Differential Scanning Calorimeter was used to determine the thermal characteristics of the powders. Masses of approximately 15 mg were placed in 30 μ L aluminium cans and stored in a dessicator over P₂O₅ for one week at room temperature under vacuum. After this pretreatment the cans were hermetically sealed and the thermograms were recorded. Each sample was heated at different scanning rates, according to its characteristics. The purge gas used was high purity N₂ supplied at a constant 35 cm³ min⁻¹ flow rate.

Attenuated Total Reflectance (ATR): The spectra recorded as function of temperature were obtained with a SPECAC temperature controller in a ATR configuration using a High Temperature Golden Gate[™] MkII ATR Accessory. The spectra were collected in 4000-500 cm⁻¹ range by averaging 64-200 scans and a resolution of 1 cm⁻¹. The range of temperatures studied was chosen for each sample according to the phase transitions observed in DSC experiments.

Polarized Optical Microscopy (POM): POM images were recorded using an OPTIKA B-600POL microscope equipped with a 8 Mpixel Digital Photo Camera. The images were analyzed using the OPTIKA Vision Pro software. The same apparatus and procedure was described in the section 1 of this chapter.

Scanning Electron Microscopy (SEM): SEM micrographs were obtained using a SEM/ESEM-FEI Quanta 400 scanning electron microscope at high acceleration voltage (20 kV). A small portion of the sample was fixed on an aluminium stub with carbon tape and then coated with Au/Pd.

High Resolution Scanning Electron Microscopy (HR-SEM): The **m-Ut(CY)-ac** samples were analyzed in a HITACHI S-5500 microscope operating at 30 kV. The samples were dispersed in ethanol and transferred to a grid. The **m-Ut(C16)@a**_x samples were analyzed with a FEI Quanta 400 FEG ESEM/ EDAXS PEGASUS x 4M. The samples were transferred to a carbon tape and coated with Au/Pd.

Photoluminescence (PL): The emission and excitation spectra and the absolute emission quantum yelds were obtained at room temperature in the same equipement and conditions as described earlier in section 2.2.

2.3.3. Results and discussion

Figures 2.3.1 (a) and (b) show the ²⁹Si CP/MAS NMR spectra of the samples under study. All the samples produce three peaks centered at -47 (T^1), -57 (T^2) and -67 (T^3) and no T^0 environments. The absence of Q-type Si atoms demonstrates the total preservation of the Si-C covalent bonds. The T^1 signal can be distinguished for the sample **@a**₂ (Figure 2.3.1 and Table 2.3.2). The spectrum of sample **@a**₃ is dominated by the T^3 environment (Figure 2.3.1 and Table 2.3.2).

The relative population of the various Si sites in the samples was estimated quantitatively through curve-fitting of the ²⁹Si CP/MAS spectra and was used to determine the condensation degrees (c) using the expression ($c = 1/3(\%T^1 + 2\%T^2 + 3\%T^3)$). The values obtained are given in Table 2.3.2.



Figure 2.3.1. ²⁹ Si CP/MAS NMR spectra of the m-Ut(CY)-ac (a) and m-Ut(C16)@a_x m (b) monoalkyl urethanesils.

The c values calculated for the m-Ut(CY)-ac samples and for m-Ut(C16)@a₃ are of the same order of magnitude than those reported earlier for di--urethanesil systems [2, 3]. In contrast, the values deduced for m-Ut(C16)@a₁ and m-Ut(C16)@a₂ practically coincide with that of the mono-amidosil m-A(14) [1]. The dominating T² site in both these samples suggests the formation of a 2D siloxane network. In the case of m-Ut(C16)@a₃ the prominent T³ signal indicates that the condensation process favored branched structures instead.

From the ¹³ C/CP MAS NMR spectra, it is clear that no cleavage of the urethane groups, Si-C, or O-alkyl bonds occurred during the synthesis. Indeed, the preservation of the urethane cross-links in the final materials is evidenced by the signal at 160 ppm (Figure 2.3.2 and Table 2.3.3). The peaks associated with the propylene chains are centred at about 44, 24 and 10 ppm (Table 2.3.3 and Figure 2.3.2). The signal observed at 64 ppm, attributed to the O-CH₂ methylene group, corresponds to that found around 65 ppm in the solution ¹³C NMR spectrum of the precursors. The peak at 14 ppm is attributed to the terminal CH₃ of the alkyl chain.

	Tab	le 2.3.2.	²⁹ Si MAS	NMR data ((8	ð in ppm) of	f the m-Ut()	/)-ac and r	n-Ut(C16)@a _x mono-a	lkyl urethanesils.	
	Sample	>	×	T ¹	T ²	Н3	J		Empirical formula	
	m-Ut(Cy)_a	c 14		3.2	56.0	41.0	78	CH ₃ (CH ₂) ₁₃ -O-C(=C	0)-NH-(CH ₂) ₃ -Si(OH	0.6001.2
		16		2.5	55.3	42.1	80	CH ₃ (CH ₂) ₁₅ -O-C(=	0)-NH-(CH ₂) ₃ -Si(ОН) _{0.60} O _{1.2}
		22		3.0	58.0	38.0	79	CH ₃ (CH ₂) ₂₁ -O-C(=	O)-NH-(CH ₂) ₃ -Si(OH	H) _{0.64} O _{1.18}
	m-Ut(C16)@a	×	1	5.5	70.6	23.9	73	CH ₃ (CH ₂) ₁₅ -O-C(=(D)-NH-(CH ₂) ₃ -Si(OH) _{0.81} O _{1.09}
			2	10.6	48.4	40.9	76	CH ₃ (CH ₂) ₁₅ -O-C(=(0)-NH-(CH ₂) ₃ -Si(OH)0.69 O 1.15
			S	3.2	39.9	56.8	84	CH ₃ (CH ₂) ₁₅ -O-C(=(O)-NH-(CH ₂) ₃ -Si(OH) _{0.46} O _{1.27}
					Sample					
	Ë	Ut(CY)-a	U					m-Ut(C16)@a _x		Attribution
Υ = 14		Υ = 16		Υ = 22		x = 1		x = 2	x = 3	
156		157		157		157		157	159	C=O groups
РЛ		Ч Ч		Ч		Ч		65	62	non-assigned
10		0		0		0 4		62		non-assigned
44		44		43		ı		ı	I	CH2NHC(=O)OCH2
33		33		33		33		33	34	(<u>C</u> H ₂)n all trans
30		ı		I		ı		30	30	(<u>C</u> H ₂)n gauche
27		27		28		28		27	27	CH ₂ NHCO <u>C</u> H ₂
24		24		24		24		24	24	SiCH ₂ CH ₂ CH ₂ CH ₂ NHCO
14		14		14		14		14	14	<u>C</u> H ₃ (CH ₂)n
10		11		11		10		10	10	Si <u>C</u> H ₂ CH ₂ CH ₂ NHCO

Hybrids organic-Inorganic materials obtained by sol-gel and self-assembly techniques



Figure 2.3.2. ¹³ C CP/MAS NMR spectra of the m-Ut(CY)-ac (a) and m-Ut(C16)@a_x m (b) monoalkyl urethanesils.

As previously discussed in sections 2.1 and 2.2, the 30.0-35.0 ppm region provides valuable information concerning the conformational disorder of the methylene groups. Densely packed all-*trans* chains produce a peak centred at 34.0 ppm, whereas the amorphous regions, characterized by *gauche* conformations, yield a more shielded peak (30.0 ppm).

For samples with **m-Ut(CY)-ac** the resonance peak is centred at 33.0 ppm indicating more ordered structures (Figure 2.3.3 (a)). This general trend is also observed for **m-Ut(CY)@a1** and **m-Ut(CY)@a2** (Figure 2.3.3 (b)). Samples with **m-Ut(C14)-ac** (Figure 2.3.3 (a)) and **m-Ut(CY)@a2** (Figure 2.3.3 (b)) also produce a shoulder at 30 ppm, indicative of the presence of more disordered conformations. The **m-Ut(CY)@a3** sample yields a considerably better resolved profile than all the other materials. The main resonances are located at 32.8 and 32.5 ppm a well-defined peak is seen at 34 ppm and a shoulder is also detected at 30 ppm (Figure 2.3.3 (b)).



Figure 2.3.3. ¹³ C CP/MAS NMR of the **m-Ut(CY)-ac** (a) and **m-Ut(CY)@a**_x (b) mono-alkyl urethanesil samples in the 24-30 ppm region.

Further evidence of the conformational degree of disorder of the pendant alkyl chains can be retrieved from FT-IR spectroscopic data in the vCH₂ and δ CH₂ regions (Figure 2.3.4). The importance of these two FT-IR regions was emphasized in section 2.2

The position of the vCH₂ modes indicates the presence of a high concentration of alkyl chains in all-*trans* conformations because of the close correspondence of the frequencies with those reported for highly crystalline *n*-alkanes (Figure 2.3.4 (A)). The signature of the vCH₂ bands at room temperature and at variable temperature will be discussed in detail below in this section in the framework of the discussion of the order/disorder phase transition undergone by these materials.

The CH₂ bending (δ CH₂) mode is sensitive to the interchain interaction and the packing arrangement of the chains [4]. Higher frequencies (~1472 cm⁻¹) indicate ordering of the methylene chains in all *trans* crystalline state

The absorption around 1470 cm⁻¹ in Figure 2.3.4 (B) is characteristic of a partially ordered phase where the chains are mobile while maintaining some orientational order. The six samples examined exhibit this band confirming the conclusion obtained from ¹³ C CP/MAS NMR data. In the case of the **m-Ut(CY)@a₃** sample the peak is split in two bands: one at 1468 cm⁻¹ and another one at 1464 cm⁻¹, corresponding to ordered alkyl chains in two sorts of environments. In sections 2.1 and 2.2 the "amide I" region was related to urea groups. In the present chapter the "amide I" region will be associated with urethane groups.

Figure 2.3.5 reproduces the global profile of the "amide I" and "amide II" regions. The band envelopes are similar for all the samples except **m-Ut(CY)@a₃**. In the FT-IR spectrum of the latter material a strong component is also visible at 1650 cm⁻¹.

The event located at 1750 cm⁻¹ is ascribed to the "free" urethane linkages (urethane linkage whose N-H and C=O groups remain non-bonded) [5]. The components at 1720 and 1705 cm⁻¹ correspond to the absorption of hydrogen bonded C=O groups in disordered urethane-urethane aggregates [5]. The bands mentioned emerge in both groups of materials (Figure 2.3.5). In the case of the m-**Ut(CY)-ac** samples the bands located at 1690, 1673 and 1657 cm⁻¹ correspond to the stronger urethane-urethane aggregates. For the m-**Ut(C16)@a**_x samples the stronger urethane-urethane aggregates give rise to bands at 1686 and 1663 cm⁻¹. The new component present in the "amide I" band of m-**Ut(C16)@a**₃ at 1633 cm⁻¹ may be ascribed to the formation of even stronger urethane-urethane aggregates.



Figure 2.3.4. FT-IR spectra in the vCH₂ stretching (A) and δ CH₂ bending (B) regions of monoalkyl urethanesils samples: **m-Ut (CY)-ac** (a) and **m-Ut(C16)@a**_x of samples (b).



Figure 2.3.5. FT-IR spectra in the "amide I" and "amide II" regions of mono-alkyl urethanesils samples and results of the curve-fitting: **m-Ut (CY)-ac** (A) and **m-Ut(C16)@a**_x of samples (B).

The XRD patterns of the mono-alkyl-urethanesil samples are reproduced in Figure 2.3.6., Figures 2.3.7 and 2.3.8 show in more detail the high and low *q* regions, respectively.



Figure 2.3.6. XRD patterns of the m-Ut(CY)-ac (a) and m-Ut(C16)@a_x (b) mono-alkylurethanesils.



Figure 2.3.7. XRD patterns of the **m-Ut(CY)-ac** and **m-Ut(C16)@a**_x mono-alkyl-urethanesils in the high *q* region.

In the high *q* region ($q > 10 \text{ nm}^{-1}$) the XRD patterns of **m-Ut(C14)-ac** and **m-Ut(C16)-ac** display a single, prominent broad band centered at 15.0 nm⁻¹ (d = 0.42 nm) and 15.2 nm⁻¹ (d = 0.41 nm), respectively (Figure 2.3.7). The XRD pattern of **m-Ut(C22)-ac** is, however, significantly better resolved: the peak observed at 14.0 nm⁻¹ (d = 0.45 nm), corresponds to urethane-urethane distances [6, 7], whereas that at 16.0 nm⁻¹ (d = 0.39 nm) and the shoulder at ca. 17.0 nm⁻¹ (d = 0.37 nm) are associated with in-plane chain-chain ordering distances [8]. The former peak is related with chains in *gauche* conformations and the latter to chains in all-*trans* conformations (highly packed and thus closer) [8]. The peak expected at about 15 nm⁻¹, attributed to order within the siliceous domains, is probably masked by the 14 and 16 nm⁻¹ peaks [8].

Comparison of the high *q* range XRD patterns of the **m-Ut(CY)-ac** and **m-Ut(C16)@a**_x mono-alkyl-urethanesils allows to immediately conclude that the latter patterns are considerably better resolved (Figure 2.3.7.). The band contour of samples **m-Ut(C16)@a**₁ and **m-Ut(C16)@a**₂ resembles closely (Figure 2.3.7): while the peak corresponding to the urethane-urethane linkage is located at 14.2 nm⁻¹ (0.44 nm), that due to the order within the siliceous domains is is found at 15.1 nm⁻¹ (d = 0.41 nm) and 15.3 nm⁻¹ (d = 0.41 nm), respectively. The ill-defined component detected at ca. 17.1 nm⁻¹ (d = 0.37 nm) is very likely associated with in-plane chain-chain ordering distances concerning highly packed all-*trans* conformers [8]. Sample **m-Ut(C16)@a**₃ differs markedly from the other materials. Its XRD pattern in the high *q* range is composed of a series of sharp and narrow peaks (Figure 2.3.7), which suggest that this material has higher order at shorter range. The attribution of these Bragg peaks, completely different from those reported in other ordered silsesquioxanes in under study.



Figure 2.3.8. XRD patterns of the **m-Ut(CY)-ac** (a) and **m-Ut(C16)@a**_x (b) mono-akyl urethanesils in the low q region. In the case of the **m-Ut(CY)-ac** samples the SAXS patterns are also included (red line, right yy' axis).

The XRD patterns represented in Figure 2.3.8 show a series of peaks which correspond to the kth order reflections of a lamellar structure. The 1st peak detected represents the fundamental order of a lamellar bilayer structure with an interlamellar spacing *I* (where $I = k2\pi/q_k$). The I_{exp} values deduced for the **m-Ut(C16)@a**_x samples (Table 2.3.4)

were based on the XRD patterns. In the case of the **m-Ut(CY)-ac** samples the l_{exp} values were estimated (Table 2.3.4) using the position of the 1st peak of the SAXS spectra (red curves in Figure 2.3.8). Assuming an average distance of 0.15 nm for the C-C, C-N, N-C=O, and C=O bonds [9] we estimated the theoretical interlamellar distance (l_{theor}) for all the samples (Table 2.3.4). Comparison of these experimental and calculated values allowed us to conclude that the three **m-Ut(CY)-ac** samples and **m-Ut(C16)@a1** and **m-Ut(C16)@a2** incorporate partially interpenetrated alkyl chains. Therefore, the interlamellar distance *l* represents the separation between the siliceous domains of a lamellar bilayer structure governed by the length of the interdigitated alkyl chains. The complex XRD pattern of **m-Ut(C16)@a3** requires an in-depth analysis. A preliminary examination of these data suggests the coexistence of two lamellar structures in this material (Figure 2.3.8). Based on the XRD data, a tentative representation of **m-Ut(C16)-ac** has been derived (Scheme 2.3.2).

Sample	<i>q</i> (nm⁻¹)	I _{exp} (nm)	I _{theor} (nm)
m-Ut(C14)- ac	1.24	5.0	5.7
m-Ut(C16)-ac	1.17	5.4	6.3
m-Ut(C22)-ac	1.50	4.2	8.4
m-Ut(C16)@a ₁	1.15	5.5	6.3
m-Ut(C16)@a ₂	1.19	5.3	6.3
m-Ut(C16)@a₃			

Table 2.3.4. XRD data of the m-Ut(CY)-ac (a) and m-Ut(C16)@a_x mono-akyl urethanesils.



Scheme 2.3.2. Tentative representation of the m-Ut(C16)-ac mono-akyl urethanesil.

Figure 2.3.9 displays the TGA curves of the **m-Ut(CY)-ac** samples. All the samples are thermally stable up to 250 °C. The samples are essentially anhydrous. The loss of water observed at **Y** = **14** it corresponds to 1.5%. Between 250 and 500 °C all the materials undergo an abrupt weight loss of ca. 75%. Beyond 500 °C a plateau is reached, which probably corresponds to a SiO₂ residue.



Figure 2.3.9. TGA curves of the **m-Ut(CY)-ac** mono-alkyl urethanesil. The derivative curve is shown in red.

Figure 2.3.10 (A) shows the DSC traces of the starting alcohols (1-tetradecanol, 1-hexadecanol and 1- docasonal). In Figure 2.3.10 (B) the DSC curves of the **m-Ut(CY)-ac** samples are represented. As referred in the literature [10] the starting materials present very important endothermic transitions (Figure 2.3.10 (a-c)). In the present work we recorded the DSC curves primarily to: (1) Confirm the occurrence of order/disorder transitions; (2) Check if, as we expected, the presence of the urethane linkage modified the order/disorder phase transition temperature with respect to that reported for the parent mono-amidosil material [1].

As expected the thermograms of 1-tetradecanol, 1-hexadecanol and 1-docosanol exhibit a single endothermic peak (Figure 2.3.10 (a-c)). The corresponding temperatures (onset and peak maxima) are listed in Table 2.3.5. The **m-Ut(CY)-ac** samples also give rise to an endothermic peak with onset temperatures, which are, as expected, different from those of the corresponding starting alcohols (Figure 2.3.10 and Table 2.3.5). In the case of **m-Ut(CY)-ac** the DSC trace exhibits two endotherms (Figure 2.3.10 and Table 2.3.5). The endothermic peaks are tentatively attributed to order-disorder phase transition[1].

Comparison of the phase transition onset temperature of the mono-alkyl urethanesils reported in Table 2.3.5 with the temperature transition observed for the parent mono-amidosil compound (which inspired this work) led us to conclude that all the mono-alkyl urethanesil compounds have lower values than m-A(14), as required [1].

	T _{onset} (°C)	T _{Peak maxima} (°C)
C14OH	36	41
C16OH	45	52
С22ОН	74	74
m-Ut(C14)-ac	62	67
m-Ut(C16)-ac	68	77
m-Ut(C22)-ac	74	81
		89

Table 2.3.5. DSC data of the starting alcohols and of the m-Ut(CY)-ac mono-alkyl urethanesils.



Figure 2.3.10. DSC curves of (A) the starting alcohols (1-tetradecanol (a), 1-hexadecanol (b) and 1- docosanol (c)) and (B) of the **m-Ut(CY)-ac** mono-alkyl urethanesils.

The temperature dependence of the FT-IR spectra of **m-Ut(C16)-ac** and the 1hexadecanol precursor was analyzed in order to check the influence of the temperature on the conformational disorder of the alkyl chains. As indicated in section 2.2, the conformation of the alkyl chains may be inferred from the position of the vCH₂ bands.

The FT-IR spectra in an ATR configuration were recorded during the heating and cooling cycles for **m-UtC(16)-ac**, from room temperature up to a temperature between the transition temperature and the decomposition temperature. Figure 2.3.11 (a) represents the ATR spectra as a function of temperature.

At room temperature the v_aCH_2 band is located at 2916 cm⁻¹, a wavenumber characteristic of the v_aCH_2 *n*-alkanes in all-*trans* conformations [4, 11]. During the heating cycle, in particular when the temperature reaches the onset of the order/disorder transition temperature of **m-Ut(C16)-ac** (68 °C), the band shifts to higher wavenumbers (2924 cm⁻¹) (Figure 2.3.11 (a)) [4, 11]. Upon increasing progressively the temperature, the proportion of alkyl chains in *gauche* conformations increases. During cooling the alkyl chains recover their original conformational state and the wavenumber of the v_aCH_2 band recovers its original value (2916 cm⁻¹). Figure 2.3.11 (b) shows that the behavior of the v_aCH_2 band of **m-Ut(C16)-ac** during the cooling cycle exhibits hysteresis, as already reported for m-A(14). However, in the present case, unlike in m-A(14), the phenomenon is also reversible, although apparently time-independent.

For comparative purposes, the same spectroscopic type of measurements were performed with the starting precursor, i.e., 1-hexadecanol (Figure 2.3.11 (c)). The shift from 2916 to 2921 cm⁻¹ occurs abruptly, in a single step when the transition temperature of this compound is reached. The same behavior was observed for 1-tetradecanol [10].



eo

2 24 2 23 2 22 2 21 2 20 2 2 2 1 0

(a)

9167

5223

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0

a_eunm_er (⊐m⁻¹)

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0

0

2 ⁰

20⁰, 24

0

0

Figure 2.3.11. Temperature dependence of the ATR spectra (a) and the v_aCH₂ band (b) of the m-Ut(C16)-ac mono-alkyl urethanesil. For comparative purposes the v_aCH₂ band shifts corresponding to 1-hexadecanol are presented in (c) (black symbols - heating cycle; open symbols - cooling cycle). The DSC curves for m-Ut(C16)-ac (a) and 1-hexadecanol (b) are also represented.

It was of the utmost interest to examine the two series of mono-alkyl urethanesil from the standpoint of morphology. The POM images reproduced in Figure 2.3.12 demonstrate that the selected samples exhibit birrefringence under crossed polarizers



Figure 2.3.12. POM images obtained under cross polarizers for representative mono-alkyl urethanesils: **m-Ut(C14)-ac** (a) and **m-Ut(C16)@a₁**(b).

The SEM images obtained for the **m-Ut(CY)-ac** materials show that this class of silsesquioxanes display complex and intrincate morphologies (Figure 2.3.13). **m-Ut(C14)-ac** exhibits an irregular texture composed of micrometric "cabbage-type leaves" (Figures 2.3.13 (a) and (b)). This samples' lamellar nature is clearly evident in the HR-SEM image of Figure 2.3.13 (c). Curiously, the texture of **m-Ut(C16)-ac** mimics the very tight arrangement of ""cabbage-type leaves" (Figure 2.3.13 (e)). The stacking of the lamellae is perfectly evident by HR-SEM (Figure 2.3.13 (g)) and AFM (Figure 2.3.13 (g)). The morphology of **m-Ut(C22)-ac** is also quite interesting, with plates organized in a such a way that globally a flower-like texture that mimics the "desert rose"-like arrangement results (Figures 2.3.13 (h) and (i)). HR-SEM and AFM confirm the lamellar nanostructure of this material (Figure 2.3.13 (j)).

The morphologies exhibited by the **m-Ut(C16)@a**_x materials (Figure 2.3.14) are completely different from those found in the **m-Ut(y)-ac** mono-alkyl urethanesils (Figure 2.3.13). All the **m-Ut(C16)@a**_x samples are composed of randomly organized microplates. Their thickness increases, however, significantly with **X** (Figure 2.3.14 (c), (f) and (i)). It is noteworthy that in **m-Ut(C16)@a**_x some of the plates (ca. 2-3 μ m thick and 20 μ m long) adopt a hexagonal shape. The edge-to-face growth gives rise to a unique "origami"-like morphology.









The emission and excitation spectra obtained for the m-Ut(CY)-ac samples are indicated in Figure 2.3.15.



Figure 2.3.15. Emission spectra excited between 275 and 420 nm for **m-Ut(C14)-ac** (a) **m-Ut(C16)-ac** (c) **m-Ut(C22)-ac** (e) and excitation spectra monitored between 420 and 520 nm for for **m-Ut(C14)-ac** (b) **m-Ut(C16)-ac** (d) **m-Ut(C22)-ac** (f).

The emission spectra recorded between 275 and 420 nm for m-Ut(C14)-ac (Figure 2.3.15 (a)), m-Ut(C16)-ac (Figure 2.3.15 (c)) and m-Ut(C22)-ac (Figure 2.3.15 (e)) are composed of a large Gaussian-shaped broad band between 320 and 600 nm, whose maximum intensity deviates towards the red as the excitation wavelengths increases. The origin of the bands is attributed to the overlap of two distinct emissions mediated by donor-acceptor pair recombinations that occur within the urethane linkages and within oxygen related defects [12, 13]. The typical excitation spectra monitored within the emission band present in Figure 2.3.15 (b, d, f) for the m-Ut(C14)-ac, m-Ut(C16)-ac and m-Ut(C22)-ac show a broad band peaking at 310 nm, 340, 350 nm respectively. The peak position deviates towards the red as the monitoring wavelengths between 330 and 400 nm. The values obtained are presented in Table 2.3.6. The maximum quantum yield values id 0.11±0.01 for all the samples under study and are poorly affected by changes in the alkyl chain length. In all the samples the maximum value is obtained at 360 nm.

Sample	330	350	360	380	400
m-Ut(C14)-ac	0.05	0.09	0.11	0.10	0.03
m-Ut(C16)-ac	0.05	0.10	0.11	0.10	0.05
m-Ut(C22)-ac	0.02	0.07	0.08	0.08	0.02

Table 2.3.6. Absolute emission quantum excited at different wavelengths (λ , nm).

2.3.4. Conclusion

In the present section the sol-gel process and self-assembly techniques were combined to create a new family of organic-inorganic hybrids compounds. These compounds were designated as mono-alkyl urethanesils (**m-Ut(CY)** Several experimental conditions were explored seeking materials with hierarchical structure.

²⁹ Si MAS and CP/MAS NMR spectroscopy were employed systematically to confirm the condensation of the samples and the presence/absence of unreacted precursor.

Two major groups of samples were prepared. The first group was prepared under acidic conditions and in the presence of a large excess of water. In the **m**-**Ut(CY)-ac** compounds the focus of the study was on the influence of the chain length. In the three cases studied (**Y** = **14**, **16** and **22**) the chains adopt preferentially *all-trans* conformations, revealing an ordered structure. This was confirmed by ¹³ C/CP NMR and FT-IR spectroscopies. For **Y** = **16** the conformational changes to which the chains are subject during heating and cooling cycles were evaluated by means of DSC and FT-IR. These analyses were fundamental, since all the **m-Ut(CY)-ac** samples undergo order/disorder phase transitions. During the cooling cycle of **m-Ut(C16)-ac** the FT-IR data exhibit hysteresis. Unlike in m-A(14), the order/disorder phase transition, although reversible, is not apparently time-dependent. The emission quantum yields are of the same order of magnitude of that reported for the parent mono-amidosil compound.

The chain length corresponding to Y = 16 was also chosen to investigate the influence of the solvent in the structuring of the samples. A second group of materials emerged: **m-Ut(CY)@a**_x. The moles of water employed (a large excess) in the preparation of the **m-Ut(C16)**-ac samples was replaced by a equimolar mixture of water/DMSO in the case of **m-Ut(CY)@a**₁ and **m-Ut(CY)@a**₂. In the latter sample, no HCl was added. In the preparation of all the samples referred up to now (i.e., **m-Ut(CY)-ac** and **m-Ut(CY)@a**_x with **x** = **1** and **2**) THF was used in the 1st stage of the synthesis. In the sixth sample prepared (**m-Ut(CY)@a**₃) no THF was used and the entire synthesis was carried out in DMSO. However, like in all the other cases, water was added to promote the hydrolysis and condensation reactions, as well as HCl, which was incorporated as catalyst.

The experimental changes introduced in the synthetic procedure in the monoalkyl urethanesils did not affect structurally the **m-Ut(CY)-ac** family of samples and **m-Ut(CY)@a**_x with x = 1 and 2. All of these materials exhibit a lamellar bilayer nanostructure. The **m-Ut(CY)@a**₃ differs markedly from all the other samples. It displays order at shorter range and it is clear that its structure deserves to be studied in the near future in more depth. In terms of morphology the two series of mono-alkyl urethanesils are very attractive. We draw the attention in particular to the complex unique textures observed in **m-Ut(C16)-ac** and **m-Ut(C22)-ac** ("cabbage-like" and "desert rose-like", respectively) and in **ac Ut(CY)@a**₃ ("origami-like").

2.3.5. References

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Chapter 3

Biohybrids organic-inorganic systems with potential application in electrochromic devices

K⁺-doped poly(ε-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

Li⁺- Eu³⁺- doped poly(ε-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

3. Biohybrids organic-inorganic systems with potential applications in electrochromic devices

The domain of electrochromic devices (ECDs) is an exciting and rapidly-growing field of research [1-5]. While some ECDs have already reached commercialization (including self-dimming rear- and side-view mirrors and sunroofs for automobile glazing, sunglasses and aircraft canopies with controllable optical transmission), current developments in the domain of ECDs are almost entirely governed by energy saving requirements and interest has shifted rapidly from non-architectural applications toward the production of large area devices for application in smart switchable and energy efficient architectural glazing, privacy glass, partitions and skylights.

A conventional solid state ECD comprises three main elements arranged in a layered, "sandwich"-type configuration composed of an electrochromic electrode and a counter-electrode separated by a solid electrolyte (*e.g.*, a Li⁺, K⁺ or H⁺ conducting polymer). A persistent and reversible color switch occurs by charging/discharging the electrochemical cell by application of an electrical potential. The colored and transparent states of ECDs are usually designated as "written" and "bleached" states, respectively. The most widely used electrochromic (EC) material is tungsten trioxide (WO₃) which undergoes a reversible color change as a result of simultaneous injection and extraction of electrons and ions (double injection) [6]. EC materials may operate either in a reflective mode (displays) or transmissive mode ("smart windows"). An attractive feature of ECDs is that once they are colored, the current may be turned off and the color preserved (*memory effect*), making them energy efficient devices.

Over the last few years the versatile sol-gel process [7] has become a popular synthetic route for ECD fabrication. Sol-gel processing has opened new opportunities for obtaining advanced, functional and high quality EC coatings with appropriate optical, chemical, electro-optical and mechanical properties [8-15]. The sol-gel method offers many advantages with respect to the traditional techniques used in the context of coating technology: (1) A high degree of homogeneity of the films is achieved, since

the starting precursors are mixed at the molecular level; (2) The precursors are relatively cheap and a large variety is commercially available; (3) The deposition equipment is inexpensive and large area coatings can be obtained by several techniques, such as spin-coating, dip-coating and spraying.

The first application of the "all sol-gel" ECD concept is thought to have taken place in 1988 with the pioneering work of Judeinstein *et al.* [16]. The device, with configuration WO_3 | titanium oxide (TiO₂) gel | tin oxide (SnO₂), failed due to irreversible SnO₂ coloration. The first successful "all sol-gel" ECD was reported in 1994 by Macêdo and Aegerter [17] who used a WO_3 | TiO₂ gel | cerium oxide (CeO₂)/TiO₂ configuration.

Several organic-inorganic hybrid electrolyte materials [18] have already been obtained *via* the sol-gel route. The use of *ormolytes* in ECDs is quite attractive because these materials are generally amorphous and highly transparent, they exhibit good mechanical properties and appropriate chemical/thermal stability. In addition, Class II [18] ormolytes can accommodate greater quantities of guest salt than polymer electrolytes (PEs) [19], thus avoiding the prejudicial effects of "salting out" on device performance.

A reduced number of proton conducting Class I hybrid systems have been proposed as electrolytes for ECDs. Examples include the hybrid gels made from tetrabutoxytitane(IV), acetic acid and glycerol [16] and the amorphous tallium oxide multi-layers dip-coated from tetraethoxytallane(IV), using acetic acid or H₂O as a stabilizer [20]. The proton conducting Class II *aminosil* ormolytes [21, 22, 23] were also considered to be good candidates for "smart windows". These materials comprise a basic hybrid structure formed from aminopropylalkoxysilanes and a strong monoacid. The highest conductivity reached was *ca.* $3x10^{-5}$ Scm⁻¹ at room temperature. An electrochemical stability domain of 1.3 V was reported for the aminosils doped with trifluoromethanesulfonic acid. A significant number of Li⁺ conducting Class II ormolyte systems have been investigated in the same context [24, 25, 26-28].

In view of their potential use as electrolytes in ECDs, in the present chapter we will report the preparation and characterization of two novel series of environmentally-friendly KCF₃SO₃- [29] and LiCF₃SO₃/Eu(CF₃SO3)₃ (50:50 molar)-doped [30] biohybrids composed of a di-urethane cross-linked siloxane-based host network incorporating short segments of the poly(ε -caprolactone) biopolymer, abbreviated as

PCL(530) (530 represents the average molecular weight in g mol⁻¹). This study is a continuation of preliminary explorations based on the PCL(530)/siloxane network doped with lithium triflate (LiCF₃SO₃) [31] and magnesium triflate (Mg(CF₃SO₃)₂) [32].

PCL, a linear poly(ester), has been chosen because, although synthetic, it is an extremely attractive biopolymer. It is an aliphatic thermoplastic, biocompatible, permeable, hydrophobic, biodegradable and non-toxic for living organisms, which is resorbed by the organism a certain interval after implantation. PCL and its copolymers have potential applications in the field of medicine, as biodegradable suture, artificial skin, resorbable prostheses and as containers for sustained drug delivery [33-35]. PCL/silica hybrids may find use as degradable bioglasses, as coating materials for bone implants and prosthetic devices, as supports for enzyme immobilization [36] and even as bone substitutes [37].

In recent years there has been a growing interest for biopolymers, as they represent viable alternatives for the development of the so-called electroactive polymers (EAPs) [44]. Most bio-based EAPs are ion conducting materials. Examples of these systems include structures based on hydroxyethylcellulose [45], modified starch [46], chitosan [41-46] or natural rubber [47] with guest ionic salts. Small all solid-state ECDs with good electrochromic properties have been successfully produced with EAPs composed of cellulose [48], starch [49-50] and gelatin [51].

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K⁺-doped poly(ε-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

This section is based on the following publication:

" K^+ -doped poly(ε -caprolactone)/siloxane biohybrid electrolytes for electrochromic devices"

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Solid State Ionics, accepted





3.1. K⁺-doped poly(ε-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

3.1.1. Brief Introduction

The high ionic conductivity exhibited by classical poly(oxyethyelene) (POE)-based PEs incorporating K⁺ ions [1-4] motivated early studies on ormolytes composed of diurea cross-linked poly(oxypropylene)/siloxane [5] and POE/siloxane [6, 7] (*di-ureasil*) matrices and potassium salts. The di-ureasils composed of long POE chains and doped with KCF₃SO₃ were proposed as electrolytes for the fabrication of "smart windows" [7]. The present section is focused on the thermal and electrochemical properties of novel PCL(530)-based biohybrid ormolytes incorporating a wide range of KCF₃SO₃ content. Optimized ormolyte compositions have been tested in prototype ECDs.

3.1.2. Experimental part

Materials

 α, ω -hydroxyl poly(ε -caprolactone) (PCL(530), Fluka, average molecular weight 530 g/mol), (3-isocyanato)propyltriethoxysilane (ICPTES, Fluka) and KCF₃SO₃ (Aldrich) were used as received. Ethanol (CH₃CH₂OH, Merck) and tetrahydrofuran (THF, Merck) were stored over molecular sieves. High purity distilled water was used in all experiments.

Synthesis of the materials

To prepare the KCF_3SO_3 -doped d-PCL(530)/siloxane-based biohybrids we applied the synthetic method described elsewhere [8], which is a modification of that reported for the LiCF_3SO_3-doped analog [9].

The synthesis of the host d-PCL(530)/siloxane hybrid involved two steps. In the first stage a urethane cross-link was formed between the hydroxyl (-OH) end groups of the PCL(530) chains and the isocyanate (-N=C=O) groups of ICPTES in THF at 70-80 °C to yield the non-hydrolyzed PCL(530)-based hybrid precursor (Scheme 3.1.1):


Scheme 3.1.1. Representation of the non-hydrolyzed PCL(530)-based hybrid precursor.

In the second stage of the synthetic procedure appropriate amounts of CH_3CH_2OH and water were added to this solution to promote the characteristic sol-gel reactions (i.e., hydrolysis and condensation). The guest KCF₃SO₃ salt was incorporated in the latter stage. The materials were obtained as transparent and flexible monoliths. The ormolytes were identified using the notation d-PCL(530)/siloxane_nKCF₃SO₃. Xerogels with n = ∞ , 200, 100, 40, 29, 21, 10, 4, 2, 1 and 0.5 were produced. Details of the synthetic procedure are provided in Table 3.1.1.

n = [C(C=O)(CH ₂)O]/K ⁺	m PCL(530)	m (KCF ₃ SO ₃)	Si/K⁺	Si/K⁺
(molmol ⁻¹)	(g)	(g)	(mol mol ⁻¹)	(g g ⁻¹)
200	1.07	0.08	92.39	68.09
100	1.04	0.01	55.49	41.09
40	1.09	0.03	21.93	16.31
29	1.19	0.05	15.37	11.43
21	1.10	0.07	11.14	8.28
10	1.13	0.15	5.39	4.01
4	1.08	0.35	2.20	1.63
2	1.07	0.64	1.18	0.87
1	1.04	1.31	0.56	0.42
0.5	1.07	2.66	0.21	0.20

Table 3.1.1. Details of the synthetic procedure of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids, where the salt content is represented by n (composition).

XRD measurements were performed at room temperature with a PANalytical X'Pert Pro equipped with a X'Celerator detector using monochromated CuK_{α} radiation ($\lambda = 1.541$ Å) over the 2 θ range between 10 and 70°. The samples, analyzed as films, were not submitted to any thermal pre-treatment.

To evaluate the morphology of the as-prepared xerogel samples, **SEM** micrographs were obtained using a SEM/ESEM-FEI Quanta 400 scanning electron microscope at high acceleration voltage (25 kV).

The **thermogravimetric** studies were done in the same equipment and with the same methods described in section 2.1. The films were pulverized and dried over phosphorus pentoxide (P_2O_5) for several days. The thermal characteristics of the xerogels were also determined using a Setaram DSC 131 Differential Scanning Calorimeter (same equipment as described in section 2.3). A disk section with a mass of approximately 20-30 mg was removed from the biohybrid film, placed in a 40 µL aluminium can and stored in a dessicator over P_2O_5 for one week at room temperature under vacuum. After this drying treatment the can was hermetically sealed and the thermogram was recorded. Each sample was heated from 25 to 250 °C at 10 °C min⁻¹. High purity nitrogen at a constant flow rate of 40 cm³ min⁻¹ (TGA) and 35 cm³ min⁻¹ (DSC) was used as purging gas in both experiments.

Prior to characterization of **conductivity behavior**, the ormolytes were vacuumdried at 80 °C for about 48 h and stored in a high-integrity, argon-filled glove box. For bulk conductivity measurements, an ormolyte disk was placed between two 10 mm diameter ion-blocking gold electrodes (Goodfellow, > 99.9%). The electrode/ormolyte/electrode assembly was secured in a suitable constant-volume support, which was installed in a Buchi TO 51 tube oven. A calibrated type K thermocouple, placed close to the ormolyte disk, was used to measure the sample temperature with a precision of about ± 0.2 °C and samples were characterized over a temperature range of between 25 and 100 °C. Bulk conductivities of the samples were obtained during heating cycles using the complex plane impedance technique (Schlumberger Solartron 1250 frequency response analyser and 1286 electrochemical interface) over a frequency range of 65 kHz to 0.5 Hz. The electrolyte behavior was found to be almost ideal and bulk conductivities were extracted in the conventional manner from impedance data by using an equivalent circuit composed of R_b in parallel with C_g, where R_b is the electrical resistance of the electrolyte and C_g is its geometric capacity. The circuit element corresponding to the blocking electrode interface was simulated by a series C_{dl} element, where C_{dl} is the double layer capacity. The experimental spectra showed a high frequency semicircle with a low frequency vertical spike. Reproducibility of measurements was better than 5%.

The **Fourier-Transform Infrared (FT-IR)** spectra were acquired at room temperature using the same equipment and with the same methods described in section 2.1.

The **FT-Raman** spectra were recorded in the same equipment and with the same methods described in section 2.1. The non-linear curve-fitting procedure provided by the PeakFit software (Jandel Corporation, 2591 Rerner Boulevard, San Rafael, CA 94901, U.S.A.) was applied to deconvolute complex band envelopes. The residuals procedure was used to automatically place hidden peaks. This procedure initially places peaks by finding local maxima in a smoothed data stream. Hidden peaks are then optionally added where peaks in the residuals occur. The best fit of the experimental data was obtained by varying the parameters of the bands (i.e., wavenumber, width and intensity) and by using Gaussian functions. A linear baseline correction with a tolerance of 3 % was employed. The standard error of the curvefitting procedure was less than 0.00006. The software parameters revealed that, in most cases, the three coefficients of the bands were significantly different from zero (α = 0.05). This was clear from the 95% confidence intervals (CI) for these parameters. The fact that the value "zero" was not included in these CIs is an indication that most bands were adequately represented by the three parameters. Frequently, the intensity was the least significant characteristic.

Solid-state ECDs were constructed using a four layer sandwich configuration which did not include an ion storage layer (Scheme 3.1.2). The external layers of the ECDs were transparent conducting oxide films made of indium-doped zinc oxide (IZO) [10]. The active layers of the ECDs were an EC film of tungsten oxide (WO₃) and a d-PCL(530)/siloxane_nKCF₃SO₃ ormolyte film with n = 29, 21 and 4. IZO films with a thickness of about 170 nm were deposited on two glass substrates by r. f. (13.56 MHz) magnetron sputtering using a ceramic oxide target In_2O_3 :ZnO (92:8 wt%; 5 cm-diameter, Super Conductor Materials, Suffern, NY, U.S.A., purity of 99.99%). Sputtering was carried out at room temperature, with an argon flow of 20 cm³ min⁻¹ and an oxygen flow of 0.4 cm³ min⁻¹. During sputtering the deposition pressure (argon and oxygen) was held constant at 0.15 Pa. The distance between the substrate and the

target was 10 cm and the r. f. power was maintained at 100 W. WO₃ (Super Conductor Materials, purity of 99.99%) films with thickness of about 300 nm were deposited on the IZO-coated glass substrates by r. f. magnetron sputtering (Pfeiffer Classic 500). Two drops of the ormolyte sol was then spread onto the surface of the WO₃/IZO-coated glass plates, a IZO-coated glass plate was placed on top of the resulting ormolyte gel and the two plates were pressed together in such a way that the two coatings faced each other inside the assembled system (Scheme 3.1.2). In this manner a surface with an area of approximately 2.7 cm² was formed. Free space was left on each side of the device for the electrical contacts. The entire assembly procedure described was carried out under atmospheric conditions. As a result of the application of a negative voltage of -4 V for period of 30 each glass/IZO/WO₃/dа S to PCL(530)/siloxanenKCF₃SO₃/IZO/glass ECD the color of the WO₃ layer changed from light yellow to uniform dark blue (Scheme 3.1.2). During coloration charge in the form of electrons and K^{\dagger} ions was transferred from the IZO and ormolyte films, respectively, to WO₃ which suffered simultaneously reduction and K⁺ insertion. Bleaching from deep blue back to light yellow (Scheme 3.1.2), corresponding to simultaneous WO₃ oxidation and K⁺ desinsertion (Equation 3.1.1), occurred upon reversing the applied voltage.

$$WO_3 + xK^+ + xe^- \leftrightarrow K_xWO_3$$
 (3.1.1)
leached (light yellow) colored (blue)

The **optical transmittance** of the ECDs was measured with a Shimadzu UV/VIS 3100PC double beam spectrophotometer and with UV-VIS Spectronic Genexys 2PCC spectrophotometer.

b



Scheme 3.1.2. Schematic representation of the glass/IZO/WO₃/d-PCL(530)_nKCF₃SO₃/IZO/glass ECDs (polarity for the coloration mode).

3.1.3. Results and discussion

The XRD patterns of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids are reproduced in Figure 3.1.1. The diffractograms of the samples with $n = \infty$, 100 and 40 reveal that these xerogels are entirely amorphous. The broad peak, Gaussian in shape, centered at *ca.* 21.3-21.6°, observed in these patterns is ascribed to ordering within the siliceous network [11]. The dilute sample with n = 200 gives rise to a peak at 21.4°, which is characteristic of PCL(530). The same feature appears as an ill-defined peak in the XRD patterns of the materials with n = 21 and 10. For n = 29 and 21 a Bragg reflection of unknown nature emerges at 28.5°. The concentrated sample with n = 4 produces a series of weak peaks which do not correspond to those of the pure salt or PCL(530). We associate them with the formation of a crystalline d-PCL(530)/siloxane-KCF₃SO₃ complex of unknown stoichiometry. In the salt-rich samples with n = 2, 1 and 0.5 this crystalline compound coexists with pure salt.



Figure 3.1.1. XRD patterns of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids.

The SEM images obtained, shown in Figure 3.1.2, are in perfect agreement with the XRD data. The occurrence of crystalline PCL(530) regions is confirmed in Figures 3.1.2(a)-3.1.2(c). Small crystalline aggregates, presumably due to the formation of the crystalline d-PCL(530)/siloxane-KCF₃SO₃ complex, are observed at n = 4 (Figure 3.1.2(d)). The high crystalline content of the two most concentrated xerogels is immediately evident in Figures 3.1.2 (e) and 3.1.2 (f).



Figure 3.1.2. SEM images of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids: (a) n = 200 (scale bar 20 μ m); (b) n= 21 (scale bar 20 μ m); (c) n= 10 (scale bar 20 μ m); (d) n = 4 (scale bar 20 μ m); (e) n= 1 (scale bar 100 μ m); (f) n = 0.5 (scale bar 20 μ m).

The DSC curves of the d-PCL(530)/siloxane_nKCF₃SO₃ xerogels with $n \le 10$ are represented in Figure 3.1.3 In the case of electrolyte samples with composition n = 10 and 2 a very weak, broad and ill-defined endothermic peak at 45 (onset at 42 °C) is readily detected. This thermal event is due to the fusion of the short polymer segments of PCL(530) (melting temperature 36-48 °C), thus corroborating the XRD data. The salt-rich biohybrid with n = 1 produces a weak, broad and ill-defined endotherm at 146 °C (onset at 132 °C), of unknown origin, and a more intense peak at 225 °C (onset at about 200 °C). The latter peak becomes more intense at n = 0.5. On the basis of the conclusions retrieved from the XRD results, we propose that this endothermic event corresponds to the fusion of the d-PCL(530)/siloxane-KCF₃SO₃ complex with a minor contribution from the melting peak of the pure salt which is located at 237 °C (onset at 228 °C) (Figure 3.1.3).



Figure 3.1.3. DSC curves of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids.

he TGA data of Figure 3.1.4 allow us to deduce that the decomposition of the xerogels with $\infty > n \ge 1$ is initiated at about the same temperature (approximately 235 °C), an indication that the thermal stability of the PCL(530)/siloxane framework in a non-oxidizing atmosphere remains practically unaffected by the presence of increasing amounts of KCF₃SO₃. The thermal degradation of the most concentrated material (n = 0.5) begins, however, at a considerably lower temperature (*ca.* 200 °C). The thermal behavior of the hybrid samples contrasts deeply with that of KCF₃SO₃ which only starts to degrade at temperatures above 450 °C. It is worth noting that even at the maximum temperature applied (700 °C), none of the samples was completely decomposed.



Figure 3.1.4. TGA curves of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids.

The Arrhenius conductivity plot and the composition dependence of the conductivity isotherms of the d-PCL(530)/siloxane_nKCF₃SO₃ samples are shown in Figures 3.1.5 (a) and 3.1.5 (b), respectively. These data reveal that in this hybrid electrolyte system the samples with compositions between n = 21 and 4 support the highest conductivities over the whole range of temperatures analyzed. At 40 °C the conductivity maximum coincides, whereas at higher temperature the material with n = 21 leads to slightly higher values.



Figure 3.1.5. Arrhenius conductivity plot (a) and isotherms (b) of the ionic conductivity versus composition of the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrids. The lines drawn are just guides for the eye.

133 Biohybrids organic-inorganic systems with potential applications in electrochromic devices The conductivity of the non-doped hybrid structure may be tentatively associated with proton hopping between neighbouring urethane groups [9]. Table 3.1.2 demonstrates that the levels of ionic conductivity exhibited by the K⁺-doped d-PCL(530)/siloxane-based hybrids are lower than those displayed by analogous biohybrids incorporating LiCF₃SO₃ [9] and a 50:50 molar mixture of LiCF₃SO₃ and Eu(CF₃SO₃)₃ [12], but higher than those measured in the case of the Mg(CF₃SO₃)₂ - containing materials [13].

Μ	Ionic	Reference		
-	T = 35 °C	T = 50 °C	T = 104 °C	-
Li ⁺ (n = 0.5)	4x10 ⁻⁶	1x10 ⁻⁶	6.7x10 ⁻⁵	[9]
Mg ²⁺ (n = 34)	8x10 ⁻⁹	3x10 ⁻⁸	9x10 ⁻⁷	[13]
Li ⁺ /Eu ³⁺ (n = 6.1)	3x10 ⁻⁶	1x10 ⁻⁵	1.6x10 ⁻⁴	[12]
K ⁺ (n = 4)	1x10 ⁻⁷	2x10 ⁻⁷	2.5x10 ⁻⁶	this work

Table 3.1.2. Conductivity maxima of d-PCL(530)/siloxane_nM(CF₃SO₃)_m biohybrids.

In an attempt to clarify the ionic conductivity/ionic association relationship, we decided to inspect the chemical environment experienced by the K⁺ and SO₃CF₃⁻ ions in the d-PCL(530)/siloxane medium over the entire salt concentration range considered. We emphasize that in this class of hybrid system the guest alkaline ions may bond, not only to the triflate ions, but also to the three types of donor oxygen atoms provided by the d-PCL(530)/siloxane network, *i.e.*, the carbonyl oxygen atoms of the urethane cross-links, the ester carbonyl oxygen atoms of the PCL(530) central oxyethylene segment.

The coordination of the cation to the urethane and ester carbonyl groups of the host matrix is manifested in the "amide I" region which corresponds to the amide I [14] region of polyamides [15]. The amide I mode is essentially a carbonyl stretching vibration [15]. As a result of its sensitivity to hydrogen bonding, the amide I band is in general composed of several distinct components which correspond to different carbonyl environments (aggregates). As the absorption coefficients of the carbonyl groups from these aggregates may differ, only changes of the same component as a function of salt concentration may be compared [16].

Curve-fitting, performed in the 1800-1650 cm⁻¹ interval of the FT-IR spectra of the d-PCL(530)/siloxane_nKCF₃SO₃ xerogels, allowed us to resolve the band profile of the d-PCL(530)/siloxane hybrid into four distinct components located at about 1762, 1736, 1720 and 1692 cm⁻¹ (Figure 3.1.6 (a)) [8, 17]. The 1762 cm⁻¹ band is associated with the presence of "free" (non-hydrogen bonded) carbonyl groups of the urethane cross-links (A1, Scheme 3.1.3) [18]. The 1736 cm⁻¹ component is characteristic of amorphous PCL(530) chains (A2, Scheme 3.1.3) [19, 20]. The band at 1720 cm⁻¹ is attributed to the presence of hydrogen-bonded oxyethylene/urethane associations (B, Scheme 3.1.3) [21], whereas that at 1692 cm⁻¹ is assigned to the formation of urethane/urethane(C, Scheme 3.1.3) [21] and ester/urethane [8,17] aggregates. The four types of carbonyl groups have been represented by the notations A1 (1762 cm⁻¹, Scheme 3.1.3), A2 (1736 cm⁻¹, Scheme 3.1.3), B (1720 cm⁻¹, Scheme 3.1.3), C1/C2 (1692 cm⁻¹, Scheme 3.1.3), respectively [18].



Scheme 3.1.3. Tentative representation of the chemical surrounding of the urethane-, estherand ether-type oxygen atoms in the host d-PCL(530)/siloxane hybrid.

The general "amide I" band profile of the non-doped and doped d-PCL(530)/siloxane hybrid materials with $n \le 29$ (Figures 3.1.6 (a) and 3.1.6 (b)) is essentially the same (the intensity maximum is located in all cases around 1736 cm⁻¹). The further addition of salt alters the band shape and the intensity maximum is shifted to 1731 cm⁻¹ for n = 10 and 4 and to 1725 cm⁻¹ for n = 21, 1 and 0.5 (Figures 3.1.6 (a) and 3.1.6 (b)), suggesting that the hydrogen bonds are generally stronger in the latter three samples. We call attention to the fact that carbonyl groups A1 (1762 cm⁻¹) exist in all the materials. Curiously, the plot of Figure 3.1.6 (c) demonstrates that the proportion of "free" carbonyl groups A1 (1762 cm⁻¹) and A2 (1736 cm⁻¹) practically coincides in the non-doped network and in the most concentrated sample. The trends observed in this graph also suggest that the disruption/formation of aggregates B (1720 cm⁻¹), which results from the addition of increasing amounts of salt, is correlated with the formation/disruption of aggregates C1/C2 (1692 cm⁻¹). Although the introduction of the alkali metal salt affects the "amide I" region over the entire range of compositions, the most significant modifications that the "amide I" components undergo take place in d-PCL(530)/siloxane₂₉KCF₃SO₃. This hybrid contains the lowest proportion of carbonyl groups A1 (1762 cm⁻¹) and the highest fraction of carbonyl groups A2 (1736 cm⁻¹) of all the series, an indication that the strong hydrogen-bonded aggregates formed at this composition are probably aggregates **C1 (1692 cm⁻¹)**. In the high salt concentration range (n = 1 and 0.5), the formation of aggregates **B** (1720 cm⁻¹) is clearly favored. At this composition, the fraction of aggregates C1 and C2 (1692 cm⁻¹) is fairly low.

The study of the anionic environment was carried out by means of FT-Raman spectroscopy. We examined the spectral region characteristic of the symmetric stretching vibration mode of the SO_3 group (v_sSO_3), since this diagnostic mode is very sensitive to coordination effects. The v_sSO_3 mode of the "free" triflate ion gives rise to a band at 1032 cm⁻¹ [22]. The coordination of the triflate ion to the K^+ ion is shown as a shift to higher wavenumbers [4]. The FT-Raman v_sSO_3 region was decomposed into several peaks (Figure 3.1.7 (a)). The most prominent band for the most dilute samples $(n \ge 10)$ is that at 1032 cm⁻¹. This feature, present over the whole salt concentration range, confirms the occurrence of "free" anions and presumably "cross-link separated ion pairs" [18, 21]. The contribution of the latter species may explain the remarkable increase of the band integral area fraction at $40 > n \ge 10$ (Figure 3.1.7 (b)). The 1038 and 1024 cm⁻¹ features, also produced by all the samples, are associated with weakly coordinated triflate ions located in two different sites [21]: (1) CF₃SO₃ species weakly bonded to K⁺ ions, which simultaneously interact with the carbonyl oxygen atom of the urethane group; (2) CF₃SO₃⁻ ions hydrogen bonded to the urethane N-H groups. The event at 1045 cm⁻¹, found in all the FT-Raman spectra, is ascribed to the existence of contact ion-pairs [7].





The components observed in the spectra of the hybrid with n = 40 at 1069, 1059 and 1052 cm⁻¹ are tentatively attributed to the formation of higher ionic aggregates [7,23]. Interestingly, at n = 10 none of these coordinated species are formed. In the v_sSO₃ region of the two most concentrated samples, the 1052 cm⁻¹ band is the most intense feature. Based on the XRD and DSC results, we suggest that in both cases free crystalline KCF₃SO₃ contributes to this feature [7]. The examination of the plot of Figure 3.1.7 (b) does not allow us to establish a direct correlation between the high room temperature ionic conductivity exhibited by the d-PCL(530)/siloxane₂₁KCF₃SO₃ sample and the proportion of "free" anions and/or weakly-coordinated species. Samples with composition n = 29 and 10 contain similar amounts of such species and exhibit considerably lower conductivity. The ionic conductivity is the result of a combination of two contributions: the concentration of charge carriers and their mobility. Clearly, the ionic association in the materials described in this study is considerable.



Figure 3.1.7. Room temperature FT-Raman spectra of d-PCL(530)_nKCF₃SO₃ biohybrids in the v_sSO₃ region (a); curve-fitting results (Note: The FT-Raman spectrum of the non-doped samples was subtracted from those of the doped samples) (b); variation of the integral area fraction of the v_sSO₃ individual components with composition (c).



The glass/IZO/WO₃/d-PCL(530)/siloxane_nKCF₃SO₃/IZO/glass ECDs with n = 29, 21 and 4 were characterized in terms of the electrochromic contrast (percent transmittance change (Δ T) in % at a particular wavelength or wavelength range), the optical density change (Δ (OD) = -log(T_{colored}/T_{bleached})), the switching time (the time required to complete the coloring/bleaching process) and the open circuit memory (the ability to maintain the absorption state while the current is off).

The transmission spectra recorded in the 325-700 nm range for the glass/IZO/WO₃/d-PCL(530)/siloxane_nKCF₃SO₃/IZO/glass ECDs with n = 29, 21 and 4 in the as-deposited, bleached and colored states are depicted in Figures 3.1.8 (a), 3.1.8 (b) and 3.1.8 (c), respectively. The 1931 CIE photopic luminosity function, with a maximum at a wavelength of 555 nm (green), is also reproduced in Figure 3.1.8 (see dotted curve).

All the spectra represented in Figure 3.1.9 display a series of maxima and minima due to interference associated with the ECDs multilayer configuration (Scheme 3.1.2).

The average Δ T in the visible (VIS) region (400-700 nm) and the optical density change Δ (OD) exhibited by the three ECDs are listed in Table 3.1.3. We note that the average Δ T of the as-deposited and bleached states are practically the same in all the devices, the value being greater than 74 % for the bleached devices (Figure 3.1.8 and Table 3.1.3). After coloration the three samples present a Δ (OD) above 0.11.

n	Т (%)			∆T(%)	$\Delta OD_{\lambda = 555 \text{ nm}}$
	as-deposited	bleached	colored	-	
29	76.4	74.6	57.0	17.6	0.13
21	76.7	75.6	55.0	20.6	0.16
4	77.7	76.5	60.1	16.4	0.11

Table 3.1.3. Average spectral transmittance (Δ T) and optical density (Δ OD) exhibited by ECDs incorporating the d-PCL(530)_nKCF₃SO₃ biohybrids.

The switching speed of the ECDs studied in the present work is fast (t \approx 30 s, see Experimental section). The electrochromic memory of the glass/IZO/WO₃/d-PCL(530)/siloxane_nKCF₃SO₃/IZO/glass ECDs with n = 4 and 29 was evaluated. Figures 3.1.9(a) and 3.1.9(b) show that after 10 days neither device reached the as-deposited non-colored state.



Figure 3.1.8. Optical transmittance as a function of wavelength for the electrochromic devices as deposited (black line), colored (blue line) and bleached (red line) states, for the d-PCL(530)/siloxane_nKCF₃SO₃ biohybrid system: n= 29 (a), n= 21(b) and n= 4 (c). On the left side are presented image of the devices in the as deposited state (top) and colored state (down).



Figure 3.1.9. Time dependence of the transmission spectra in the VIS region of the $glass/IZO/WO_3/d$ -PCL(530)_nKCF₃SO₃/IZO/glass ECDs with n= 4 (a) and n= 29 (b) and average transmittance in the VIS region (c). The curves drawn in (c) are guides for the eye. The transmittance of the colored state was measured after 2 cycles (as-deposited (black line) and colored (red line)).

3.1.4. Conclusions

A series of di-urethane cross-linked PCL(530)/siloxane biohybrids doped with KCF₃SO₃ have been characterized by XRD, SEM, DSC, TGA, ionic conductivity, FT-IR and FT-Raman spectroscopy. Preliminary studies of the performance of prototype ECDs incorporating these xerogel materials as electrolytes demonstrated that further research is necessary in order to improve our understanding of critical parameters and permit optimization of device performance.

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Li⁺- and Eu³⁺-doped poly(ϵ -caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

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"Li⁺- and Eu³⁺-Doped Poly(ɛ-caprolactone)/Siloxane Biohybrid Electrolytes for Electrochromic Devices"

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3.2. Li⁺- and Eu³⁺-doped poly(ε-caprolactone)/siloxane biohybrid electrolytes for electrochromic devices

3.2.1. Brief introduction

The *mixed cation* approach, which basically involves the use of two guest salts instead of a single one, is an attractive procedure that usually results in a significant enhancement of the ionic conductivity of PEs [1-6]. It is manifested in the following cases: (1) With salts containing cations of the same or different valence; (2) With salts composed of the same or different anionic species; (3) With variable relative amounts of the two salts. Although the origin of the increase of conductivity observed in PEs doped with a pair of ionic salts remains uncertain, changes in charge carrier type and concentration or in the microscopic viscosity have been pointed out as possible explanations. In some cases, however, the *mixed cation* effect does not emerge, a situation found for instance by Chowdary *et al.* [7] in systems composed of mixtures of poly(ethylene glycol) dimethylether and POE containing various ratios of zinc and lithium bromides.

With the primary goal of developing a new family of environmentally friendly multifunctional biohybrid materials displaying simultaneously high ionic conductivity and high luminescence we have produced in this section, by means of the sol-gel route [8], *ormolytes* comprising biopolymer chains and have doped them with a mixture of LiCF₃SO₃ and Eu(CF₃SO₃)₃ (molar ratio LiCF₃SO₃:Eu(CF₃SO₃)₃ \approx 50:50), in the light of the *mixed cation effect*. The integration of different hybrid components in a single device is of the utmost interest. This "lab-on-a-chip technology" is expected to have a tremendous impact on information and communication technologies, global health and biomedicine, structural engineering and environment monitoring systems in the near future. Requirements such as, speed, sensitivity, specificity, ease of use, shelf-life, cost, scalability and recyclability are critical [9].

We note that, although a significant number of Li⁺-doped POE-based ormolytes have been investigated in the last decades [10-19], the references dealing with POE/siloxane ormolytes incorporating europium salts are considerably less abundant [20-22]. We must also emphasize that the work of Morita *et al.* [23] focused on POEgrafted poly(methylmethacrylate) matrices doped with LiCF₃SO₃ and lanthanum triflate or ytterbium triflate, is the only known study of a PE system including a mixture of an alkaline salt and a lanthanide salt. Finally, we would also like to stress that to the best of our knowledge this is the first time that the *mixed cation* approach is combined with the hybrid concept.

We have decided to employ the d-PCL(530)/siloxane structure for two reasons: (1) The electrolyte behavior of the di-urethane cross-linked d-PCL(530)/siloxane network doped with lithium triflate LiCF₃SO₃ [24], Mg(CF₃SO₃)₂ [25] and KCF₃SO₃ [26] (section 3.1.) is quite encouraging. (2) The incorporation of Eu(tta)₃(H₂O)₂ (tta⁻ is 2thenoyltrifluoracetonate) into the d-PCL(530)/siloxane matrix, not only results in a significant increase of the D₀ quantum efficiency value of the aquocomplex (from 29.0 to 44.2 %), but also yields a hybrid that displays high photostability (under UVA exposure, the emission intensity decreased less than 10 % in 11 h) [27].

The materials studied here have been identified using the notation d-PCL(530)/siloxane_nLi_mEu_{m'}, where n (called composition) corresponds to the number of $(C(=O)(CH_2)_5O)$ repeat units of PCL(530) per mixture of Li⁺+Eu³⁺ ions and m and m' represent the individual compositions of LiCF₃SO₃ and Eu(CF₃SO₃)₃, respectively.

3.2.2. Experimental part

Materials

 α, ω -hydroxyl poly(ε -caprolactone) (PCL(530), Fluka, MW = 530 gmol⁻¹), (3isocyanato)propyltriethoxysilane (ICPTES, Fluka, 95%), anhydrous LiCF₃SO₃ (Aldrich, 99.995%) and Eu(CF₃SO₃)₃.xH₂O (Aldrich, 98%) were used as received. Ethanol (EtOH, Merck, PA grade) and tetrahydrofuran (Merck, puriss. PA grade) were stored over molecular sieves. High purity distilled water was used in all experiments.

The synthetic method described in section 3.1 was adopted to prepare the $LiCF_3SO_3$ - and $Eu(CF_3SO_3)_3xH_2O$ -doped d-PCL(530)/siloxane-based biohybrids. The molar ratio ICPTES: EtOH:H₂O used here was 1:4:1.5. Xerogels with different concentrations were produced as transparent and flexible monoliths (Figure 3.2.1). Relevant details of the synthetic procedure are presented at Table 3.2.1.

Cation	Li ⁺	Eu ³⁺	Li⁺	Eu ³⁺	Li⁺	Eu ³⁺	Li⁺	Eu ³⁺
	n		n		n		n	
	52.6		27.0		6.1		3.2	
	m	m'	m	m'	m	m'	m	m'
	99	111	50	56	12	12	6	7
1/n 1/m	0.01	0.009	0.02	0.017	0.083	0.083	0.167	0.142
1/n+1/m	0.019	52.6	0.037	27.0	0.163	6.1	0.309	3.2
m _{PCL(530)} (g)	1.24		1.04		1.09		1.06	
V_{CPTES} (μL)	1155		972		1024		988	
V _{H2O} (μL)	126		106		111		108	
ν _{etoH} (μL)	1006		929.78		979		945	
m _{triflate salt} (g)	0.015	0.060	0.025	0.101	0.115	0.497	0.221	0.887

Table 3.2.1. Details of the synthesis of the d-PCL(530)/siloxane_nLi_mEu_{m'} hybrids.



Figure 3.2.1. Representative image of d-PCL(530)/siloxane_nLi_mEu_{m'} hybrid ormolyte.

The samples were characterized by means of DSC, TGA, SEM, XRD, complex impedance spectroscopy and FT-IR using the the same equipments and procedures described in detail in section 3.1.

The room temperature **photoluminescence** spectrum of the complex was obtained using a ISS PC1 spectrofluorometer. The excitation device was equipped with a 300 W xenon lamp and a photographic grating. Emission spectra were collected with a 25 cm monochromator (resolution of 0.1 nm) connected to a photomultiplier. The excitation and emission slit width were fixed at 1.0 mm, with all used monochromators having 1200 grooves/mm. The experimental set up used for these lifetime measurements comprises a Nd:YAG (third harmonic) coherent laser of with λ = 355 nm used as excitation the source (frequency of 5 Hz and pulse width of 7 ns), a Tektronix TDS a 1012 oscilloscope and a fast detector ET 2000. The photoluminescence features of the hybrid material were recorded at room temperature with a modular double grating excitation spectrofluorimeter with a TRIAX 320 emission monochromator (Fluorolog-3, Horiba Scientific) coupled to a R928 Hamamatsu photomultiplier, using the front face acquisition mode. The excitation source was a 450 W Xe arc lamp. The emission spectra were corrected for detection and optical spectral response of the spectrofluorimeter and the excitation spectra were weighted for the spectral distribution of the lamp intensity using a photodiode reference detector. The lifetime measurements were acquired with the setup described for the luminescence spectra using a pulsed Xe-Hg lamp (6 μ s pulse at half width and 20-30 μ s tail).

The construction of the prototype **ECDs** was performed according to the procedure adopted in section 3.1.

The **optical transmittance** of the ECDs was measured in the 800-350 nm range using the the same equipment referred in section 3.1.

Chronoamperometric (CA) tests were performed using a potentiostat/galvanostat (Autolab model 100) by monitoring device current response as a function of time while the applied voltage was stepped between -4 V and +4 V with a delay time at each voltage of 50 s. The ECD was cycled 30 times between the colored and bleached states, respectively. In the set-up used for measurements the electrolyte/WO₃/IZO substrate played the role of working electrode (W in Scheme 3.2.1) and the IZO substrate acted as counter and reference electrodes (C and R in Scheme 3.2.1). The cathodic and anodic charge densities were determined through integration of the CA curves during the coloring and bleaching processes, respectively.



Scheme 3.2.1. Close view of the set-up used to carry out the CA tests.

3.2.3. Results and discussion

The well known hygroscopic nature of the two guest triflate salts employed prompted us to examine the thermal behavior of the as-received compounds.

The TGA curve of LiCF₃SO₃ shown in Figure 3.2.2 (a) reveals that the decomposition of this salt is a two-step process. Below 80 °C, an initial mass loss of *ca*. 4 % is evident, followed by a stability plateau that ends with an abrupt mass drop stage with onset at about 425 °C. The latter event represents the main degradation stage. At 800 °C a residue that represents 15% of mass loss remains. The DSC curve of LiCF₃SO₃

(Figure 3.2.2 (a)) displays an endothermic peak centered at 59 °C (T_{onset} at *ca*. 57 °C) that correlates well with the initial mass loss observed in the TGA curve. According to Lu *et al.* [28] this thermal event is due to the removal of free hydrogen fluoride (HF), a product that remains after the salt production process. The associated enthalpy ($\Delta H = 33 \text{ Jg}^{-1}$) is much lower than the value reported by the same authors (164 J g⁻¹) [28]. On the basis of the TGA data, we have been able to estimate the number of HF moles initially present in the as-received LiCF₃SO₃ and thus deduce that the exact formula of the salt is LiCF₃SO₃.0.4HF. Below 300 °C, another endothermic event, less intense than the former, slightly broader and centered at 135 °C (T_{onset} at *ca*. 126 °C) is detected in the DSC curve (Figure 3.2.2 (a)). As it does not imply a mass variation (see TGA curve), it might be due to a solid state phase transition [28]. The fusion of LiCF₃SO₃ (423 °C) occurs shortly before its decomposition (425 °C) [28]. The melting temperature is thus higher than the maximum temperature value considered in our DSC analysis (300 °C) and consequently our data do not enable us to detect this thermal event. The final residue may be associated with 1 mole of lithium fluoride (LiF) [28].

Close analysis of the TGA curve of Eu(CF₃SO₃)₃.xH₂O (Figure 3.2.2 (b)) reveals that the thermal decomposition of this compound occurs in several stages. Below 160 °C three mass losses of *ca*. 16% (T < 90 °C), 5% (90 < T < 137 °C) and 3% (137 < T < 160 °C) are visible. They correspond to the loss of seven, two and one water molecules, respectively. At about 400 °C the TGA suffers an abrupt drop, which corresponds to a major, although not complete, thermal degradation of the salt. These results may be interpreted as a clear indication that three of the ten water molecules present in the decahydrated compound are strongly bonded to the Eu³⁺ ion and thus presumably belong to its 1st coordination sphere. Their complete removal requires temperatures of at least 160 °C. In contrast the remaining seven water molecules are considerably more labile and may be removed readily below 90 °C through simple drying procedures. The correct formula of the compound purchased is therefore $[Eu(CF_3SO_3)_3(H_2O)_3]$.7H₂O. The prominent and sharp endothermic peak centered at 129 °C (Tonset difficult to determine) and that less intense and broader centered at 188 °C (T_{onset} = 141 °C) discerned in the DSC curve of this salt (Figure 3.2.2 (b)) are typical of dehydration of a compound comprising water molecules bound with different strength. The former DSC peak detected presumably corresponds to two processes:

the first takes place in the low temperature range and implies the removal of the seven labile water molecules of the compound; the second process, occurring at higher temperature, represents the cleavage of the bonds that ensure strong coordination of two water molecules in the 1st coordination shell of the lanthanide ion. The 188 °C peak is clearly associated with the most strongly Eu³⁺-bonded water molecule of the salt.

The TGA data reproduced in Figures 3.2.2 (c) and 3.2.2 (d) demonstrate that the thermal d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ ddegradation of the and PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ hybrid samples is initiated at ca. 238 and 220 °C, respectively. The TGA curves also reveal that decomposition takes place in two and three steps, respectively. Beyond about 500 °C a plateau is attained in both cases, that persists up to the maximum temperature analyzed (800 °C). At the latter temperature the samples are not fully decomposed and a considerable amount of residue still remains (40-45% of the sample mass). In the case of the salt-rich sample d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂ (Figure 3.2.2 (e)), after an initial mass loss of about 8%, the TGA curve is subject to two major drops at 220 °C and at about 400 °C (Figure 3.2.2 (e)). At 800 °C the degradation of this material may be considered practically accomplished. At last, in the case of the most concentrated sample d-PCL(530)/siloxane_{3.2}Li₆Eu₇ (Figure 3.2.2 (f)), thermal decomposition starts immediately from room temperature and is a multi-step process below 500 °C. Between this temperature and 800 °C no mass losses occur. At the maximum temperature examined ca. 20% of the sample mass persists. It is worth noting that in the four hybrid samples examined the value of the decomposition onset temperature is lower than that reported for the non-doped d-PCL(530)/siloxane (300 °C) [24], an indication that the mixture of the two guest salts exerts a non-stabilizing effect on the host d-PCL(530)/siloxane framework. This effect is critical in the case of the most concentrated hybrid d-PCL(530)/siloxane_{3.2}Li₆Eu₇ (Figure 3.2.2 (f)).

The hybrid samples with $n \ge 6.1$ are semi-crystalline. In the case of the dilute d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ and d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ samples, a weak endothermic peak centered near 47 °C is seen in the DSC thermograms (Figures 3.2.2 (c) and 3.2.2 (d), respectively). As the melting temperature of the crystalline organic precursor PCL(530) ranges from 36 to 48 °C, the thermal event found in both DSC

curves is definitely associated with the fusion of a minor proportion of free, crystalline PCL(530) chains in the PCL(530)/siloxane matrix. Based on the value reported in the literature for the bulk enthalpy of melting of 100% crystalline PCL (ΔH_m^{0} = 166.7 Jg⁻¹ [29]) and on the experimental data retrieved from the DSC thermograms of PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ and PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ samples ($\Delta H_m = 1.49$ and 5.69 Jg^{-1} , respectively), we concluded that the proportion of cristallinity in both samples is indeed negligible (0.9 and 3.4%, respectively). The formation of free crystalline PCL(530) regions in both hybrids is in perfect agreement with the presence of the pair of intense and sharp Bragg peaks characteristic of PCL(530) (not shown) at 23.8 and 21.6° in their XRD patterns (Figure 3.2.3). In both diffractograms this pair of peaks coexists with a broad band centered near 21°, Gaussian in shape, also produced by the non-doped d-PCL(530)/siloxane structure and due to the coherent diffraction of the siliceous domains [30]. In contrast with previous results that supported the amorphous character of the non-doped matrix [24], in the present case the XRD pattern of d-PCL(530)/siloxane evidences the existence of crystalline PCL(530) chains (Figure 3.2.3). It is noteworthy that the formation of crystalline domains of PCL(530) was also reported in the case of d-PCL(530)/siloxane-based materials doped with the $Eu(tta)_3(H_2O)_2$ and $Eu(tta)_3$ phen (phen is 1,10-phenantroline) complexes [27]. The nature of the second peak centred at 200 °C in the DSC thermogram of d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ hybrid is unknown. In the case of the d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂ material, as the Bragg peaks discerned in its XRD pattern (Figure 3.2.3) do not coincide with those produced by LiCF₃SO₃ (not shown), $[Eu(CF_3SO_3)_3(H_2O)_3]$.7H₂O (not shown) or PCL(530) (not shown), we are led to conclude that a new crystalline phase is formed. The DSC curve depicted in Figure 3.2.2 (f) confirms that the thermal decomposition of the most concentrated sample studied is a highly complex process that is initiated immediately after the beginning of the measurement, all the endothermic peaks observed being entirely attributed to degradation reactions.



Figure 3.2.2. Thermal behaviour of LiCF₃SO₃ (a), [Eu(CF₃SO₃)₃(H₂O)₃].7H₂O (b), d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ (c), d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ (d), d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂ (e) and d-PCL(530)/siloxane_{3.2}Li₆Eu₇ (f). The black and red lines represent the TGA (left axis) and DSC (right axis) curves, respectively.



Figure 3.2.3. XRD patterns of the d-PCL(530)/siloxane_nLi_mEu_m, hybrids.

In the SEM images recorded for d-PCL(530)/siloxane_{52.6}Li₅₀Eu₅₆ (Figures 3.2.4 (c) and 3.2.4 (d)) and d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ (Figures 3.2.4 (e) and 3.2.4 (f)) the presence of crystalline PCL(530) chains (Figures 3.2.4 (a) and 3.2.4 (b)) is visible. As expected, the texture of these samples contrasts deeply with that reported earlier for amorphous d-PCL(530)/siloxane based materials [31]. The formation of a new crystalline phase in the d-PCL(530)/siloxane_nLi_mEu_{m'} system at high salt content is clearly recognized in the SEM images of Figures 3.2.4 (g) and 3.2.4 (h)). Figures 3.2.4 (i) and (j) show the high crystalline nature of the most concentrated sample, which confirms XRD data (Figure 3.2.3).



Figure 3.2.4. SEM images of the d-PCL(530)/siloxane_nLi_mEu_{m'} hybrids with n = ∞ (scale bars = 100 \mathbb{P} m (a) and 20 μ m (b)), n = 52.6 (scale bars = 200 μ m (c) and 20 μ m (d)), n = 27 (scale bars = 200 μ m (e) and 20 μ m (f)), n = 6.1 (scale bars = 200 μ m (g) and 10 μ m (h)) and n = 3.2 (scale bars = 100 μ m (i) and 20 μ m (j)).

High ionic conductivity (higher than 10^{-5} Scm⁻¹) is definitely one of the most important requirements that need to be fulfilled in a PE system if practical applications in electrochemical devices are envisaged. The main conclusion derived from our earlier work conducted on the d-PCL(530)/siloxane biohybrid system doped with LiCF₃SO₃ was that the conductivities exhibited by these materials are modest [24] with respect to those observed in classical LiCF₃SO₃-containing PEs extensively reported in the literature.

The Arrhenius conductivity plot of the d-PCL(530)/siloxane_nLi_mEu_m biohybrids is reproduced in Figure 3.2.5 (a). This graph also shows the temperature dependence of the ionic conductivities of some of the PCL(530)/siloxane_nLiCF₃SO₃ samples studied previously. [24] Examination of Figure 3.2.5 (a) allows us to state that the addition of a mixture of LiCF₃SO₃ and [Eu(CF₃SO₃)₃(H₂O)₃].7H₂O to the host d-PCL(530)/siloxane matrix instead of simply LiCF₃SO₃ was successful, as a remarkable enhancement of the ionic conductivity resulted [24], a clear manifestation of the cation mixed effect. For instance, while at 25 °C the conductivity of the d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ hybrid is *ca.* 2x10⁻⁸ S cm⁻¹, at about 100 °C it attains 2.3x10⁻⁶ Scm⁻¹ (Figure 3.2.5 (a)). These values are approximately one order of magnitude higher than those measured previously for the d-PCL(530)/siloxane matrix doped solely with LiCF₃SO₃ and n = 93 (5.44x10⁻⁹ and 5.93x10⁻⁷ Scm⁻¹ at 27 and \approx 100 °C, respectively) [24] (Figure 3.2.5 (a)). In the high temperature range (at ca. 100 °C), the conductivity of the d-PCL(530)/siloxane_{3.2}Li₆Eu₇ sample practically coincides with that of the most conducting composition of the d-PCL(530)siloxane_nLiCF₃SO₃ series (n = 0.5) (2.94x10⁻⁵ and 3.2x10⁻⁵ Scm⁻¹, respectively [24]). The conductivity maximum of the d- $PCL(530)/siloxane_nLi_mEu_{m'}$ system is located at n = 6.1 over the whole range of temperatures studied $(3.7 \times 10^{-7} \text{ and } 1.71 \times 10^{-4} \text{ Scm}^{-1} \text{ at } 20 \text{ and } 102 \text{ °C, respectively})$ (Figure 3.2.5 (c)).

The microelectrode cyclic voltammogram of the d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ hybrid over the -2.0-8.0 V potential range obtained at 30 °C is depicted in Figure 3.2.6. This voltammogram demonstrates that in the anodic region the sample is stable up to about 5.0 V *versus* Li/Li⁺, whereas the cathodic region lithium deposition is not detected (see Experimental Section). This means that the overall redox stability of d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ spans more than 7 V, an indication that this material displays an acceptable stability window for an application in a solid state electrochemical device. These results are in perfect agreement with those found for d-PCL(530)siloxane_{0.5}LiCF₃SO₃ [24].





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Figure 3.2.6. Cyclic voltamogram of the d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ hybrid obtained at about 30 °C with a 25 μ m gold microelectrode as working electrode and lithium as counter and reference electrodes (sweep rate = 100 mVs⁻¹).

To elucidate the role played by the carbonyl (C=O) oxygen atoms of the urethane cross-links in the coordination of the Eu³⁺ and Li⁺ ions, we have inspected the signature of the d-PCL(530)/siloxane_nLi_mEu_m hybrids in the "amide I" region of the FT-IR spectra. After incorporation into the hybrid host framework, several types of interactions may be enviasaged for the Li^+ and Eu^{3+} ions [27]: (1) bonding to the "free" urethane C=O groups of the cross-links; (2) bonding to "free" esther C=O groups of the PCL(530) chains; (3) bonding to C=O groups belonging to hydrogen-bonded aggregates (oxyethylene/urethane aggregates, urethane/urethane aggregates and esther/urethane aggregates) [27]. Obviously, coordinating situation (3) implies the hydrogen-bonded array formed throughout pristine drupture of the PCL(530)/siloxane.

The "amide I" region of the di-urethane cross-linked d-PCL(530)/siloxane_nLi $_{m}Eu_{m'}$ hybrids corresponds to the amide I region (1800-1600 cm⁻¹) of polyamides [32].

The "amide I" region of the FT-IR spectrum of the non-doped d-PCL(530)/siloxane matrix contains four distinct components located at about 1762, 1736, 1720 and 1692 cm⁻¹ [31]. The high frequency bands at 1762 and 1736 cm⁻¹ are associated with "free" C=O groups of the urethane cross-links (A1, Scheme 3. 1.3, section 3.1) [31] and "free" C=O groups of the esther groups of amorphous PCL(530) chains (A2, Scheme 3.1.3, section 3.1) [33]. The component at 1720 cm⁻¹ is attributed to oxyethylene/urethane aggregates (B, Scheme 3.1.3, section 3.1), whereas the 1692 cm⁻¹ feature is assigned to C=O groups belonging to considerably more ordered hydrogen-bonded urethane/urethane aggregates (C1, Scheme 3.1.3, section 3.1) and ester/urethane aggregates (C2 Scheme 3.1.2, section 3.1) [31].

Figure 3.2.7 (a) proves that the inclusion of LiCF₃SO₃ and $[Eu(CF_3SO_3)_3(H_2O)_3]$.7H₂O into d-PCL(530)/siloxane produces a series of marked modifications in the environment of the C=O groups which are manifested in the "amide I" region in terms of band redistribution. Globally the incorporation of increasing amounts of the guest salts leads to a strengthening of the hydrogen bonds, to the saturation of the urethane free C=O groups A1 and to the formation of new, very strong and cation-coordinated hydrogen-bonded aggregates **D**. Further conclusions may be drawn from the analysis of the plot of Figure 3.2.7 (b): (a) The fraction of "free" urethane C=O groups A1 is subject to a regular reduction. No such groups remain at n = 3.2; (b) The fraction of "free" esther C=O groups A2 increases slightly in d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ and then is significantly reduced, reaching a minimum value in the d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂ material. In the most concentrated sample the proportion of these C=O groups increases, recovering the value observed at n = 27.0; (c) The most dramatic effect resulting from salts addition is undoubtedly the marked increase in the proportion of oxyethylene/urethane aggregates B which become dominant in the sample d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂. At n = 3.2 a considerable fraction of these aggregates B are, however, disrupted; (d) The variation of the fraction urethane/urethane aggregates C1 with the incorporation of increasing amount of salts resembles closely that of the "free" esther C=O groups A2. This means that in samples with n = 27.0 and 6.1 a partial breakdown of these aggregates occurs, but that in contrast they are formed again at higher salt content; (e) The proportion of esther/urethane aggregates C2 does not suffer major changes over the whole salt concentration range examined, although we note a regular increase in samples with $n \leq 52.6$; (f) New hydrogen-bonded aggregates D, stronger than all the others already existent, are formed in d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂. Their fraction increases in the most concentrated sample studied.



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Figure 3.2.7. Curve-fitting results of the "amide I" region of d-PCL(530)/siloxane_nLi mEum' biohybrids (a) and composition dependence of the integral fraction area of the different resolved components (b, left axis, black curves) and of the ionic conductivity (b, right axis, red curve). The variations detected in the integral fraction of the various C=O environments present in the d-PCL(530)/siloxane_nLi_mEu_m, hybrids upon introduction of increasing amounts of the two guest salts clearly point out that at n = 6.1 – the conductivity maximum of this electrolyte system – major modifications take place. This sample is very rich in oxyethylene/urethane aggregates B, formed at the expense of the breakdown of urethane/urethane aggregates C1 and of "free" urethane C=O groups A1. In parallel, a drastic reduction of the "free" esther C=O groups A2 is necessary for the formation of more esther/urethane aggregates C2 and especially of the new very strong aggregates D.

To investigate the chemical surroundings of the triflate ions at increasing content of the mixed salts we analyzed the FT-IR spectra of the d-PCL(530)/siloxane_nLi _mEu_m' hybrids in the region of the symmetric stretching vibration mode of the SO₃ (v_sSO_3) group. This non-degenerated mode of the triflate ion is very sensitive to coordination effects. We note that in the light of this spectroscopic analysis the two populations of triflate ions present (i.e., that originating from LiCF₃SO₃ and that originating from Eu(CF₃SO₃)₃) are indistinguishable.

Figure 3.2.8 (a) reproduces the v_sSO_3 region of three representative d-PCL(530)/siloxane_nLi mEu_m hybrids. The v_sSO_3 band was resolved into four components Figure 3.2.8 (b): a prominent band at 1032 cm⁻¹, two shoulders positioned around 1038 and 1025 cm⁻¹ and a weak peak centered at about 1045 cm⁻¹. The detection of the 1031 cm⁻¹ band indicates the presence of free anions in the three samples [34]. The contribution of the so-called "cross-link separated ion pairs" to this feature is very likely [35]. The shoulders at 1038 and 1025 cm⁻¹ are ascribed to weakly coordinated triflate ions located in two different anionic environments [35]. Based on the literature, the event at 1045 cm⁻¹ may be associated with the formation of monodentate $Li^{+}CF_{3}SO_{3}^{-}$ ions pairs or negatively charged triplets $[Li(CF_{3}SO_{3})_{2}]^{-}$ [36-38]. Although in the case of mono-urethanesil POE/siloxane compounds doped with $Eu(CF_3SO_3)_3$, we assigned the 1045 cm⁻¹ band to the formation of a POE/Eu(CF_3SO_3)_3 crystalline compound of unknown stoichiometry [35], in the present series of hybrids the contribution of the Eu^{3+} ions to the 1045 cm⁻¹ feature is uncertain. Figure 3.2.8 (c) shows that d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ contains a high concentration of "free" ions (1031 cm⁻¹) and weakly coordinated triflate ions (1037 cm⁻¹). Upon introduction of more salt (n =6.1) the fraction of "free" ions decreases at the expense of a further

increase of the percentage of weakly coordinated anions (1037 and 1025 cm⁻¹). In addition, the proportion of associated ions is also subject to an increase (1045 cm⁻¹). In contrast with the expected situation, these trends are accompanied by a significant increase of the room temperature ionic conductivity. In the salt-rich d-PCL(530)/siloxane_{3.2}Li₆Eu₇ material, in spite of the fact that the fraction of "free" ions displays a slight increase and that the fraction of associated species decreases significantly, the ionic conductivity suffers a dramatic decrease.

Figure 3.2.9 (a) shows the d-PCL(530)/siloxane₂₇Li₅₀Eu₅₆ emission under different excitation wavelengths. The emission spectra are composed of a large band, whose energy depends on the excitation wavelength, superimposed on a series of sharp peaks attributed to the $Eu^{^{3+}~^5}D_0\!\!\rightarrow^7\!\!F_{0.4}$ transitions. A similar broad emission was already observed in the non-doped d-PCL(530)/siloxane hybrid, being ascribed to electron-hole recombination occurring within oxygen-related defects present in the siliceous domains and within the cross-linkages groups [27]. The emission energy dependence on the excitation wavelength was modeled as radiative recombinations involving thermal relaxation within localized states, in the framework of the extended multiple trapping approach [39-40]. The presence of the host-related band indicates a non-efficient energy transfer PCL(530)/siloxane-to- Eu³⁺ ions, which in fact can be used to produce multi-wavelength light-emitters. In particular, taking advantage of the relative intensity variation of the d-PCL(530)/siloxane broad band emission and of the Eu³⁺ lines, the fine tuning of the emission color coordinates within the Commission Internationale d'Éclairage (CIE) chromaticity diagram becomes easy (Figure 3.2.9 (b)). The emission color of the d-PCL(530)/siloxane₂₇Li₅₀Eu₅₆ sample can be easily tuned from the pink region (0.43,0.29) excited at 260 nm to the yellow-green area (0.37,0.54) under 464 nm, crossing the white region (0.29,0.28) at 393 nm excitation wavelength, as illustrated in the CIE chromaticity diagram.

Focusing our analysis on the intra-f⁶ lines, we observe that the energy, full width at half maximum (fwhm) and number of Stark components of the ${}^{5}D_{0}\rightarrow{}^{7}F_{1-4}$ transitions are almost independent of the selected excitation wavelength, suggesting that the Eu³⁺ occupy a single average local environment. Moreover, the presence of the ${}^{5}D_{0}\rightarrow{}^{7}F_{0}$ line and the Stark splitting of the ${}^{7}F_{1,2}$ levels in 3 and 4 components, respectively, points out a low local-symmetry for the Eu³⁺-coordination site with the absence of an inversion centre, in agreement with the high relative intensity of the ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ transition.







The emission features were further quantified by the measurement of the ${}^{5}D_{0}$ decay curves (monitored within the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ transition). The curves are well reproduced by a single exponential function, in good agreement with the presence of a single average Eu³⁺-local environment. The single exponential fit yielded ${}^{5}D_{0}$ lifetime values of 0.225 ±0.001 ms and 0.262 ±0.002 ms, for d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ and d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁, respectively.



Figure 3.2.9. (a) Room temperature emission spectra of d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ excited at (1) 260, (2) 300, (3) 360, (4) 393, (5) 430 and (6) 464 nm. (b) CIE chromaticity diagram (1931) showing the (x,y) color coordinates of the room temperature emission excited between 260 and 464 nm.

A preliminary assessment of the potential interest of the d-PCL(530)/siloxanebased ormolytes introduced here as electrolytes in an all solid-state ECDs was performed using the four layer-sandwich configuration represented in Scheme 3.2.3.



Scheme 3.2.2. Configuration of the glass/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECDs investigated (polarity for the coloration mode).

We draw the attention to the fact that it did not include, as usual, an ion storage layer [41]. The outermost layers included (transparent conducting oxide (TCO) films made of indium-doped zinc oxide (IZO) [42]) provided the electronic contacts through which a voltage difference was applied to the active layers of the device. The active layers were an electrochromic (EC) film of tungsten oxide (WO₃) and an ion conducting (IC) film of d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂, the most conducting ormolyte sample of the series studied in the present work (Figure 3.2.5 (c)).

The electrochromic contrast of an ECD may be expressed in terms of the percent transmittance change (Δ %T) at a specified wavelength (or over a specified wavelength range) for which the EC material exhibits the highest optical contrast. Optical switching of the glass/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD from light yellow to uniform dark deep blue occurred by charging/discharging the electrochemical cell through the application of a potential of -4 V and +4 V during 50 s, respectively (see

pictures at the bottom of Figure 3.2.10). We note that potential values lower than this did not lead to any color change. The transmission spectra obtained in the wavelength range between 340 and 800 nm for the as-deposited, colored and bleached states are reproduced in Figure 3.2.10.



Figure 3.2.10. Transmission spectra of the as-deposited (black line), bleached (red line) and colored (blue line, 1^{st} cycle) glass/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD. The pictures shown below the graphic reproduce the bleached and colored states of this ECD.

All the spectra display a series of maxima and minima in this spectral region assigned to interference, resulting from the presence of a multilayer structure (Scheme 3.2.2). The average transmittance of the d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂-based ECD in the VIS region (400-700 nm) is practically identical for the as-deposited and bleached states (64.6 and 60.2%, respectively), being 44.9 % for the colored state. The change in optical density (Δ (OD)) (where Δ (OD) = -log (T_{colored}/T_{bleached})) in the VIS region is thus 0.13. This value coincides with that calculated at 555 nm (T_{bleached} = 41 % and T_{colored} = 58 %). We recall that the human eye is sensitive to light waves for which the wavelength is between about 400 and 700 nm (visible region). Under abundant

illumination (daylight) the maximum eye sensitivity lies in the green region at 555 nm (*photopic vision*) (dotted curve in Figure 3.2.10).

The switching speed (or device response time) of an ECD corresponds to the time required for the coloring/bleaching process. Among other factors, the switching speed depends on the ionic conductivity and thickness/morphology of the electrolyte and on the magnitude of the applied potential [43]. The response times of the prototype ECD reported here (t \approx 50 s) are fast.

The coloration efficiency (CE) of the glass/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD was determined on the basis of CA measurements (Figure 3.2.11). The CE is a spectrally dependent parameter which measures the amount of charge necessary to produce the optical change. It is defined as the change in optical density per unit of inserted charge (CE = Δ (OD)/ Δ Q). A high CE represents a large optical modulation at small charge insertion/desinsertion. During coloration from light yellow to uniform dark blue, a voltage of -4 V was applied during 50 s (Figure 3.2.11 (a)) and charge, in the form of electrons and Li^{\dagger} ions, was transferred from the TCO and IC layers, respectively, to the EC layer (Scheme 3.2.3). Under these conditions, WO₃ suffered reduction and simultaneous Li⁺ insertion. Upon reversing the polarity of the applied voltage, bleaching resulted (*i.e.*, WO₃ was oxidated and Li⁺ was desinserted) and the device recovered its initial state, *i.e.*, from uniform dark deep blue to light yellow. In the present study, the device was cycled during a very short period of time (1500 s corresponding to 15 cycles) (Figure 3.2.11 (b)).

Figure 3.2.12 shows that the charge density decreases gradually with cycling, although this tendency is more abrupt during the first 5 cycles. It may be also inferred from Figure 3.2.12 that the ratio of the cathodic to the anodic charges (Q_{in}/Q_{out}) of the device decreases with cycling, demonstrating a progressive improvement of the charge insertion/desinsertion reversibility. For the 2nd cycle a high CE value of 577 cm²C⁻¹ was estimated for an Δ (OD) of 0.15. The short period of time covered by the CA measurements (only 15 cycles) does not enable us to comment of the stability of the glass/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD.



Figure 3.2.11. Time dependence of the current density of the glass/IZO/WO₃/d PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD with potential steps of -4 and + 4 V at every 50 s after: 3 cycles (a) and 15 cycles (b). The area of the device was assumed to be ideally 4 cm².



Figure 3.2.12. Charge density of the glass/IZO/WO₃/d PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD as a function of the number of cycles: The area of the device was assumed to be ideally 4 cm². The data corresponding to the 1^{st} insertion were discarded.

The electrochromic memory of an ECD is the ability to hold its absorption state while the current is off. Figure 3.2.13 demonstrates that the open circuit memory of our prototype ECD is quite good (approximately 1 month). The extremely encouraging results observed in this exploratory study confirm the advantages that derive from the use of the d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂ material in ECDs. Further optimization of the procedures is obviously required, since improvements in switching speed, stability and optical memory and the application of lower operating voltages should be expected. Long-term operation of ECDs is known to depend critically on the production of defect-free ormolyte thin films and air-free sealing of the device.[43] The inclusion of a counter-electrode layer with high ion-storage capacity in future tests of this ECD is absolutely necessary to ensure the existence of a sufficient number of ions to produce a deep coloration of the WO₃ active EC layer and for the device to remain stable.



Figure 3.2.13. Time dependence of the transmission spectra (a) and average transmittance in the VIS region (b) of the glass/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/glass ECD. The transmittance of the colored state was measured after 15 cycles. The curve drawn in (b) is just a guide for the eyes.

3.2.4. Conclusions

The thermal (DSC and TGA), structural (XRD and FT-IR spectroscopy), electrochemical (ionic conductivity and CV) and photoluminescence properties of a novel series of LiCF₃SO₃- and Eu(CF₃SO₃)₃-doped di-urethane cross-linked

PCL(530)/siloxane biohybrids induced us to carry out preliminary tests of the performance of prototype ECDs incorporating these luminescent materials as electrolytes. The extremely promising results obtained for the switching time, optical density change, open circuit memory and high coloration efficiency lead us to foresee that these materials may find application in "smart windows" and other ECD-based devices, thus justifying further studies. However, several aspects will have to be taken into account in future for the improvement of their performance. The inclusion of counter-electrode layer with high ion-storage capacity is mandatory to ensure a sufficient number of ions for deeper coloration of the WO_3 layer at lower voltage, and therefore for the enhancement of both device stability and cyclability. The optimization of the ECD assembly procedure is another requirement that needs to be fulfilled. Problems related with the presence of air and/or defects in the electrolyte films produced during sealing might explain why the parameters deduced for the three prototype ECDs tested in this work, although not significantly different, did not match exactly. The control of moisture during device construction is also advisable. Another aspect that remains to examined is the variation of the Δ (OD) with ormolyte composition.

3.2.5. References

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Chapter 4

Biomimetic growth of calcium carbonate

Ionic-liquid assisted morphology tuning of calcium carbonate in ethanolic solution

Bio-inspired morphology tuning of calcium carbonate in ethanolic solution mediated by non-ionic surfactants

Polymer-mediated precipitation of amorphous calcium carbonate

4. Biomimetic growth of calcium carbonate

Calcium carbonate (CaCO₃) has been one of the most extensively investigated minerals due not only, to its abundance in Nature [1, 2], but especially because of its important applications in industry (*e.g.*, toothpastes, paints, cosmetics, paper, fillers, plastics and rubber). In recent years the potential of this inorganic compound in orthopedics [3] and drug delivery [4, 10] have been recognized. The CaCO₃ biomineral of invertebrates, such as mollusks shells and a sea urchin spines, have been particularly well studied due to their accessibility and because of the high degree of crystallographic control that is achieved in these biologically formed crystals.

CaCO₃ crystallizes into three anhydrous polymorphic forms: rhombohedral calcite (the most stable), orthorhombic aragonite and hexagonal vaterite (the least stable and the most rare). Their conventional morphologies are rhomboedral, needle-like and spheroidal, respectively. In addition, $CaCO_3$ has three metastable polymorphs: two well-defined hexahydrate and monohydrate compounds and an amorphous form which occurs in many biological organisms [11]. The hydrated forms are calcium carbonate monohydrated, calcium carbonate hexahydrated and amorphous CaCO₃ (ACC). Calcite and aragonite are by far the most widely produced forms of calcium carbonate in biology. The less stable phases can be transformed to calcite, the thermodynamically most stable phase. Because magnesium ions are readily accommodated in calcite lattice, many biological calcites contains Mg²⁺ ions up to levels of 30% mol [12]. Biogenic ACC was first identified at the beginning of the twentieth century when investigators noted that certain CaCO₃ deposits were isotropic when observed between crossed Nichols using polarized light. These phases do not diffract x-rays. Many organisms use ACC as a transient intermediate to form single crystals of calcite and aragonite with elaborate shapes.

Besides its importance as a structural biomaterial, CaCO₃ is also of interest for fundamental studies on templates-mineral interactions due to its sensitivity for templates effects. Both in a biological and in a synthetic environment, the formation of

 $CaCO_3$ can be controlled through the interference of organic molecules and surfaces with the mineral formation process.

Additives can inhibit the development of the energetically most stable product, thus yielding one of the other polymorphs. This means that the crystal size is kept below the critical size for the formation of the crystalline polymorphs or that the dissolution-reprecipitation step that allow the formation of crystals is prevented [13].

Many examples of adittives can be found in the literature. One of the most popular examples is the magnesium ion [12, 14,]. But the field of research has been enlarged to polymers/block copolymers [15, 16], dendrimers [17], surfactants [18, 19] and more recently ionic liquids [20].

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Ionic liquid-assisted morphology tuning of calcium carbonate in ethanolic solution

This section is based on the following publication:

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M. Fernandes, F. A. Almeida Paz, V. de Zea Bermudez European Journal of Inorganic Chemistry



4.1. Ionic liquid-assisted morphology tuning of calcium carbonate in ethanolic solution

4.1.1. Brief Introduction

Ionic liquids (ILs) are a very attractive class of salts, composed of organic cations and inorganic or organic anions, which are generally liquid below 100 °C. ILs display a series of unique characteristics, such as high fluidity, thermal and chemical stability, ability to dissolve a variety of materials and high ionic conductivity. Because of their low toxicity, non-flammability, non-measurable vapour pressure and recyclability, they are considered as "green" solvents in contrast with classical organic compounds [1]. The potential of ILs is further emphasized by the fact that they have tuneable physicochemical properties that can be finely tailored to suit a particular purpose simply through a judicious adjustment of their chemical structure (i.e., through the variation of both the cation and the anion).

Applications of ILs in organic synthesis [2], catalysis [3], extraction [4] and electrochemistry [5] have been widely reported. More recently, ILs have started to be explored as environmentally benign reaction media for the production of inorganic materials [6-8]. Interestingly, ILs can sometimes act, not only as solvents, but also as reactants and morphology templates for the fabrication of inorganic matter with novel or improved properties [6-12]. Apart from their morphology-modifying effect, ILs may also lower nucleation energies and influence polymorph selectivity [13]. In this sense, ILs may be considered as chemically simple all-in-one systems suitable for "crystal tectonics", i.e., for the synthesis of advanced inorganic crystal architectures with hierarchically complex structures and optimized features [14].

In spite of its natural abundance and tremendous potential for conventional industry and biomedicine, the precipitation of CaCO₃ mediated by ILs has been little explored. Hollow calcite spheres were obtained in a solution of CO₂-saturated 1,1,3,3-tetramethylguanidinium lactate [15], whereas high surface area mesoporous CaCO₃

with straw-like bundles morphology was synthesized in 1-methyl-3-pentylimidazolium pyruvate [16]. More recently, Zhao *et al.* [17] produced unusual rod-like and dendrite-like aragonite nanoparticles in the presence of 1-dodecyl-3-methylimidazolium bromide and 1-butyl-3-methylimidazolium bromide, respectively.

In the present work we have investigated the structure and morphology of CaCO₃ samples crystallized in the presence of five different ILs whose chemical structure and notation are indicated in Scheme 4.1.1. While four of these compounds are composed of imidazolium-based cations, the fifth contains a pyrrolidinium-based cation. Two types of counter-anions have been considered in this study: the chloride (CI) and tetrafluoroborate (BF₄) ions. To precipitate CaCO₃ we have adopted Lee *et al.* [18] s straightforward method which relies on the presence of ethanol as the reaction medium and calcium chloride (CaCl₂) and ammonium carbonate ((NH₄)₂CO₃) as the sources of calcium and CO₂, respectively. This procedure is extremely attractive, because it does not require any elaborate pH control or the addition of additives. The use of (NH₄)₂CO₃ instead of CO₂ allows the reaction medium to maintain at neutral or weakly basic pH caused by the dissolution of ammonia. Moreover, the water vapour derived from the sublimation of (NH₄)₂CO₃ presumably participates in the formation of bicarbonate, carbonate, and ammonium ions, though in small amounts, in ethanol [18].

We have tested several parameters, in particular the influence of the C/Ca ratio, the IL concentration and the reaction temperature.

4.1.2. Experimental part

Materials

Calcium chloride dehydrate (CaCl₂.2H₂O, Panreac), ammonium carbonate ((NH₄)₂CO₃, Riedel-de Haën) and the ionic liquids 1-ethyl-3-methylimidazolium chloride ([Emim]Cl, Solvionics), 1-butyl-3-methylimidazolium chloride ([Bmim]Cl, Solvionics), 1-butyl-1-methylpyrrolidinium chloride ([Bmpyr]Cl, Solvionics), 1-ethyl-3-methylimidazolium tetrafluoroborate ([Emim]BF₄, Solvionics) and 1-ethanol-3-methylimidazolium tetrafluoroborate ([HOmim]BF₄, Solvionics) (Scheme 4.1.1) were

used as received. Ethanol (Merck, PA grade) was stored over molecular sieves prior to being used.

Cl

1-ethyl-3-methylimidazolium chloride [Emim]Cl

1-butyl-1-methylpyrrolidinium chloride

[Bmpyr]Cl





1-butyl-3-methylimidazolium chloride [Bmim]Cl

 $\Box F_{4}^{-}$

1-ethyl-3-methylimidazolium tetrafluoroborate

[Emim][BF₄]



1-ethanol-3-methylimidazolium tetrafluoroborate

[HOmim][BF₄]

Scheme 4.1.1. Chemical structures of the ionic liquids.

Preparation of the materials

A Becker with an appropriate mass of $(NH_4)_2CO_3$ was placed next to a Petri dish containing 20 ml of an ethanolic solution of $CaCl_2.2H_2O$ and a certain amount of IL (Table 4.1.1). The whole set was then covered with a vessel, to allow the diffusion of CO_2 vapour from $(NH_4)_2CO_3$ into the solution (Scheme 4.1.2), and maintained at room temperature in a fume hood (Figure 4.1.1 (a)) or inside a refrigerator at 9 °C (Figure 4.1.2 (b) and Table 4.1.1). As the reaction progressed the solution phase became milky white. A white precipitate deposited at the bottom of the Petri dish after 24 hrs or *ca*. one week, respectively. The jelly-like precipitate was then centrifuged with 5 ml of distilled water at 2000 r.p.m. for 5 min. After repeating this washing operation several times, the precipitate was transferred to an oven at 50 °C, where it remained for several days to remove the adsorbed water.



Scheme 4.1.2. Scheme of the experimental set-up.



Figure 4.1.1. View of the experimental set-up used to carry out the experiments at 24 °C (a) and 9 °C (b).

Table 4.1.1.	Synthetic conditions	s of CaCO ₃ precipi	tation, crystalline phase	s and morphology. C-	calcite, F – fluorite, A1 and A2 – two forms of NH_4CI .
Sample	IL	Molar	Ca:C:IL	Crystalline	Morphology
		D° 6	room temperature	Phases	
CC#1	No		1:1.29	C, A1	microcubes
CC#2	No		1:2.26	C, A2	microcubes
CC#3	[Emim]C1		1:1.30:0.12	C	microcubes and microframes
CC#4	[Emim]Cl	1:1.25:0.12		C	microcubes
CC#5	[Emim]C1		1:1.23:0.26	C	microboxes
CC#6	[Emim]Cl	1:1.25:0.25		C	microcubes
CC#7	[Emim]Cl		1:2.39:0.13	C	nanocubes and nanocorn-like objects
CC#8	[Emim]Cl	1:2.52:0.13		C, A2	nanocubes and nanocorn-like objects
CC#9	[Bmim]Cl		1:1.28:0.11	C	microboxes
CC#10	[Bmim]Cl		1:1.24:0.21	C	microcubes
CC#11	[Empyr]Cl		1:1.33:0.11	C	microboxes
CC#12	[Empyr]Cl		1:1.19:0.23	C	microboxes
CC#13	[Emim]BF ₄		1:2.54:0.10	C, F, A1, A2	microcubes and nanostructured microspheres
CC#14	$[Emim]BF_4$	1:2.71:0.10		C, F, A1	microcubes, microframes and microspheres
CC#15	[HOmim]BF ₄		1:2.16:0.08	C, F, A1, A2	shapeless micro-objects
CC#16	[HOmim]BF ₄	1:2.65:0.09		C, F	microcubes,
					nanostructured jar-like micro-objects ice-cream ball-like micro-objects
					6

Characterization.

Scanning Electron Microscopy (SEM) and High Resolution (HR-SEM): The HR-SEM/EDS and SEM images were obtained at CEMUP-Porto with a FEI QUANTA 400 FEG/EDAX Pegasus X4M and a JEOL JSM 35C/Noran Voyager, respectively. Prior to being analyzed the samples were coated with Au/Pd. X-ray Diffraction (XRD): Powder X-ray diffraction data (PXRD) suitable for phase identification were collected at ambient temperature on a X'Pert MPD Philips diffractometer (Cu K_{α 1,2} X-radiation, $\lambda_1 = 1.540598$ Å and $\lambda_2 = 1.544426$ Å), equipped with a X'Celerator detector and a flatplate sample holder in a Bragg-Brentano para-focusing optics configuration (40 kV, 50 mA). Intensity data were collected by the step-counting method (step 0.04°), in continuous mode, in the *ca*. $5 \le 2\theta \le 50^{\circ}$ range. Fourier Transform Infrared (FT-IR): The FT-IR spectra were acquired at room temperature in the 4000-400 cm⁻¹ range by averaging 64 scans at a resolution of 4 cm⁻¹, using a Unicam FT-IR spectrophotometer. To prepare the pellets, 2 mg of the samples were mixed and finely ground with 175 mg of potassium bromide (KBr, Merck, spectroscopic grade) and pressed under vacuum.

4.1.3. Results and discussion

Microcube-shaped crystals of CaCO₃ were obtained when **no IL** was added to the reaction medium, independently of the C:Ca ratio used (Figure 4.1.2). As expected, the rhombohedra formed correspond to calcite (see XRD patterns in Figure 4.1.3 (a), although a minor amount of NH₄Cl remained in both samples. The FT-IR spectra reproduced in Figure 4.1.3 (b) exhibit the characteristic absorption bands of calcite at 875 and 712 cm⁻¹, ascribed to the v₂ mode (due to carbonate out-of-plane bending vibration) and v₄ mode (due to in-plane bending vibration), respectively [19].



Figure 4.1.2 SEM images of CaCO₃ precipitated at room temperature in the absence of any IL. Molar ratios C/Ca \approx 1 (CC#1: (a) and (b)) and C/Ca \approx 2 (CC#2: (c) and (d)).

The addition of ILs to the ethanolic solution of $CaCl_2$ affected the crystallization of $CaCO_3$ leading to a series of more or less marked morphological changes.





 \approx 2 (CC#2). C – calcite, A1 - NH₄Cl (01-089-2786) and A2 - NH₄Cl (00-007-0007).

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CaCO₃ precipitation in the presence of [Emim]Cl

With a stoichiometric molar ratio of C:Ca and a low [Emim]Cl content, calcite (Figure 4.1.4) aggregates of **CC#3** where a mixture of microcubes and microframes (see red arrows) coexist were produced at room temperature (Figure 4.1.5 (b)) Signs of erosion are evident in many of these objects. At lower temperature the aggregates became significantly denser, comprising essentially calcite (Figure 4.1.4) microcubes of **CC#4** with regular, plate-like faces Figure 4.1.5 (d)).



Figure 4.1.5 SEM images of CaCO₃ precipitated at room temperature (**CC#3**: (a) and (b)) and 9 °C (**CC#4**: (c) and (d)). Molar ratios C/Ca \approx 1 and [Emim]Cl/Ca = 0.12.



Figure 4.1.4. XRD patterns of CaCO₃ precipitated at room temperature (CC#3) and 9 °C (CC#4) (a) and FT-IR spectrum of sample CC#4 (b).

Molar ratios C/Ca \approx 1 and [Emim]Cl/Ca = 0.12. C – calcite.

The increase of [Emim]Cl concentration yielded dense aggregates of calcite (Figure 4.1.6) **CC#5** microboxes at room temperature (see red arrow in Figure 4.1.7 (b)). In contrast, when the reaction was carried out at much lower temperature these "gruyère"-type objects were no longer observed Figure 4.1.7 (d). Under the latter experimental conditions the aggregates of **CC#6** produced were smaller and less dense (Figure 4.1.7 (d)) and comprise essentially calcite (Figure 4.1.6). It is also worth noting that the rhombohedral morphology produced resembles closely that of sample **CC#2**, obtained in the absence of any IL (Figure 4.1.2 (c)).



Figure 4.1.7. SEM images of CaCO₃ precipitated at room temperature (**CC#5**: (a) and (b)) and 9 °C (**CC#6**: (c) and (d)). Molar ratios C/Ca \approx 1 and [Emim]Cl/Ca = 0.26.



Figure 4.1.6. XRD patterns of CaCO₃ precipitated at room temperature (CC#5) and 9 °C (CC#6) (a) and FT-IR spectrum of sample **CC#6** (b). Molar ratios C/Ca \approx 1 and [Emim]Cl/Ca = 0.26. C – calcite.

The occurrence of microframes in **CC#3** and in particular microboxes in **CC#5** are results of the utmost interest in the context of the development of hollow structures with foreseen application in drug delivery [20]. Considering that **CC#3** and **CC#5** were thoroughly washed with water (see Experimental section) we may draw a possible scenario for the formation of these two sorts of microstructures. If we assume that in both samples [Emim]Cl was essentially concentrated in the core of the growing micro-objects, during washing leaching of the IL must have taken place to balance the ionic liquid chemical potential difference. The IL probably left the solid structure of the microcube through surface defects. At this stage the reason why microframes are not formed at high [Emim]Cl concentration is not clear.

When an excess of $(NH_4)_2CO_3$ was employed (C/Ca = 2.5) and a low concentration of [Emim]Cl was introduced, highly dispersed sphere/cocoon-shaped microaggregates of **CC#7** (Figure 4.1.8 (a) and (b)), composed of a mixture of calcite (Figure 4.1.9) nanocubes and nanocorn-like objects (Figure 4.1.8 (c)) resulted at room temperature. At 9 °C, the size of these aggregates increased and their substructure became less regular. The XRD pattern of **CC#8**, reproduced in Figure 4.1.9, confirms that this sample contains NH_4Cl besides calcite, a result that indicates that it was not possible to remove all the NH_4Cl formed through washing.



Figure 4.1.8. SEM images of CaCO₃ precipitated at room temperature (CC#7: (a)-(c)) and 9 °C (CC#8: (d)-(f)). Molar ratios C/Ca = 2.5 and [Emim]Cl/Ca = 0.13.




CaCO₃ precipitation in the presence of [Bmim]Cl

To evaluate the consequences arising from the replacement of an ethyl group by a butyl group at position 1 of the imidazolium-based ILs, we incorporated [Bmim]Cl instead of [Emim]Cl in the reaction medium and carried out the synthesis of CaCO₃ at room temperature, using a stoichiometric content of C:Ca and two different IL concentrations (Table 4.1.1).

Comparison of the morphology of sample **CC#9** shown in Figures 4.1.10 (a) and (b) with that exhibited by sample **CC#3** (Figures 4.1.5 (a) and (b)) demonstrates that at low [Bmim]Cl concentration the length of the alkyl substituent exerts a major effect. Although no microcubes or microframes are produced Figures 4.1.10 (a) and (b), the irregular calcite (Figure 4.1.11) objects formed in **CC#9** show great resemblance with those exhibited by sample **CC#5** (Figures 4.1.7 (a) and (b), also fabricated at room temperature, but at high [Emim]Cl concentration. Curiously, at higher [Bmim]Cl content, the morphology of the calcite (Figure 4.1.11) **CC#10** sample (Figures 4.1.10 (c) and (d)) does not differ significantly from that displayed by **CC#4** obtained at 9 °C and at a low [Emim]Cl concentration (Figures 4.1.5 (c) and (d))



Figure 4.1.10. SEM images of CaCO₃ precipitated at room temperature with molar ratios C/Ca \approx 1, [Bmim]Cl/Ca = 0.11 (**CC#9**: (a) and (b)) and [Bmim]Cl/Ca = 0.21 (**CC#10**: (c) and (d)).





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Biomimetic growth of calcium carbonate

CaCO₃ precipitation in the presence of [Bmpyr]Cl

When the imidazolium-based cation of [Bmim]Cl was replaced by pyrrolidinium-based one, the morphology of the CaCO₃ fabricated at room temperature with a stoichiometric content of C:Ca changed considerably at low IL content, since the calcite (Figure 4.1.12) microboxes of **CC#11** formed in the presence of [Bmpyr]Cl are significantly more perfect (Figure 4.1.13 (a) and (b)) than those displayed by sample **CC#9** (Figure 4.1.10 (a) and (b)). However, the calcite (Figure 4.1.12) microboxes of **CC#12** that emerge at higher [Bmpyr]Cl content (Figure 4.1.13 (c) and (d)) resemble those of sample **CC#9** (Figure 4.1.10 (a) and (b)). Moreover, we note that the microboxes produced within the [Bmpyr]Cl-based solution at low content are similar to those of **CC#5** (Figure 4.1.7 (a) and (b)), synthesized under the same conditions, but at high [Emim]Cl content. The tentative explanation given above for the formation of microboxes **CC#5** should apply here too.









Figure 4.1.13. SEM images of CaCO₃ precipitated at room temperature with molar ratios C:Ca \approx 1, [Bmpyr]Cl/Ca = 0.11 (CC#11: (a) and (b)) ⁵ and [Bmpyr]Cl/Ca = 0.23 (CC#12: (c) and (d)).

CaCO₃ precipitation in the presence of [Emim][BF₄]

To inspect the influence of the counter-anion on the crystallization of $CaCO_3$ in the presence of [Emim]⁺, we compared the morphologies formed in the presence of [Emim][BF₄] and [Emim]Cl, using a molar ratio C/Ca = 2.5 and low IL concentration, at room temperature (sample CC#13 in Figures 4.1.14 (a-c) and sample CC#7 in Figures 4.1.8 (a-c) respectively) and 9 °C (sample CC#14 in Figures 4.1.14 (d-f) and sample CC#8 in in Figures 4.1.7 (d-f), respectively). These data lead us to conclude that there is in both series of samples a clear tendency for the formation of micro-aggregates. However, it seems that in the case of [Emim][BF₄]-derived CC#13 and CC#14 materials this effect is favored: the size of the calcite (Figure 4.1.15) aggregates increases, although they become more irregular (Figure 4.1.14). In the case of sample CC#13 these aggregates are composed of a mixture of spherical particles (ca. 1 μ m diameter) and eroded rhomboedra (Figure 4.1.14 (b) of calcite, fluorite and two forms of NH₄Cl (Figure 4.1.15). Figure 4.1.14 (b) demonstrates that the spherical micro-objects are nanostructured. Low temperature conditions yielded denser CC#14 aggregates of calcite, fluorite and a form of NH_4Cl (Figure 4.1.15) where irregular microframes, microcubes and microspheres are visible (Figure 4.1.14 (f)).

The occurrence of fluorite in **CC#13** and **CC#14**, both synthesized in the presence of BF_4^- -based ILs (Table 4.1.1), suggests that in both samples the IL played the role of reactant. Clearly in the ethanolic reaction medium used, the BF_4^- ion released the fluoride ion (F^-).



Figure 4.1.14. SEM images of $CaCO_3$ precipitated at room temperature (**CC#13**: (a)-(c)) and 9 °C (**CC#14**: (d)-(f)). Molar ratios C/Ca = 2.5 and [Emim][BF₄]/Ca = 0.10.



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Figure 4.1.15. XRD patterns (a) and FT-IR spectra (b) of CaCO₃ precipitated at room temperature (CC#13) and 9 °C (CC#14). Molar ratios C/Ca = 2.5 and [Emim][BF₄]/Ca = 0.10. C- calcite, F – fluorite, A1 - NH₄Cl (01-089-2786) and A2 - NH₄Cl (00-007-0007).



CaCO₃ precipitation in the presence of [HOmim][BF₄]

The second BF_4 -based IL explored in the present work contains an ethanol group instead of an ethyl group at position 3 of the imidazolium cation. Analysis of Figure 4.1.16 lead us to conclude that the presence of the terminal OH group has a dramatic effect on the morphology of the CaCO₃ crystals.

When [OHmim][BF₄] was employed the sample obtained at room temperature (**CC#15**) was produced as shapeless aggregates (Figure 4.1.16 (a) considerably bigger that those found in sample **CC#13** prepared with [Emim][BF₄] (Figure 4.1.14 (a-c)). Sample **CC#15** contains calcite, fluorite and two forms of NH₄Cl (4.1.17). At 9 °C the aggregates of **CC#16** that grow in the [OHmim][BF₄] medium display a highly complex and intricate texture (Figure 4.1.16 (b)). According to Figure 4.1.17, the latter material only contains calcite and fluorite.



Figure 4.1.16. SEM images of CaCO₃ precipitated at room temperature (**CC#15**: (a)) and 9 °C (**CC#16**: (b)). Molar ratios C/Ca = 2.5 and [OHmim][BF₄]/Ca = 0.09.

Figure 4.1.17. XRD patterns (a) and FT-IR spectra (b) of CaCO₃ precipitated at room temperature (CC#15) and 9 °C (CC#16). Molar ratios C/Ca = 2.5 and [OHmim][BF_4]/Ca = 0.09. C- calcite, F – fluorite, A1 - NH_4Cl (01-089-2786) and A2 - NH_4Cl (00-007).



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The higher magnification SEM images obtained in different regions of **CC#16** Figure 4.1.18 and the EDS data Figure 4.1.19-Figure 4.1.21 allowed us to identify at least three different types of objects for which the shape, size and composition differ considerably: (1) Spherical calcite- and fluorite-based micro-objects that mimic icecream balls (Figure 4.1.18 (a) and (b) and 4.1.19); (2) Calcite microcubes with regular faces Figure 4.1.18 (a) and (b) and Figure 4.1.20; (3) Finely structured calcite- and fluorite-based micro-objects that mimic the shape of jar flowers Figure 4.1.18 (b) and Figure 4.1.21.



Figure 4.1.18. SEM images of sample **CC#16**: (b)). Molar ratios C/Ca = 2.5 and [OHmim][BF₄]/Ca = 0.09. The EDX spectra for selected areas Z1, Z2 and Z3 can be found in Figures 4.1.19 - 4.1.21.

The presence of fluorite in samples **CC#15** and **CC#16** gives support to the above claim that the BF_4^- ion decomposes in the reaction medium, releasing F^- ions which give rise to the crystallization of fluorite concomitantly with that of calcite.



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Figure 4.1.19. EDX spectrum of selected area Z1 of sample **CC#15**. Molar ratios C/Ca = 2.5 and [OHmim][BF₄]/Ca = 0.09.



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Figure 4.1.20. EDX spectrum of selected area Z2 of sample **CC#15**. Molar ratios C/Ca = 2.5 and [OHmim][BF₄]/Ca = 0.09.

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Figure 4.1.21. EDX spectrum of selected area Z3 of sample **CC#15** in. Molar ratios C/Ca = 2.5 and [OHmim][BF₄]/Ca = 0.09.

2.2.4. Conclusions

In the present work we have examined how the crystallization of $CaCO_3$ from $CaCl_2$ and $(NH_4)_2CO_3$, in ethanolic medium, is affected by the presence of five different ILs based on imidazolium- and pyrrolidinium-based cations and Cl^- or BF_4^- anions. We have chosen methyl, ethyl, butyl and alcohol groups as substituents of the cationic rings.

Irrespective of the chemical structure and concentration of the IL, of the reaction temperature and of the C:Ca ratio employed, the only polymorph found in all the CaCO₃ samples synthesized was calcite. A second crystalline phase, fluorite, was formed only in the case of the samples synthesized in the presence of BF₄⁻-based ILs, an indication that these ILs played the role of reactants. Within the ethanolic medium employed the decomposition of the anion was induced, resulting in the formation of fluorite in parallel to the crystallization of calcite. In some of the samples a minor proportion of one or sometimes two forms of NH₄Cl were detected, suggesting that the washing procedure was not always efficient. Performing crystallization at low temperature slowed down the precipitation process (cf. Experimental section).

The present work has illustrated the quite extraordinary ability of ILs to tune the morphology (i.e., shape and size) of CaCO₃. Materials with a large variety of forms, ranging from microcubes, microframes and microboxes to nanocubes and nano-corn like objects, have been produced with the three Cl⁻-based ILs. Interestingly, the addition of BF₄⁻-based ILs has generated hierarchically structured materials, displaying considerably more complex shapes, such as nanostructured microspheres, nanostructure jar-like micro-objects and ice-cream ball-like micro-objects.

The encouraging results derived from the present investigation justify further studies. Clearly, the production of calcite microboxes as promising drug carriers must be explored in more detail, using other washing methods, such as for instance, dialysis. Monitoring of dialysis progression with time may provide useful information about the transformation of microcubes, to microboxes and ultimately to microframes. Other reaction conditions and changes in the chemical structure of the IL used must be considered to try to control the size of these structures.

4.1.2. References

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Bio-Inspired morphology tuning of calcium carbonate in ethanolic solution



4.2. Bio-Inspired morphology tuning of calcium carbonate in ethanolic solution mediated by non-ionic surfactants

4.2.1. Brief Introduction

In the last decades biomineralization processes have inspired researchers seeking to mimic the morphologies and properties of the CaCO₃ found in biological organisms. In this context the production of CaCO₃ crystals assisted by surfactants has emerged as an attractive strategy to control polymorphism and crystal orientation [1-11]. Most of the research in this domain has involved the use of cationic or anionic surfactants or mixtures of both. A reduced number of reports deal with the use of non-ionic surfactants. Amphiphilic polymers, such as poly(oxyethylene)-poly(oxypropylene-poly(oxyethylene) (POE-POP-POE) block copolymers (commercially known as Pluronics), fall into the latter category of surfactants. Yan *et al.* [12] concluded that the mixture of the anionic surfactant sodium dodecyl sulfate with Pluronic127 in ethanol/water solution favored the formation of vaterite. Xie *et al.* [13] precipitated calcite and vaterite with low and high poly(ethylene glycol) concentration, respectively.

In the present work we have examined the influence of three different nonionic surfactants on the structure, shape and size of precipitated $CaCO_3$ crystals. The compounds, which belong to the class of fatty alcohols, have been represented by the notation C_nOH , with n = 14, 16 and 22 (Scheme 4.2.1). The crystallization of $CaCO_3$ has been performed using the straightforward method proposed by Lee *et al.* [14], which implies the use of ethanol as the reaction medium, calcium chloride ($CaCl_2$) as the source of calcium and ammonium carbonate ((NH_4)₂CO₃) and the source of CO₂. This method is suitable because does not require the control of the pH or the addition of additives.

4.2.2. Experimental part

Materials

Calcium chloride dihydrate (CaCl₂.2H₂O, Panreac), ammonium carbonate $((NH_4)_2CO_3, Riedel-de Haën, purissim.), 1-tetradecanol (C₁₄OH, Aldrich, 97%), 1-hexadecanol (C₁₆OH, Sigma-Aldrich, 99%), 1-docasanol (C₂₂OH, Aldrich, 98%) were used as received. Ethanol (Merck, PA grade) was stored over molecular sieves prior to being used. A schematic representation of the non-ionic surfactants employed are reproduced in Sheme 4.2.1.$



1-docasanol (C₂₂OH)

Synthesis of the materials

The procedure used to precipitate CaCO₃ has been described in detail in section 4.2.1. The samples prepared, in the different experimental conditions, are listed in table 4.2.1. The characterization of the samples by **HR-SEM**, **XRD** and **FT-IR** was done with the same conditions as described in section 4.1.

Scheme 4.2.1. Chemical structures of the surfactants employed.

of NH₄CI.					
Sample	Surf	Molar	· Ca:C:Surf	Crystalline	Morphology
	C _n OH	D ° 6	room temperature	Phases	
CC#1	n = 14		1:1.25:0.08	C, A2	microcubes
CC#2	n = 16		1:1.22:0.08	C, A2	microcubes
CC#3	n = 22		1:1.22:0.06	U	microcubes
CC#4	n = 16		1:2.47:0.11	U	microcubes
CC#5	n = 16	1:1.23:0.08		U	microspheres
CC#6	n = 16		1:1.25:0.16	U	microcubes microboxes
CC#7	n = 16	1:1.25:0.15		U	irregular microcubes

Table 4.2.1. Synthetic conditions of CaCO₃ precipitation, crystalline phases and morphology. Surf - surfactant, C- calcite, F - fluorite, A1 and A2 - two forms

4.2.3. Results and discussion

Influence of the chain length of the surfactant

In the absence of any additive in the reaction medium, microcube-shaped crystals of calcite CaCO₃ were obtained at room temperature, independently of the molar C/Ca ratio considered (Figure 4.1.2, section 4.1). Figures 4.2.1 (a-c) shows that at room temperature and low surfactant concentration, the rhombohedral shape is preserved in the dispersed aggegates of CC#1. However, upon increasing the chain length of the surfactant, the aggregates formed become larger and more irregular (CC#2 (Figures 4.2.1 (d-f) and CC#3 (Figures 4.2.1 (g-i)). Concomitantly, the rhombohedra observed in these aggregates become smaller and less abundant. Figures 4.2.1 (a), 4.2.1 (d) and 4.2.1 (e). In CC#1 and CC#2 calcite coexists with traces of a form of NH₄Cl, an indication that it was not possible to remove all the NH₄Cl formed through washing (Figure 4.2.2 (a)). In contrast in CC#3 calcite was the sole crystalline phase detected (Figure 4.2.2). The FT-IR spectra represented in Figure 4.2.2 (b) exhibit the characteristic absorption bands of calcite at 875 and 713 cm⁻¹, ascribed to the $v_2(CO_3^{2-})$ mode (due to carbonate out-of-plane bending vibration) and $v_4(CO_3^{2-})$ mode (due to in-plane bending vibration), respectively [15]. The origin of the shoulders detected in the high-frequency side of the $v_4(CO_3^{2-})$ band of **CC#3** is unknown.



Figure 4.2.1. SEM images of $CaCO_3$ precipitated at room temperature: CC#1: (a-c); CC#2: (d-f)); CC#3: (g-i) . Molar ratios C/Ca \approx 1 and Surf/Ca = 0.08.



Figure 4.2.2. PXRD patterns (a) and FT-IR spectra (b) of $CaCO_3$ precipitated at room temperature with molar ratios C/Ca \approx 1 and Surf/Ca = 0.08. C – calcite and A2 - NH₄Cl.

Influence of the C/Ca molar ratio

Figures 4.2.3 (a-c) demonstrate that when an excess of $(NH_4)_2CO_3$ was employed (C/Ca = 2.5), while maintaining a low concentration of C₁₆OH, the morphology changed dramatically (*cf.* **CC#2** in Figures 4.2.1 (d-f)). In **CC#4**, perfect submicrometer cubes (Figure 4.2.3(c)) assemble forming interconnected microspheres (Figures 4.2.3 (a) and (b)) of variable size. The objects formed are composed of calcite, although NH₄Cl was also detected (Figure 4.2.4 (a)).



Figure 4.2.3. SEM images of CaCO₃ precipitated at room temperature (**CC#4**). Molar ratio C/Ca = 2.5 and Surf/Ca = 0.11.



Figure 4.2.4. PXRD patterns (a) and FT-IR spectra (b) of $CaCO_3$ precipitated at room temperature with molar ratio C/Ca = 2.5 and Surf/Ca = 0.11(**CC#4**) and 9 °C with molar ratio C/Ca \approx 1 and Surf/Ca \approx 0.08 (**CC#5**). C – calcite and A2 - NH₄Cl.

Influence of the reaction temperature

When a low concentration of $C_{16}OH$ and a stoichiometric C:Ca molar ratio was used, but CaCO₃ precipitation was carried out at 9 °C, calcite (Figure 4.2.4) aggregates smaller (Figure 4.2.5 (a)) than those of **CC#2** (Figure 4.2.1 (d)) were obtained. Moreover in **CC#5** the rhombohedra that form these aggregates are also smaller (Figure 4.2.5 (b)) than those produced at room temperature (Figure 4.2.1 (f)).



Figure 4.2.5. SEM images of CaCO₃ precipitated at 9 °C (**CC#5**). Molar ratio C/Ca \approx 1 and Surf/Ca \approx 0.08.

Influence of the surfactant concentration

With a stoichiometric molar ratio of C:Ca and a high C₁₆OH content, calcite (Figure 4.2.6) aggregates of **CC#6** composed of a mixture of microcubes and microboxes (red arrows in Figures 4.2.7 (a) and (b)) with regular, plate-like faces were precipitated at room temperature. At lower temperature the aggregates of **CC#7** became shapeless and irregular (Figures 4.2.7 (a) and (b)). The presence of microboxes in **CC#6** makes this sample potentially attractive as drug carrier [16].

These findings differ significantly from those observed at lower $C_{16}OH$ concentration both at room temperature in **CC#2** (Figures 4.2.1 (d-f)) and at low temperature in **CC#5** (Figure 4.2.5).



Figure 4.2.6. PXRD patterns (a) and FT-IR spectra (b) of $CaCO_3$ precipitated at room temperature (**CC#6**) and 9 °C (**CC#7**). Molar ratios C/Ca \approx 1 and Surf/Ca \approx 0.16.

The formation of microboxes in **CC#6** may be associated with the fact that the surfactant was probably located in the core of the growing crystals. During the washing procedure leaching of the surfactant must have occurred through surface defects.

We must note, however, that some molecules of surfactant must have remained bonded to the calcite crystals. This conclusion derives from the fact that practically all the PXRD patterns recorded included peaks ascribed to the surfactant employed in each case. In particular we draw the attention to the PXRD patterns of **CC#4** (Figure 4.2.4 (a)) and **CC#6** (Figure 4.2.6 (a)) where the occurrence of this effect is clearly evident.

It is of interest to refer at this stage that fatty alcohols exhibit a polymorphic behavior which has been known for a long time [17-22]. In 1960 Abrahamsson et al. [19] reported an orthorhombic low temperature phase for odd alcohols and two different forms for even alcohols (between dodecanol and eicosanol) depending on the temperature: a hexagonal high temperature form (α) stable just below the melting point and two low temperature forms an orthorhombic (β) with the chains perpendicular to the planes formed by the hydroxyl group and another one monoclinic (γ) with inclined chains. In the literature it is possible to find some studies reporting the polymorphic behavior of fatty alcohols: 1-heptadecanol (C₁₇H₃₅OH), 1-octadecanol (C₁₈H₃₇OH), 1-nonadecanol (C₁₉H₃₉OH)) and 1-eicosanol (C₂₀H₄₁OH) [21]. The even *n*-alkanols (C₁₈H₃₇OH) and (C₂₀H₄₁OH) are isostructural at 298 K with the molecules in an all-t*rans* conformation presenting a different behavior if compared with the odd alcohols ((C₁₇H₃₅OH) and (C₁₉H₃₉OH)) [21]



Figure 4.2.7. SEM images of CaCO₃ precipitated at room temperature (**CC#6**: (a) and (b)) and 9 °C (**CC#7**): (c) and (d)). Molar ratios C/Ca \approx 1 and Surf/Ca \approx 0.16.

4.2.4. Conclusion

In the present work we have investigated the crystallization of CaCO₃ from CaCl₂ and (NH₄)₂CO₃, in ethanolic solution, in the presence of three different fatty alcohols that acted as non-ionic surfactants. Independently of the experimental conditions considered, calcite was the sole polymorph formed. In general, objects with more irregularities were obtained at low temperature. With the three surfactants employed rhombohedra were obtained in practically all the reaction conditions. The only exceptions were the microspheres composed of microcubes produced at room temperature, high molar ratio C/Ca and low surfactant concentration, as well as the microboxes obtained at room temperature, using a stoichiometric molar ratio C/Ca and a high surfactant concentration.

4.2.5. References

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Polymer-mediated precipitation of amorphous calcium carbonate (Poly(vinyl)pyrrolidone)



4.3. Polymer-mediated precipitation of amorphous calcium carbonate (Poly(vinyl)pyrrolidone)

4.3.1. Brief Introduction

Poly(vinylpyrrolidone) (PVP) (scheme 4.3.1) is a water soluble polymer that shows unusual colloidal and complexing properties, allowing the interaction with many inorganic materials [1].



Scheme 4.3.1. Representation of comercial poly(vinyl)pirrolidone (PVP)

Its biomedical applications have been known for many years [2], for example as a blood plasma substitute and extender, and the corresponding ability to bind to certain drugs [3], dyes and toxins have been explored. More recently [4] an engineered *in vitro* process was reported which allows enamel recristallization and dentine tubule occlusion. It involves the use of metastable calcium fosfate/polymer hydrogels produced *in situ* on acid-etched dental hard tissues by hydration of electrospun mats of amorphous calcium pohosphate/PVP in fluoride containing saliva solution.

The interaction of PVP with surfactants has been also reported in the literature [5]. Mixtures of PVP with surfactants have been proposed as a medium to promote the crystallization of $CaCO_3$ [1, 6-8]. The PVP dispersing capability for the solid particles, as well the mechanical stirring, prevents the direct precipitation of $CaCO_3$ [7]. Depending on the surfactant employed and on the surfactant concentration [6], several polymorphs and morphologies were obtained. Wei *et. al* [8]. found that the crystallization of $CaCO_3$ in a certain amount of PVP (1 mg/L) in the presence of a low amount of sodium sodecylsulfonate (DDS) the polymorph obtained was calcite with a

rhombohedral shape and *ca*. 5 μ m of dimension, but when they increased the concentration of surfactant, keeping the same amount of PVP, they obtained a mixture of rhombohedra and a flower-shape objects. The same group reported the change of calcite to vaterite in the presence of PVP and sodium dodecylbenzenesulfonate (SDBS), with an increasing amount of surfactant [8]. To evaluate the influence of the polymer in the precipitation process of CaCO₃ the same authors carried out a study in the presence/absence of PVP at various incubation times [1]. After ten minutes they observed the appearance of vaterite. Two main conclusions could be drawn: (1) The presence of PVP had no influence on the polymorphs obtained, but for higher concentration of PVP the morphologies of calcite and vaterite could be changed [1]. (2) The weak affinity between PVP molecules and Ca²⁺ ions, together with the high colloid-stabilizing ability of PVP made it clear that before the transformation from ACC to crystalline phases, CaCO₃ aggregated into bigger spherulites [1].

In the present work we decided to use a different experimental method [9] and employ PVP with different molecular weight in order to inhibit the crystallization of CaCO₃ for a longer time, in an attempt to optimize the conditions that maintain CaCO₃ in the amorphous form (ACC).

Various organisms use CaCO₃ as a constituent of their skeleton, as protective shell or as optical medium [10,11]. ACC is widely found in biological organisms as temporary storage site for calcium and carbonate [12]. Because of its in-growth rate, immunogenicity and mechanical strength of the grown bones, biogenic CaCO₃ is an attractive candidate for bone replacement/regeneration. A considerable amount of research done on materials for prostheses/implants has used biomimetic and/or bioinspired approaches to develop new biomaterials with improved performance

In the present work ACC crystallisation process was monitored over a long period of time right after ACC synthesis using standard techniques, such as X-ray Diffraction, FT-IR, Scanning Electronic Microscopy and Polarized Optical Microscopy [13].

4.3.2. Experimental part

Materials

Calcium chloride di-hydrated (CaCl₂.2H₂O, Panreac, PA-ACS, 147,02 g/mol), ammonium carbonate ((NH₄)₂CO₃, Riedel de Haën, purissim), ethanol absolute (Panreac, PA) and poly(vinylpyrrolidone) (PVP, Mw~70 000, Across) were used as received.

Synthesis of the materials

The general method employed in the preparation of the samples was mentioned in section 4.2.1. PVP was dissolved in the ethanolic solution of $CaCl_2.2H_2O$ (Scheme 4.3.2). After approximately one year selected samples were washed by centrifugation in the way described in section 4.2.1.



Scheme 4.3.2. Representation of the experimental procedure employed.

Table 4.3.1. shows the appropriate amounts of compounds involved in the preparation of the samples as a function of time. For the sake of simplicity, we decided to divide the samples under study in three groups: Without template (I), 500-100 mg range of PVP (II) and 50-10 mg range of PVP (III).
			Mass of $CaCl_2$	Mol CaCl ₂	Mass of	Mol	Mass of PVP
			(g)		NH ₄ (CO ₃) ₂ (g)	NH ₄ (CO ₃) ₂	(mg)
	I	CC#0	1.48	0.01	1.99	0.02	0
	II	CC#500	1.48	0.01	1.98	0.02	500
		CC#300	1.48	0.01	1.94	0.02	300
		CC#100	1.48	0.01	1.92	0.02	100
	III	CC#50	1.48	0.01	1.95	0.02	50
		CC#25	1.48	0.01	1.93	0.02	25
		CC#10	1.50	0.01	1.94	0.02	10

Table 4.3.1. Preparation of samples analyzed as function of time.

Characterization of the materials

The experimental procedures (equipments and methods) were already described in section 2.1 for Fourier Transform Infra-Red Spectroscopy (FT-IR) and Polarized Optical Microscopy (POM) and in section 3.1 for X-ray diffraction.

To examine the morphology of the samples two different equipments were employed. To check the evolution of the samples as function of time a SEM/ESEM-FEI Quanta 400 equipment operating at a high acceleration voltage (25 kV) was employed. To access the final morphology a FEI Quanta 400 FEG ESEM / EDAXS Pegasus x44 was used. All the samples were coated with Au/Pd.

We note that the samples were analyzed by different techniques with small delays between each technique.

4.3.3. Results and discussion

I- Without template

Figure 4.3.1 shows the XRD patterns of samples prepared without any template recorded as function of time. The appearance in the first hour (1h) of residual peaks at 22.9 and 29.4° suggest the presence of calcite (C), whereas the peak at 32.6° indicates the presence of vaterite (V). These peaks remain during the first month (1m) of

analysis. The presence of the peak at 27° corresponding to aragonite (A) is clear in the XRD pattern corresponding to the first day (1d).



Figure 4.3.1. XRD patterns of the sample without template as function of time. On the right side it is possible to observe the SEM Images corresponding to the sample after one hour (bottom) and one day (top)

The corresponding SEM images are represented in Figure 4.3.1. After one hour the SEM image (bottom of Figure 4.3.1) exhibits an heterogeneous aspect composed of elongated objects that end-up with spherical aggregates. No specific morphologies can be detected and the same applies to the SEM image recorded after 1 day.

The POM image, represented in Figure 4.3.2, was obtained between crossed polarizers after 4 days. This technique is a useful tool to monitor the development of the crystallinity [13]. It reveals birefringence corresponding to the anisotropic character of the sample.



Figure 4.3.2. POM image recorded between crossed polarizers of the sample prepared without any template.

The XRD pattern obtained on the first day does not display any peak. However a close analysis of different regions of the FT-IR spectrum (Figure 4.3.3) reveals the presence of aragonite, represented by the shoulder at 1080 cm⁻¹ (Figure 4.3.3 (a)) and the band at 700 cm⁻¹ (Figure 4.3.2 (c)) [14, 15]. In fact the presence of aragonite was detected by FTIR since the first hour (Figure 4.3.3 (a) and (c)). The evolution of the system to calcite/vaterite after the 4th day was clearly manifested in the FT-IR spectra by the shift of the band from 700 cm⁻¹ up to 710 cm⁻¹ (Figure 4.3.3 (c) and the presence of the band at 875 cm⁻¹ (Figure 4.3.3 (b)).





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II- 500-100 mg range of PVP

The first technique employed here was XRD (Figure 4.3.4), followed by FTIR (Figure 4.3.5). The POM and SEM images were recorded simultaneously.

According to the XRD data obtained in the first hour, all the samples remain amorphous (Figure 4.3.4 (a-c)). After 24 hours the first peaks of polymorphs with different morphologies start to appear, more specifically, the peaks corresponding to vaterite (27.97 and 32.7°). This result is more evident in the samples with a high and low amount of polymer (Figure 4.3.4 (a) and (c) respectively). The POM image in the bottom of Figure 4.3.4, obtained after one day between crossed-polarizers, shows the characteristic needle-like shapes which confirm the presence of vaterite in the 100 mg PVP-based sample [13]. After two days, the POM image, obtained for the same sample and with the same conditions, reveals the presence of the rhombohedra shapes associated with calcite (Figure 4.3.4 top) [14]. The latter result is in good agreement with XRD, since the pattern (Figure 4.3.4 (c)) shows the 29° calcite peak after the second day and until the last analysis made for the sample with 100 mg of polymer (Figure 4.3.4 (c)). The presence of a peak suggesting the formation of vaterite is observed from the first up to the third day.

In the case of the sample with 200 mg of PVP, the calcite peak at 29.4° appear just after two weeks (Figure 4.3.4 (b)). In fact, for this amount of polymer and in five months of analysis the presence of calcite was not easy to detect by this technique. In contrast, the presence of vaterite is easily identified because of the existence of a peak located at 33° (Figure 4.3.4 (b)).

For the sample with the highest amount of PVP the presence of vaterite is revealed by the appearance of the corresponding peak (33°) after one day. This peak remains present for 21 days (Figure 4.3.4 (a)). Due to the evolution of the mechanical properties of the samples, the XRD analysis from the 5th month were very difficult to perform (Figure 4.3.4 (b)), suggesting that the samples were amorphous, a conclusion which was not confirmed by FT-IR spectroscopy. This point will be discussed below.



Figure 4.3.4. XRD patterns of the samples doped with different amounts of PVP: 500 mg (a), 300 mg (b), 100 mg (c) (inset the POM image of the sample with 100 mg of polymer, under crossed polarizers, after 1 day (bottom) showing the vaterite crystals, and 7 days (up) showing calcite crystals).

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III- 50-10 mg range of PVP

The samples containing 50-10 mg of PVP were prepared in two series (room temperature changes significantly throughout the year in Vila Real). The main goal was to check the reproducibility of the experiments, but unfortunately, as expected, the resulting data were not reproducible. We tried to perform the analyses within the same time intervals, but sometimes this was not possible. As it was reported in the first range of concentrations studied, the absence or presence of the different polymorphous by XRD and FTIR is not always in agreement.

For the sample prepared with 50 mg of PVP the XRD results obtained are displayed in Figure 4.3.6 (a) and the FTIR data in Figures 4.3.6 (b) and (c). According to the XRD pattern (Figure 4.3.6 (a)) the first peak on the XRD pattern crystallites, visible after 48 hours, is located at 32.8° (vaterite). Small traces at 29° (calcite) are seen too. In the corresponding FT-IR spectra the 875 cm⁻¹ band characteristic of calcite is evident after four hours, but the 715 cm⁻¹ band also characteristic of calcite is observable just after three days.

The POM images recorded between crossed polarizer (Figure 4.3.7) beautifully demonstrates the amorphous character of the sample after 4 hours (Figure 4.3.7 (a) [14] and the presence of needles of aragonite after one day (Figure 4.3.7 (b))



Figure 4.3.7. POM images obtained between crossed polarizers for the sample prepared with 50 mg of PVP after 4 hours (a) and one day (b).

The XRD patterns of the sample prepared with 25 mg of PVP are reproduced in Figure 4.3.8 (a). In all the analyses just small peaks were discerned, the presence of

crystallites being observed after 2 days. The 900-940 cm⁻¹ (Figure 4.3.8 (b)) and 770-690 cm⁻¹ (Figure 4.3.8 (c)) regions of the FTIR spectra, *i.e.* confirm the presence of calcite after 4 days, because of the occurrence of its characteristic bands. In the FTIR region represented in Figure 4.3.8 (c) it is possible to observe the band at 698 cm⁻¹ corresponding to aragonite [14] on the first and second days of analysis. No such information is retrieved, however, from the XRD pattern (Figure 4.3.8 (a)).

The sample prepared with 10 mg of PVP produced the same kind of XRD patterns (Figure 4.3.9 (a)), with small crystallites appearing all over the period of analysis. In the FTIR spectra the most relevant feature is the band at 865 cm⁻¹, corresponding to the v_2 mode of carbonate and characteristic of ACC [15]. It is observed after two days (Figure 4.3.9 (b)). In the same period of time aragonite (700 cm⁻¹, v_4 mode) and vaterite (738 cm⁻¹, v_4 mode) are also detected. The presence of aragonite after two days is confirmed by POM (Figure 4.3.10) which displays the characteristic needles associated with this polymorph.After four days the presence of calcite is indicated by the bands at 875 cm⁻¹ and 715 cm⁻¹ (Figure 4.3.9 (b-c)).



Figure 4.3.10. POM images obtained between crossed polarizers (a) for the sample prepared with 50 mg of PVP after 4 hours (a) and one day (b).





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Figure 4.3.6. Results of the analyses obtained with 50 mg of PVP: XRD patterns (a); 900-840 cm⁻¹ (b) and 770-690 cm⁻¹ region of FTIR spectra.











Biomimetic growth of calcium carbonate

After one year the samples were washed in order to remove PVP. The XRD patterns obtained after the washing process, presented in Figure 4.3.11 (a), clearly show the diffraction peaks corresponding to calcite. The FTIR data presented in Figure 4.3.11 (b) also reveal the presence of calcite, represented by the bands located at 875 and 713 cm⁻¹, as expected.



Figure 4.3.11. XRD patterns (a) and FTIR spectra (b) of the samples with different amounts of polymer (50, 25, 10 mg of PVP) after the washing/drying process.

The main goal washing was to access the morphologies of the samples. The washed samples present a well-defined texture over the whole range of PVP concentrations considered. Figures 4.3.12 (a-c) show that after one year the samples exist under the form of aggregates. Irrespetively of PVP concentration, all the aggregates are composed of nonocorn-like objects.







4.3.4. Conclusion

The biomimetic growth of $CaCO_3$ was performed, in a laboratory scale, in the presence of different amounts of PVP, in an ethanolic medium in order to inhibit/retard the growth of the crystalline polymorphs. The different experiences were monitored from the first hour. In the case of the samples prepared with low amount of polymer the study was extended to one year.

During this work some difficulties in the attribution of the correct polymorph present were evident, due to the different information retrieved from the techniques employed. FT-IR spectroscopy is a more powerful technique giving the first clear indication of the appearance of vaterite and the interval time that is necessary for its transformation to calcite. Is also the only technique that allowed us to identified the presence or aragonite.

The long-time inhibition of the growth of crystalline CaCO₃ was not achieved. The growth of crystalline forms took longer when low amounts of PVP were employed (50-25 mg of PVP). In particular, aragonite, together with small traces of vaterite, were detected after two days for the sample prepared with 10 mg of PVP and after one day for the sample prepared with 20 mg of PVP.

Although the main goal of this work was not completely achieved, the analyses performed after one year demonstrated that the polymorph formed for all the samples under analysis calcite, presented dimensions in the nanometric range, suggesting that PVP did not affect polymer selectivity, but influenced the size of the calcite crystals.

4.3.5. References

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Chapter 5

Conclusions and perspectives futures

5. Conclusions and perspectives futures

This thesis was divided into three main Chapters of experimental results, which in turns are sub-divided into several sections. All the chapters have in common the fact that they deal with organic-inorganic materials differing from each other in the methodology employed in their preparation. The motivation on the preparation of each family of compounds, as well the main conclusions drawn from their study is reported in the corresponding sections.

The advantages of combining the sol-gel method and self-assembly techniques were discussed in Chapter 2. All the materials reported in this Chapter were based on this synthetic strategy.

In section 2.1 a hybrid silica prepared through acidic hydrolysis/condensation of the (EtO)₃Si(CH₂)₃NHC(=O)NH(CH₂)₁₂NHC(=O)NH(CH₂)₃Si(OEt)₃ (**P12**) precursor using a water/DMSO mixture was proposed. The final morphology of the lamellar silsesquioxane produced from the (**P12**) was changed from rigid platelets obtained in the lamellar hybrid (**L12**) to micro-objects that resemble sea sponges (**L12D**) upon simple mixing with dimethylsulfoxide (DMSO). The microstructural modifications observed were ascertained by several techniques. A mechanism for the morphology tuning based on the polarity of the solvent mixture was proposed. The results reported here represent an important step forward in the comprehension of the processes governing the formation of self-organized hybrid siliceous materials and highlight that the nature of the solvent plays a major role on the shaping of the final material. This conclusion was of particular importance in the preparation of some other materials studied in the Chapter 2.

In particular, DMSO and an excess of water were employed in the preparation, through the combination of self-directed assembly and an acid-catalyzed sol-gel route, of di-urea cross-linked bridged silsesquioxanes (BSs) $C_{10}C_nC_{10}$ derived from organosilane precursors including decylene chains as side spacers and alkylene chains with variable length as central spacers (EtO)₃Si-(CH₂)₁₀-Y-(CH₂)_n-Y-(CH₂)₁₀-Si(OEt)₃ (n = 7, 9-12; Y = urea group and Et = ethyl). This new family of hybrids, discussed in section

2.2, enabled us to conclude that the length of the side spacers plays a unique role in the structuring of alkylene-based BSs, although their morphology remains unaffected. All the samples adopt a lamellar structure. While the alkylene chains are totally disordered in the case of the $C_{10}C_7C_{10}$ sample, a variable proportion of all-trans and gauche conformers exist in the materials with longer central spacers. The highest degree of structuring occurs for n = 9. The inclusion of decylene instead of propylene chains as side spacers leads to the formation of a stronger hydrogen-bonded urea-urea array. The emission spectra and emission quantum yields of the C₁₀C_nC₁₀ materials are similar to those reported for di-urea cross-linked alkylene-based BSs incorporating propylene chains as side spacers and prepared under different experimental conditions. The emission of the $C_{10}C_nC_{10}$ hybrids was ascribed to the overlap of two distinct components that occur within the urea cross-linkages and within the siliceous nanodomains. Time-resolved photoluminescence spectroscopy provided evidence that the average distance between the siliceous domains and the urea cross-links is similar in the C₁₀C_nC₁₀ BSs and in oxyethylene-based hybrid analogues incorporating propylene chains as side spacers (di-ureasils), an indication that the longer side chains in the former materials adopt gauche conformations. It also allowed us to demonstrate for the first time that the emission features of the urea-related component of the emission of alkylene-based BSs depend critically on the length of the side spacers.

In section 2.3 a novel family of silsesquioxanes were prepared using as organic precursors three fatty alcohols ($C_{Y}OH$) of variable length. These compounds are suitable because the reaction of the terminal OH group with the isocyanate group of ICPTES gives rise to the urethane linkage. This new family of compounds were designated by mono-alkyl urethanesils (**m-Ut(CY)**). A first group of samples was prepared under acidic conditions (**ac**) and in the presence of a large excess of water to study the influence of the chain length giving origin to the **m-Ut(CY)-ac** group of samples. In the **m-Ut(CY)-ac** compounds with **Y** = **14**, **16** and **22** the chains adopt preferentially *all-trans* conformations, revealing an ordered structure. For **Y** = **16** the conformational changes to which the chains are subject during heating and cooling cycles were evaluated by means of DSC and FT-IR. These analyses were fundamental, since all the **m-Ut(CY)-ac** the FT-IR data exhibit hysteresis. Unlike in m-A(14),

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the order/disorder phase transition, although reversible, is not apparently timedependent. The emission quantum yields are of the same order of magnitude of that reported for the parent mono-amidosil compound.

The chain length corresponding to Y = 16 was also chosen to investigate the influence of the solvent in the structuring of the samples. Several experimental changes were introduced in the synthetic procedure (being represented by @ax where x = 1, 2 or 3). A second group of materials emerged: $m-Ut(CY)@a_x$. The experimental changes did not affect structurally the $m-Ut(CY)@a_x$ samples with x = 1 and 2. All the materials exhibit a lamellar bilayer nanostructure. The $m-Ut(CY)@a_3$ differs markedly from all the other samples. It displays order at shorter range and it is clear that its structure deserves to be studied in the near future in more depth. In terms of morphology the two series of mono-alkyl urethanesils are very attractive. We draw the attention in particular to the complex unique textures observed in m-Ut(C16)-ac and m-Ut(C22)-ac ("cabbage-like" and "desert rose-like", respectively) and in ac $Ut(CY)@a_3$ ("origami-like").

During the study of these materials many other questions were raised, related with the preparation and characterization of the samples. In terms of preparation should be interesting, for example, to inspect in the future:

- The influence of different ratios H_2O / HCl / DMSO in different steps of reaction
- The possibility of obtaining materials starting from fatty alcohols with other chain lengths or with chains comprising an odd number of carbons
- The possibility of incorporating lanthanide ions, or other cations in order to create/enlarge the range of applications

In terms of characterization it will be mandatory to characterize thermally the m-Ut(CY)@ax samples in order to check the existence of order/disorder phase transitions. Based on the systems answer to the thermal characterization many other techniques as function of temperature could be employed.

In Chapter 3 the sol-gel method was employed to prepare two series of diurethane cross-linked poly(ε -caprolactone) (PCL(530))/siloxane ormolytes doped with potassium triflate (section 3.1) and a mixture of lithium triflate / europium triflate (section 3.2). As stated before (PCL stands for the poly(ε -caprolactone) biopolymer and 530 is the average molecular weight in gmol⁻¹ (d-PCL(530)/siloxane)

In section 3.1 the KCF₃SO₃-doped di-urethane cross-linked poly(ε -caprolactone) system was studied with different concentrations of salt. The concentration was represented by n, being n the number of (C(=O)(CH₂)₅O) repeat units per K⁺ ion. In the present work we analyzed xerogels with $n = \infty$, 200, 100, 40 29, 21, 10, 4, 2, 1 and 0.5. Ormolyte samples with $n \ge 1$ are thermally stable up to 235 °C. A minor proportion of PCL crystallites occur in some dilute-to-concentrated samples. At $n \le 4$ a crystalline PCL(530)/siloxane-KCF₃SO₃ complex with unknown stoichiometry emerges. At $n \le 2$ this complex coexists with pure salt. At temperatures higher than 40 °C the composition which exhibits the highest ionic conductivity is n = 21. "Free" anions, weakly coordinated $CF_3SO_3^-$ ions, contact ion pairs and several higher ionic aggregates emerge in all the samples. The K^+ ions bond to the oxygen atoms of the carbonyl groups of the urethane and ester groups, of the PCL (530) ether chain and of the triflate ions at all salt concentrations. The ormolytes were successfully used in the production of prototype electrochromic devices (ECDs) that exhibit low switching time and good open circuit memory. The ECD incorporating the ormolyte with n = 21displayed an average transmittance in the visible region of ca. 55 % in the colored state and 76 % in the bleached state

In section 3.2. the sol-gel process was successfully combined with the "mixed cation" effect to produce novel luminescent and ion conducting biohybrids composed of a d-PCL(530)/siloxane doped with a wide range of concentrations of lithium and europium triflates (LiCF₃SO₃ and Eu(CF₃SO₃)₃, respectively) (molar ratio of *ca*. 50:50). The hybrid samples are all semi-crystalline: while at n = 52.6 and 27.0 (n, composition, corresponds to the number of (C(=O)(CH₂)₅O) repeat units of PCL(530) per mixture of Li⁺ and Eu³⁺ ions) a minor proportion of crystalline PCL(530) chains is present, at n = 6.1 a new crystalline phase emerges. The latter electrolyte is thermally stable up to 220 °C and exhibits the highest conductivity over the entire range of temperatures studied (3.7x10⁻⁷ and 1.71x10⁻⁴ Scm⁻¹ at 20 and 102 °C, respectively). According to infrared spectroscopic data, major modifications occur in terms of hydrogen bonding interactions at this composition. The electrochemical stability domain of the biohybrid sample with n = 27 spans about 5.5 V *versus* Li/Li⁺. This sample is a room temperature

white light emitter. Its emission color can be easily tuned across the Commission Internationale d'Éclairage (CIE) chromaticity diagram upon simply changing the excitation wavelength. Preliminary tests performed with a prototype electrochromic device (ECD) comprising the sample with n = 6.1 as electrolyte and WO₃ as cathodically coloring layer are extremely encouraging. The device exhibits switching time around 50 s, an optical density change of 0.15, good open circuit memory under atmospheric conditions (ca. 1 month) and high coloration efficiency (576 cm²C⁻¹).

The results obtained in this Chapter encourage us to explore the possibility of incorporating different salts or ionic liquids into d-PCL(530)/siloxane bio-hibrid in order to increase the conductivity of the materials and enlarge the applications on prototype ECDs.

Chapter 4 concerns biomineralization and the concept of organic inorganic materials are slightly different from that applied in Chapters 2 and 3. These studies involved the formation of calcium carbonate in laboratory scale through the use of different templates that tuned the characteristic morphologies of CaCO₃. The possibility of inhibiting the crystalline forms of CaCO₃ was investigated using poly(vinylpyrrolidone) as inhibitor. Unfortunattely the amorphous form of CaCO₃ was not kept longer than two days, which motivates us to continue exploring the optimal conditions necessary to retard the growth of crystalline forms and allow the further application of ACC for instance in the orthopedic field.

In section 4.1 the influence of 1-ethyl-3-methylimidazolium chloride, 1-butyl-3methylimidazolium chloride, 1-butyl-1-methylpyrrolidinium chloride, 1-ethyl-3methylimidazolium tetrafluoroborate and 1-ethanol-3-methylimidazolium tetrafluoroborate ILs on the morphology and structure of CaCO₃ was investigated in ethanolic medium using calcium chloride and ammonium carbonate as calcium and carbon sources, respectively. The syntheses were carried out at 9 °C and room temperature, at different IL concentrations and different C:Ca molar ratio.

No polymorph selectivity was detected, calcite being the only crystalline form obtained under all the reactions conditions considered. In the case of the BF₄⁻-based ILs, anion decomposition occurred, leading to the formation of fluorite. Low temperature induced a reduction of the precipitation rate.

With the ILs used the morphology of CaCO₃ was finely tailored. Calcite microcubes, microframes and microboxes, with potential application in drug delivery, as well as nanocubes and nano-corn like objects, have been produced with Cl⁻-based ILs. With BF₄⁻-based ILs, hierarchically structured materials, in which calcite coexists with fluorite, complex and intricate shapes have been produced, such as nanostructured microspheres, nanostructure jar-like micro-objects and ice-cream ball-like micro-objects.

In section 4.2 the same methodology with the same goals was employed in the preparation of other class of materials. But instead of ionic liquids were employed as templates the same fatty alcohols used in section 2.3 in the preparation of the mono-alkyl urethanesil samples.

Once again no polymorph selectivity was detected, calcite being the only crystalline form obtained under all the reactions conditions considered. The rombohedral shape of calcite was the major form found in the experiences carried out.

In section 4.3 the major goal was not completely achieved, but the analysis after one year demonstrated that the polymorph formed for all the samples under analysis, calcite, presented dimensions in the nanometric range, suggesting that PVP did not affect polymer selectivity, but influenced the size of calcite crystals. Appendix A

Résumé en français

Introduction

Pour une bonne compréhension des travaux exposés ci-dessous, des concepts de base doivent être rappelés dans un premier temps.

La chimie des matériaux occupe une place importante à l'interface de la chimie, de la physique et de la biologie. Les réactions chimiques permettent la formation de nouveaux **matériaux** qui sont caractérisés par des techniques physiques. L'inspiration par la Nature est une constante [1-3]. Beaucoup d'idées viennent de la Nature, ce qui donne lieu à des **matériaux bio-inspirés**, aussi appelés **matériaux biomimétiques**. Les matériaux naturels présentent un haut degré de sophistication, de miniaturisation (ils contiennent un maximum de fonctions élémentaires dans un petit volume) réalisant un compromis entre les différentes propriétés ou fonctions [2]. Ils montrent une complexité et une structure hiérarchique entre les échelles nanométriques, micrométriques et millimétriques. Les propriétés de la plupart des matériaux dépendent de leur **échelle** [2] et de leur **forme** [4, 5].

Un des buts principaux de la science des matériaux consiste en la production de **matériaux à structuration hiérarchique** qui sont organisés à différentes échelles. Les approches du bas vers le haut (*bottom-up*) et du haut vers le bas (*top-down*) sont employées dans la production de nanomatériaux. La stratégie *bottom-up* emploie des processus chimiques comme le sol-gel.

L'importance de la production de matériaux hybrides organiques-inorganiques [6] à structure hiérarchique et morphologie contrôlée par l'emploi des techniques **solgel** [7] et de l'**auto-assemblage** [8] a été démontrée.

Le procédé sol-gel a aussi été employé pour préparer des matériaux bio-hybrides organiques-inorganiques dopés utilisés comme couche conductrice dans des prototypes de dispositifs électrochrome, afin d'illustrer les applications potentielles des matériaux sol-gel.

Il est possible de trouver dans la Nature des exemples d'approches *bottom-up* dans la production de **biominéraux** en conditions douces. Ces biominéraux sont des composites organiques-inorganiques qui ont des propriétés intéressantes et des structures hiérarchiques contrôlées. Beaucoup d'exemples d'organismes vivants

comportant des biominéraux ont été rapportés: dans les crustacées [9-11], des cristaux intracellulaires dans les prokariotes, les exosquelettes des algues protozoa, les invertébrés, les spicules [12, 13] et lentilles[14], les os, les dents, les statolithes et les otolithes, les coquilles d'œuf, les plantes ou les structures minérales [15, 16]. Dans quelques exemples, les biominéraux formés sont si stables qu'ils ne précipitent jamais dans les conditions ambiantes [12]. La **biominéralisation** [3] peut être considérée comme un phénomène très répandu dans la Nature, permettant la formation d'une grande variété de structures inorganiques solides par des organismes vivants.

Chapitre 2: Matériaux hybrides organiques-inorganiques obtenus par les techniques sol-gel et d'auto-assemblage

Ce chapitre est divisé en trois sections, chacune correspondant à une famille différente de matériaux. Ces matériaux ont en commun qu'ils ont été obtenus par le procédé sol-gel en employant les techniques d'auto-assemblage, et qu'ils présentent des structures hiérarchiques avec des morphologies bien définies.

La première section est focalisée sur l'étude de l'influence du solvent sur la morphologie finale d'un silsesquioxane lamellaire produit à partir du précurseur **P12** ((EtO)₃Si(CH₂)₃NHC(=O)NH(CH₂)₁₂NHC(=O)NH(CH₂)₃Si(OEt)₃). Les modifications structurales observées ont été établies par différentes techniques. Un mécanisme a été proposé pour expliquer la modification de la morphologie comme une conséquence du changement de polarité du mélange de solvants.

Dans la seconde section, des silsesquioxanes pontés (BS) appelés $C_{10}C_nC_{10}$ contenant des liens urée capables d'auto-assemblage ont été synthétisés. Ils sont dérivés de précurseurs organosilanes ((EtO)₃Si-(CH₂)₁₀-Y-(CH₂)_n-Y-(CH₂)₁₀-Si(OEt)₃ (n = 7, 9-12; Y = fonction urée and Et = éthyle)) contenant des chaînes décylène comme espaceurs latéraux, et des chaînes alkylène comme espaceurs centraux. Cette nouvelle famille de silices hybrides nous a permis de conclure que la longueur des espaceurs latéraux joue un rôle unique dans la structuration des BS à base d'alkylènes, bien que leur morphologie ne soit pas altérée.

La troisième section de ce chapitre s'intéresse à une nouvelle famille de matériaux hybrides à structuration hiérarchique, appelés mono-uréthanesils, comportant des liens uréthane formés par la réaction d'une série d'alcools (C_nH_{2n+1}OH, avec n = 14, 16 et 22) avec le (3-isocyanatopropyl)triéthoxysilane. Les effets du lien uréthane et de la polarité du solvant sur la morphologie des échantillons ont été étudiés, ainsi que la possibilité d'un comportement thermique hystérétique.

2.1. Contrôle de la morphologie des silsesquioxanes lamellaires par le solvant : des plaquettes aux microéponges

Dans ce travail, nous avons pu produire un matériau hybride de type silsesquioxane ponté à partir du précurseur P12 avec une morphologie totalement inédite. La nouvelle méthode de synthèse adoptée ici est une modification de celle employée précédemment pour préparer le matériau L12, le seul changement introduit étant l'incorporation d'un large excès de DMSO dans le milieu réactionnel [17]. La présence de ce solvant a induit la formation d'un matériau (appelé L12D) avec une morphologie d'éponge. Ce matériau L12D a été synthétisé à partir d'un mélange de P12, d'eau, de DMSO et de HCl avec un rapport molaire P12: DMSO: H_2O : HCl = 1:388:527:0.175 à 80 °C. L12D a été obtenu sous la forme d'une poudre blanche après filtration, lavages et lyophilisation. Le thermogramme ATG de L12D révèle que ce matériau hybride est stable thermiquement jusqu'à 245 °C en atmosphère non oxydante. Le spectre RMN ²⁹Si CP/MAS montre des signaux à -48, -57 et -67 ppm, attribuées aux environnements T¹ (C-Si(OSi)(OR)₂), T² (C-Si(OSi)₂(OR)) et T³ (C-Si(OSi)₃) du silicium, respectivement, avec R = H ou Et). Le degré de condensation c (où c = 1/3 $(\%T^{1} + 2\%T^{2} + 3\%T^{3}))$ a été estimé à *ca* 71%. La similarité trouvée entre cette valeur et celle rapportée pour le matériau L12 [18-21] et d'autres alkylsiloxanes[22] suggère la formation d'un réseau siloxane 2D dans le silsesquioxane L12D, et par conséquence l'existence d'un polymère linéaire de liaisons siloxanes malgré l'encombrement stérique significatif induit par les groupes alkyle. Le spectre RMN ¹³ C CP/MAS de L12D présente les pics escomptés: les groups urée donnent un signal fin à 160 ppm (largeur à mi-hauteur (fwhm) = 2,2 ppm), signaux faibles à 58 et 18 ppm correspondant à quelques fragments éthoxy résiduels (CH_3CH_2-O and CH_3CH_2-O , respectivement), démontrant que l'hydrolyse a été quasi-complète, et les signaux associés aux fragments méthylène internes entre 30 et 35 ppm. Le pic à 12 ppm typique des groupes CH_2 -Si est aussi présent.

Les clichés de microscopie électronique à balayage (MEB) démontrent que, à la différence de L12 qui était obtenu sous la forme de plaquettes, L12D est produit sous la forme de sphères micrométriques de diamètre compris entre 10 et 50 μ m. Une plus grande amplification révèle clairement que ces microsphères ont une morphologie d'éponge qui consiste en des films très fins repliés et liés les uns aux autres selon un assemblage côté contre face. L'existence de films recourbés a été confirmée par microscopie électronique en transmission (MET). De façon intéressante, L12D a un caractère anisotropique qui a été démontré par des clichés de microscopie optique obtenus sous lumière polarisée (POM) entre polariseurs croisés. La bi-réfringence observée suggère une anisotropie à l'échelle sous-micrométrique. Les images par microscopie à force atomique (AFM) enregistrées en scannant la surface de L12D en mode de modulation d'amplitude, dit *tapping*, indiquent une organisation lamellaire. La périodicité discernée dans les images 2D peut aussi être observée à partir du profil. La comparaison des diffractogrammes de rayons X obtenus à partir de poudres de L12D et L12 indique que le tracé de L12D est clairement moins bien résolu que celui de L12. Le diffractogramme de L12D présente trois pics principaux à 2,17, 6,52 et 8,72 nm⁻ ¹ dans la région des petits angles, correspondant aux premier, troisième et quatrième harmoniques d'une structure lamellaire avec une distance interlamellaire caractéristique / (où / = $n 2\pi/qn$, et n est l'ordre de réflexion) de 2,85 nm. Dans la région des grands angles, le pic à 13,0 nm⁻¹ (d = 0,48 nm) est associé avec la séparation entre deux groupes urée voisins dans le réseau urée-urée auto-assemblé par liaisons hydrogène [18, 19]; la bande large proéminante à 15,1 nm⁻¹ (d = 0,42 nm) est attribuée à l'ordre dans les domaines siloxane [18, 19]. Le pic mal défini à 16,3 nm⁻¹, mais aussi l'épaulement observé à 17,0 nm⁻¹ (d = 0,39 et 0,37 nm, respectivement) donnent des informations sur la densité de l'empilement des chaînes et sur l'ordre dans les distances chaîne-chaîne dans le plan. Ce premier pic est associé avec les chaînes en conformation gauche, alors que le second est caractéristique des chaînes en conformation *all-trans* (mieux empilées, et donc plus proches) [18, 19]. Toutes les distances caractéristiques dans **L12D** indiquées ci-dessus sont en parfait accord avec celles rapportées précédemment pour **L12** [20].

Pour comprendre l'influence du DMSO sur la force des liaisons hydrogène, nous avons décidé d'éxaminer la signature spectrale de L12D dans la région 1800-1500 cm⁻¹ du spectre infrarouge à transformée de Fourier (FT-IR) et de la comparer avec celle de L12. Cette région spectrale est d'un très grand intérêt, car c'est là que les modes de vibration amide I et amide II absorbent. Le mode amide I (1800-1600 cm⁻¹) est essentiellement dû aux vibrations d'élongation C=O [23]; il est sensible à la spécificité et à l'amplitude des liaisons hydrogène. Habituellement, la bande amide I consiste en plusieurs composants distincts qui correspondent à des aggrégats ou environnements des C=O différents [23, 24]. Le mode amide II (1600-1500 cm⁻¹) est principalement associé à des vibrations de torsion dans le plan des groupes N-H, et est sensible à la fois aux conformations des chaînes et aux liaisons hydrogène intermoléculaires, donnant des informations précieuses sur la distribution en intensité des liaisons hydrogène [23]. Une analyse plus poussée des profils des bandes de L12 et L12D révèle qu'ils diffèrent de façon significative, comme conséquence d'une redistribution des composantes. En effet, la proportion d'aggrégats désordonnés responsables de la composante à 1647 cm⁻¹ [18] augmente dans L12D aux dépens de la destruction des aggrégats ordonnés qui donnent la composante à 1625 cm⁻¹ [18]. En conséquence, la surface correspondant au composant amide II à 1564 cm⁻¹ augmente, alors que celle à 1583 cm⁻¹ diminue. Ces résultats sont en faveur de l'explication dans laquelle l'addition de DMSO dans le milieu réactionnel a pour conséquence la formation d'aggrégats urée-urée moins ordonnés [18]. Une explication mécanistique basée sur les propriétés physico-chimiques de ces deux solvants a été proposée pour expliquer les différences observées dans la morphologie finale de L12 et L12D. Par rapport au DMSO, qui est aprotique, l'eau est un solvant à plus haute constante diélectrique ($\varepsilon_{20 \circ C}$ = 46,68 and 80,10, respectivement), mais avec un moment dipôlaire plus faible ($\mu_{25 \circ C}$ = 4,1 D and $\mu_{20 \text{ °C}}$ = 1,87 D, respectivement). De plus, les deux solvants ont des indices de polarité importants (7,2 et 10,2, respectivement). La constante diélectrique du mélange eau/DMSO utilisé dans cette étude (ratio molaire 527/328) a été estimée à 68 ± 6 [25] Nous pensons que la cause de cette différence de morphologie entre L12 et L12D est à trouver à un stade avancé du mécanisme réactionnel. Dans la première étape de la

procédure, l'hydrolyse acide de P12 conduit à la formation d'un composé amphiphilique bis(silanetriol). Des interactions intermoléculaires fortes entre molécules voisines, telles que les liaisons hydrogène entre les groupes urée ou entre les fonctions silanol [26], mais aussi les interactions de van der Waals entre les chaînes alkyle promeuvent la formation du réseau siloxane, menant finalement à la formation et à l'organisation de rubans lamellaires fins. L'influence de la nature du solvant dans la structuration des matériaux dérivés de P12 à l'échelle micrométrique devrait s'opérer à cette étape. Une explication plausible pour la différence de morphologie est la suivante: dans l'eau, les interactions hydrophobes entre les chaînes alkyle promeuvent un empilement face contre face des rubans lamellaires, menant finalement à la formation de plaquettes 3D (L12). Un tel empilement est favorisé par la forte mobilité des charges et les faibles répulsions entre rubans chargés qui ont lieu dans l'eau. A l'opposé, le DMSO interagit avec les chaînes alkyle lipophiles en stabilisant les rubans qui grandissent. De plus, la faible mobilité des charges dans le mélange DMSO/eau et la plus faible constante diélectrique défavorisent les empilements face contre face, en privilégiant les approches face contre côté entre les rubans chargés, ce qui conduit au final à des micro-objets ressemblant à des éponges (L12D). Le repliement des films, qui est rendu possible par leur faible épaisseur, contribue à la morphologie finale observée.

2.2. Auto-structuration de silsesquioxanes pontés lamellaires comportant des espaceurs latéraux longs

Dans cette section, nous avons étudié l'influence des espaceurs latéraux sur la structuration, la morphologie, et finalement les propriétés optiques des matériaux dérivés de **P12**. Nous avons pour cela étudié une série de matériaux hybrides à base de chaînes alkylène (appelés **C**₁₀**C**_n**C**₁₀) dérivés de précurseurs de silsesquioxanes similaires au **P12**, mais incluant des espaceurs latéraux composés de chaînes décylène au lieu de propylène ((EtO)₃Si-(CH₂)₁₀-Y-(CH₂)_n-Y-(CH₂)₁₀-Si(OEt)₃ avec n = 7, 9-12 (**P10-n-10**)). La structure des matériaux finaux a été inspectée par RMN ²⁹Si MAS et ¹³C CP/MAS. Dans le spectre RMN ²⁹Si MAS, les matériaux donnent trois signaux larges à -47, -58 et -68

ppm, attribués aux environnements T^1 , T^2 et T^3 du silicium, respectivement. Les degrés de condensation calculés sont du même ordre que ceux rapportés précédemment pur le matériau **L12** [20, 27, 28] et plus récemment pour le matériau **L12D** à morphologie d'éponge (cf Section 2.1) [29]. Ces résultats suggèrent que dans $C_{10}C_nC_{10}$ les ponts siloxane sont inclus dans un réseau 2D composé de polymères linéaires de siloxane. En RMN ¹³C CP/MAS, il est possible de distinguer les signaux attendus (cf Table 2.2.1, section 2.2), ce qui confirme la structure des matériaux finaux.

Les images MEB donnent la preuve que la morphologie de C10CnC10, qui varie entre de micro-objets irréguliers à des microparticules sphéroïdales denses, diffère clairement de la morphologie de plaquettes des matéraiux L8-L12, mais ressemble à celle de L12D. L'analyse des clichés de MEB révèle que la morphologie de C₁₀C₇C₁₀ est plutôt irrégulière, alors que celle des échantillons C10C9C10 et C10C10C10 ressemble beaucoup à celle de L12D. Ces deux matériaux forment des micro-objets avec une morphologie d'éponge, et consistent en de très fins rubans assemblés côté contre face (n=9), ou en des rubans recourbés et enchevêtrés (n=10). Pour C₁₀C₁₁C₁₀, les rubans semblent considérablement plus repliés, et forment des objets moins réguliers. Le processus finit avec C10C12C10 et la production de particules sphéroïdales homogènes denses de 10 μ m de diamètre qui tendent à se lier les unes aux autres. La contribution croissante du processus de repliement auquel les films sont sujets lorsque la longueur de l'espaceur central augmente est clairement reconnaissable dans les images de MET. L'organisation intrinsèque dans les films/rubans est parfaitement évidente dans le cas des échantillons avec n = 9, n = 10, et n = 12. Des preuves additionnelles de la texture organisée de C10C12C10 et en particulier de C10C10C10 ont été obtenues par AFM en scannant la surface des échantillons en mode tapping. Le mode d'organisation observé dans les deux derniers matériaux est cependant moins bien reconnaissable dans le cas du matériau avec n = 9. La nature anisotropique de $C_{10}C_{10}C_{10}$ est démontrée dans l'image de POM enregistrée entre polariseurs croisés. La biréfringence observée indique une anisotropie sous-micrométrique. Les diffractogrammes de rayons X des différents échantillons montrent des profils complètement différents dans la région des grands angles (q > 10 nm⁻¹). Alors que le matériau $C_{10}C_7C_{10}$ produit un pic large, mal défini centré à environ 15 nm⁻¹, le maximum d'intensité de la bande est décalé vers 15,7 nm⁻¹ pour n = 9 et 11, et un épaulement est visible du côté des plus petits angles, en particulier dans le cas de ce dernier. Dans le cas du silsesquioxane ponté avec l'espaceur central le plus long ($C_{10}C_{12}C_{10}$), le profil de la bande devient mieux résolu, et deux pics centrés à 14,7 et 16,2 nm⁻¹ sont discernés. La modélisation des courbes, réalisée entre 12 et 19 nm⁻¹ par des Gaussiennes nous a permis d'identifier quatre composants dans le profil des diffractogrammes des échantillons avec n = 7, 9, 11 et 12, attribuables à la séparation entre deux fragments urée adjacents du réseau urée-urée formé par l'intermédiaire de liaisons hydrogène (**U**), à l'ordre entre au sein du domaine siloxane (**S**) et aux espacements chaîne-chaîne (**c-c**). Les valeurs correspondantes sont rapportées dans la Table A.1.

Région des grands angles (q > 10 nm ⁻¹)							
<i>q</i> (nm⁻¹)	d (nm)	Attribution					
13.54	0.464	U					
14.65	0.429	S					
15.85	0.392	C-C					
17.15	0.366	C-C					

Table A.2.1. Données de PXRD pour la région des grands angles des échanillons C10CnC10.

L'analyse de la région des petits angles des diffractogrammes XRD et SAXS permet de trouver des indications précieuses sur la conformation des chaînes alkyle. En comparant les distances interlamellaires / dérivées des données de SAXS pour les matériaux **C**₁₀**C**_n**C**₁₀ (avec n = 9, 10, et 12) avec les longueurs calculées pour les chaînes alkylène des espaceurs centraux et latéraux adoptant des conformations totalement étirées *all-trans* (en zig-zag), nous pouvons conclure que les conformères *all-trans* et *gauche* coéxistent dans les échantillons. Nous pouvons de plus conclure qu'il n'y a pas de relation linéaire entre l'augmentation de la longueur de chaîne de l'espaceur central de **C**₁₀**C**₉**C**₁₀, **C**₁₀**C**₁₀**C**₁₀ et **C**₁₀**C**₁₂**C**₁₀ et la déviation des valeurs longueur expérimentales de la longueur *I* de celles calculées pour des chaînes alkylène parfaitement étirées *all-trans*. Ainsi, il apparait clairement qu'avec l'introduction de groupes méthylène supplémentaires dans l'espaceur central, la proportion de conformères *gauche*

augmente et que les chaînes alkylène deviennent moins bien empilées. C'est un processus qui mène au final vers la compression des domaines silylés. Sur la base de ces données, il est raisonnable de penser que les chaînes alkylène des matériaux $C_{10}C_nC_{10}$ avec n= 9, 10, et 12 sont très probablement orientés de façon non-perpendiculaire par rapport aux plans des réseaux siloxane. Les données de RMN CP/MAS du ¹³C corroborent les conclusions des expériences de SAXS.

Afin d'avoir une meilleure appréhension du degré d'empilement régulier des chaînes et du rapport conformationnel trans/gauche dans les matériaux hybrides C10CnC10, nous avons enregistré les spectres FT-IR et FT-Raman et examiné les modes diagnostiques des chaînes alkylène: (1) les modes d'élongation CH₂ symétrique et antisymétrique (v_sCH_2 and v_aCH_2 , respectivement). (2) Le mode de torsion CH₂ (δCH_2). L'analyse de la localisation et l'intensité du mode v_sCH_2 est rendue compliquée à cause de la résonnance de Fermi entre le mode fondamental de v_sCH₂ avec les nombreux harmoniques des vibrations δCH_2 [27, 30-33]. Le mode v_aCH₂ est affecté par le couplage avec les mouvements de rotation et de torsion des chaînes [27-30]. Dans le spectre Raman des chaînes alkyle ordonnées (conformation *all-trans*), le mode v_aCH_2 émerge comme une bande intense dans l'intervalle 2884-2878 cm⁻¹, alors que le mode v_{s} CH₂ produit une bande à 2930 cm⁻¹ (faible), 2900-2898 cm⁻¹ (moyen) et 2850-2844 cm⁻¹ (fort) [27-30]. Dans le cas des chaînes alkylène (en conformation *gauche*), le mode v_a CH₂ apparaît à 2897-2890 cm⁻¹, et les bandes v_s CH₂ sont typiquement observées à 2920 cm⁻¹ (moyen), 2904 cm⁻¹ (moyen) et 2858-2853 cm⁻¹ (fort) [27-30]. Un décalage vers les hauts nombres d'ondes, et un élargissement des bandes indiquent une proportion croissante des conformères qauche. Les spectres FT-Raman dans la région des vCH₂ des matériaux C₁₀C_nC₁₀ avec n pair ou impair sont dominés par deux bandes à 2885 cm⁻¹ (très fort, vS)/ 2837 cm⁻¹ (fort, S) et 2884 cm⁻¹ (vS)/2858 cm⁻¹ (S), respectivement. Dans les deux cas, un évènement intense, qui se manifeste comme un épaulement et est localisé à 2850 et 2848 cm⁻¹, respectivement, est discerné. Les pics à environ 2885 et 2859 cm⁻¹ sont attribuables aux modes v_aCH_2 and v_sCH_2 des conformères all-trans des chaînes alkylène [34,35]. La composante à ca 2858 cm⁻¹, aussi associée avec le mode v_sCH₂ est caractéristique des conformères gauche [35]. Le rapport des hauteurs de pics (r) entre les bandes v_aCH_2 and v_sCH_2 est un outil de choix

pour déterminer le désordre conformationnel des chaînes alkylène et leur arrangement par empilement [31]. Des hautes valeurs de r (1.61-1.72) sont produites par des chaînes alkylène cristallines, tandis que les chaînes à l'état amorphe conduisent à des valeurs qui vont de 1.39 à 1.48 [31]. La représentation du rapport des intensités r en fonction du nombre d'atomes de carbone des chaînes alkylène de l'espaceur central des matériaux C₁₀C_nC₁₀ suggère que les chaînes alkylène de l'échantillon C₁₀C₇C₁₀ (*i.e.* les chaînes des espaceurs latéraux et celles des espaceurs centraux) sont complètement désordonnées et par conséquent adoptent des conformations gauche. Dans les matériaux hybrides avec un espaceur central plus long (n > 7) la proportion des chaînes alkylène densément empilées et totalement étirées (conformères all-trans) est augmentée considérablement. Pour C10C9C10 la valeur atteinte pour r coïncide pratiquement avec la valeur minimum rapportée pour les alcanes linéaires solides, ce qui suggère que la présence des chaînes décylène latérales et d'une chaîne centrale nonylène promeut un haut degré d'ordre et un empilement serré. De plus, ces données pointent aussi le fait que les matériaux avec n = 10, 11 et 12 contiennent plus de conformères gauche que C10C9C10. L'inspection de la région des δCH_2 est aussi très intéressante, puisque la fréquence, l'intensité, et la forme de la bande du mode δCH_2 sont sensibles aux interactions interchaînes et au mode d'empilement des chaînes [35, 36]. Les plus hautes fréquences (~1472 cm⁻¹) dans le spectre IR indiquent un ordonnement des chaînes alkylène en conformation all-trans (état cristallin), tandis qu'à des fréquences plus basses (~1466 cm⁻¹), un élargissement des bandes et une intensité plus faible indiquent une augmentation de la mobilité des chaînes, (état proche du liquide) et donc un rapport gauche/trans plus élevé [35].

Les bandes centrées à environ 1479 et 1466 cm⁻¹ dans la région des δ CH₂ du spectre FT-IR des hybrides **C**₁₀**C**_n**C**₁₀ révèlent l'occurrence de chaînes alkylène ordonnées mais aussi désordonnées, et donc la coexistence de conformères *all-trans* et *gauche* [35, 37]. La bande située à environ 1440 cm⁻¹ discernée dans le même spectre représente une preuve supplémentaire de l'existence d'arrangements *gauche*, [38,39]. Le mode δ CH₂ est sensible à la parité du nombre d'atomes de carbone de l'espaceur central. Alors que les matériaux **C**₁₀**C**_n**C**₁₀ avec un nombre *n* impair montrent un épaulement à environ 1460 cm⁻¹, cette contribution est absente dans le cas des

échantillons avec un nombre *n* pair. Un effet similaire a été rapporté pour les matériaux voisins **L8-L12** [40].

Les spectres d'émission des échantillons sélectionnés $C_{10}C_nC_{10}$ sont pratiquement indépendants de la longueur de l'espaceur alkylène central, et similaires à ceux rapportés pour les matériaux hybrides contenant des espaceurs latéraux propylène comme le silsesquioxane ponté non structuré A12 [19], les di-uréasils [41, 42], les diuréthanesils [43], les di-amidosils, et les mono-amidosils structurés en bicouches lamellaires[45]. L'émission est attribuée au recouvrement de deux composantes distinctes qui ont proviennent des réseaux urée, uréthane ou amide dans le cas des diuréasils, di-uréthanesils et amidosils, respectivement, et des nanodomaines silylés. Les données de spectroscopie en temps résolu nous ont permis de démontrer pour la première fois que les caractéristiques d'émission de la composante liée aux groupes urée de l'émission des silsesquioxanes structurés par liaisons hydrogène entre les fragments urée dépend de façon critique de la longueur des espaceurs alkylène latéraux. Cela nous a permis de déduire que la distance moyenne entre les régions silylées et les liens urées est pratiquement la même dans les silsesquioxanes à chaîne latérale propyle ou décyle, ce qui suggère que les chaînes latérales longues adoptent préférentiellement des conformations gauche. Les spectres d'excitation des matériaux C10CnC10 ressemblent à ceux de A12 [19]. Cependant, alors que le temps de vie des composantes liées au réseau siloxane ressemble à ceux mesurés pour les di-uréasils, le temps de vie de la composante liée aux urées est bien plus court, ce qui témoigne du rôle crucial joué par les espaceurs longs dans la dynamique des deux émissions.

Le rendement quantique absolu d'émission de C₁₀C₁₁C₁₀ est considérablement plus faible que la valeur la plus haute rapportée pour les matériaux dérivés de P12 (A12), mais, à la différence de ce dernier, est constant dans le temps.

2.3. Synthèse de matériaux hybrides mono-alkyl-uréthanesils à structuration hiérarchique

Dans cette partie, nous souhaitons étudier une nouvelle famille de composés hybrides à structuration hiérarchique appelés mono-alkyl uréthanesil. Cette famille de composés a été préparée par réaction d'une série d'alcools (C_YOH, avec Y=14, 16 et 22) avec le (3-isocyanatopropyl)triéthoxysilane, ce qui permet la formation de liens uréthane. Les effets de la nature du lien et de la longueur de la chaîne alkyle ont été évalués. Pour plus de simplicité, les matériaux seront appelés **m-Ut(CY)-ac** (Y = 14, 16 et 22). Nous souhaitons aussi évaluer l'effet de l'incorporation d'un co-solvant (DMSO) sur la morphologie finale, d'où la synthèse d'un autre lot de matériaux préparés pour une longueur de chaîne donnée (Y = 16), en employant le DMSO comme co-solvant sous différentes conditions. Ces échantillons seront appelés **m-Ut(C16)-@a_x** (avec @a_x = @a_x, @a_x and @a_x qui représentent les différentes conditions expérimentales employées pour la préparation des échantillons) (Cf section 2.3 pour les détails expérimentaux).

Les spectres RMN ²⁹Si CP MAS ont été étudiés: tous les échantillons produisent des pics centrés à -47 (T^1), -57 (T^2) et -67 (T^3) ppm, sans qu'il ne reste de pic à -46 ppm caractéristique des environnements T^0 . L'absence d'atome de silicium de type Q démontre la préservation totale des liaisons Si-C. Les signaux T¹ sont plus intenses dans le matériau @a2. L'échantillon @a3 est dominé par les environnements T³. Les degrés de condensation sont plus hauts que ceux rapportés précédemment pour L12 (64-67%) [18], mais sont similaires à ceux rapportés pour L12D [29], pour les matériaux C10CnC10 [46] (Section 2.2) et pour les mono-uréthanesils (74%) [47]. En analysant les spectres RMN¹³ C CP MAS, il apparaît que les groupes uréthane, les liaisons Si-C et C-O ont été préservés au cours de la synthèse. En effet, la préservation des liens uréthane dans les matériaux finaux est prouvée par le signal à 160 ppm, alors que les signaux associés avec les chaînes propylène sont centrés aux environs de 44, 24 et 10 ppm. Le signal observé à 64 ppm est attribué au groupe méthylène CH₂-O, ce qui correspond à la valeur de 65 ppm trouvée dans le spectre en solution (CDCl₃) du précurseur. Le signal à 14 ppm est attribué au CH₃ terminal de la chaîne alkyle. Pour les échantillons avec Y = 14, 16 et 22, la résonnance centrée à 33.0 ppm est typique de structures ordonnées. Cette tendance générale est aussi observée pour les échantillons @a1 et @a2 pour lesquels le signal principal est centré à 33 ppm. Pour les échantillons y = 14 et @a₃, un épaulement à 30 ppm indique la présence de conformations gauche. L'échantillon @a₃ présente un profil complètement différent, et mieux résolu. Des indications supplémentaires sur les conformations des chaînes peuvent être obtenues par
spectroscopie FT-IR dans les régions correspondant à l'élongation et à la torsion des groupes CH₂. Comme dans les parties précédentes (2.1 et 2.2), la spectroscopie FT-IR a aussi été employée pour analyser les régions amide I et amide II [43, 48]. Ici, ces régions correspondent aux groupes uréthane. Le profil global des spectres dans cette région est similaire pour tous les échantillons (avec une légère différence pour @a₃ où un épaulement important est visible à 1650 cm⁻¹). Les diffractogrammes de rayons X sur poudre ont été analysés dans la région des grands angles (> 10 nm) et des petits angles (< 10 nm). Aux grands angles, des informations sur les distances uréthane-uréthane (**U**), les répétitions ordonnées dans les réseaux siloxane (**S**), et les distances chaîne-chaîne (c-c) peuvent être obtenues. Il est à noter que l'échantillon @a₃ présente une structure hautement cristalline.

Le comportement thermique des matériaux m-Ut(CY)-ac a été analysé par les techniques TGA et DSC. Les courbes d'analyse thermogravimétrique des échantillons m-Ut(CY)-ac avec Y = 14, 16 et 22 démontrent que les matériaux sont stables thermiquement jusqu'à 250 °C; il est possible de distinguer des pics endothermiques dans les courbes de DSC avec des températures de transition différentes de celles des précurseurs. Ces transitions nous ont conduits à réaliser des analyses FT-IR à température variable. Les spectres FT-IR de l'échantillon m-Ut(C16)-ac ont été enregistrés en fonction de la température, avec des cycles de réchauffementrefroidissement afin de détecter un éventuel comportement hystérétique. A température ambiante, la bande v_aCH_2 est située à 2916 cm⁻¹, fréquence caractéristique des v_aCH₂ des alcanes linéaires. Dans la phase de montée en température, au dessus de la température critique (onset) de transition de m-Ut(C16)ac (68 °C), la band est décalée vers de plus hauts nombres d'onde. Dans la phase de refroidissement, la fréquence de v_aCH₂ retrouve sa valeur initiale, ce qui démontre clairement que m-Ut(C16)-ac présente un comportement hystérétique réversible quand l'échantillon revient à température ambiante.

Les variations dans les conditions expérimentales ont un impact sur les morphologies à l'échelle du nanomètre. A l'échelle micrométrique, tous les matériaux sont biréfringents lorsqu'on les observe en POM entre polariseur et analyseur croisés. Les images de MEB montrent que pour Y = 14, des "feuilles" avec des dimensions de 20-30 μ m sont obtenues. Tous les échantillons sont lamellaires, mais lorsque l'on

compare Y = 14 avec Y = 16, le premier présente une morphologie sans caractéristique particulière, alors qu'une amplification forte du second permet de distinguer des paquettes fines qui semblent cristallines, avec une épaisseur de l'ordre du nanomètre et des dimensions latérales de l'ordre du micromètre. Leur assemblage résulte en une morphologie de "chou rouge". L'empilement de plaquettes fines est aussi visible dans l'image AFM obtenue en mode tapping. Le balayage d'une section de l'échantillon Y = 22 révèle deux orientations perpendiculaires pour les plaquettes, ce qui pourrait expliquer les données recueillies en XRD et DSC. Cette morphologie est de type "rose des sables". Les matériaux m-Ut(C16)@an révèlent l'influence des conditions expérimentales sur la morphologie. Tous ces échantillons sont composés de plaquettes fines micrométriques, mais par exemple, l'échantillon préparé en l'absence de catalyseur HCl (@a₂) est organisé de façon aléatoire. Pour @a₁, il est possible d'observer des morphologies distinctes selon l'amplification employée. Pour les plus faibles grossissements, la morphologie de "rose des sables" est discernable, comme nous l'avions décrite pour m-Ut(C22)ac. A plus fort grossissement, les microplaques sont parfaitement ordonnées, de façon parallèle.

En photoluminescence, les spectres d'émission et d'excitation, mais aussi les rendements quantiques d'émission ont été étudiés. Les valeurs de rendement quantique sont inférieures à 0.11 pour tous les échantillons étudiés, et sont peu affectés par les variations étudiées (longueur de chaîne, conditions expérimentales).

Chapitre 3: Systèmes biohybrides organiques-inorganiques à application potentielle comme dispositifs électrochromes

Le chapitre 3 est dédié à l'étude de prototypes de dispositifs électrochromes. Un dispositif électrochrome conventionnel comporte trois éléments principaux arrangés en une structure en couche de type sandwich composée d'une électrode électrochrome et d'une contre électrode séparés par un électrolyte solide (par exemple un polymère conducteur contenant des ions Li⁺, K⁺ or H⁺) (schéma A.1).



Schéma A.1. Exemple représentatif de dispositif électrochrome utilisé: verre/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/verre (polarité associée à l'état coloré).

Au cours des années précédentes, le procédé sol-gel est devenu une voie de synthèse populaire pour la fabrication de dispositifs électrochromes [49-53]. La méthode sol-gel offre de nombreux avantages par rapport aux techniques traditionnelles utilisées dans le contexte des technologies de revêtement: (1) un degré élevé d'homogénéité des films est atteint, car les précurseurs sont mélangés au niveau moléculaire; (2) les précurseurs sont relativement peu onéreux, et une grande variété d'entre eux est disponible dans le commerce; (3) les équipements de dépôt sont relativement peu chers, et des grandes surfaces de revêtement peuvent être déposées grâce à quelques techniques comme les dip-coating et spray coatings.

Une commutation persistante et réversible de couleur a lieu en chargeant/déchargeant la cellule électrochimique lors de l'application d'une différence de potentiel. Les états colorés et transparents des dispositifs électrochromes sont habituellement appelés "écrits" (*written*) et "décolorés" (*bleached*), respectivement. Les matériaux électrochromes peuvent opérer soit en mode de réflexion (pour l'affichage), ou de transmission (pour les fenêtres "intelligentes"). Une caractéristique importante des dispositifs électrochromes lorsqu'ils sont colorés est que la couleur peut être préservée lorsque le courant est éteint. Cet effet mémoire en fait des dispositifs efficaces en énergie.

En vue d'une utilisation potentielle comme électrolytes pour des dispositifs électrochromes, nous montrerons dans ce chapitre la préparation et la caractérisation de deux nouvelles séries de biohybrides dopés soit au triflate de lithium (Chapitre 3.1), soit avec un mélange de triflate de lithium et de triflate d'europium 1:1 (Chapitre 3.2). Ces biohybrides sont composés de silsesquioxanes pontés comportant comme fragment organique pontant un segment poly(ε -caprolactone) (PCL 530 M_n = 530 g mol⁻¹) lié au réseau siloxane par des liens uréthane. Cette étude vient en continuation d'explorations préliminaires basées sur les systèmes PCL(530)/siloxane dopés au triflate de lithium ou au triflate de magnésium.

La haute conductivité ionique montrée par les polyélectrolytes classiques à base de poly(oxyéthylene) (POE) incorporant des ions K^+ ont motivé l'emploi du triflate de potassium pour doper les biohybrides d-PCL(530) (Section 3.1)[54-57]. Le choix des sels dans la section 3.2 a été stimulé par l'*effet de mélange cationique (mixed cationic effect*) [58], qui implique classiquement l'utilisation de deux sels au lieu d'un seul (c'est une procédure attractive qui a habituellement pour conséquence une augmentation de la conductivité ionique des polyélectrolytes). Nous souhaitons de plus obtenir une luminescence importante pour produire des matériaux biohybrides multifonctionnels éco-compatibles avec simultanément des propriétés de luminescence et de conductivité ionique. Nous avons alors décidé d'employer les triflates d'europium et de lithium (Section 3.2).

Le poly(ε -caprolactone) (PCL) est un polyester linéaire qui a été choisi car c'est un biopolymère extrêmement attractif, bien que synthétique. C'est un thermoplastique aliphatique, biocompatible, perméable, hydrophobe, biodégradable et non toxique pour les organismes vivants, qui peut être résorbé par l'organisme après un certain temps postérieur à l'implantation. Les PCL et leurs copolymères ont des applications potentielles dans le domaine de la médecine comme fils de suture biodégradables, peau artificielle, prothèses résorbables et comme conteneurs pour la libération contrôlé de médicaments [59-61]. Les hybrides PCL/silice pourraient trouver des applications comme bio-verres dégradables, comme matériaux de revêtement pour les implants d'os et autres dispositifs prothétiques, comme supports pour l'immobilisation d'enzymes [62], et même comme substituts d'os [63].

Les structure, morphologie, stabilité thermique, conductivité ionique et stabilité électrochimique des deux séries de matériaux ont été caractérisées. Des études exploratoires ont été entreprises sur les performances des prototypes de dispositifs électrochromes dans lesquels les biohybrides organiques-inorganiques de composition optimisée ont été utilisés comme couche active conductrice d'ions. Ces dispositifs ont été caractérisés selon différents paramètres: le contraste électrochrome, changement de densité optique, temps de commutation, et mémoire en circuit ouvert. L'efficacité de coloration pour le prototype exploré dans la section 2.2 a aussi été étudié.

3.1. Electrolytes biohybrides poly(ε-caprolactone)/siloxane dopés K⁺ pour les dispositifs électrochromes

Biohybride à base de d-PCL(530)/siloxane dopé au KCF₃SO₃

Afin de préparer des biohybrides à base de d-PCL(530)/siloxane dopés au KCF₃SO₃ nous avons appliqué une méthode de synthèse décrite par ailleurs [63], qui est une modification de celle rapportée pour l'analogue dopé au triflate de lithium [64] [64]. Les matériaux ont été obtenus sous la forme de monolithes transparents et flexibles Ces ormolytes ont été identifiés en utilisant la notation d-PCL(530)/siloxane_nKCF₃SO₃. Des xérogels avec n = ∞ , 200, 100, 40, 29, 21, 10, 4, 2, 1 et 0 ont été produits.

Les diffractogrammes des échantillons avec $n = \infty$, 100 and 40 révèlent que ces xérogels sont complètement amorphes. L'échantillon dilué avec n = 200 donne lieu à un pic à 21,4°, qui est caractéristique du PCL(530). La même caractéristique apparaît comme un pic mal défini dans le profil XRD des matériaux avec n = 21 et 10. Pour n = 29 et 21, une réflexion de Bragg de nature inconnue émerge à 28.5°. L'échantillon concentré avec n = 4 produit une série de pics faibles qui ne correspondent pas à ceux du sel pur ou du PCL(530). Nous les avons associé avec la formation d'un complexe d-PCL(530)/siloxane-KCF₃SO₃ cristallin de stœchiométrie inconnue. Dans les échantillons les plus riches en sel, avec n = 2, 1 et 0.5, ce composé cristallin coexiste avec le sel pur. Les clichés de MEB obtenus sont en parfait accord avec les données de diffraction des rayons X; celles de DSC corroborent aussi ces conclusions. Les données d'analyse thermogravimétrique nous ont permis de déduire que la décomposition des xérogels avec $1 < n < \infty$, est initiée à la même température (environ 235 °C), ce qui est une indication que la stabilité thermique du réseau PCL(530)/siloxane sous atmosphère

non oxydante n'est pratiquement pas affectée par la présence de quantités croissantes de KCF₃SO₃. Les données de conductivité révèlent que dans ce système électrolyte hybride les échantillons de composition entre n = 4 et 21 ont les meilleures conductivités sur l'ensemble de la gamme de température analysée. A 40 °C, les maxima de de conductivité coïncident, alors qu'à plus haute température le matériau avec n = 21 donne des valeurs sensiblement plus hautes que les autres.

Afin de clarifier la relation entre conductivité ionique et association ionique, nous avons décidé d'inspecter l'environnement chimique ressenti par les ions K⁺ et CF₃SO₃⁻ dans le milieu d-PCL(530)/siloxane sur l'ensemble de l'intervalle de concentration considéré. La modélisation des bandes IR, réalisée sur l'intervalle 1800-1650 cm⁻¹ nous a permis de résoudre le profil de la courbe de l'hybride d-PCL(530)/siloxane en 4 composantes distinctes localisées à environ 1762, 1736, 1720 et 1692 cm⁻¹ [63, 65]. La bande à 1762 cm⁻¹ est associée avec la présence de groupes carbonyles "libres" (non associés par liaisons hydrogène) des liens uréthane. La composante à 1736 cm⁻¹ est caractéristique des chaînes du PCL(530) amorphe. Celle à 1720 cm⁻¹ est attribuée à la présence d'associations oxyéthylène/uréthane par liaisons hydrogène, tandis que celle à 1692 cm⁻¹ est assignée à la formation d'agrégats uréthane/uréthane et uréthane/ester [63, 65]. L'étude de l'environnement anionique a été réalisée en utilisant la spectroscopie FT-Raman. Nous avons examiné la région spectrale caractéristique du mode de vibration par élongation des groupes SO₃ [66, 67] Le mode v_sSO₃ des ions triflates libres donne une bande à 1032 cm⁻¹. La région des v_sSO₃ en FT-Raman a été décomposée en plusieurs pics. La bande proéminente pour les échantillons les plus dilués est celle à 1032 cm⁻¹. Cette caractéristique, présente sur l'ensemble de l'intervalle de concentration considéré, confirme la présence d'anions libres, et possiblement des paires d'ions "cross-link separated ion pairs". Les composantes à 1038 et 1024 cm⁻¹, aussi détectées pour tous les échantillons, sont associés avec des ions triflate faiblement coordinés et localisés dans deux types de sites: (1) des espèces CF₃SO₃⁻ faiblement liées aux ions K⁺, qui interagissent simultanément avec l'atome d'oxygène des carbonyles des groupes uréthane; (2) les ions CF₃SO₃⁻ liés par liaison hydrogène aux groupes N-H des uréthanes. La composante à 1045 cm⁻¹, que l'on trouve dans tous les spectres FT-Raman, est associée à l'existence de paires d'ions en contact. Les composantes observées dans le spectre de l'hybride avec n = 40 à 1069, 1059 et 1052 cm⁻¹ sont provisoirement attribués à la formation de plus grands agrégats ioniques.

Caractérisation des dispositifs électrochromes

Trois dispositifs électrochrome avec des concentrations différentes (n) de d-PCL(530)/siloxane_nKCF₃SO₃ été l'hybride ont preparés. Les dispositifs verre/IZO/WO₃/d-PCL(530)/siloxane_nKCF₃SO₃/IZO/verre avec n = 29, 21 et 4 ont été caractérisés en terme de contraste électrochromique, (pourcentage de variation de transmittance (ΔT) en % à une longueur d'onde déterminée où sur un intervalle de longueurs d'onde), de changement de densité optique ($\Delta(OD) = -\log(T_{coloré}/T_{décoloré}))$, de temps de commutation (le temps nécessaire pour finaliser le processus de coloration/décoloration) et de mémoire en circuit ouvert (la capacité à maintenir l'état d'absorption quand le courant est éteint). Les spectres de transmission ont été enregistrés sur l'intervalle 325-700 nm pour les dispositifs verre/IZO/WO₃/d- $PCL(530)/siloxane_nKCF_3SO_3/IZO/verre avec n = 29, 21 et 4 dans les états "juste$ déposé", décolorés et colorés. Le ∆T moyen dans la région du visible (400-700) et la variation de densité optique $\Delta(OD)$ montrés par les trois dispositifs sont listés dans la Table A.3.1. La mémoire électrochrome des dispositifs verre/IZO/WO₃/d-PCL(530)/siloxane_nKCF₃SO₃/IZO/verre avec n = 4 et 29 a été évaluée, ce qui a montré qu'après 10 jours les deux dispositifs n'ont pas atteint l'état non-coloré correspondant à l'état "juste déposé".

Table A.3.1. Transmittance spectral moyenne (Δ T) et densité optique (Δ OD) obtenue par les
dispositifs électrochromes à base du biohybride d-PCL(530)nKCF3SO3.

n	Т (%)			∆T(%)	$\Delta OD_{\lambda = 555 \text{ nm}}$
	Juste déposé	décoloré	coloré	-	
29	76.4	74.6	57.0	17.6	0.13
21	76.7	75.6	55.0	20.6	0.16
4	77.7	76.5	60.1	16.4	0.11

Electrolytes biohybrides poly(ε-caprolactone)/siloxane dopés Li⁺- et Eu³⁺pour les dispositifs électrochromes

<u>Biohybrides poly(ε-caprolactone)/siloxane dopés Li⁺- et Eu³⁺-</u>

Les matériaux étudiés ici ont été nommés d'après la notation PCL(530)/siloxane_nLi_mEu_{m'}, où n (appelé composition) correspond au nombre d'unités de répétition (C(=O)(CH₂)₅O) du PCL(530) par mélange d'ions Li⁺+Eu³⁺ et m et m' représentent les compositions individuelles de LiCF₃SO₃ et Eu(CF₃SO₃)₃, respectivement. Des xérogels avec n = 52,6 (m = 99, m' = 111), 27,0 (m = 50, m' = 56), 6,1 (m = 12 et m' = 12) et 3,2 (m = 6, m' = 7) ont été produits. Les propriétés thermiques (DSC et TGA), structurales (XRD et spectroscopie FT-IR), électrochimiques (conductivité ionique et voltamétrie cyclique) et de luminescence d'une nouvelle série de biohybrides PCL(530)/siloxane à liens urethane dopés LiCF₃SO₃ et Eu(CF₃SO₃)₃ ont été étudiées.

Les données d'analyse thermogravimétrique démontrent que la dégradation matériaux hybrides $PCL(530)/siloxane_{52.6}Li_{99}Eu_{111}$ thermique des et d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ est initiée à 238 et 220 °C, respectivement. Les thermogrammes d'ATG révèlent aussi que la décomposition a lieu respectivement en deux et trois étapes. Dans le cas de l'échantillon riche en sels d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂, après une perte en masse initiale de 8% environ, le thermogramme montre deux chutes importantes à 220 °C et 400 °C. Dans l'échantillon le plus concentré d-PCL(530)/siloxane_{3.2}Li₆Eu₇, la décomposition thermique commence directement à partir de la température ambiante, et consiste en un processus multiétapes au dessous de 500 °C. Les échantillons hybrides avec n ≥ 6,1 sont semicristallins. Dans le cas des échantillons dilués d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ et d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆, un pic endothermique faible centré aux alentours de 47 °C est visible dans le thermogramme de DSC. La formation de régions de PCL(530) libres cristallins dans les deux hybrides est en parfait accord avec la présence d'une paire de pics de Bragg fins et intense caractéristiques du PCL(530) à 23,8 et 21,6° dans les profils de XRD. Dans les clichés de MEB pris pour d-PCL(530)/siloxane_{52.6}Li₅₀Eu₅₆ et d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆, la présence de zones correspondant à des chaînes cristallines de PCL(530) est visible. La formation d'une nouvelle phase cristalline dans le système hybride d-PCL(530)/siloxane_nLi_mEu_m, à haute concentration en sel est clairement identifiable dans les clichés de MEB.

La courbe de conductivité d'Arrhénius du biohybride d-PCL(530)/siloxane_nLi_mEu_m' montre une dépendance en température des conductivités ioniques de certains des échantillons PCL(530)/siloxane_nLiCF₃SO₃ étudiés précédemment. L'addition d'un mélange de LiCF₃SO₃ and $[Eu(CF_3SO_3)_3(H_2O)_3]$.7H₂O à la matrice hôte d-PCL(530)/siloxane au lieu du simple triflate de lithium est une réussite, car une augmentation remarquable de la conductivité ionique en a résulté, ce qui est une manifestation claire de l'effet de mélange de cations. Par exemple, alors qu'à 25 °C la conductivité de l'hybride d-PCL(530)/siloxane_{52.6}Li₉₉Eu₁₁₁ est d'environ 2x10⁻⁸ S cm⁻¹, il atteint 2.3x10⁻⁶ S cm⁻¹ à 100 °C. Ces valeurs sont d'une magnitude plus haute d'un ordre de grandeur par rapport à celles précédemment mesurées pour les matrices d-PCL(530)/siloxane dopées seulement au triflate de lithium avec n = 93 $(5.44 \times 10^{-9} \text{ et})$ 5.93×10^{-7} Scm⁻¹ à 27 et ≈ 100 °C, respectivement). Dans l'intervalle des hautes températures, (à environ 100 °C), la conductivité de l'échantillon d-PCL(530)/siloxane_{3.2}Li₆Eu₇ coïncide pratiquement avec celle de la composition la plus conductrice de la série des d-PCL(530)siloxane_nLiCF₃SO₃ (n = 0.5) (2.94×10^{-5} et 3.2×10^{-5} Scm⁻¹, respectivement). Le maximum de conductivité pour le système d-PCL(530)/siloxane_nLi_mEu_m est situé à n = 6,1 sur l'intervalle entier de températures étudié (3.7x10⁻⁷ et 1.71x10⁻⁴ Scm⁻¹ à 20 et 102 ºC, respectivement). Le voltamogramme cyclique à microélectrode du matériau d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ sur l'intevalle de potentiel -2,0 – 8.0 V obtenu à 30 °C démontre que la région anodique de l'échantillon est stable jusqu'à environ 5.0 V par rapport à Li/Li⁺, tandis que dans la région cathodique, la déposition de lithium n'est pas détectée. Cela signifie que le système d-PCL(530)/siloxane_{27.0}Li₅₀Eu₅₆ est globalement stable sur plus de 7 V, ce qui indique que ce matériau montre une fenêtre de stabilité acceptable pour des applications comme dispositif électrochimique à l'état solide. Ces résultats sont en parfait accord avec ceux trouvés pour les matériaux d-PCL(530)siloxane_{0.5}LiCF₃SO₃.

Pour comprendre le rôle joué par les atomes d'oxygène des groupements carbonyle des fonctions uréthane dans la coordination des ions Li⁺ et Eu³⁺, nous avons examiné la signature spectrale des hybrides d-PCL(530)/siloxane_nLi_mEu_m, dans la région

amide I des spectres FT-IR [63, 65]. L'inclusion de LiCF₃SO₃ et [Eu(CF₃SO₃)₃(H₂O)₃].7H₂O dans la matrice d-PCL(530)/siloxane produit une série de modifications marquées dans l'environnement des groupes C=O qui se manifestent dans la région amide I par une redistribution des bandes. Globalement, l'incorporation de quantités croissantes de sels "invités" dans l'hôte hybride conduit à un renforcement des liaisons hydrogène, à la saturation des groupes C=O libre des uréthanes, et à la formation de nouveaux et très forts agrégats par liaison hydrogène d'uréthane coordinés au cation. Pour étudier les environnements chimiques des ions triflates à des concentrations croissantes de sels mélangés, nous avons analysé les spectres FT-IR des matériaux hybrides d-PCL(530)/siloxane_nLi mEum' dans la région des modes de vibrations d'élongation des groupes SO₃ (v₅SO₃). La bande v₅SO₃ a été résolue en quatre composantes: une bande proéminente à 1032 cm⁻¹, deux épaulements positionnés à environ 1038 et 1025 cm⁻¹ indique la présence d'anions libres dans les trois échantillons [66, 67].

L'émission des matériaux d-PCL(530)/siloxane₂₇Li₅₀Eu₅₆ a été enregistrée sous différentes longueurs d'onde d'excitation. Les spectres d'émission sont composés d'une bande large, dont l'énergie dépend de la longueur d'onde d'excitation, superposée sur une série de pics fins attribués aux transitions ${}^{5}D_{0} \rightarrow {}^{7}F_{0-4}$ des ions Eu $^{3+}$. Une bande large d'émission similaire avait déjà été observée pour les matériaux hybrides non dopés d-PCL(530)/siloxane [63], et avait été attriuée à des recombinaisons électron-trou à partir de défauts dans le réseau siloxane et dans le réseau de liens croisés ente les groupes uréthane. Les caractéristiques d'émission ont ensuite été quantifiées par la mesure des courbes de déclin des états excités ${}^{5}D_{0}$.

Caractérisation des dispositifs électrochromes

La construction des prototypes de dispositifs électrochromes a été réalisée pour une concentration spécifique: n = 6.1, m= 12, m'=12. La commutation optique du dispositif électrochrome verre/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/verre du jaune clair au bleu foncé uniformément sombre a lieu en chargeant/déchargeant la cellule électrochimique par l'application de potentiels de -4 V et + 4 V pendant 50 s. La transmittance moyenne (T) du dispositif basé sur le matériau d-

PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂ dans la région du visible (400-700 nm) est pratiquement identique pour les états "juste déposé" et décoloré. (64,6 et 60,2%, respectivement), atteignant 44,9% pour l'état coloré. La variation de densité optique Δ (OD) dans la région du visible est donc de 0,13. Cette valeur coïncide avec celle calculée à 555 nm $(T_{décoloré} = 41 \% \text{ and } T_{coloré} = 58 \%)$. Il faut rappeler que l'œil humain est sensible aux ondes lumineuses dont les longueurs d'onde sont comprises entre 400 et 700 nm (visible). Sous illumination forte (lumière du jour) la sensibilité maximale de l'œil est dans la région spectrale correspondant au vert (555 nm, vision photopique). L'efficacité de coloration (CE = Δ (OD)/ Δ Q) du dispositif verre/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/verre a été déterminée sur la base de mesures de chronoampérométrie. Une efficacité de coloration haute correspond à une grande modulation optique pour une petite charge d'insertion/désinsertion. Durant la phase de coloration de l'état jaune clair au bleu foncé uniforme, un courant de -4 V a été appliqué pendant 50 s : la charge, sous la forme d'électrons et d'ions Li⁺ a été transférée des couches d'oxyde conducteur (IZO) et conducteur ionique, respectivement, à la couche électrochrome. Sous ces conditions, le WO₃ a été réduit, et a subi simultanément une insertion d'ions Li⁺. En renversant la polarité du courant appliqué, la décoloration a résulté (c'est-à-dire que le WO₃ a été oxydé, et les ions Li⁺ ont été retirés) et le dispositif a retrouvé son état initial, c'est-à-dire qu'il est passé du bleu foncé au jaune pâle. Au cours de cette étude, le dispositif n'a été cyclé que pour une période très courte (1 500 s, soit 15 cycles).

La densité de charge décroît graduellement au cours du cyclage, bien que cette tendance soit plus abrupte durant les 5 premiers cycles. On peut aussi déduire de la Figure 3.2.12 que le rapport entre les charges cathodiques et anodiques (Q_{in}/Q_{out}) des dispositifs décroît au cours du cyclage, ce qui démontre une amélioration progressive de la réversibilité d'insertion/désinsertion. Pour le second cycle, une valeur haute d'efficacité de coloration de 577 cm²C⁻¹ a été estimée pour un Δ (OD) de 0,15. La courte période de temps couveerte par les mesures de chronoampérométrie (seulement 15 cycles) ne nous permet pas de conclure sur la stabilité du dispositif électrochrome verre/IZO/WO₃/d-PCL(530)/siloxane_{6.1}Li₁₂Eu₁₂/IZO/verre. La mémoire électrochrome éteint. Notre prototype est assez bon dans ce domaine, avec une mémoire en circuit ouvert d'environ un mois.

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