Hybrid Organic-Inorganic Coatings Synthesized from Sol-Gel Chemistry of Organosilanes and Polyamidines

PhD student: Coustal Cécile

Coordinator:
Prof. José M. Kenny

Supervisors:
Pr. J.F. Gérard
Dr. J. Galy
Hybrid Organic-Inorganic Coatings Synthesized
from Sol-Gel Chemistry of Organosilanes and Polyamidines

PhD student: Cécile Coustal

Supervisors:
Prof. Jean-François Gérard
Dr. Joselyne Galy

Coordinator:
Prof. José M. Kenny

This PhD thesis was performed within the framework of the European Network of Excellence NANOFUN-POLY
ACKNOWLEDGEMENTS

First of all, I would like to sincerely thank the persons who supervised this work, Prof. Jean-François Gérard and Dr. Jocelyne Galy, for their shrewd advices, availability and constructive guidance.

I would like to express my gratitude to Prof. José Kenny, coordinator of the Nanofun project.

I wish to convey my sincere thanks to Dr. Frank Böhme who hosted me in this laboratory and for his precious help during all my Ph.D.

I express my deep sense of gratitude to Dr. Fernande Boisson for his timely NMR spectral measurements and valuable discussions.

I would like to thanks Pierre Alcouffe for his microscopics observations.

I also would like to thanks Pr. Sandra Dire for her advices and precious help.

A special thanks to all my friends of laboratory and all the people from Laboratoire des Matériaux Macromoléculaires whith who I shared interesting scientific discussions and also great conviviality time.

I’d like to thank Sebastien for his supporting.

I would like to also acknowledge the EU NoE “NANOFUNPOLY” and the LMM for the financial support.
### ABBREVIATIONS

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>DP</td>
<td>Degree of polymerization</td>
</tr>
<tr>
<td>DPn</td>
<td>Average number degree of polymerization</td>
</tr>
<tr>
<td>DSC</td>
<td>Differential Scanning Calorimetry</td>
</tr>
<tr>
<td>GPTS</td>
<td>3 Glycidyloxypropyltriethoxysilane</td>
</tr>
<tr>
<td>MALDI-TOF</td>
<td>Matrix Assisted Laser Desorption-Ionisation Time-Of-Flight</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance</td>
</tr>
<tr>
<td>PA12</td>
<td>Polyamide12</td>
</tr>
<tr>
<td>POA</td>
<td>Poly(1,8-octamethyleneacetamidine)</td>
</tr>
<tr>
<td>POA F1:1</td>
<td>POA functionalised with a primary amine to epoxy ratio of 1:1</td>
</tr>
<tr>
<td>POA F1:2</td>
<td>POA functionalised with a primary amine to epoxy ratio of 1:2</td>
</tr>
<tr>
<td>POC&lt;sub&gt;80&lt;/sub&gt;</td>
<td>Poly(1,8-octamethyl-co-1,4-cyclohexylacetamidine) 80:20</td>
</tr>
<tr>
<td>POC&lt;sub&gt;20&lt;/sub&gt;</td>
<td>Poly(1,8-octamethyl-co-1,4-cyclohexylacetamidine) 20:80</td>
</tr>
<tr>
<td>POC F1:1</td>
<td>Poly(1,8-octamethyl-co-1,4-cyclohexylacetamidine) a primary amine to epoxy ratio of 1:1</td>
</tr>
<tr>
<td>POC F1:2</td>
<td>Poly(1,8-octamethyl-co-1,4-cyclohexylacetamidine) a primary amine to epoxy ratio of 1:2</td>
</tr>
<tr>
<td>TEOS</td>
<td>Tetraethylorthosilicate</td>
</tr>
<tr>
<td>TGA</td>
<td>Thermogravimetric Analysis</td>
</tr>
<tr>
<td>Tg</td>
<td>Glass transition temperature</td>
</tr>
<tr>
<td>Tm</td>
<td>Melting temperature</td>
</tr>
</tbody>
</table>
I.1.1 Identification of the chemical structure by NMR and MALDI spectrosopies 46
I.1.2 Molar mass characterization (NMR, MALDI) 49
I.1.3 Thermal characterization of polyamidine POA (TGA, DSC) 50
I.2 Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine)( POC) 51
I.2.1 Identification of the chemical structure by $^1$H NMR and MALDI spectrosopies 51
I.2.2 Molar masses characterization (NMR, MALDI) 55
I.2.3 Characterization of thermal properties of polyamidines POC (DSC, TGA) 57

II Functionalisation of Polyamidines with an epoxysilane 57

II.1 Functionalisation of the Poly(1,8-octamethylacetamidine) with epoxysilane 57
II.1.1 Model reactions 58
II.1.1.a Study of the reaction between the epoxy and the secondary amine 58
II.1.1.b Study of the reaction between the epoxy and the amidine functions: model compound 64
II.1.2 Study of the alkoxysilane- functionalised oligomers by RMN and MALDI spectrosopies 71
II.1.2.a Functionalisation of the POA with a amine: epoxy ratio of 1:1 71
II.1.2.b Functionalisation of the POA with a amine NH$_2$: epoxy ratio of 1:2 76
II.2 Functionalisation of the Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) POC$_{20}$ 78
II.2.1 Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) with 20% of cycloaliphatic units with a amine: epoxy ratio of 1:1 79
II.2.1 Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) with 20% of cycloaliphatic units with a amine: epoxy ratio of 1:2 80

III. Conclusion 81

CHAPTER III: Organic-inorganic hybrid materials a new strategy for using polyamidine 83

I Processing of the hybrid coatings based on polyamidine 83
I.1 Polyamidine-based hybrid materials 84
<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>I.1.1 Starting polymers</td>
<td>84</td>
</tr>
<tr>
<td>I.1.2 Processing of O/I hybrid materials as films</td>
<td>85</td>
</tr>
<tr>
<td>I.2 Optimization of the silica content in the hybrid materials</td>
<td>86</td>
</tr>
<tr>
<td>II Characterization of the inorganic-rich phase</td>
<td>87</td>
</tr>
<tr>
<td>II.1 Study of the inorganic phase from solid state NMR</td>
<td>87</td>
</tr>
<tr>
<td>II.2 Study of morphology of O/I hybrid materials</td>
<td>90</td>
</tr>
<tr>
<td>II.2.1 Hybrid organic-inorganic materials from POA</td>
<td>90</td>
</tr>
<tr>
<td>II.2.1.a Influence of the functionalisation ratio for POA-based hybrid materials</td>
<td>94</td>
</tr>
<tr>
<td>II.2.1.b Influence synthesis conditions the dynamic mechanical behaviour of O/I hybrid materials</td>
<td>101</td>
</tr>
<tr>
<td>II.2.2 Hybrid organic-inorganic materials from POC₂₀</td>
<td>107</td>
</tr>
<tr>
<td>II.2.2.a Influence of the structure of the polyamidine and of the functionalisation ratio: POC₂₀-based materials</td>
<td>107</td>
</tr>
<tr>
<td>II.2.2.b Influence synthesis conditions the dynamic mechanical behaviour of O/I hybrid materials</td>
<td>113</td>
</tr>
<tr>
<td>III Conclusion</td>
<td>114</td>
</tr>
<tr>
<td>GENERAL CONCLUSION</td>
<td>117</td>
</tr>
<tr>
<td>Annex A</td>
<td>121</td>
</tr>
<tr>
<td>Annex B</td>
<td>125</td>
</tr>
<tr>
<td>Annex C</td>
<td>133</td>
</tr>
</tbody>
</table>
Polyamidines -(R1-N=C(R2)-NH)_n- are attractive polymers due to their ability to interact with proton donors and to form ionic complexes [1]. As a consequence, applications such as compatibilizers, polymeric acid traps, or surface modifiers was envisaged [2]. Recently, their ability to form ionic complexes was considered to immobilize drugs and used polyamidines as drug delivery systems [3]. The basicity of polyamidines depends on the nature of R1 and R2 substituents. Polyamidines where R1 and R2 are alkyl residue [4] are the most basic. As a consequence, we focused on this kind of polyamidines. Among them, previous results lead to interest in aliphatic polyacetamidine (R2 = CH₃). Until now, only aliphatic polyacetamidine with low $D\bar{P}n$ and therefore with rather poor mechanical behaviour have been synthesized. To overcome this problem, we propose in this work to design new O/I (organic/inorganic) hybrid materials based on polyamidines. Organic-inorganic hybrid materials combine advantages of organic polymers (flexibility, lightweight, good impact resistance, and ability to be processed) and inorganic materials (high mechanical strength, good chemical resistance, thermal stability, etc.) [5]. For example, Frings et al. studied polyester-based hybrid coatings to combine the hardness of inorganic phase and the flexibility of organic phase for coil coating applications. [6] Inorganic phase can be introduced in an organic matrix by several means: introduction of nanobuilding blocks such as metal-oxo clusters, preformed nanoparticles such as silica or layered silicates, or sol-gel process. In the sol-gel process, the inorganic phase is generated in-situ by hydrolysis and condensation of inorganic precursor and could act as crosslinker of the organic phase if covalent bonds between the organic and inorganic phases are generated. Advantages of sol-gel process are numerous: from an experimental point of view the sol-gel reaction proceeds in a low viscosity medium and at low temperature. Moreover, the in situ generation of inorganic phase favours the development of interactions between the two components from the development of inorganic-rich nanostructures, i.e. a large amount of interfacial zones.

The objectives of this work are to develop new hybrid organic-inorganic materials based on various polyamidines as organic phase. Such O/I materials have not been investigated yet and could lead to the use of polyamide-based materials as coatings and/or free standing films for membrane applications which cannot be obtained from neat polyamidines. Poly (1,8-octamethylacetamidine) as well as cycloaliphatic polyamidine copolymers will be used as organic matrix to design O/I nanomaterials.
having an organic phase as continuous phase (matrix), i.e. containing few percents of inorganic compounds.

The first chapter is devoted to a literature survey of the synthesis methods of polyamidines. This overview also reports the influence of the microstructure of polyamidines on final properties of those polymers. In the second part of Chapter I, the chemistry of the sol-gel reactions used to design organic/inorganic materials will be described. A focus will be done on the influence of synthesis parameters on the morphology of the generated inorganic phase. Finally, the different routes for processing O/I hybrid materials from sol-gel chemistry and the type of O/I hybrid materials obtained will be described. In fact, according to the type of interactions created between the two phases, hybrid materials could be divided in two classes (class I and class II). Strong chemical bonds between the two components allow to increase the compatibility between the systems and to reach better intermixing of the phases. The creation of covalent bonds required beforehand reactivity or functionalisation of the polymers with the inorganic phase precursors.

In our case, the sol-gel route selected for preparing hybrid organic-inorganic materials from polyamidines involves the functionalisation of those ones with an organo-alkoxysilane which could be hydrolyzed and condensed in second step. The synthesis of polyamidines and the study of their functionalisation by an organo-triethoxysilane precursor will be examined in Chapter II. This study will be supported by the synthesis of model compounds. The characterization of the chemical structure of both organic matrices, i.e. aliphatic and cycloaliphatic polyamidine polymers, will be previously studied.

The third Chapter will describe the processing of O/I hybrid materials based on polyamidines as free standing films from a sol-gel process. A special attention will be done onto the morphologies of the resulting O/I hybrid materials, i.e. the type of the inorganic phase (dispersed as nanoclusters vs. co-continuous phases), the nature of the phases (composition of phases – purity-, distribution of sizes), and the condensation state of the inorganic phase (silanol condensation rates). The influence of functionalisation ratio of polyamidines and processing parameters on the dynamic mechanical properties will be investigated.

This project was a part of the activities of the NANOFUN-POLY Network of Excellence within the 6th PCRD of the European Community. This work was performed in the frame of a co-supervised Ph.D. thesis between the University of Perugia (Italy) and INSA Lyon (France). A third partner, the IPF (Institut
für Polymerforschung, Dresden, Deutschland), was included in this project (Dr. F. BOHME) for the synthesis of polyamidines.
REFERENCES

CHAPTER I: Literature survey

First of all, in the 1st part of this bibliographic chapter, we will introduce the polyamidine as this polymer is not known as conventional polymers. This presentation will lead to describe the various synthesis routes, the different possible architectures, and the applications along with the properties involved. As reference polymer we also considered polyamide 12 which is well documented and close to the polyamidine structure. The second part will be devoted to the sol-gel process, namely chemical reactions involved and influence of synthesis conditions. Finally, the different route for synthesizing hybrid materials using sol-chemistry will be detailed.

I. Polyamidine: overview of a non conventional polymer

Although the amidines are well-known molecules and are used in numerous applications such as catalysts, the polyamidine remains a little widespread polymer. Polymers having an amidine group in their repetitive unit are denoted polyamidines.

The amidine are compounds of the general formula [1]:

\[
\begin{align*}
\text{R}_4 & \quad \text{N} \\
\text{R}_1\text{R}_2 & \quad \text{N}\text{R}_1\text{R}_2
\end{align*}
\]

with \( \text{R}_1, \text{R}_2, \text{R}_3 = \text{H} \) or alkyl.

If \( \text{R}_1, \text{R}_2, \text{R}_3 \) are hydrogen atoms then the amidines are denoted as unsubstituted, and if \( \text{R}_1, \text{R}_2, \text{R}_3 \) are alkyl chains, amidines are denoted as tetrasubstituted. According to the nature of the substituent \( \text{R}_4 \), one defines several types of amidine: the formamidines (Figure 1), acetamidines (Figure 2), and benzamidines (Figure 3).
A lot of different polyamidine structures are available. One can find cyclic [2] or linear [3], aliphatic [4] or aromatic polyamidine [5][6]. The nitrogen atoms can be out of the backbone of the polymer [7] or included in the skeleton [8]. One can also find polyamidine with only one nitrogen included in the polymer backbone [9][10]. This part is concerned with examining the polyamidine synthesis, i.e. the main synthesis routes of polyamidine and specifically the steps for synthesis that will be used in the experimental part, as well as advantages of such a polymer and potential application domains.

Scheme 1: General structure of polyamidine with nitrogen atoms in the backbone (R: alkyl or phenyl substituents; R’: alkyl or aromatic groups)
I.1 Synthesis of polyamidines

In 1959, C. Grundmann and A. Kreutzberger [11] described the synthesis of aliphatic oligamidines with $2 < n < 5$ from S-triazine and diamine (Figure 4).

\[
\text{HC} \quad \text{N} \quad \text{CH} \quad + \quad 6\text{NH}_2\left(\text{CH}_2\right)_4\text{NH}_2 \quad \xrightarrow{2\text{h}, \ 80^\circ\text{C}} \quad 3\text{H}_2\text{N}\left(\text{CH}_2\right)_4\text{NH} - \text{CH} = \text{N}\left(\text{CH}_2\right)_4\text{NH}_2
\]

\[
\xrightarrow{-3\text{NH}_3} \quad \text{H}_2\text{N}\left[\left(\text{CH}_2\right)_4\text{NH} - \text{CH} = \text{N}\left(\text{CH}_2\right)_4\right]_{5}\text{NH}_2
\]

\[
\xrightarrow{-\text{NH}_2\left(\text{CH}_2\right)_4\text{NH}_2} \quad \text{H}_2\text{N}\left[\left(\text{CH}_2\right)_4\text{NH} - \text{CH} = \text{N}\left(\text{CH}_2\right)_4\right]_{5}\text{NH}_2
\]

Figure 4: Synthesis of oligoamidines from S-triazine

The reaction is exothermic and accompanied by production of ammonia. By heating and condensation of these oligomers (Figure 5), polyamidine with higher polymerization degree could be synthesized. Molar masses could reach 6,000 g.mol$^{-1}$ for amino-terminated polymers. Nevertheless, the resulting polymers were sensitive to air contact.

\[
\text{H}_2\text{N}\left[\left(\text{CH}_2\right)_4\text{NH} - \text{CH} = \text{N}\left(\text{CH}_2\right)_4\right]_{5}\text{NH}_2
\]

\[
\xrightarrow{6\text{h}, \ \text{from} \ 140-180 \ \text{to} \ 200^\circ\text{C}} \quad -\text{NH}_2\left(\text{CH}_2\right)_4\text{NH}_2
\]

\[
\text{H}_2\text{N}\left[\left(\text{CH}_2\right)_4\text{NH} - \text{CH} = \text{N}\left(\text{CH}_2\right)_4\right]_{5}\text{NH}_2
\]

Figure 5: Formation of higher oligomers by heating and condensation
Kurita et al. [12] obtained amorphous polyamidine by a polyaddition reaction between a bisketenimine and hexamethylenediamine (HMDA) (Figure 6) with a molar ratio of 1:1

![Synthesis of polyamidine from Bisketenimine](image)

The syntheses were performed in various organic solvents (toluene, dioxane, anisole and dimethylacetamide) to seek the optimum polymerization conditions. The highest yield (95%) was obtained with dioxane as solvent while the anisole used as solvent gave the lowest yield (60%).

Brand et al. [10] attempted to synthesize aromatic polyamidine with NH group as side group (Figure 7) from reaction of methylenedianiline and isophthalonitrile introduced in equimolar ratio and reacted at 190°C. Low molar mass oligomers with low yield having a high melting point (265-280 °C) were synthesized from this route.

![Synthesis of polyamidine by Brand et al.](image)

Aliphatic polyamidine with one atom nitrogen out of the backbone have been prepared by polycondensation of hexamethylenediamine and dimethylsuberimidate-2HCl (Figure 8) which are both of them commercially available. The yield of the reaction was rather low (13%) and the corresponding amidium salt was synthesized [9].
As mentioned previously one can also find polyamidine where the amidine is a side group of the polymer backbone. This type of polyamidine has been studied by Batres et al. [13]. The authors considered two general routes for the synthesis of this polymer. These two methods consist in modifying a poly(acrylonitrile) polymer either by a reaction with a an alkali amide of a primary amine (Figure 9), either with a primary amine in presence of AlCl₃ (Figure 10). In fact, they obtained polyamidine copolymers in both cases.
Recently, another way, consisting in the polymerization of styryl amidine monomers (Figure 11) where R is a hydrogen atom or a methyl group or an ethyl group was reported [7].

![Figure 11: Chemical structure of styryl amidine monomer](image)

Monomers can be homopolymerized or copolymerized with other monomers such as styrene or methyl methacrylate by radical initiation.

I.2 Synthesis of polyamidines from the reaction with a diamine and an orthoester

At the beginning, this reaction has been investigated for the synthesis of low-molecular weight amidine. The mechanism has been firstly underlined by Roberts and De Wolfe [14] during the preparation of aromatic formamidine from aniline and triethylorthoformate (TEOF) (Figure 12).

![Figure 12: Reactive schema for amidine preparation](image)

They demonstrated that the reaction proceeds in two steps, namely, a first one which leads to the formation of an imidoester and a second one in which the imidoester reacts with a second molecule of amine to give the amidine product. This reaction is accompanied by alcohol formation. The authors showed that the reaction of an aromatic amine with TEOF in the absence of acid catalysis leads exclusively to the amidine reaction product. However, if a small amount of acid is added, the second step becomes reversible and the reaction products are the imidoester and the amidine.
In 1962, A.C. Taylor and W.A Ehrhart broadened the study to the synthesis of formamidines and acetamidines from aliphatic amines and aromatic amines. They showed that the yield of the reaction between aromatic amines and the triethylorthoacetate (TEOA) is dependent on the acid catalysis in contrast with the TEOF case. Nevertheless the aliphatic amines react in a similar way with TEOF and TEOA. The higher yields for aliphatic amines are obtained with a molar ratio amine/TEO of 2 to 1 and a molar ratio acid/TEO of 1 to 1.

This reaction between an amine orthoester can easily be applied to the amidine polymerization by the introduction of a diamine. This has been investigated for the first time in 1979 by L. J. Mathias and C.G. Overberger [5] for synthesis of polyformamidime. The authors used four different aromatic diamines and triethylorthoformate (TEOF) in excess for the preparation of polyformamidines. The synthesis was performed both in solution using hexamethylphosphoric triamide (HMPT) as solvent (Figure 13) and in bulk (Figure 14).

![Figure 13](image1.png)  
**Figure 13**: Synthesis of polyamidine from TEOF in HMPT (R: aromatic substituent)

![Figure 14](image2.png)  
**Figure 14**: Synthesis of polyamidine from TEOF in bulk (R: aromatic substituent)

In the same way, they investigated a second polymerization technique using \(\alpha,\alpha\)-dichloromethyl methyl ether (DCME) of general formula \(\text{CH}_3\text{O-CH-Cl}_2\) and the same aromatic diamines as reagents in tetrahydrofuran or in hexamethylphosphoric triamide (HMPT) as solvents.

![Figure 15](image3.png)  
**Figure 15**: Synthesis of polyamidine from DCME in THF (R: aromatic substituent)
These last procedures have both disadvantages to use carcinogenic products (HMPT and DCME) and to involve a long reaction time. The authors concluded that the techniques using TEOF as comonomer “was the more practical and gave more tractable polymers” [5].

Later, in 1993, Rillich et al. [15] [16] [6] started a broad study on the preparation and the characterization of aliphatic and aromatic polyformamidine which has been reported in a series of publications. They developed, from Taylor et al. works, a synthesis method for aliphatic polyformamidine (Figure 17) by solution polycondensation in dimethyl sulfoxide (DMSO). This synthesis is catalysed by acetic acid and fails without it. Seven polyformamidines (Figure 17) have been prepared from seven different alkyl diamines, each of them having a yield higher than 85 % and a degree of polymerization, DPN, between 12 and 17 (Table 1). All these polyformamidines show melting points close to 100°C, i.e. are semi-crystalline polymers.

![Figure 17: Chemical structure of aliphatic formamidines (4<n_a<12)](image)

Table 1: Yield and properties of aliphatic polyformamidines (Figure 17) prepared from triethyl orthoformate and various aliphatic diamines [15]

<table>
<thead>
<tr>
<th>R</th>
<th>Yield (%)</th>
<th>n inh a) (dl/g)</th>
<th>DPN b)</th>
<th>Tm (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(CH₂)₄</td>
<td>85</td>
<td>0.16</td>
<td>-</td>
<td>105-108</td>
</tr>
<tr>
<td>(CH₂)₆</td>
<td>86</td>
<td>0.16</td>
<td>17</td>
<td>108-112</td>
</tr>
<tr>
<td>(CH₂)₇</td>
<td>88</td>
<td>0.14</td>
<td>17</td>
<td>95-97</td>
</tr>
<tr>
<td>(CH₂)₈</td>
<td>92</td>
<td>0.19</td>
<td>16</td>
<td>102-105</td>
</tr>
<tr>
<td>(CH₂)₉</td>
<td>87</td>
<td>0.15</td>
<td>14</td>
<td>104-107</td>
</tr>
<tr>
<td>(CH₂)₁₀</td>
<td>91</td>
<td>0.17</td>
<td>18</td>
<td>104-106</td>
</tr>
<tr>
<td>(CH₂)₁₂</td>
<td>94</td>
<td>0.14</td>
<td>12</td>
<td>105-107</td>
</tr>
</tbody>
</table>

a) Inherent viscosity measured at 25°C with c = 0.5 g/dl in CHCl₃
b) Number-average degree of polycondensation determined by ¹H NMR using the intensities of the end-group signals and the CH-proton intensity of formamidine groups
The following article [6] was aimed, from a base process, to seek the best synthesis conditions for preparation of aromatic polyformamidines by solution polycondensation. In a first part the authors improved the synthesis method considering a model system based on 4,4'-diaminodiphenyl methane and triethylorthoformate, TEOF (Figure 18) in an amine:TEOF molar ratio of 1:1:1.

\[
\begin{align*}
    \text{H}_2\text{N}-\text{C}_6\text{H}_4-\text{CH}_2 &- \text{H}_2\text{N} + \text{HC}(-\text{OC}_2\text{H}_5)_3 \\
    \text{N} &- \text{C} - \text{NH} \rightarrow \\
    \text{CH}_2 &- \text{NH}_2 + 3\text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

Figure 18: Synthesis of polyamidine from 4,4'-diaminodiphenyl methane and TEOF

Opposite to the aliphatic polyformamidines, this synthesis does not require any catalyst to be achieved. Authors considered numerous parameters such as monomer concentration, temperature, reaction time and solvent medium, in order to increase the yield of the reaction and the inherent viscosity which is correlated to the molar mass.

In the second part, authors applied this optimum synthesis method, i.e. 10 mol% excess TEOF, 4h at 140°C and 4h at 180°C, 25 mmol aromatic diamine in 25 mL DMSO, to a series of aromatic diamines (Figure 19).

\[
\begin{align*}
    \text{H}_2\text{N} - \text{C}_6\text{H}_4 &- \text{R} - \text{C}_6\text{H}_4 - \text{NH}_2 \\
    \text{R} &- \text{O} , \text{R} = \text{CH}_2 , \text{R} = \text{CH}_2-\text{CH}_2 , \text{R} = \text{O}(-\text{CH}_2-\text{CH}_2-\text{O})_2
\end{align*}
\]

Figure 19: Chemical structure of various aromatic diamines (R= O , R= CH₂ , R= CH₂-CH₂, R = O(CH₂-CH₂-O)₂)

The characterization of the resulting polyformamidines (Figure 20) is reported in the Table 2.

\[
\begin{align*}
    \text{N} &- \text{C} - \text{NH} \rightarrow \\
    \text{CH}_2 &- \text{NH}_2 + 3\text{C}_2\text{H}_5\text{OH}
\end{align*}
\]

Figure 20: Chemical structure of aromatic polyformamidines (R= O , R= CH₂ , R= CH₂-CH₂, R = O(CH₂-CH₂-O)₂)
Table 2: Yield of the reaction and thermal characterization of polyformamidines from various aromatic diamines and TEOF

<table>
<thead>
<tr>
<th>Nature of R</th>
<th>Yield (%)</th>
<th>Tg a) (°C)</th>
<th>Tm a) (°C)</th>
<th>T for 5% of weight loss b) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>96</td>
<td>-</td>
<td>350 c)</td>
<td>310</td>
</tr>
<tr>
<td>CH₂</td>
<td>92</td>
<td>161</td>
<td>286</td>
<td>331</td>
</tr>
<tr>
<td>CH₂-CH₂</td>
<td>95</td>
<td>125</td>
<td>255</td>
<td>332</td>
</tr>
<tr>
<td>O(CH₂-CH₂-O)₂</td>
<td>90</td>
<td>62</td>
<td>-</td>
<td>342</td>
</tr>
</tbody>
</table>

a) DSC measurements at heating and cooling rate of 10 K/min, 2nd heat after removal of solvents and cooling from the melt
b) Thermogravimetric analysis with a heating rate at 10 K/min in nitrogen
c) Due to the decomposition Tg or Tm could not be observed by DSC. The value was detected by optical microscopy equipped with a heating stage.

These polyamidines were obtained in excellent yields. The polymers are soluble in strong acid and aprotic dipolar solvent such as N,N-dimethylacetamide (3 wt.%/LiCl). All the polyamidines start to decompose about 300°C in both air and nitrogen atmosphere.

This synthesis method was also shown suitable for preparing other numerous aromatic polyformamidines as described in [16]. The influence of the nature of monomers on the final material properties is clearly stated from WAXS analyses: polyamidines with rigid para structures showed a high crystallinity rate whereas polyformamidines with flexible groups in the polymer backbone have a lower crystalline rate or are amorphous.

The works previously described established the impact of the chemical structure of the amine monomer and synthesis conditions. However, the nature of the orthoester is also an important parameter on the final properties of polyamidines.

Böhme et al. [8] studied the influence of the orthoester on the final properties of aromatic polyamidines (Table 3). Six different orthoester were used: triethylorthoformate, triethylorthoacetate, triethylorthopropionate, trimethylorthobutyrate, trimethylorthovalerate and triethylorthobenzoate. As amine monomer they used 4, 4''-diaminodiphenyl methane (DDM):

![Chemical structure of 4,4''-diaminodiphenyl methane](image)

The solution polycondensation which was successful for the synthesis of polyformamidines [16][6][15] was inappropriate for polyamidines synthesized from alkyl and phenyl substituted orthoester due to the weaker reactivity of these orthoester and intermediates imidoester with respect to...
triethylorthoformate. As a consequence, the synthesis was performed in bulk using an acid as catalyst as described: two moles of DDM were mixed with a slight excess of the respective ortho ester and with 1-10 mol% (based on DDM) of 2,4,6-trimethylbenzoic acid. The mixture was heated to 80-120°C with stirring and continuous removing of the resulting alcohol by distillation. After 10-45 minutes the temperature was raised to 200-250°C and the temperature was reduced to 0.1-10 mbar for 1-3 hours.

Table 3: Chemical structure of the polyamidines as a function of the structure of the orthoester used.

<table>
<thead>
<tr>
<th>Orthoester</th>
<th>Polyamidines</th>
<th>DPn</th>
<th>Tg (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH(OC₂H₅)₃</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>7</td>
<td>30</td>
</tr>
<tr>
<td>CH₃C(OC₂H₅)₃</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>16</td>
<td>142</td>
</tr>
<tr>
<td>CH₃CH₂C(OC₂H₅)₃</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>9</td>
<td>130</td>
</tr>
<tr>
<td>CH₃CH₂CH₂C(OCH₃)₃</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>7</td>
<td>110</td>
</tr>
<tr>
<td>CH₃CH₂CH₂CH₂C(OCH₃)₃</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>13</td>
<td>106</td>
</tr>
<tr>
<td>C₆H₅C(OC₂H₅)₃</td>
<td><img src="image" alt="Chemical structure" /></td>
<td>21</td>
<td>158</td>
</tr>
</tbody>
</table>

* Degree of polymerization determined by NMR end group analysis

The authors examined if the resulting polyacetamidines and polybenzamidine had better properties than polyformamidines. All polymers were amorphous excepted polyformamidines. The four polyacetamidines and the polybenzamidine exhibited a better thermal stability than the
polyformamidine and were more hydrolytically stable. They also have better solubility in common organic solvents.

In 2001, Böhme et al [4] investigated the surface properties of aromatic and aliphatic polyamidines -(R1-N=C(R2)-NH)-, as a function of the nature of subsituents R$_1$ and R$_2$ of reagents, namely various diamine of general formula NH$_2$-R$_1$-NH$_2$ and various triethylorthoester R$_2$-C-(OCH$_2$CH$_3$)$_3$. The different combinations of amines and orthoester for the synthesis of different polyamidine are reported in the Table 4.

Table 4: Synthesized polyamidines and nature of the substituents in the diamine and orthesters reagents

<table>
<thead>
<tr>
<th>Polyamidines</th>
<th>R$_1$ in NH$_2$-R$_1$-NH$_2$</th>
<th>R$_2$ in R$_2$-C-(OCH$_2$CH$_3$)$_3$.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aromatic polyformamidine</td>
<td>CH$_2$-H</td>
<td>-H</td>
</tr>
<tr>
<td>Aromatic polyacrylamidine</td>
<td>CH$_2$-CH$_3$</td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>Aromatic polyacrylamidine</td>
<td>CH$_2$-CH$_2$CH$_3$</td>
<td>-CH$_2$CH$_3$</td>
</tr>
<tr>
<td>Aromatic polyacrylamidine</td>
<td>CH$_2$-(CH$_2$)$_2$CH$_3$</td>
<td>-(CH$_2$)$_2$CH$_3$</td>
</tr>
<tr>
<td>Aromatic polybenzimidine</td>
<td>CH$_2$</td>
<td></td>
</tr>
<tr>
<td>Aliphatic polybenzimidine</td>
<td>-(CH$<em>2$)$</em>{10}$-</td>
<td></td>
</tr>
<tr>
<td>Aliphatic polyacrylamidine</td>
<td>-(CH$<em>2$)$</em>{10}$-</td>
<td>-CH$_3$</td>
</tr>
<tr>
<td>Aromatic polyacrylamidine</td>
<td>H$_2$C-CH$_2$</td>
<td>-CH$_3$</td>
</tr>
</tbody>
</table>

The aromatic polyamidines were synthesized as described in the paper [8] on the influence of orthoesters on final properties except the aromatic polyamidine where R$_1$ =CH$_2$-C$_6$H$_5$-CH$_3$ which was synthesized by following a similar protocol than for aliphatic ones. Aliphatic polyamidines was synthesized according to the following scheme:
The study revealed that polyamidines in which orthoester bears electron providing substituent, have higher pKa values than polyamidines based on phenyl or hydrogen substituted orthoesters. This inductive effect on basicity is even more pronounced in the case of polyamidines substituted with aliphatic groups on both nitrogens. The authors concluded that the basic behaviour of polyamidines can be classified according to the following sequence:

Lower basicity

<table>
<thead>
<tr>
<th>aromatic polyformamidines</th>
<th>&lt; aromatic polyacrylamidines</th>
<th>&lt; aliphatic polybenzamidines</th>
<th>&lt; aliphatic polyacrylamidines</th>
</tr>
</thead>
<tbody>
<tr>
<td>= aromatic polybenzamidines</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The term polyacrylamidine is used for polyamide -(R1-N=C(R2)-NH)- where the group R2, coming from the orthoester, is an aliphatic residue. These results have conduced Sharavan et al.[3] to investigate in depth and improve the synthesis of aliphatic polyacetamidines which have a much more pronounced basicity than aromatic ones. Indeed, the acid-catalysed melt polycondensation as described in [4] worked but the acid catalyst is difficult to be completely removed. Sharavan et al. [3] overcame this problem by the replacing acetic acid by phenol which can easily be taken out from the system at the end. This compound is less acidic than acetic acid but its catalytic activity is strong enough. The reagents, i.e. diamine, TEOA and phenol, were introduced in the following ratio: 1:1:0.5: 0.8 (with respect to TEOA).
I.3 Applications of polyamidines

In most of the applications, the ability of polyamidines to form proton-donor complexes is used. For example, in the molecularly imprinted polymers (MIP) domain which consist in the crosslinking of polymers in the presence of interacting monomers around a molecule that acts as a template. At the end, the template is removed and a shape remains in the polymer (Figure 23). This cavity can be used for many applications. During the polymerization the interactions between the binding sites of the polymer and the template must to be stable but, after, the template has to be easily removable.

Figure 23: Scheme of molecularly imprinted polymers [17]

Styryl-amidine has been introduced in a polymer to act as binding sites and interact with a template namely phosphonic monoester. It shows interesting results because after removal of the template the amidium sites are used for their catalytic effects.[7]

Styryl-amidine monomer was also introduced in methacrylate polymers to prepare MIPs in a bead form. [18]

Styryl amidine-containing copolymers could find an application in the formulation of both adhesives and varnishes which require strong adhesion and cohesion. Wulff et al. [7] studied the cohesion of polymer resin films (butyl acrylate, methyl acrylate, acrylamide, and 1% of an active comonomer). When styryl-amidine is used as comonomer, the cohesion is improved with respect to standard additives
(dimethylaminoethylmethacrylate (DMAEME) and 2-acetoacetoxyethylmethacrylate (AAEM)). The cohesion was evaluated by the measure of tensile strength K, breaking elongation D and degree of swelling Q: “The larger the K value is and the smaller the D and Q values are, the stronger the cohesion.”

Some researchers [19] find an interest to the polyamidine for the preparation of polymeric complexes of calyx[8]arene complexes. These complexes would allow the combination of the useful properties of both calixarenes and polymers. Calixarenes are macrocycles made of phenolic units linked by methylenic bridges and which have cavities able to accommodate a guest molecule. The authors succeeded in the preparation of binary complexes between poly-1,8-octamethylacetamidine and \( p \)-tert-Butylcalix[8]arene or octa-\( p \)-calix[8]arene. They demonstrated that these complexes could respectively accommodate the guest molecules fullerene C60 and uranyl ions.

![Figure 24: Formation of ternary (a) hydrophilic-hydrophobic and (b) ion-ion complexes [19]](image)

A series of amidines and polyamidines have been also developed to solve toxicity problem in the field of oil-producing industry. Scavengers of hydrogen sulphide which is a toxic gas encountered during the drilling and processing of crude oil [20].

**II- Polyamide 12**

Polyamide 12 has some common features with aliphatic polyamidines: NH\(_2\) chain ends, and NH in the chain backbone. This is the reason why we will
described below the chemical modifications performed on PA12 with epoxy compounds. They will inspire our strategies for the synthesis of polyamidine-based hybrid materials.

II.1 General introduction on Polyamide 12

The polyamide 12 (Figure 25) is obtained from the polymerization of laurolactam monomer either by anionic ring opening polymerization [21] either by a two-step process comprising the hydrolysis of the monomer [22].

![Chemical structure of polyamide 12](image)

Figure 25: Chemical structure of polyamide 12

This polymer is semi-crystalline and crystallizes in the γ form which is composed of pleated sheets joined by hydrogen bonds [23]. The polyamide has some specific properties such as its low sensitivity to hydrolysis as it has low equilibrium moisture absorption. As polyamides it also shows a good chemical resistance and as a consequence it could be used in many application such as automotive industry, medical articles, etc.[22].

II.2 Polyamide modification with epoxy compounds

The modification of a polyamide by the reaction with an epoxy can take place either on the nitrogen of the amide groups or on the nitrogen of amino terminal groups. The former functionalisation requires a catalyst to convert the amide in its conjugated base in reason of the weak basicity [24]

II.2.1 Reaction on the amide groups

In 2000, Y. W. Park and J. E. Mark [25] described the modification of an aromatic polyamide, commercially called Trogamid, by the 3-gycidoxypropyl triethoxysilane (GPTS). The polymer was dissolved in the N,N-Dimethylacetamide( DMAc) and reacts by means of the nitrogen from the amide group along the chain. The reaction is catalysed by a basic reagent: the 1,4-diazabicyclo[2,2,2]-octane (DABCO) (also called triethylenediamine)( Figure 26). The reaction between PA12 and GPTS is confirmed by I.R spectroscopy.
In 2006 Balas et al. [26] followed a similar protocol to modify polyamide 6. A square piece of nylon 6 is soaked in a solution of GPTMS and DMAc at 50°C for five days. The reaction is catalysed by DABCO. The apparition of a Si2p peak in X-ray photoelectron spectroscopy (XPS) revealed that the silane agent is correctly grafted to the polymer. As in the previous cited articles, GPTS reacts with the amide group’s nitrogen.

In the literature, the generation of anionic active sites on secondary amide groups could be done from the use of potassium tert-butoxide as catalyst (Figure 27). Such a catalyst is used in the synthesis of ethoxylated PA12 in DMSO. Activated, the nitrogen attacks the ethylene oxide monomer, allowing the ring opening, followed by the propagation of the reaction and formation of PEO chains along the backbone. On the 1H NMR (Nuclear Magnetic Resonance) spectra, the shift of the two methylene groups is attributed to the influence of the electronegative neighboring groups coming from the grafting. In Infra-Red spectroscopy (IR), the disappearance of a band containing a large contribution from the N-H bond in plane bending shows that the grafting worked leading to the consumption of the NH groups [27].
Jia et al. [24] also used potassium tert-butoxide for creating anionic sites on a polyamide backbone and initiating a ring opening polymerization of 3-glycidoxypropyl(triethoxysilane) (GPTS). The grafting was confirmed by XPS.

**Figure 28:** Surface modification of polyamide 6/6 by N-alkylation and subsequent reactive labeling [24]

II.2.2 Reaction on the amino end groups

In the frame of a study dealing with the protein absorption on polyamide 6/6 membranes, the authors described, among others, the activation of nylon by a bisoxirane reagent. The amino terminal groups of nylon 6/6 are modified by the 1,4-butanediol diglycidyl ether in an addition reaction leading to a secondary amine bonds [28].
III Polymer based hybrid-materials from sol-gel chemistry

A hybrid material is an organomineral or biomineral system in which one of the components has a dimension in the range of one to few tens of nanometers [29]. Traditionally, hybrid materials can be designed by using different methods: by sol-gel chemistry, by incorporation of nanobuilding blocks (NBBs), by incorporation of pre-formed nanoparticles such as silica, nano-core-shells, layered clays, and by infiltration/insertion of the polymers in nanoporous ordered inorganic materials such as zeolites, MCM-41[30][31]. In our study, we are especially interested in sol-gel chemistry derived hybrid materials. Usually, the hybrid materials are divided in two classes; this classification is based on the nature of interface between the organic and inorganic moieties. In class I, the organic part interacts with the organic phase by weak interactions such as Van der Wall’s forces, hydrogen bonds and electrostatic interactions (Figure 29).

Class-II hybrid materials (Figure 29) are characterized by strong chemical bonds (covalent or ionocovalent) between the two parts [29].

![Diagram of class-I and class-II hybrid materials](image)

**Figure 29: Scheme of class-I and class-II hybrid materials [29]**

The mechanisms and the reactions involved in the sol-gel chemistry will be detailed as well as the processing methods.
III.1 Sol-gel chemistry

The sol-gel process is a technique based on hydrolysis and condensation of precursors (starting materials) which leads to the formation of an inorganic phase. As precursors, the most employed are the metal alkoxides M(OR)n where M is a metal or metalloid such as Si, Ti, Zr, Ce atom and OR an alkoxide group [32]. Among them, tetraethoxysilane (TEOS: Si(OCH₂CH₃)₄) and tetramethoxysilane (TMOS: (Si(OCH₃)₄) are the most largely spread [33]. Organo (functional) alkoxysilane R’xSi(OR)₄-x where R’ is an organic functionality which improves the compatibility with an organic matrix or can copolymerize with the organic matrix to improve interfacial interactions between the organic and inorganic phases could be also considered. In this part we will focus on alkoxysilane precursors.

“The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension of solid species in a liquid called sol, which is converted into a gel through polycondensation of the sol. A gel is a interconnected, rigid network with polymeric chains, whose average length is greater than a micrometer, and pore width of nanometer dimensions [34].” This synthetic technique enables to process inorganic materials (glassy or ceramic) and inorganic-organic (hybrid) polymers or nanocomposites [35].

Indeed, the compatibility of the mild synthetic conditions, i.e. organic solvents, low temperature, with organic components allows preserving the integrity of the organic part during the preparation of the hybrid materials. For this reason sol-gel chemistry is also called “chimie douce”.

III.1.1.Mechanisms of sol-gel reaction

This process breaks down into two steps [36]: the hydrolysis of the precursor (Figure 30) and subsequent condensation (Figure 31). The former permits to replace alkoxy groups by silanol groups and the latter leads to the formation of siloxane bridge.

\[ \text{Hydrolysis: } \text{Si-OR} + \text{H}_2\text{O} \rightarrow \text{Si-OH} + \text{ROH} \]

Figure 30: Hydrolysis step of silicon alkoxides
The reactivity of alkoxysilane toward the hydrolysis and condensation depend on its ability to increase its coordination number and the partial charge ($\delta$) of the silicon atom. However, in reason of a rather high electronegativity (1.74) the silicon presents a partial charge rather small [32]. The use of catalyst appeared necessary in order to work with reasonable reaction time.

**III.1.1.a Hydrolysis**

The hydrolysis occurs by the attack of the oxygen atom from water on the silicon atom and the subsequent displacement of an OR group. The reaction proceeds by bimolecular nucleophilic substitution reaction (SN$_2$) involving pentacoordinates intermediates. The same behaviour is observed for organoalkoxysilane [33].

Acid-catalyzed hydrolysis:
The acidic catalysis implies the protonation of the silicon-attached OR group (Figure 32). It makes the silicon more electrophilic, therefore more susceptible to a nucleophilic attack [32].

![Figure 32: Acid-catalysed hydrolysis](image-url)
Base-catalyzed hydrolysis:
The basic medium allows generating better nucleophilic agent, i.e. OH\(^-\) anion, by water dissociation which attacks the silicon atom. According to the type of mechanisms proposed, either this attack is accompanied by simultaneous displacement of an OR- anion with inversion of silicon tetrahedron (Figure 33) or leads to a SN\(_2\) mechanism reaction involving a stable 5-coordinated intermediate in which the silicon acquires a negative charge.

\[
\begin{align*}
H_2O & \rightleftharpoons H^+ + OH^- \\
OH^- + SiOR & \rightleftharpoons R-O---Si-OH \\
& \rightleftharpoons HO-SiOR + OR^-
\end{align*}
\]

*Figure 33: Basic-catalysed hydrolysis*

Re-esterification, transterification reactions:
The reaction of hydrolysis is reversible: an alcohol molecule can attack the silicon atom to regenerate an alkoxy ligand and produce a water molecule as by-product. This phenomenon could be non suitable during the drying of the gel as resulting materials will be porous. Indeed, the excess of water can be evaporated in the azeotropic mixture which has a higher vapour pressure than the pure solvent or water. This reaction path leads to a rich alcohol system which favours re-esterification and even if the hydrolysis goes to completion one can obtained etherified gels [33]. Transesterification reaction results in an exchange between the alkoxy ligand of the precursor and the OR’ of an alcohol molecule [33]:

\[
R’OH + Si(OR)_4 \rightarrow Si(OR)_3OR’ + ROH
\]

The new steric and inductive effects of the exchange alkoxide can modify the hydrolysis kinetics.

*III.1.1.b Condensation*

This step, which leads to the creation of a siloxane bridge, can be either a water-producing or a alcohol-producing reaction [33]. The condensation starts before hydrolysis goes to completion but it cannot take place if hydrolysed species are not present in a sufficient amount [37].
Acid-catalyzed condensation:
This reaction involves protonated silanol species (Figure 34). Protonation of the silanol makes the silicon more electrophilic and more susceptible to nucleophilic attack. The most likely silanols to be protonated are the most basic. The basicity of an alkoxide group (and its ability to be protonated) increases as the electron-providing power of the three other substituents. The substituents are classified by increasing character of electron-donor: OSi <OH< OR< R [32].
As the consequence, the condensation reactions occur preferentially between neutral species and a protonated silanol situated on monomer or end group chains.

Base-catalyzed condensation:
A nucleophilic deprotonated silanol attacks a neutral silicon species to form the Si-O-Si linkage (Figure 35). The probability to be protonated for a silanol depends on its acidity which is directly connected to the three other substituents on silicon atom. The substituents with a high electron withdrawing power increase the partial charge on silicon and increase the acidity of remaining silanols. As a consequence, the basic catalysis favours the condensation reaction of highly condensed species, containing acidic silanols, and smaller, less weakly branched species.[33]

Most of the time, the sol-gel reaction is carried in presence of 4 components: a precursor, water for hydrolysis, a solvent as suspending agent, a catalyst
which promotes the reaction. Each of them can influence the hydrolysis and condensation reaction kinetics and the microstructure of final materials.

III.1.2 Influence of parameters and role of the reagents

The gelation time which is the time to form a gel, i.e. a 3D network, gives an indication of the overall rate and the competition between the hydrolysis and condensation reactions. For example, the simultaneous effect of pH and temperature for the gelation of tetraethoxysilane in ethanol and water as a function of molar ratio was reported [34]. Gelation time could vary, by changing these parameters, from 5 hours to 1440 hours.

Figure 36: Response surface of the gelation time as a function of: (a) temperature and water:TEOS molar ratio, and (b) pH and ethanol:TEOS molar ratio [34]
A. Influence of the H$_2$O/Si molar ratio

Theoretically a H$_2$O/Si molar ratio of 2 is enough to complete hydrolysis and condensation reactions according to the following equation:

\[ n\text{Si(OR)}_4 + 2n\text{H}_2\text{O} \rightarrow n\text{SiO}_2 + 4n\text{ROH} \]

Water is a by-product of the condensation reaction (Figure 31) and by consequence can react again after regeneration [33].

J.J. van Beek et al.[38] studied the effects of the initial molar H$_2$O/Si ratio on the incipient polymerization of SiO$_2$ in the case of tetramethoxysilane. Figure 37 gives an overall view of the evolution of each species, i.e. SiOR, SiOH and Si-O-Si, as a function of H$_2$O/Si molar ratio.

![Figure 37](image)

Figure 37: Functional groups distribution for 20 min of reaction as a function of H$_2$O/Si molar ratio. (The dash line indicates the ideal case of full hydrolysis for the remaining percentage of SiOR groups)[38]
Table 5: Hydrolysis and condensation rate in function of H$_2$O/Si molar ratio from [33][38]

<table>
<thead>
<tr>
<th>H$_2$O/Si</th>
<th>Hydrolysis degree</th>
<th>Condensation degree</th>
</tr>
</thead>
<tbody>
<tr>
<td>≤ 2</td>
<td>relatively low</td>
<td>relatively fast max for 2.5 Decrease (dilution effect)</td>
</tr>
<tr>
<td>2 &lt; H$_2$O/Si ≤ 4</td>
<td>promoted</td>
<td></td>
</tr>
<tr>
<td>≥ 4</td>
<td>extensive</td>
<td></td>
</tr>
</tbody>
</table>

For those studies, increasing of H$_2$O to Si molar ratio promotes hydrolysis rate. The value of H$_2$O/Si also influences the nature of condensed species since the authors observed that an under-stoechiometric ratio of water favours the alcohol-producing condensation whereas an excess of water promotes a water-producing condensation.

B. Influence of the catalyst
The main catalysts used in such hydrolysis and condensation reactions are mineral acids, ammonia, acetic acid, KOH, amines, KF, HF and oxides as well as metal alkoxides such as titanium or vanadium alkoxides [36].

In a study dealing with the kinetics of reaction of four organoalkoxysilanes, i.e. an amino, a mercapto, a methacryloxy and an alkyl, it is shown that in the absence of catalyst no polymerization occurred except for the 3-aminopropyltriethoxysilane, APES, which probably leads to an autocatalysis. It was also demonstrated that while the basic catalysis enhances the rate of hydrolysis but also drastically the self condensation rate, the acid catalysis increases the rate of hydrolysis and limits the self condensation [39].

As reported before, the catalyst influences the hydrolysis and condensation rates but also leads, in agreement with its basic or acidic character, to specific polymeric shapes [32]. Acid-catalysed hydrolysis with low H$_2$O/Si ratio results in weakly branched polymeric network while basic-catalysed hydrolysis with large H$_2$O/Si ratio gives highly branched colloidal particles (Figure 38).
Vasconcelos et al. [41] have synthesized spherical silica particles by the basic-catalysed sol-gel processing using molar ratios of TEOS:NH₄OH:H₂O:C₂H₅OH equal to 1: 1-10:4-16:6-60. The particles have diameters varying from 0.35 to 1.06 µm. Intermediate conditions leads to structure intermediates to these extremes [36].

C. Influence of solvent
The first role of the solvent (alcohols, dioxane, THF, acetone, etc.) is to act as an homogenizing agent because of the immiscibility of water and alkoxy silane [33]. Solvents could also facilitate the hydrolysis reaction and could be beneficial in promoting the hydrolysis of silanes containing bulky organic or alkoxy ligands. The solvent could have an active role and generate esterification or alcoholysis reactions.

C. Mutter et al. [42] studied the condensation state of SiO₂ powder obtained by drying an hydrolysis mixture based on TEOS, ethanol and water diluted either with ethanol or propanol. In the case of ethanol, the water is the last liquid to evaporate, these rich water systems causes silicon sites with only hydroxyl on the remaining which easily condense. In the case of propanol, as the solvent forms a azeotropic mixture with water the last liquid to be evaporated is the propanol. This alcohol rich system causes re-esterification leading to the formation of silicon sites with many attached propoxy groups.
which does not easily condensate. As a consequence, the condensation will be higher for ethanol diluted mixture. The authors also showed the influence of the steric hindrance of solvents, used for the dilution, on the re-esterification. They attempted four alcohols (2-methyl-x-butanols with \(1 \leq x \leq 4\)) with different degree of branching (Table 6). The cross linking degree increases in the following order: \( \text{C-OH(I)} < \text{C-OH(II)} < \text{C-OH(III)} \). Bulky substituents hinder the re-esterification which leads to hydroxyl-rich \( Q \) species and to a higher condensation.

<table>
<thead>
<tr>
<th>Value of x</th>
<th>Structure formula of alcohol</th>
<th>Type of alcohol</th>
<th>Alkoxy percentage</th>
</tr>
</thead>
</table>
| 1          | \[
\begin{array}{c}
\text{H}_2\text{C} \equiv \text{CH} \equiv \text{CH}_2 \equiv \text{CH}_3 \\
\text{CH}_3
\end{array}
\] | Primary | 22.1 |
| 2          | \[
\begin{array}{c}
\text{H}_2\text{C} \equiv \text{CH} \equiv \text{CH}_2 \equiv \text{CH}_3 \\
\text{OH}
\end{array}
\] | Tertiary | 0    |
| 3          | \[
\begin{array}{c}
\text{H}_3\text{C} \equiv \text{CH} \equiv \text{CH} \equiv \text{CH}_3 \\
\text{OH}
\end{array}
\] | Secondary | 13.4 |
| 4          | \[
\begin{array}{c}
\text{H}_3\text{C} \equiv \text{CH} \equiv \text{CH}_2 \equiv \text{CH}_2 \\
\text{OH}
\end{array}
\] | Primary | 21.5 |

D. Influence of the substituents
As silane precursors one can find the four-folded alkoxy coordinated or the organo substituted alkoxy silanes \( R’x\text{-Si-(OR)}n \).

The chemical nature of silicon-bonded groups modifies the reactivity of silicon and of the surrounded oxygen, influencing thus the hydrolysis and condensation rate. Indeed, in reason of the difference of electronegativity between the atoms, these groups have an electron-providing or electron
withdrawing effect on the silicon atom (Figure 39) which will affect the silicon partial charge and also the basicity of oxygen atoms borne by silicon [37].

![Figure 39: Inductive effects of substituents attached to the silicon][36]

Although the OH group has a higher electron withdrawing power than OR, the subsequent replacement of OR by OH groups causes a downfield shift (toward more positive values) on the $^{29}\text{Si}$ NMR spectra. As general rule, it is admitted that an increase of the positive partial charge on the silicon involves an upfield shift (more negative value)[43]. This means that the subsequent replacement of OR by OH groups tends to decrease the positive partial charge on the silicon.

The inductive effects of some organic groups are summarized in the Table 7.

<table>
<thead>
<tr>
<th>Effect and strength</th>
<th>Groups</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weak Electron withdrawer</td>
<td>Vinyl, Phenyl</td>
</tr>
<tr>
<td>Moderate Electron withdrawer</td>
<td>Alkoxy, hydroxy</td>
</tr>
<tr>
<td>Weak electron provider</td>
<td>Methyl</td>
</tr>
</tbody>
</table>

Table 7: Inductive effects classification of substituents[37][43]

In acid-catalysed hydrolysis, providing-electron substituents such as alkyl group help to stabilize the positive charges developed in transition state. It has been demonstrated, in a paper dealing with the study of acid-catalysed hydrolysis-polycondensation of organic modified Si-alkoxides comparatively with TEOS, that the hydrolysis-polycondensation rate increased in the following order: TEOS<VTEOS<MTEOS (V for vinyl and M for methyl). The replacement of an ethoxy group by a less withdrawer substituent or by a electron provider substituent allows the decreasing of the positive partial charge of the silicon and by consequence the increase of the negative charge on oxygen of remaining alkoxy groups[43].

In base-catalysed hydrolysis withdrawing-electron substituents such as OR and OH groups help to stabilize the negative charges developed in the
transition states. Reactivity decreases with the size of alkoxy groups and steric hindrance plays a role during the transition state of hydrolysis.[32]

The other factor susceptible to have an impact on the reactions is the extent of the steric hindrance. The length of the alkyl chain has a retarding effect on the hydrolysis but this latter is even more affected by the degree of branching [36]. Study [37] of the hydrolysis and condensation of various organoalkoxysilanes in the acidic conditions shows the impact of the steric hindrance and inductive effect of substituents.

Inductive effects are also dependent of experimental conditions. At higher acid concentration, in the case of a series of methylethoxysilane (\(\text{CH}_3\))_n-Si-(OCH_2CH_3)_{4-n} with 0≤n≤3 the degree of hydrolysis and condensation increases with the increase of methyl groups. At low acid concentration the hydrolysis rate is greater for more substituted species except for trimethyl which has a similar behaviour to the unsubstituted compound. At low acid concentration, free of the effects of condensation, the hydrolysis is more sensitive to other substituent effect and in this case the steric effect overwhelmed the inductive effect.

III.2 Hybrid materials: how to process them

The sol-gel chemistry could be used to synthesize hybrid organic-inorganic materials from hydrolysis and condensation reactions of metal-alkoxides (mainly silicon-based ones). Three different methods could be considered depending on the degree of nanostructuration required for the final materials [30]:

- Method A in which metal alkoxides and/or organo-functional metal alkoxides are hydrolyzed and condensed to form hybrid organic-inorganic materials. Such a method could imply also organic monomers, oligomers, or polymers to design O/I hybrids with a higher organic content and materials for which the continuous medium is an organic polymer. For those O/I hybrids an inorganic phase is generated from a microphase separation occurring during hydrolysis and condensation reactions of metal alkoxides.

- Method B in which the sol-gel chemistry is done in an organized medium, i.e. a template obtained from organic components. For example, this method was performed from organic components to prepare nanoporous and mesoporous silicas (from degradation of the organic compounds in a second step).
- Method C in which the sol-gel chemistry is performed in solution and in specific conditions to synthesize metal-oxo nanoclusters, denoted as nanobuilding blocks which could be associated in a second step with organic monomers or polymers. These nanoclusters have a metal-oxo core bearing organic (reactive or not) ligands.

In the following part, only method A will be detailed as this one was selected for the experimental study. Such a method allows to process nanomaterials with an organic polymer-rich matrix in which inorganic-rich nanophases perfectly dispersed and with a careful control of the interactions at the O/I interfaces. Such a method overcomes the problems encountered for processing nanocomposites from the introduction of preformed nanoparticles. In fact, a perfect dispersion of nanoparticles within organic monomers or polymers remains very difficult to achieve as those ones tend to stay as agglomerates even if the interface is matched from surface treatments of fillers.

The method A for synthesizing hybrid O/I nanomaterials having an organic-rich matrix could itself be divided in three different routes:

Route #1 - Combination of a polymer with metal-alkoxides, i.e. the hydrolysis and condensation reaction occur in a polymer medium (polymer solution or polymer in molten state).

Route #2 - Simultaneous polymerization of organic monomers and sol-gel reactions.

Route #3 - Hydrolysis and condensation reactions of metal alkoxide-terminated oligomers or polymers. Of course, this route will require a first step in which the functionalization of the oligomer or polymer will be performed with organo-functional metal-alkoxides.
Figure 40: Use of sol-gel chemistry of silicon alkoxides for synthesis of hybrid organic-inorganic materials [30]

### III.2.1 Route 1: Polymer combined with a metal alkoxide precursor

This method consists in the hydrolysis and condensation of an organic/inorganic precursor in a polymer or oligomer solution. The solvent which solubilizes the polymer and the O/I precursor acts as an homogeneizing agent. From hydrolysis and condensation reactions combined with a phase separation process which occurs during condensation and drying of the solvent, a dispersed inorganic-rich nanophase is obtained within a polymer-rich continuum (matrix).

This type of preparation method leads normally to O/I hybrids of class I [44] for which only physical interactions are created at the organic-inorganic interface. However, in the case of a polymer or oligomer chains bearing OH along the chain such as polyvinyl alcohol or α- or α,ω-hydroxyl chains, the hydroxyl groups could react with silanol groups to create Si-O-C bridges. These ones are very stable in hydrothermal conditions. Nevertheless, it is possible from this method to obtain transparent materials if appropriate conditions during gel forming and drying process are adopted, i.e. in order to avoid macrophase phase separation [45].

A limited number of polymers could be combined with hydrolyzed and condensed species of the O/I precursors in solution as the solubility parameters of these compounds change a lot during hydrolysis and condensation reactions. In addition, the final morphology, i.e. the size and
composition of the inorganic-rich dispersed phase, is strongly dependent on the drying conditions. An important shrinkage could be associated during drying [45].

For example, Frings et al.[46] prepared polyester-based hybrid coatings to combine the hardness of an inorganic phase and the flexibility of organic phase for coil coating applications. They used two organic matrices: hydroxyl-terminated polyester and a carboxylic-terminated polyester crosslinked with epoxy resin as terminal groups and as inorganic precursor tetraethoxysilane, TEOS. Whereas O/I hybrid transparent coatings with improvement of the hardness and Tg with respect to the neat polymer could be obtained from hydroxyl-terminated polyester, it appeared difficult to incorporate silica in the polyester epoxide matrix. This is probably due to the basic character of the catalyst used to promote the reaction between carboxylic end-groups and epoxy function. In the successful O/I hybrid, the interactions take place between the hydroxyl end groups of the polymer and the hydroxyl of hydrolyzed TEOS. The authors claim for the likely formation of Si-O-C bond via condensation reaction [46].

This route was also performed in polymer melt, i.e. without solvent. According to the viscosity of molten polymers, this route requires high shear tools such as extruders. The reactive extrusion process is involved and the specific features of this approach are the high viscosity of the medium in which the sol-gel chemistry is performed, the high temperatures compared to conventional sol-gel, and the short residence time, i.e. time available for sol-gel reactions. In addition, only few polymers could be considered for a direct in-situ sol-gel chemistry due to polar nature of the hydrolyzed and condensed species. In fact, matching of the miscibility of the various components in the reactive system could limit the types of polymers to polar ones such as polyamides.

III.2.2 Route 2: Simultaneous organic and inorganic polymerizations

The organic matrix is generated from a polymerizable organic monomer (R’’) or from the polymerizable organic part of an organoalkoxysilane R’-Si-(OR)₃ (Table 8) simultaneously with the growth of the inorganic network. The latter one is generated from the hydrolysis and condensation reactions of alkoxysilanes. Organoalkoxysilanes bearing the same reactive group than the organic monomer could be used to act as coupling agents between the inorganic and organic phases (Class II hybrid organic/inorganic materials are generated).
Table 8: Examples of organoalkoxysilanes with polymerizable organic groups: vinyl, [30]

\[
\begin{align*}
&\begin{array}{c}
\text{N} \\
\text{O} \\
\text{O} \\
\text{Si(OEt)}_3
\end{array} \\
&\begin{array}{c}
\text{CH}_2 \\
\text{O} \\
\text{Si(OEt)}_3
\end{array} \\
&\begin{array}{c}
\text{H}_2\text{C} \\
\text{Si(OEt)}_3
\end{array}
\end{align*}
\]

Depending on the combination of monomers and silicon alkoxides, the systems leads to class-I or class-II hybrid. Three main schemes of polymerization can be considered:

Table 9: Main schemes of simultaneous polymerization

<table>
<thead>
<tr>
<th>Scheme</th>
<th>R’</th>
<th>R’-Si-(OR)₃</th>
<th>Si-(OR)₄</th>
<th>Hybrid class</th>
</tr>
</thead>
<tbody>
<tr>
<td>Scheme 1</td>
<td>√</td>
<td></td>
<td>√</td>
<td>I or II</td>
</tr>
<tr>
<td>Scheme 2</td>
<td></td>
<td>√</td>
<td></td>
<td>II</td>
</tr>
<tr>
<td>Scheme 3</td>
<td>√</td>
<td>√</td>
<td>√</td>
<td>III</td>
</tr>
</tbody>
</table>

This route implies that the organic monomers and the inorganic or organic/inorganic components are miscible in the initial steps of the process. The ‘simultaneous polymerization’ leading to the creation of homogeneous materials at the macroscale requires conditions which could be difficult to fit. In fact, as reported previously, the solubility parameters of the non-hydrolyzed and hydrolyzed species change in a large range. Thus, in most of the cases, the O-I precursors are previously pre-hydrolysed, then mixed with the organic monomers and finally further hydrolysis and condensation are carried out simultaneously to the polymerization of the organic monomers. As for route 1, during reactions, a microphase separation occurs leading to the generation of Si-rich nanodomains.

Numerous studies were carried out with organic monomers such as styrene, acrylates or methacrylates, epoxy and amine comonomers, etc.

For example, the simultaneous polymerization of hydroxyethylmethacrylate, HEMA, and tetraethoxysilane, TEOS, in acid-catalyzed conditions leads to transparent monolithic samples. As it is demonstrated this transparency results from an intimate mixing of the components at the initial state, i.e. miscibility is achieved between initial and hydrolyzed species of TEOS due to the presence of a polar (OH) group onto the HEMA monomer. In addition, condensation reactions could occur between the silanols and the hydroxyl groups of the polyhydroxylmethacrylate polymer. In fact, organic phase is
covalently bonded to the inorganic-rich phase at the O/I interface. Nevertheless, the amount of generated inorganic phase remains limited to get nanomaterials with an organic matrix as for equivalent SiO₂ content up to 15 wt. %, a phase inversion occurs, i.e. the continuous phase is inorganic [47]. Compared to this study, Hung et al [48] prepared PHEMA-SiO₂ by hydrolysis and condensation of the PHEMA polymer in solution (Route 1). Whereas, hybrid materials of Class II are also obtained, a macrophase separation occurs with increasing of silica up to 33 to 67 wt % of TEOS, i.e. corresponding to 9.5 SiO₂ wt %.

III.2.3 Route 3: Hydrolysis and condensation of alkoxyisilane-functionalized polymers or oligomers

In this case the oligomer or polymer functionalisation and the growth of silicon-rich phase via hydrolysis-condensation of alkoxyisilane groups are two completely independent steps. First, the polymer is synthesized and functionalized by an organosilane of a general structure R’Si(OR)₃, i.e. having an organic R’ group reactive (α- or α,ω-oligomers or polymers are used) and/or in-chain reactive groups to introduce alkoxyisilane groups. This functionalisation will lead latter to the creation of covalent bonds between the polymer and the inorganic-rich which will result from the second step for which hydrolysis and condensation reactions will be performed. Moreover, as the Si-C bond is hydrolytically stable, the organic-inorganic interface is very strong.[49]

The different architectures deriving from this polymer functionalization are reported in Figure 41.

![Figure 41: Possible structures that can be obtained by functionalization of organic polymers with trialkoxysilane groups](image)

The alkoxyisilane functionalization could be also reached via the copolymerisation of an organic monomer and an organo-functional silane
taking care of the non-occurrence of hydrolysis and condensation reactions during copolymerisation (as in Route#2 described previously). For example, a side-chain functionalization was achieved from the copolymerization of methyl methacrylate (MMA) and 3-(trimethoxysilyl)propylmethacrylate (MSMA). Numerous polymers and oligomers have been functionalized by various types of organosilanes. L. Matejka et al. described the preparation of hybrid materials from alkosilane end capped oligomers such as difunctional oligomers: poly(oxypropylene) diamine, poly(oxypropylene)diol and polycaprolactone functionalized by ITES (3-Isocyanatopropyl)triethoxysilane. These functionalized oligomers undergo hydrolysis and condensation to synthesize hybrid O/I materials [50].

IV Conclusion

This bibliographic study gives an overview on the numerous synthesis methods for polyamidine preparation. The experimental conditions, i.e. in solvent or in bulk, with catalyst or without, depend on the reactivity of the monomers considered and have to be adapted in each specific case.

The properties of the polyamidines can be varied as a function of starting monomers used: the polyamidines with the highest basicity, i.e. which have the most ability to interact with proton donor, are the aliphatic polyacrylamidine. As a consequence, aliphatic polyacetamidine will be considered in the frame of this study. The literature showed that these polyamidines can be obtained by acid-catalysed melt polycondensation, starting from aliphatic diamine and triethylorthoester, with reasonable reaction time. Acid acetic added in high ratio give good results but it cannot be completely removed from the mixture, then the authors replaced it by phenol which can be easily removed.

The second and third part of this chapter, showed how organic silica phase can be designed from the sol-gel chemistry and how hybrid materials can be processed via different routes. The influence of process parameters on the morphology of the inorganic phase was evidenced. As a consequence, the basicity of polyacetamidine will determine the final morphology of future hybrid materials.
REFERENCES

CHAPTER II: Characterization of Polyamidines and Functionalisation

I Synthesis and characterization of a series of polyamidines

We selected further polyamidines for this study, each one having different chemical structure and therefore different glass transition temperature, $T_g$. The first one is an aliphatic polyamidine (POA) whereas the two others are cycloaliphatic polyamidine copolymers. The introduction of a cycloaliphatic monomer allows designing thermal properties. Trans-1,4-diaminocyclohexane monomer is introduced according to the cycloaliphatic/aliphatic molar ratios: 20:80 and 80:20. The corresponding copolymers will be called POC$_{20}$ and POC$_{80}$.

I.1. Poly (1,8-octamethylacetamidine) oligomers (POA)

POA has been synthesized following the protocol described by Böhme [1] and reported in annex A. POA is obtained by a polycondensation reaction from 1,8 diaminoctane, triethyl orthoacetate and acetic acid as a catalyst, i.e. a bulk polycondensation without any purification. A study on polyacetacetamidine done by Shravananan [2] showed that interesting results are obtained using phenol as a catalyst. Indeed the number-average degree of polymerization ($DP_n$) are higher and the phenol is easier to remove from the medium with respect to acetic acid. However, we preferred to use acetic acid for safety reason as phenol is classified as a C.M.R. (Carcinogenic, Mutagenic and Reprotoxic) substance.

The POA chains bear amine and acetamide end-groups. The acetamide groups come from the hydrolysis of imidoester groups by traces of water in the medium.

Scheme 1: General structure of the Poly (1,8-octamethylacetamidine)
I.1.1 Identification of the chemical structure by NMR and MALDI spectroscopies

The $^1$H NMR spectrum of POA (aliphatic polyamidine) is reported in Figure 1. Chemical shift values are given in ppm with reference to internal tetramethylsilane.

![Scheme 2: Expected structure of the POA with assigned groups](image)

**Figure 1: $^1$H NMR spectrum of the POA (400MHz; solvent: CD$_3$OD; TMS)**

The assignments have been done according to the data of the Shravanan’s paper [3]. The spectrum reveals that we correctly synthesized the polyacetamidine. The peak at 2.61 ppm show that the POA bears amine end-groups and the peaks at 1.92 and 3.14 ppm correspond to the acetamide end-groups.

For the protons H$_1$ and H$_1’$ two distinct signals could be expected [3]. Nevertheless, due to the tautomerism of the amidine group (R$_1$-NH-C(CH$_3$)=N-R$_2$)/ R$_1$-NH-C(CH$_3$)=N-R$_2$) which is fast with respect to the $^1$H NMR time scale, coalescence of the signals is observed.
Although, a high vacuum and high temperature was applied to remove the acetic acid (catalyst), the signal at 1.88 ppm (CH$_3$C00H) proves that some of acids remain in the reactive medium. This acid is in fact under the acetate form, i.e. bounded to the amidine, and therefore the largest part of the amidine groups are as amidium forms. This hypothesis can be confirmed by the $^1$H NMR. Indeed, a study done by Sharavan’s [3] showed that when free polyacetamidine is analysed in CD$_3$OD solvent, a proton-deuteron exchange tautomerism occurs between the four hydrogens from amidine groups and the solvent which leads to the nearly disappearance of the peak of the methyl from amidine at 2.1 ppm. If the amidine is protonated, the proton-deuteron exchange tautomerism on the CH$_3$ cannot take place and therefore the methyl (H$_6$) group gives a peak. That is why the presence of the peak at 2.1 ppm indicates that some of the amidine are protonated. Moreover, the methyl group of the acetic acid shows up a peak at 1.99 ppm when it is considered alone in CD$_3$OD, while in the POA solution this peak is shifted to 1.88 ppm pointing out the presence of the acetate form.

It has been reported [3] that when polyacetamidine spectra are recorded in deuterated trifluoroacetic acid CF$_3$COOD, because of the high excess of acid, the polyamidinium salt is formed. This protonation results in the splitting of the signals H$_1$ and H$_1’$, because in the predominant configuration adopted by the protonated amidine groups, the protons H$_1$ and H$_1’$. have different chemical environment.

On our POA spectrum, this splitting is not observed for the proton H$_1$ and H$_1’$. It can be concluded that the amidine groups are in equilibrium with the protonated form.

The study of the architecture from NMR spectroscopy could confirm of the microstructure of polyamidine chains and the calculation of the percentage of each terminal group. The polyamidine has two different terminal groups: an amine and an acetamide group. Then each sample of polyamidine can be composed of three different kinds of chains as shown below:

\[
\begin{align*}
\overset{\text{O}}{\text{H}} & \overset{\text{N}}{\text{P}} \overset{\text{-}}{\text{NH}}  \\
& \overset{\text{H}}{\text{N}} \overset{\text{P}}{\text{-}} \overset{\text{NH}_2}{\text{O}}  \\
\text{H}_2\text{N} & \overset{\text{P}}{\text{-}} \overset{\text{NH}_2}{\text{O}}  \\
& \overset{\text{O}}{\text{H}} \overset{\text{N}}{\text{P}} \overset{\text{-}}{\text{NH}_2}
\end{align*}
\]

The signal used to quantify the amine termination is the signal of protons labelled 1d at 2.6 ppm. The signal taken into account for the acetamide termination is the one of protons H$_6$c at 1.92 ppm.

The amino and acetamide end-group percentages are calculated as follows:

\[
\begin{align*}
\% \text{ amine end-groups} &= \frac{(I_{1d}/2)}{((I_{1d}/2)+(I_{6c}/3))} \\
\% \text{ acetamide end-groups} &= \frac{(I_{6c}/2)}{((I_{1d}/2)+(I_{6c}/3))}
\end{align*}
\]
The results for six POA synthesized in the same experimental conditions denoted POA1, POA2,….,POA6 were reported Table 1.

Table 1: Percentage of amino and acetamide end-chains for different POA

<table>
<thead>
<tr>
<th>Samples</th>
<th>POA1</th>
<th>POA2</th>
<th>POA3</th>
<th>POA4</th>
<th>POA5</th>
<th>POA6</th>
</tr>
</thead>
<tbody>
<tr>
<td>% amine termination</td>
<td>35</td>
<td>25</td>
<td>50</td>
<td>35</td>
<td>50</td>
<td>27</td>
</tr>
<tr>
<td>% amine termination</td>
<td>65</td>
<td>75</td>
<td>50</td>
<td>65</td>
<td>50</td>
<td>72</td>
</tr>
</tbody>
</table>

It appears that the percentage of amino end-groups is comprised between 25 and 50%. The percentage of each termination depends on the initial amine-orthoester ratio. Nevertheless, during reaction, some monomer could be released from the mixture by evaporation leading to variable chain end ratios. In our case the monomers were introduced in a stoechiometric ratio, so statistically we can expect to obtain the same amount of each termination. We notice that that di-acetamido terminated and amino-acetamido chain-ends are preferentially formed with respect to di-amino terminated structures. These results have been confirmed by mass-spectrometry (MALDI-TOF).

A conventional MALDI spectrum of POA is reported Figure 2. The notation a, b, c, respectively designated the di-amino terminated, amino-acetamido terminated, di-acetamido terminated chains. The notation d corresponds to the cyclic POA. The associated number corresponds to the polymerization degree (DP). For example the notation b2 is used for an amino-acetamido terminated chain with a DP of two. The spectrum shows that the three different kinds of chains are present as well as the presence of cyclic compounds.

Figure 2: MALDI spectrum of the polyacetamidine
I.1.2 Molar mass characterization (NMR, MALDI)

In the case of polyamidines, the molar mass cannot be calculated from a conventional technique as Size Exclusion Chromatography (SEC). Indeed, the results obtained are not reliable because of interactions created between the polymer chains and the column. This problem is generally met with polar polymers able to form strong hydrogen bonds. To overcome this problem, we chose to use the \(^1\)H NMR and the MALDI-TOF spectroscopies to calculate the molar masses of the oligomers. The NMR spectroscopy gives us an average of the molar mass while the MALDI allows reaching the value of all molar masses of each kind of chains presents in the sample.

Molar mass determined by \(^1\)H NMR:
This technique will not allow to obtain the weight-average molecular weight \(M_w\) and consequently the polydispersity index (Ip) but gives only the \(DP_n\) and \(M_n\)

The \(DP_n\) is calculated from the signal of the protons from repeating units and from terminations.

The repeating unit can be characterized by the signals of protons 2, 2’ to 4, 4’ (1.3-1.7 ppm) or protons: 1, 1’, 1c, 1d. According to the chain-ends, the signal of protons 1d is used for the amino group and the signal of protons 6c for the acetamide chain-ends.

![Scheme 3: structure of POA with assigned nomenclature](image)

Chain-ends distribution by MALDI-TOF:
In addition to the NMR analyses, MALDI-TOF gives information on the distribution of each kind of polyamidine chains depending on their chain ends. Unfortunately MALDI is not quantitative, and could not give the percentage of in function of the DP. However the intensity of the peaks of chains with similar terminations but different masses can be compared. On the Figure 2, if we compare separately each type of chains, we notice that the chains with polymerization degree of 1, 2 and 3 are predominant.

We have analyzed four aliphatic polyamidines synthesized in the same conditions. The results are summarized in the following table, the \(DP_n\) calculated by \(^1\)HNMR is also reported.
| Table 2: Comparison of DPn from MALDI and from \(^1\)H NMR |
|-----------------|-----|-----|-----|-----|
| Synthesis       | 1   | 2   | 3   | 4   |
| range of acyclic DP (MALDI) | 0\(^\text{a}\)-7 | 0-6 | 0-8 | 0-11 |
| Cyclic DP (MALDI) | 2   | 2 and 3 | 2   | 2,3 and 4 |
| DPn \(^1\)H NMR) | 6.8 | 8.2 | 3.2 | 5.5 |

\(^{a}\) a degree of polymerization of zero corresponds to the reaction of one molecule of diamine with one molecule of triethylorthocacetate.

From the NMR results it appears that polyamidine oligomers were synthesized with \(\overline{DPn}\) from 3 to 8. Although these polyamidines have been synthesized in the same conditions the value of \(\overline{DPn}\) are variable. In the case of the sample 1, the value of the \(\overline{DPn}\) is very close to that of the longer chain lengths determined by MALDI and for the sample 2 the average \(\overline{DPn}\) calculated from NMR spectrum is higher than the polymerization degree determined by MALDI. These two results are not logical could be explained by an evolution of the polyamidine in solution during the MALDI analyses. It means that the results from MALDI measurements would be underestimated.

I.1.3 Thermal characterization of polyamidines POA (TGA, DSC)

The thermal stability of the POA has been studied performing thermogravimetric analysis, TGA, measurements under nitrogen up to a temperature of 600°C.

Studies on aliphatic polyamidines show that the stability increases with the number of carbon in the amine monomer. From the TGA thermogram, the temperature for which the weight loss is of 5% (T\(_{5\%}\)) and the maximum temperature of the derivative weight loss curves (Tmax) were determined for a given heating rate. The T\(_{5\%}\) are found between 190°C and 210 °C and Tmax is equal to 468°C.

The thermal behaviour was also studied by differential scanning calorimetry, DSC. The polyamidine was found to be an amorphous polymer. In our case, the glass transition temperature is molar mass dependent (Table 3) due to the low molar masses of polyamidines.
Table 3: \(DPn\) and corresponding glass transition temperature of different POA

<table>
<thead>
<tr>
<th>Synthesis</th>
<th>1</th>
<th>3</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg (°C)</td>
<td>6</td>
<td>-8</td>
<td>8</td>
</tr>
<tr>
<td>DPn ((^{1})HNMR)</td>
<td>6.8</td>
<td>3.2</td>
<td>7.3</td>
</tr>
</tbody>
</table>

The polyamidines have low Tg comprised in the range from -3 to 8 °C. The evolution of the Tg are in agreement with the variation of the \(DPn\).

I.2 Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine)( POC)

Copolymers are obtained by a melt polycondensation reaction from 1,8 diaminoctane and trans-1,4-diaminocyclohexane as amine monomers, triethyl orthoacetate and phenol as a catalyst. The reagents were introduced with an amine: orthoester: phenol molar ratio of 1.05:1:0.8 (with respect to the orthoester). The protocol is the same as for the POA synthesis but the phenol is used as a catalyst. These samples have been made at IPF Dresden according to the synthesis protocol described in [3]. Two types of POC have been prepared:

- with a trans-1,4-diaminocyclohexane/1,8 diaminoctane molar ratio of 20/80
- with trans-1,4-diaminocyclohexane/1,8 diaminoctane molar ratio of 80/20. These samples will be respectively denoted as \(POC_{20}\) and \(POC_{80}\). The copolymers present two types of repeating unit: aliphatic and cycloaliphatic.

I.2.1 Identification of the chemical structure by \(^{1}\)H NMR and MALDI spectroscopies

The NMR spectrum of \(POC_{20}\) and \(POC_{80}\) are reported in Figure 3 and Figure 4 respectively, with the assignments of the various resonances. The structures of the possible chain-ends are shown in Scheme 5, four types have been identified and they are the same for both polymers.
Figure 3: $^1$HNMR spectrum of POC$_{20}$

Scheme 4: Expected chemical structure of the POC$_{20}$ with assignment of hydrogen and carbon

Scheme 5: Different chain-ends of the POC$_{20}$ and POC$_{80}$
Figure 4: $^1$H NMR spectrum of POC$_{80}$

Scheme 6: Expected chemical structure of POC$_{30}$ with nomenclature

We can notice on the spectrum that all intensity of resonances (m, m$_2$, p1, n$_a$, n$_{2b}$) due to the cyclic part increased and all the ones (1c, 1’, 6c, 2’, 2d) from the acyclic monomers decreased. This confirms that the concentration of cycloaliphatic monomer is higher.

MALDI measurements were performed on these samples to determine more precisely the molecular structure. A mixing of homopolymers and copolymers with different kind of terminations is obtained.

For polyamidine POC$_{20}$ (20% cycloaliphatic monomer) the following ten different structures:
Table 4: Molecular structures of POC$_{20}$ determined by MALDI-TOF spectroscopy

<table>
<thead>
<tr>
<th>Structure</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{H}_2\text{N} - \left[ \text{A} \right]_x x \text{NH}_2)</td>
<td>(x = 1)</td>
</tr>
<tr>
<td>(\text{H}_2\text{N} - \left[ \text{B} \right]_y \text{NH}_2)</td>
<td>(y = 1) and 2</td>
</tr>
<tr>
<td>(\text{H}_2\text{N} - \left[ \text{A} \right]_x \left(\text{CH}_2\right)_y \text{NH}_2)</td>
<td>(x = 1) and 2; (y = 1) and 2, ...6</td>
</tr>
<tr>
<td>(\text{A} = \left[ \text{N} - \text{C} - \text{NH} \right] \quad \text{B} = \left[ \text{N} - \text{C} - \text{NH} \left(\text{CH}_2\right)_8 \right])</td>
<td></td>
</tr>
</tbody>
</table>

For polyamidine POC$_{80}$ (80% cycloalipahtic monomer), the composition determined by MALDI-TOF is reported in the Table 5:
Table 5: Molecular structures of POC\textsubscript{80} determined by MALDI-TOF spectroscopy

\begin{align*}
\text{H}_2\text{N} & \quad \begin{array}{c}
\text{A} \\
x = 1,2, \ldots, 7
\end{array} \\
\text{H}_2\text{N} & \quad \begin{array}{c}
\text{A} \\
x = 1,2, \ldots, 9 ; y = 1 \text{ and } 2
\end{array} \\
\text{H}_3\text{C} & \quad \begin{array}{c}
\text{A} \\
x = 1,2 \text{ and } 3
\end{array} \\
\text{NH}_2 & \quad \begin{array}{c}
\text{B} \\
x = 1,2, \ldots, 8 ; y = 1 \text{ and } 2
\end{array}
\end{align*}

I.2.2 Molar masses characterization (NMR, MALDI)

$^1$H NMR analyses were performed at IPF Dresden. $\overline{DPn}$ can be approximated from the resonance intensities of the repeating units and terminations. The protons used for the calculations are reported in the table below.

<table>
<thead>
<tr>
<th>Groups</th>
<th>Protons considered</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aliphatic moiety</td>
<td>H1'</td>
</tr>
<tr>
<td>Cyclic moiety</td>
<td>H m</td>
</tr>
<tr>
<td>Acetamide end-groups</td>
<td>H 6c and H p\textsubscript{1}</td>
</tr>
<tr>
<td>Amine end-groups</td>
<td>H m\textsubscript{2} and H 1d</td>
</tr>
</tbody>
</table>

As reported in Figure 3 and Figure 4, the signals H m\textsubscript{2} and H 1d are too close to be integrated separately. To overcome this, two limit cases can be considered: one assumes that the signal at 2.62 ppm is exclusively caused by either cyclic or n-aliphatic terminal groups, therefore two different normalized intensities are available by division of the signal intensity by 1 (case a) or 2 (case b). With other words, we obtain for each sample two sets of normalized signal intensities representing one polymer with only cyclic terminal groups (case a) and one with only n-aliphatic ones (case b). With these assumptions two different compositions can be calculated. In the case of POC\textsubscript{20} (20% cyclic monomer), we suppose that the signal at 2.62 ppm only comes from n-aliphatic terminal groups, and for POC\textsubscript{80} we assume that the signal is only due to the proton of cyclic terminal groups.
Each kind of moiety (cyclic and aliphatic) is considered and added to obtain the $\overline{DPn}$.

For the cyclic moiety of POC$_{20}$ the number of pattern is:

$$\left[ \frac{(I_{Hm}/2) *2}{(I_{Hm2} + H_{1d}/2) + (I_{Hp1} \text{ and } I_{H6c}/3)} \right]$$

For the aliphatic moiety POC$_{20}$ the number of pattern is:

$$\left[ \frac{(I_{H1}/4) *2}{(I_{Hm2} + H_{1d}/2) + (I_{Hp1} \text{ and } I_{H6c}/3)} \right]$$

On the spectrum of the copolymer POC$_{80}$:

For the cyclic moiety, the number of pattern is:

$$\left[ \frac{(I_{Hm}/2) *2}{(I_{Hm2} + H_{1d}/1) + (I_{Hp1} \text{ and } I_{H6c}/3)} \right]$$

For the aliphatic moiety the number of pattern is:

$$\left[ \frac{(I_{H1}/4) *2}{(I_{Hm2} + H_{1d}/1) + (I_{Hp1} \text{ and } I_{H6c}/3)} \right]$$

The results of the $^1$H NMR calculations are reported and compared to the MALDI results in the Table 6.

**Table 6: Comparison of DPn from MALDI and from NMR**

<table>
<thead>
<tr>
<th></th>
<th>POC$_{20}$</th>
<th>POC$_{80}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>range of acyclic DP</td>
<td>0-7</td>
<td>1-10</td>
</tr>
<tr>
<td>(MALDI)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclic DP (MALDI)</td>
<td>2 and 3</td>
<td>2 and 3</td>
</tr>
<tr>
<td>$\overline{DPn}$ ($^1$HNMR)</td>
<td>12</td>
<td>9</td>
</tr>
</tbody>
</table>

$^a$ degree of polymerization of zero corresponds to the reaction of only one molecule of diamine with one molecule of triethylorthoacetate

For polyamide POC$_{20}$ the average $\overline{DPn}$ calculated from NMR spectrum is higher than the polymerization degree determined by MALDI and for POC$_{80}$, the value of the $\overline{DPn}$ is very close to that of the longer chain lengths determined by MALDI. These two results are not logical could be explained by an evolution of the polyamide in solution during the MALDI analyses or by a poor solubility of the longer chains which are not detected.
I.2.3 Characterization of thermal properties of polyamidines POC (DSC, TGA)

The value of the, Tg, T5% and Tmax are reported in the Table 7.

<table>
<thead>
<tr>
<th></th>
<th>Tg (°C)</th>
<th>T5% a (°C)</th>
<th>Tmax b (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>POC20</td>
<td>20</td>
<td>300</td>
<td>419</td>
</tr>
<tr>
<td>POC80</td>
<td>84</td>
<td>339</td>
<td>412</td>
</tr>
</tbody>
</table>

a) temperature for which one the weight loss is of 5%
b) the maximum temperature of the derivative weight loss curve

The effect of the introduction of cycloaliphatic groups in the oligomer backbone is very important. In fact, the glass transition temperature and the value of T5% are increased for the copolymer having more cycloaliphatic groups due to the stiffness of the cycloaliphatic group compared to the methylene groups in the main chain.

II Functionalisation of Polyamidines with an epoxysilane

As reported, the neat polyamidines can be used directly to prepare class-I hybrids materials, i.e. no covalent bonds between the organic and inorganic phase. For the preparation of the class-II hybrid materials in which a covalent bond exists between the two phases, the oligomers have to be functionalised first. For that purpose the chain ends of the polyamidine oligomers will be reacted with organoethoxysilane compounds.

II.1 Functionalisation of the Poly(1,8-octamethylacetamidine) with an epoxysilane

For polyamidines POA there are two types of terminal groups: (i) amino and (ii) acetamide groups. Because of the low reactivity of the acetamide groups we considered amino-end groups for grafting alkoxy silane functions. We used the 3 glycidyloxypropyltriethoxysilane (GPTS) as organosilane to functionalise POA, taking profit of the well-known and quantitative epoxy-amine condensation reaction.
The experimental protocol of the polyamidine functionalisation is described in annex A.
The structure of the expected compound is shown below:

Scheme 7: Expected chemical structure of the triethoxysilane functionalised POA

Functionalised POA with two different NH₂/epoxy molar ratios: 1:1 and 1:2 were synthesized and denoted POA F1:1 and POA F1:2, respectively. The samples have been analyzed by NMR spectroscopy to check if the functionalisation took place. The interpretation of the spectra is not obvious because the reaction of some amino terminal groups with two epoxy functions is possible even in the case of an epoxy amine ratio of 1/1. Moreover, amidine group could also react with glycidyl group. Thus, for a better understanding, the reaction was studied using model compounds.

II.1.1 Model reactions

The first model compound was prepared in order to study the reaction between the secondary amine (amino end group) and the epoxy function of the GPTS. With the second one, we want to elucidate which peaks could be attributed to a possible reaction between the amidine groups and the epoxy function of the GPTS.

II.1.1.a Study of the reaction between the epoxy and the secondary amine

The model compound, 3-aminodecyl-1-oxypropyltriethoxysilane-propane-2-ol, was synthesized from the reaction of decylamine and glycidyloxypropyltriethoxysilane (GPTS) in equimolar ratio. The protocol is described in the part of the annex A. It means that for two active hydrogen there is one epoxy ring. The main expected reaction is the nucleophilic attack of the epoxy ring by the electronic pair of the amine leading to the formation of the secondary amine and the hydroxide function [4]. This reaction can be followed by the attack of a second epoxy ring by the electronic pair of the secondary amine leading to the formation of the tertiary amine and a second hydroxide function. This second step occurs with a lower reaction rate because of the lower reactivity of the secondary amine[5].
Even in the case of an initial epoxy-amine ratio of 1:1, two epoxy can react with one primary amine group. Indeed, the reaction of the butylamine (BA) with phenylglycidylteher (PGE) with a PGE/BA ratio of 1:1 yields three products: residual butylamine (21%), secondary amine resulting from the addition of one butylamine on the epoxy ring (53%), and tertiary amine (26%) [6]. Secondary reactions may occur such as the homopolymerization of epoxy functions [5] and also the condensation of the hydroxide from opened epoxy with silanol groups [7].

To study the reaction in our case, $^1$H and $^{13}$C NMR analyses were carried out on the coupling agent (GPTS) and on the reaction product.

A- $^1$H NMR characterisation

The $^1$H NMR spectrum of GPTS (structure shown below) exhibits 10 peaks having the following assignment: 3.31 and 3.72 ppm (6e), 3.12 ppm (5e), 2.58 and 2.76 ppm (4e), 3.47 ppm(3e), 1.67 ppm (2e), 0.64 (1e), 3.72(7e) and at 1.17 ppm (8e).

![Scheme 8: Chemical structure of γ-glycidoxypropyltrihoxysilane GPTS](image)

The main compound that we are supposed to obtain is the reaction product between the amino group and the epoxy ring with formation of a hydroxyl ether and a secondary amine function:

![Scheme 9: Expected chemical structure of the reaction product from GPTS and decylamine](image)

On the spectrum of this compound shown in Figure 5, the 5e and 6e resonances of the epoxy ring are no more present. It indicates that all the epoxy groups have reacted to completion.

Unreacted amine could be present in the final product: the following nomenclature is used for designating the starting amine.

![Scheme 10: Chemical of the starting amine](image)
The overlay of the $^1$H NMR spectrum of GPTS and model compound is reported below:

![NMR spectra](image)

**Figure 5:** $^1$H NMR spectra of GPTS (bottom) and GPTS-decylamine reaction product (top) (0-4.5 ppm) (400MHz; solvent: CD$_3$OD; TMS)

The peak b at 3.84 ppm is characteristic of protons like CH$_2$-OH arising from the epoxy opening by the amino group [8]. The signals of the ethoxy groups are replaced by up-field shifted signals which correspond to ethanol. This ethanol could come either from the hydrolysis of ethoxy groups by residual traces of water or from the condensation between the hydroxyl function (arising from the epoxy ring opening) and the ethoxy groups. When C-O-Si bridge is formed, the -CH$_2$ of the epoxy ring gives a peak at 4.2 ppm for in the case of a GPTMS/oligo(NH$_2$) system [8]. On our spectrum such peak is not observed.

**B- $^{29}$Si NMR characterisation**

The study of the model compound by $^{29}$SiNMR (Figure 9) demonstrates that six different Si-containing species, corresponding to different degree of hydrolysis and condensation on silicon, are present. The silicon sites are labelled by the Q, T, D notation (Q= Si(RO)$_4$; T= R’Si(OR)$_3$; D= R’$_2$-Si-(OR)$_2$) where j denotes the number of siloxane bridges (Si-O-Si) on the considered silicon atom.
The subscript i indicates the degree of hydrolysis of the alkoxy groups attached to the given silicon. For example, $T_2^0$ represents a di-hydrolysed silicon. Therefore the number of ethoxy groups on the Q silicon is 4-i-j.

The analysis of the GPTS in the same conditions allows to conclude that the peak at -45 ppm correspond to the R'Si(OR)$_3$ species. The subsequent hydrolysis of Si-OCH$_2$CH$_3$ to Si-OH causes a downfield shift. Signals are caused by mono, bi and hydrolysed species presents in the samples and also condensed species ($T^1$). The spectra was recorded in presence of tris(acetylacetonato)chromium III Cr(acac)$_3$ which allows to decrease the relaxation time and obtain quantitative spectra. As a consequence, we can conclude that only a few part of ethoxysilane groups are condensed. Identifications of the peaks were made using the data reported in the references [9][10]. Few articles related to the $^{29}$SiNMR of the GPTS with
respect to GPTMS have been published. It is generally known that the initial difference of chemical shift between two organoethoxysilane is kept during the hydrolysis and condensation processes.

![Figure 9: $^{29}$Si NMR spectrum of the model compound prepared from reaction of GPTS with decylamine (79.5 MHz; solvent: CD$_3$OD; Cr(acac)$_3$;TMS)](image)

C - $^{13}$C NMR characterisation

The spectra reported in Figure 10 show that GPTS is characterised by 10 carbon resonances: at 44.61 ppm (6e), 51.82 ppm (5e), 74.51 ppm (4e), 72.68 ppm (3e), 24.09 ppm (2e), 7.31 ppm (1e), 59.39 ppm (7e) and at 18.66 ppm (8e).

The main peaks that characterize the epoxy ring opening by the amine function are those at 69.9 ppm, 53.7ppm, 50.7 ppm from carbons labelled b (CHOH), a (NH$\text{C}_2\text{H}_2\text{CHOH}$) and 1i ($\text{CH}_2\text{NHCH}_2\text{CHOH}$) respectively. The assignments were performed according to the data found in the literature [8][6].

The peaks 6e (44.61 ppm) and 5e (51.82 ppm) of the epoxy ring are no more present which tends to show that all epoxy functions have reacted. But the spectrum shows that the peak from the carbon 1d (CH$_2$-NH$_2$) (42 ppm) is still present which means that it remains some unreacted amine. The reagents have been introduced in an NH$_2$: epoxy ratio of 1:1. Therefore the signal amino group should not be present. Different hypotheses may explain why it remains some unreacted amino group whereas the signals of the epoxy totally disappeared:

(i) the epoxy could react twice with the same amine and formed the tertiary amine. In this case, for the carbon CH$_2$$\alpha$-N, a peak shift of + 6 ppm with respect to the carbon 1i of the secondary amine is expected [6].

(ii) the hydroxyl of opened ring could react on an epoxy leading to the formation of an ether link. In $^{13}$C solid-state NMR oligo- and poly (ethyleneoxide) species give a broad shoulder at 74 ppm [11].

(iii) Finally, residual water could open the epoxy ring to form a diol whose the presence is indicated by peaks at 72.1 (-CH-OH) and 61.5 (-CH$_2$-OH) ppm in the case of GTMS. The respective carbons groups shows up at 53.8ppm (-CH-) and 46.5 ppm (-CH$_2$-) in the starting oxirane ring [9].

None of these hypotheses is suitable.
The explanation could be the partial condensation of epoxy silane to give solid species which are no longer detectable by liquid NMR. But, on the spectrum (Figure 9), as condensed species only $T^1$ species are observed. If in the medium there was highly condensed species which cannot be detected, we should also observe intermediate species, i.e. $T^2$ and $T^3$.

The presence on the spectrum (Figure 10) of both signals of ethoxy groups and ethanol shows that the hydrolysis and condensation of ethoxy groups occurred partially. This condensation reaction only happened between the silanol and ethoxyilane silane groups. Indeed, the condensation reaction between an ethoxysilane group and the hydroxyl function of the opened epoxy leads to the formation of a a C-O-Si link. This link is characterized by a peak at 60 ppm [7][12] which is not observed in our case.

![Model compound spectrum](image1.png)

![GPTS spectrum](image2.png)

**Figure 10:** $^{13}$C NMR spectrum of model compound prepared from reaction of GPTS with decylamine (100.6 MHz; solvent: CD$_3$OD; TMS)

In summary, this NMR study allows to:

- show that the epoxy ring of GPTS is opened by the addition reaction with the secondary amine. But the reaction does not go to completion.
- identify the signals of the different carbons coming from the epoxysilane/amine reaction. These signals will be used as references in the characterization of the functionalised polyamidines.
- exhibit that the hydrolysis and condensation of the ethoxysilane groups started and induced the formation of insoluble GPTS.
II.1.1.b Study of the reaction between the epoxy and the amidine functions: model compound

A second model compound was synthesized in order to study the reactivity of amidine functions with the epoxysilane. It was prepared in two steps: first by the synthesis of N, N'-dioctylacetamidine then by its reaction with γ-glycidyloxypropyltriethoxysilane GPTS to obtain the final model compound, i.e. triethoxysilane-functionalised dioctylacetamidine.

II.1.1.b.1 Synthesis of N, N'-dioctylacetamidine

N, N'-dioctylacetamidine was obtained from the reaction of octylamine and triethylorthoacetate with acetic acid as a catalyst (cf. annex A). The scheme of reaction is shown below:

\[
2 \text{H}_3\text{C} \text{N} \text{H}_2 + \text{H}_3\text{C} \left( \text{O} \text{CH}_3 \right)_3 \rightarrow \text{H}_3\text{C} \left( \text{N} \text{H} \right)_7 \text{N} \text{NH} \left( \text{CH}_3 \right)_7
\]

If the reaction does not go to completion intermediate species can be hydrolysed to give the corresponding acetamide:

\[
\text{H}_3\text{C} \left( \text{N} \text{H} \right)_7 \text{N} \text{O} \text{CH}_3 \rightarrow \text{H}_3\text{C} \left( \text{N} \text{H} \right)_7 \text{C} \text{O}
\]

As explained earlier, in the presence of acid, amidine functions are protonated. This is the reason why we certainly synthesized the acetate of N, N'-dioctylacetamidinium. The synthesis procedure was described by Sharavananan [2].
A- $^1$H NMR characterisation

Figure 11: $^1$H NMR of N,N'-dioctylacetamidine (400 MHz; solvent: CD$_3$OD; TMS)

Scheme 11: Expected chemical structure of N,N'-dioctylacetamidine

The $^1$H spectrum of N,N'-dioctylacetamidine is shown Figure 11. The main resonances are those of the expected amidine but there are also minor signals: the peak at 2.6 ppm correspond to residual octylamine, the signals of octyl acetamide are found at 3.28 ppm (1,1’) and 2.15 ppm (9) and the signal (3c) at 1.88 ppm comes from the methyl of acetate functions.
B. $^{13}$C NMR characterisation
The $^{13}$C spectrum of N,N'-dioctylacetamidine is shown in Figure 12.

![13C NMR spectrum of N,N'-dioctylacetamidine](image)

**Figure 12: $^{13}$C NMR of N,N'-dioctylacetamidine (100.6 MHz; solvent: CD$_3$OD; TMS)**

The carbon spectrum confirms the presence of octylacetamide (signal of C10 at 163.7 ppm), of N-octylacetamide (peak 3c at 22.5 ppm and peak 2c at 172.74 ppm) and of residual octylamine (40.38 and 33.84 ppm).

II.1.1.b.2 Reaction of N, N'-dioctylacetamidine with GPTS

The synthesis protocol is reported in annex A. The starting model compound (N, N'-dioctylacetamidine) was not purified before the reaction with the epoxysilane (which makes the interpretation of the spectra more difficult). As previously mentioned, the aim of this experiment is to check if the epoxy ring reacts with the secondary nitrogen of the amidine function. According to the wide spectrum of amine structures which react with the epoxy in an addition reaction, we assumed that the imino nitrogen of the amidine could open the epoxy ring.
The following scheme shows the expected structure of the reaction product:

Scheme 12: Expected structure from functionalisation of N,N'-dioctylacetamidine with GPTS

The molecules that could be found in the final product of the reaction between the N, N'-dioctylacetamidine and GPTS are:
- the octylamine (Scheme 13),
- unreacted N, N'-dioctylacetamidine (Scheme 11),
- N-octylacetamide (Scheme 11),
- unreacted GPTS (Scheme 8),
- 3-aminoctyl-1-oxypropyltriethoxysilane-propan-2-ol (Scheme 9)
- and the functionalised N, N'-dioctylacetamidine (Scheme 14).

Scheme 13: Chemical structure of the octylamine with assignments of group

Scheme 14: Expected structure of functionalised N, N'-dioctylacetamidine
A- $^1$H NMR characterisation

Figure 13: $^1$H NMR spectrum of functionalised N,N'-dioctylacetamidine (400 MHz; solvent: CD$_3$OD; TMS)

The main information which can be drawn from the $^1$H NMR spectrum is that the signals of the GPTS are still present. In this case, the $^1$H NMR does not give us further information. The assignments of characteristic peaks of reaction are done in Figure 13.

B- $^{29}$Si NMR characterisation

The analysis of the spectrum shows the presence the GPTS is mainly fully hydrolysed and a small part is condensed to form dimers (T$^1$ species) (see II.I.I.a.B).

B- $^{13}$C NMR characterisation

The $^{13}$C NMR spectrum of the model compound is shown in Figure 14. The different resonances were assigned from comparison of the $^{13}$C spectrum of this last model compound with the spectra of GPTS, the model compound prepared from decylamine-GPTS reaction product and N,N'-dioctylacetamidine. The signals of the epoxy ring of the starting GPTS are present. It means that if the reaction between the amidine and GPTS occurred, the yield remains very low.
Chemical shifts of signals from carbons C1, C1’ and C9 that could be influenced by the possible addition reaction, because they are in the close environment of the imino nitrogen, are only slightly modified. Therefore these signals do not allow to give rise the reaction.

The signal of carbon C10 (163.6,ppm) is shifted to 160.90ppm, this resonance could be attributed to carbon 10m.

New resonances, at 64.5 72.1, 73.1 and 74.4 ppm are also observed and could characterise carbons am, bm, cm and dm. In the literature, no paper dealing with the NMR characterization of the reaction between a trisubstituted amidine and epoxy is reported presently.
Figure 14: $^{13}$C NMR spectrum of the functionalised N,N'-dioctylacetamidine (100.6 MHz; solvent: CD$_3$OD; TMS)
From this study, we can conclude that we correctly synthesized the N, N'-
dioctylacetamidine and identified all the reaction products. Concerning the
reaction of the amidine with the GPTS, a part of GPTS did not react; another
part was involved in a secondary reaction i.e. the addition of the remaining
octylamine on the epoxy and a third part reacted with amidine. A small
amount is maybe as insoluble form which cannot be detected as Si NMR
showed the presence of condensed species.

II.1.2 Study of the alkoxysilane- functionalised oligomers by RMN
and MALDI spectroscopies

The aim of this part is to characterise the products of the reaction of
polyamidine with epoxysilane, which were synthesised with different molar
ratio: \( \text{NH}_2/\text{epoxy} = 1 \) and 2. The corresponding model compounds are 3-
aminodecyl-1-oxypropyltriethoxysilane-propan-2-ol and N,N'-
dioctylacetamidine-GPTS reaction product respectively.

II.1.2.a Functionalisation of the POA with a amine: epoxy ratio of 1:1

The expected structure which corresponds to the reaction product between
the epoxy groups and the amino chain ends is represented in Scheme 15. The
structure does not consider the possible reaction between the imino nitrogen
of the amidine and the epoxy ring.

![Scheme 15: Expected chemical structure of the functionalised polyamidine](image)

A- \(^1\)H NMR characterisation

\(^1\)H NMR does not allow the exact elucidation of the whole structure. On the
spectrum the peaks of the epoxy ring of starting GPTS are no more present.
We noticed the presence of new resonances (with respect of the POA) at
0.66, 1.69, 2.69, 3.47 and 3.76 ppm which, in agreement with the model
compound, are due to the reaction of the epoxy group from GPTS with an
amino group. Thus, one can conclude the expected functionalisation of the
POA from the amino end groups occurred.
The comparison of the POAF1:1 and GPTS shows that the peak at 1.17 ppm
and 3.6 ppm are due to the ethanol and then that the ethoxy groups started to
be hydrolysed.
B- $^{13}$C NMR characterisation

The resonances of epoxy ring at 44.6 ppm and 51.9 ppm are no more present in the $^{13}$C NMR spectrum. Nevertheless, as showed in the paragraph C of the part II.1.1., the disappearance of these peaks may be partially due to the formation insoluble condensed GPTS. Therefore, this observation is not sufficient to conclude to the complete reaction of the GPTS.

If we compare the spectra of POA (Figure 16), before and after functionalisation, 9 new resonances can be evidenced. The chemical shifts and the corresponding assignments are reported in Table 8.
Table 8: Assignments of alkoxyisilane-functionalised POA resonances ($^{13}$C NMR)

<table>
<thead>
<tr>
<th>δ (ppm)</th>
<th>Type of carbon (DEPT)</th>
<th>Corresponding carbon in model compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.45</td>
<td>CH or CH$_3$</td>
<td>CH$_2$CH$_2$OH</td>
</tr>
<tr>
<td>50.7</td>
<td>CH$_2$</td>
<td>1i of DeG</td>
</tr>
<tr>
<td>53.68</td>
<td>CH$_2$</td>
<td>a of DeG</td>
</tr>
<tr>
<td>58.2</td>
<td>CH$_2$</td>
<td>CH$_3$CH$_2$OH</td>
</tr>
<tr>
<td>64.61</td>
<td>CH$_2$</td>
<td>am of DiG</td>
</tr>
<tr>
<td>69.92</td>
<td>CH or CH$_3$</td>
<td>b DeG</td>
</tr>
<tr>
<td>72.21</td>
<td>CH or CH$_3$</td>
<td>bm peak of DiG</td>
</tr>
<tr>
<td>73.27</td>
<td>CH$_2$</td>
<td>cm or dm of DiG</td>
</tr>
<tr>
<td>74.42</td>
<td>CH$_2$</td>
<td>d of DeG</td>
</tr>
<tr>
<td>74.89</td>
<td>CH$_2$</td>
<td>c of DeG</td>
</tr>
</tbody>
</table>

a) DeG: decylamine – GPTS reaction product

b) DiG: N, N’-dioctyamidine – GPTS reaction product

The NMR-DEPT (distorsionless enhanced polarization transfer) spectroscopy allows differentiating the four types of carbons. On the $^{13}$C spectrum the signals of the -CH- and -CH$_3$- are unchanged, the signal of the CH$_2$ is reversed and the signal of the -C- is absent.

Signals at 18.4 ppm and 58.22 ppm are those of ethanol indicating that some ethoxy groups are hydrolysed.

The comparison with the spectrum of model compound synthesized from reaction of GPTS and decylamine shows that signals at 50.67 (1i: CH$_2$NHCH$_2$CHOH), 53.8 (a: NHCH$_2$CHOH), 69.92 (b:CHOH), 74.45 and 74.84 (c and d) ppm come from the functionalisation of amino-terminal groups. The resonance of the amine as chain end at 42.5 ppm is still present therefore the whole of the amino end groups was not functionalised.
The comparison of spectra from both model compounds, decylamine-GPTS and functionalised N,N'-dioctylacetamidine, and functionalised and POA F1:1 (Figure 17) shows that the peaks at 64.63, 69.92, and 74.45 ppm can be attributed to the reaction of epoxy functions with amidine groups.
Figure 17: Comparison of the $^{13}$C NMR spectra of POA F1:1 (top) with the model compounds between 60-80 ppm (100.6 MHz; solvent: CD$_3$OD; TMS)

C-$^{29}$Si NMR characterisation

The Si NMR spectrum of alkosilane-functionalised POA with NH$_2$:epoxy molar ratio 1:1 is reported Figure 18.

Figure 18: $^{29}$Si NMR spectrum of the POAF1:1 (79.5 MHz; solvent: CD$_3$OD; TMS)

No resonance corresponding to the hydrolysed species $T^0$ and to the condensed species $T^1$ and $T^2$ are observed. The small intensity resonance close to -66 ppm is characteristic of the fully condensed GPTS.
D – MALDI-TOF spectroscopy

We expected to evidence species with molar masses equal to the sum of POA and GPTS or hydrolysed GPTS molar mass (278.42 g mol⁻¹). But the MALDI-TOF spectra display only peaks of the starting POA. The reaction compounds are probably a mixture of the neat oligomer and functionalised POAs. As the $^{29}$Si NMR shown, the alkoxy silane groups are condensed and the functionalised POAs form probably insoluble dimers and trimers. These species are therefore cannot be detected by MALDI (maybe the matrix used for MALDI analyses is not convenient for the alkoxy silane-functionalised POA in contrast to the neat polymer).

In summary, NMR and MALDI showed that:
- the functionalisation of the amino end groups of the polyamidine take place
- the GPTS also reacted on the amidine groups at a low extent
- some POA chains remain unfunctionalised
- a large amount of alkoxy silane groups condense

II.1.2.b Functionalisation of the POA with a amine NH₂: epoxy ratio of 1:2

![Figure 19: Expected chemical structure of the polyamidine F1:2](image)

$^{13}$C NMR characterization
The spectra of the $^{13}$C NMR spectra of POAF1:2 and POAF1:1 (Figure 20) are almost identical. As a consequence, the assignments are only done on the POAF1:1 spectrum.
Therefore the conclusions drawn about the functionalisation are the same. As the GPTS was introduce with amine (NH$_2$) to epoxy ratio of 1:2, one can expect a resonance at about 50.7 +6 ppm corresponding to the carbon
CH₂α-N (tertiary amine). This peak is not observed, it means that only the secondary amine is formed. However, the epoxy functions disappeared. The explanation could be that:
(i) the other half of GPTS reacts with the amidine groups,
(ii) the reaction occurred but the POA formed dimers by condensation of alkoxy groups which insoluble compounds due to the condensation,
(ii) a part of the GPTS didn’t react but formed insoluble particles.
As shown in NMR spectrum in Figure 22 shown, compounds are composed of hydrolysed and condensed species T² and T³ (T¹ specie are not detected).

![NMR Spectrum](image)

**Figure 22:** ²⁹Si NMR of POA F1:2 (79.5 MHz; solvent: CD₃OD; TMS)

Due to its poor solubility this compound cannot be analyzed by MALDI-TOF spectroscopy.

II.2 Functionalisation of the Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) POC

The polyamidines were functionalized with an primary amine to epoxy molar ratio of 1:1 and 1:2. Two types of amino end-groups are susceptible to attack the epoxy ring: the aliphatic and the cycloaliphatic.

![Scheme 16](image)

**Scheme 16:** Amino-end groups on copolymers
II.2.1 Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) with 20% of cycloaliphatic units with a amine: epoxy ratio of 1:1

As the functionalisation may happen on two kind of amino groups two structures are possibles (Figure 23).

![Chemical Structures](image)

**Figure 23: Expected chemical structures of the POC20 F1:1**

A. $^{13}$C NMR characterization

The $^{13}$C spectrum of the triethoxysilane-functionalised POCc20 in reported in Figure 24.

![NMR Spectrum](image)

**Figure 24: $^{13}$C NMR spectrum of POC20 F1:1**
The resonances at 44.6 and 51.8 corresponding to the epoxy ring of starting GPTS cannot be seen. In the case of the POC\textsubscript{20}, the functionalisation only happened on amino end chains. Indeed, the signals am and bm 64.6 and 72.2 corresponding to the reaction imino nitrogen of amidine on GPTS are not observed. The synthesis of the POC\textsubscript{20} was catalysed by the phenol. And the spectrum shows that it has been almost completely removed from the medium. The amidine group is mainly under the underprotonated form in opposition to the POA.

II.2.1 Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) with 20\% of cycloaliphatic units with a amine: epoxy ratio of 1:2

![Figure 25: \textsuperscript{13}C NMR spectrum of POC\textsubscript{20} F1:2](image)

The POC\textsubscript{20} F1:2 have a poor solubility and as the polyamidine change in solution, the solubilization time has to be limited. It is likely that the whole polyamide chains were not analysed. As a consequence, the spectra are not completely representative of the synthesized polyamidines. On the spectrum the resonances at 44.6 and 51.8 corresponding to the epoxy ring of starting GPTS are not present.

The polyamidines alkosilane-functionalised Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) with 80\% cycloaliphatic could not be analyzed by
NMR and MALDI because of their very poor solubility. We couldn’t investigate the functionalisation of these copolymers.

III. Conclusion

The structural characterization of the aliphatic polyamidines showed oligomers were synthesized since the highest $DP_n$ is equal to 8. The reaction products are a mixture of three types of chains. Amino-acetamido and di-acetamido terminated oligomers are preferentially formed. For similar experimental conditions were identical, polyamidines cannot be easily obtain with the same molar masses. In agreement with the $DP_n$ values, these POA oligomers have low Tg low comprised in the range from -8 to 8 °C. The catalyst was not completely removed from the medium and the protonated amidine is in equilibrium with the unprotonated form. As expected, the introduction of cycloaliphatic monomers in the main chain of polyamidines increases the glass transition temperature. The $DP_n$ of the copolymers are slightly higher than the POA ones. The structural investigation showed that in the both cases (POC$_{20}$ and POC$_{80}$) a mixture of homopolymers and copolymers is obtained. Concerning the alkoxy silane functionalisation, $^{13}$C NMR showed that the reaction between $\gamma$-glycidoxypropyltriethoxysilane GPTS and the amino end groups of polyamidines POA and POC$_{20}$ occurred. Nevertheless, in the case of the aliphatic polyamidine, the GPTS reacts also with the imino nitrogen of the amidine groups. The remaining acetic acid present in the aliphatic polyamidine, POA could promote the reaction between the GPTS and the imino-nitrogen of amidine group. Thus, the GPTS is an appropriate precursor for the synthesis of alkoxy silane-functionalised polyamide. For functionalised polyamidines, the alkoxy silane groups could undergo, during synthesis and characterization, steps hydrolysis and condensation. As we will see in the chapter III, the hybrid materials made from the functionalised POC$_{80}$ are too brittle to prepare free standing films. Therefore the thermo-mechanical characterization couldn’t be performed. We didn’t further investigate these materials and focused our attention on the hybrid materials from POC$_{20}$. 
REFERENCES

CHAPTER III: Organic-inorganic hybrid materials: a new strategy for using polyamidine

I Processing of the hybrid coatings based on polyamidine

As reported in part I (bibliography) three routes for synthesis of polymer-based hybrid materials exist:

- from simultaneous polymerization of an monomer organic and an inorganic precursor (metal alkoxide)
- from a polymer or an oligomer combined with a metal alkoxide precursor
- from an alkoxysilane-functionalised polymer or oligomer combined or not with a metal alkoxide precursor.

The first route is frequently used as the organic matrix is synthesized from free radical polymerization. In this work, we focused our studies on the other routes as the objective was to prepare hybrid materials from non-functionalised polyamidine and from functionalised polyamidine. The inorganic content, i.e. SiO$_2$ equivalent content, of O/I materials was increased by adding tetraethoxysilane (TEOS) which could be co-condensed with the alkoxysilane groups from functionalised polyamidines. The schema of the hybrid synthesis is reported in Figure 1.

![Figure 1: Schema of synthesis and processing of hybrid materials](image-url)
We will first recall in the paragraph below the chemical structure of our starting oligomers, and then we will explain how the amount of inorganic phase in the hybrid materials was chosen.

I.1 Polyamidine-based hybrid materials

I.1.1 Starting polymers

Two polymer matrices have been used to prepare the films: 

Poly (1,8-octamethylacetamidine): POA

\[
\text{NH} - \overline{\text{N}}_8 \]

-Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) with a molar ratio of aliphatic/cyclophatic monomers equal to 80:20 as denoted POC\textsubscript{20}

In addition, we also prepared the corresponding alkoxysilane-functionalised polyamidines (as described in part 2 of this manuscript). The epoxysilane, GPTS, was chosen in order to functionalise the polyamidines due to the fact that the condensation reaction between amino (and amidine) and epoxy groups is very sufficient. The polyamidines were functionalised with primary amine to epoxy molar ratios of 1:1 and of 1:2. The denominations of the resulting polymers are given in the Table 1.

<table>
<thead>
<tr>
<th>Primary amine to epoxy</th>
<th>POA</th>
<th>POC\textsubscript{20}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1:1</td>
<td>POA F1:1</td>
<td>POC\textsubscript{20} F1:1</td>
</tr>
<tr>
<td>1:2</td>
<td>POA F1:2</td>
<td>POC\textsubscript{20} F1:2</td>
</tr>
</tbody>
</table>

The glass transition temperature of neat polyamidines and alkoxysilane-functionalised polyamidines are reported in Table 2.
Table 2: Glass transition temperatures of polyamidines

<table>
<thead>
<tr>
<th></th>
<th>POA</th>
<th>POA F1:1</th>
<th>POA F1:2</th>
<th>POC 20</th>
<th>POC 20 F1:1</th>
<th>POC 20 F1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tg (°C)</td>
<td>6</td>
<td>-4</td>
<td>-11</td>
<td>18</td>
<td>5</td>
<td>13.5</td>
</tr>
</tbody>
</table>

The functionalisation induces a decrease of the glass transition temperature, Tg, for all the triethoxysilane-functionalised polyamidines POA and POC. For aliphatic polyamidines the functionalisation, which also occurred on amidine groups tends to decrease the inter-chains interactions, i.e. decreasing Tg. On the DSC thermogram of neat polyamidines (POA and POC20) no endothermic phenomenon is observed which demonstrates that the polyamidines are amorphous compounds as confirmed by X-ray diffraction (Figure 2)

Figure 2: X-ray diffraction, WAXS, pattern of (a) POA and (b) POC20

I.1.2 Processing of O/I hybrid materials as films

All the films have been prepared according to the same procedure illustrated in Figure 3. First the polymer was dissolved in anhydrous ethanol (step 1) at a concentration of 87.5g/L. The amount of solvent tended to be minimized. Anhydrous ethanol was used in order to control the total amount of water, because the polyamidine hydrolyses in presence of water. When the dissolution was completed, the TEOS was introduced in one step (step 2) and the mixture is stirred for one hour under reflux of ethanol. During this step, the hydrolysis of TEOS takes place. After that, acidified water (pH = 2) corresponding to a ratio H₂O/Si equal to 1 was added (step 3). The mixture was stirred under reflux for two additional hours. At the end, the solution was poured (step 4) on a PTFE plate and the solvent was evaporated at room temperature for 12 hours. Then, the sample underwent a curing at 80°C in an oven for 24 hours followed by a drying under vacuum at 50°C for about 12 hours.
The pH of the medium cannot be determined as the solution is mainly based on alcohol. Due to the low amount of added acidified water the pH medium remains basic. According to the value of pKa of POA the condensation reactions are favoured compared to the hydrolysis one.

I.2 Optimization of the silica content in the hybrid materials

Our final objective was the processing of polyamidine-based materials based on poly(1,8-octamethylacetamidine).

Preliminary experiments were performed with POA and POA F1:1 in order to synthesize class I and class II hybrids, respectively.

In our results, the amount of inorganic phase will be expressed in percentage of Si. Indeed, in such O/I hybrid materials, the silicon is present under several forms and not only as silica SiO$_2$.

In fact, the complete hydrolysis and condensation of the ethoxysilane groups from organosilane leads to the formation of SiO$_{3/2}$ and secondly, the condensation could be not completed.

a-Class I O/I hybrids

Films from POA with various contents of silicon 1.3, 2.54, and 4.7 wt% (theoretical) have been prepared. When the percentages were of 1.3 and 2.54, the samples were sticky and were too soft to be remove from the substrate. It appeared that in this case the percentage of silicon was not sufficient to obtain a material. But, when the Si percentage was equal to 4.7 wt%, the films have no cohesion. It was impossible to obtain good materials whatever the percentage of silicon introduced. These results are due to the low molar mass of the polyamidine and a lack of compatibility between the inorganic (hydrolysed TEOS species) and polyamidine phase.

The poor physical properties of O/I hybrids of class I indicate that:

i) a better compatibility is required between organic and inorganic species and
ii) that it is necessary to create strong interactions between phases such as covalent bonds, i.e. by designing hybrids of class II.

b- Class II O/I hybrids
Preliminary studies were done on films prepared from a POA functionalised by \(\gamma\)-glycidoxypropyltriethoxysilane, with a primary amine to epoxy molar ratio equal to 1:1. We studied films of different compositions by varying the final amount of equivalent SiO\(_2\) from the amount of TEOS introduced. These attempts showed that the range of SiO\(_2\) content allow to synthesize free standing films was narrow. For the films with Si percentage lower than 5 wt %, the inorganic phase was not sufficient to ensure a good behaviour. However, if the percentage of Si was higher than 9 wt% the inorganic part is too important and it leads to a too important shrinkage to get films. The optimal percentage of Si content was determined to be in a range from 5.5 to 6.5 wt%.

II Characterization of the inorganic-rich phase

This part is devoted to the study of the morphology of O/I hybrid materials synthesized from aliphatic (POA) and cycloaliphatic copolymer polyamidine (POC\(_{20}\)). As mentioned in the part I, a wide range of morphologies are reported. The condensation degree of the inorganic phase was probed by Si NMR. Mechanical properties of the hybrid materials were studied and correlated to the microscopy results. The effects of the alkoxysilane-functionalisation ratio of polyamidines on organisation and thermal properties were investigated. The influence processing parameters were also demonstrated.

The designation of the triethoxysilane-functionalised polyamidines (aliphatic and cycloalipahtic copolymers) studied in this work are reported in Table 3.

<table>
<thead>
<tr>
<th>Starting polyamidines</th>
<th>POA F1:1</th>
<th>POA F1:2</th>
<th>POC(_{20}) F1:1</th>
<th>POC(_{20}) F1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hybrid materials</td>
<td>hybPOA F1:1</td>
<td>hybPOA F1:2</td>
<td>hybPOC(_{20}) F1:1</td>
<td>hybPOC(_{20}) F1:2</td>
</tr>
</tbody>
</table>

II.1 Study of the inorganic phase from solid state NMR

\(^{29}\)Si NMR is a useful tool for the structural characterization of the inorganic network. It permits detection of different intermediate species resulting from
the sol-gel process: ranging from fully-alkoxy coordinated form to condensed structure going through hydrolyzed species.

The silicon sites are denoted by using the $Q^j$, $T^j$, $D^j$ notation (Figure 4, Figure 5) ($Q= \text{Si(RO)}_4$; $T= \text{R’Si(OR)}_3$; $D= \text{R’}_2\text{-Si-(OR)}_2$) where $j$ denotes the number of siloxane bridges (Si-O-Si) on the considered silicon atom.

![Diagram of silicon species](image1)

**Figure 4:** Nomenclature of silicon species as a function of condensation state for tetraalkoxysilane ($Y = \text{R or H}$)

![Diagram of silicon species](image2)

**Figure 5:** Nomenclature of silicon species as a function of condensation state for trialkoxysilane ($Y = \text{R or H}$) ($R = \text{organic group}$)

The assignments were done according to references [1] and [2] for $^{29}\text{Si}$ NMR in Figure 6, Figure 7 and Figure 8. All conditions of experiments are described in annex C.

![NMR spectrum](image3)

**Figure 6:** $^{29}\text{Si}$ solid-state NMR of hybPOA F1:1 with a silicon content of 5.83 wt % (elemental analysis)
The $^{29}$Si CP-MAS NMR demonstrates that the silanol species are well condensed since mainly Q$^4$ and T$^3$ silicon species are evidenced. No Q$^2$ species (~ -90 ppm)[3][4] and T$^2$ (~ -60 ppm) species are detected except for the POC$_{20}$ F1:2-based films. Nevertheless, because of the high noise to signal ratio, the absence of these species is not totally confirmed. These results suggest the formation of fully condensed particles rather than polymers which would exhibit principally Q$^2$ and Q$^3$ resonances [5]. This fact is in agreement with the basic-catalysed synthesis conditions used for the processing of O/I hybrid materials. In fact, the high pKa of the polyamidines provides to the medium a basic character. The residual acetic acid (catalyst of the polyamidine synthesis) and the small amount of acid contained water added for the hydrolysis are not sufficient to lead to acidic conditions of the reactive medium, i.e. to the formation of linear species.
One can also conclude that the protocol applied for the elaboration of films is appropriate for the elaboration of highly condensed and 3-D inorganic phase.

**II.2 Study of morphology of O/I hybrid materials**

The O/I hybrid materials were studied by dynamic thermomechanical analysis, DMA in tension mode. Usually the characterization of polymers-based hybrid materials is performed by comparison with the starting polymers, i.e. the systems without inorganic compounds. Due to the low molar masses ($3 < DPn < 8$) of the starting polyamidines the processing of free standing films cannot be done therefore this comparison is not possible.

The evolution of $E'$, $E''$, and tan delta as a function of the temperature are studied. $T_{E'' \text{max}}$ is determined from the maximum of $E''$ as this method allows to determine a temperature of relaxation close to the glass transition temperature [6]. A decrease of $E'$ as a function of temperature is simultaneously observed [1].

Details concerning the conditions of experiments are given in annex C.

**II.2.1 Hybrid organic-inorganic materials from POA**

POA F1:1-based film (synthesized in the conditions described in the part I.1.2) is considered as the reference sample. The study of the influence of process parameters will be performed by comparison with it. Thus this method will be used to compare the $T_g$ of the neat POA (which cannot be studied as free standing films) with one from POA-based O/I hybrid materials. The value of $T_\alpha$ and $T_{E'' \text{max}}$ are given in Table 4.
A Dynamical mechanical analysis

Figure 9: Storage modulus $E'$ and loss modulus $E''$ modulus as a function of temperature for hybPOA F1:1 (a) $E'$, (b) $E''$ (at 1 Hz)

Table 4: Transition temperatures obtained from DMA and DSC for hybPOA F1:1

<table>
<thead>
<tr>
<th>Si (wt%)</th>
<th>$T_{E''\text{max}}$ (°C)</th>
<th>$T_\alpha$ (°C)</th>
<th>$T_g^b$</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOA F1:1</td>
<td>5.83</td>
<td>-8</td>
<td>10</td>
</tr>
</tbody>
</table>

$^a$ temperature of the maximum of the loss factor $\tan \delta$

$^b$ measured by D.S.C

The starting triethoxy-functional polyamidines POA F1:1 has a $T_g$ of -4 °C (DSC measurement, Table 2).

The expected rubbery plateau (constant value of $E'$ vs. temperature) which is characteristic of the formation of a network is not observed. Nevertheless, above the main relaxation zone the storage modulus $E'$ slowly decreases with temperature. In fact, this behaviour is very different than the one from initial polyamidines which have a low molar mass ($3<DP_n<8$), i.e. lower than the molar mass needed for entanglements, and as a consequence should undergo a sharp decrease of $E'$ above $T_\alpha$ to a rapid liquid flow.

The glass transition obtained by DSC is in agreement with the $T_{E''\text{max}}$ obtained from DMA. The $T_g$ of the polyamidine is -14°C in the hybrid materials whereas the opposite effect is generally observed in the hybrid materials. In class-II hybrids materials, a chemical bonding with inorganic precursor of the organic matrix causes a loss of molecular mobility of polymer chains [7][8]. This effect
could be explained by the fact that the polyamide is water sensitive and could be hydrolysed during the sol-gel process.

B Microscopy

(a)

(b)
From the transmission electron microscopy (TEM) micrographs, it is clear that a phase separation occurred during synthesis of O/I hybrids (Figure 10). The TEM micrographs obtained on non-modified samples (i.e. without any staining) show two distinct regions:
i) a dark region composed of small (from 500 to 800 nm) aggregated particles
ii) and a uniform white region.
The first one could be assigned to a silicon-rich phase whereas the second corresponds mainly to polyamidine-rich phase.
TEM-EA (TEM combined with elemental analysis) was performed on the sample. Different regions of the samples were probed with the beam and a spectrum of the counts as a function of the energy (keV) is obtained. Unfortunately as Si is observed all over the specimen, it is not possible to conclude on phase composition as the two phases are strongly intermingled at a low scale.
We also performed S.E.M-EDX on the same sample in order to study the sample at larger scale length and obtain Si-mapping (Figure 11).
The mapping of Si element shows a uniform distribution which confirms that the structure of the hybrid is based on a mixed O/I composition with higher local concentration of Si. This observation shows also that the hybrid O/I material is based on a very fine microstructure, i.e. the two components (O and I) are present in all the volume of the materials. Such microstructure could result from the fact that the POA chain length is very low. As a consequence, the distance between two silicon-rich domains remains very low compared to the O/I reported in the literature for which the molar mass of alkoxy functionalised oligomers is commonly about 1,000 or 2,000 g.mol\(^{-1}\) ref [9]. In the later cases a two phases morphology is observed most of the time.

**II.2.1.a Influence of the functionalisation ratio for POA-based hybrid materials**

The polyamidines were functionalised with a primary amine to epoxy molar ratio of 1:1 and 1:2, i.e. for the latter ones the trialkoxysilane functionality is higher. The influence of the hydrolysable and condensable functions on the final morphologies was studied. From a conventional approach, a higher ratio should lead to higher crosslinked (average crosslink density) material.

A Dynamical mechanical analysis

The spectra of both materials: i) a POA F1:1-based ones and ii) POA F1:2-based O/I material are reported Figure 12 and Figure 13.
Figure 12: Comparison of storage modulus, $E'$ as a function of temperature for (a) hybPOA F1:1, and (b) hybPOA F1:2 (at 1 Hz)

Figure 13: Comparison of loss modulus, $E''$ for (a) hybPOA F1:2, and (b) hybPOA F1:1; Comparison of tan delta for (c) hybPOA F1:2, and (d) hybPOA F1:1

The modulus $E'$ at the glassy plateau is not influenced by the functionalisation whereas larger changes are observed for higher temperatures between the two types of O/I hybrid materials. For the mono-functionalised samples, only one broad relaxation peak is observed. As mentioned previously, this broad
relaxation is associated to an intimate co-existence of O and I phases. On the opposite, the loss factor of the material based on a higher functionality of POA displays two relaxation peaks indicating a more clearly microphase separation [10]. The narrow first peak corresponds to the organic rich phase as the second one could be attributed to a mixed O/I phase. In fact, higher number of strong interactions (covalent bonds) between the two phases induces a phase separation phenomenon leading to the creation of richer inorganic phase (in term of Si content). For hybPOA F1:2-based material, the first relaxation peak (-6°C) corresponds with the one from POA chains indicating that the phase separation occurring during the condensation step leads to the purification of the polyamidine phase. In fact, the POA F1:2 used for the synthesis of O/I hybrids has of a Tg equal to -11°C.

Table 5: Transition temperatures obtained from DMA and DSC for hybPOA F1:1 and hybPOA F1:2

<table>
<thead>
<tr>
<th></th>
<th>Si (wt %)</th>
<th>T_{E''\text{max}} (°C)</th>
<th>T_{α} (°C)</th>
<th>T_{g} (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOA F1:1</td>
<td>5.83</td>
<td>-8</td>
<td>10</td>
<td>-14</td>
</tr>
<tr>
<td>hybPOA F1:2</td>
<td>5.5</td>
<td>-16</td>
<td>-6 (first peak)</td>
<td>-14</td>
</tr>
</tbody>
</table>

B Microscopy
The TEM micrograph of the films made from hybPOA F1:2 is presented Figure 14 and the SEM in Figure 15. The film is characterized by a two-phase structure with large zones from 10 to 20 µm. The morphology is quite different of the POA F1:1-based films where the smaller domains have a size in a range from 500 to 800 nm.
Figure 15: S.E.M analysis of hybPOA F1:2

From the observations from microscopy and DMA spectra one can assign the second relaxation peak (hybPOA F1:2) to the dispersed domains. Those ones are based on an O/I mixed structure. Unfortunately, the films based on a high functionalised POA remain very brittle and the second relaxation cannot be entirely observed.

C Small Angle X-ray scattering

The SAXS profiles are displayed on the plot I(q) scattered intensity as a function of the scattering vector q. The scattering vector is described by the following equation:

$$q = \frac{4\pi}{\lambda}\sin\theta$$

$\lambda$: wavelength of the radiation
$\theta$: scattering angle

The low q region is characteristic of the smaller scale length and high q region is representative of higher length scale.
The SAXS profiles of the hybPOA F1:1 and hybPOAF1:2 are reported in Figure 16.

![SAXS profiles of hybPOAF1:1 and hyb POAF1:2](image)

Figure 16: SAXS profiles of hybPOAF1:1 and hyb POAF1:2

The lower limit of the size of Si-O domains can be determined from SAXS from the low-q region given by the resolution of SAXS apparatus. The size of Si structures is larger than 30 nm. The interference maxima for the sample hybPOA F1:2 exhibit well-ordered two-phase structures. The profiles of the hybPOA F1:1 indicates no or much less ordering.

The correlation distances $\frac{2\pi}{q_{\text{max}}}$, corresponding to the distance characteristic between scattering domain, can be calculated from the interference maximum. The correlation distance is equal at 35 Å for hyb POA F1:2. The correlation distance is quite large ca 35 Å because it includes also the size of Si domains.

D Wide Angle X-ray scattering

As observed by TEM micrographs the O/I materials made from POA F1:2 exhibit structures inside the dispersed phase which were assigned to the silicon rich one. No ordering is expected in such materials as all the components (initial and in situ ones) are amorphous. Moreover the functionalisation of the polyamidine takes place on the end-chains but maybe also on the imino nitrogen of amidine of the chains and
cannot improve ordering. In addition, the generated inorganic phase may hinder the probable hydrogen bond between the polyamidine chains. The WAXS patterns of triethoxysilane-functionalised POA-based O/I hybrid materials with different degrees of alkoxy silane functionalisation are reported in Figure 17 and Figure 18.

![Figure 17: X-ray diffraction, WAXS, pattern hybPOA F1:1](image1)

![Figure 18: X-ray diffraction, WAXS, pattern hybPOA F1:2](image2)

We clearly see the appearance of diffraction peaks with respect to the neat polymers. These peaks suggest the presence of an ordered phase. From the integration of the deconvoluted peaks a crystallinity rate can be calculated as follows:

\[ \chi(\%) = \frac{A_{\text{crystalline peaks}}}{(A_{\text{crystalline peaks}} + A_{\text{amorphous peak}})} \]
The peak deconvolution and the attribution of the peak (crystalline or amorphous) were done on the basis of the results obtained with the neat polyamidine. The calculated crystallinity rate cannot be considered as absolute since the amorphous phase identified in the films is certainly different of the amorphous neat polyamidine. In the films the polyamidine has been modified and also undergone the sol-gel process. The crystallinity rates are reported in the table:

<table>
<thead>
<tr>
<th>Hybrid materials</th>
<th>hybPOAF 1:1</th>
<th>hybPOA F1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\chi$ (%)</td>
<td>6</td>
<td>4.5</td>
</tr>
</tbody>
</table>

The rates are very low but the existence of “organized” species is clearly stated.

E Thermal properties

The thermal stability for the hybrid materials is improved with respect to the neat polyamidine POA, i.e. the one which is not combined with alkoxysilane compounds. The final weight percentage is the same for the hybrid O/I materials based on the functionalised-POA whatever the rate of alkoxysilane-functionalisation (POA F1:1 vs. POA F1:2). This is due to the fact that the two systems are based on the same amounts of silicon. The thermal stability of the POA F 1:2-based hybrid materials, with a two step process of degradation, is better. The first loss at about 420°C could be associated to the degradation of organic compounds in the organic rich phase and the second one to organic
compounds in the Si-rich phase. This phenomenon is correlated to the existence of two distinct phases in such O/I materials.

This part showed that the morphology is dependent on triethoxysilane functionalisation ratio of polyamidine. For both O/I hybrid materials, a phenomenon of phase separation is evidenced by microscopy. Nevertheless, as TEM-EA demonstrated the silicon is dispersed all over the film and there is no exclusively organic or inorganic phase. But, although the silica contents are similar, the microphase separation is more pronounced for POA F1:2-based hybrid materials as it confirmed by SAXS analysis which show an organised two-phase structure for hybPOA F1:2. In fact, as it is confirmed by dynamic mechanical analysis, the higher ratio of functionalisation, i.e. a higher number of strong chemical bonds between the organic and inorganic phase, leads to a purification of inorganic phase although a better intermixing of phase should occurred.

Characterization of thermal properties showed that the introduction of silica phase improved the thermal stability of organic matrix and in a greater extent for POA F1:2 which confirms the higher number of strong chemical bonds between the organic and inorganic phase.

II.2.1.b Influence synthesis conditions the dynamic mechanical behaviour of O/I hybrid materials

Then the experimental conditions (see part I.1.2) were subsequently varied (Table 7) in order to study the parameter effect on the final properties. We studied the influence of:
Mixing time with TEOS
Reaction time between silane and water
Curing time
Curing temperature

The POA F1:1-based hybrid material was considered to analyse the influence of these parameters.
Table 7: Conditions of POAF1:1-based O/I hybrid synthesis

<table>
<thead>
<tr>
<th></th>
<th>( t_{\text{TEOS}} )</th>
<th>( t_{\text{H2O}} )</th>
<th>( t_{\text{curing}} )</th>
<th>( T_{\text{curing}} )</th>
<th>Si (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOA F1:1 (ref)</td>
<td>1 h</td>
<td>2 h</td>
<td>24 h</td>
<td>80°C</td>
<td>5.83</td>
</tr>
<tr>
<td>hybPOA F1:1t_{\text{TEOS}}</td>
<td>½ h</td>
<td>2 h</td>
<td>24 h</td>
<td>80°C</td>
<td>6</td>
</tr>
<tr>
<td>hybPOA F1:1 ( t_{\text{H2O/2}} )</td>
<td>1 h</td>
<td>1 h</td>
<td>24 h</td>
<td>80°C</td>
<td>5</td>
</tr>
<tr>
<td>hybPOA F1:1t_{\text{curing}*3}</td>
<td>1 h</td>
<td>2 h</td>
<td>72 h</td>
<td>80°C</td>
<td>5.45</td>
</tr>
<tr>
<td>hybPOA F1:1T_{50°C}</td>
<td>1 h</td>
<td>2 h</td>
<td>24 h</td>
<td>50°C</td>
<td>5</td>
</tr>
</tbody>
</table>

\( a \) mixing time of TEOS with polymer solution  
\( b \) reaction time of water  
\( c \) curing time  
\( d \) curing temperature  
\( e \) determined by elemental analysis

A Influence of the time \( t_{\text{TEOS}} \), for mixing POA F1:1 with TEOS

\( t_{\text{TEOS}} \) is the time of mixing tetraethoxysilane, TEOS, with the triethoxysilane-functionalised polyamidine. The dynamic mechanical analyses of O/I hybrid materials as free-standing films prepared with \( t_{\text{TEOS}} \) of 30 minutes and one hour are reported in Figure 20.

![Figure 20: Variation of the storage modulus, \( E' \) and loss modulus, \( E'' \) as function of temperature: (a) \( E' \) hybPOA F1:1, (b) \( E' \) hybPOA F1:1t_{\text{TEOS/2}}, (c) \( E'' \) hybPOA F1:1 (d) \( E'' \) hybPOA F1:1t_{\text{TEOS/2}}](image-url)

102
Table 8: Transition temperatures obtained from DMA and D.S.C. for POA F1:1 \( t_{\text{TEOS/2}} \) and POA F1:1-based hybrid

<table>
<thead>
<tr>
<th>Material</th>
<th>Si (wt%)</th>
<th>( T_{E''_{\text{max}}} ) (°C)</th>
<th>( T\alpha^a ) (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOA F1:1 ( t_{\text{TEOS/2}} )</td>
<td>6</td>
<td>-10</td>
<td>4</td>
</tr>
<tr>
<td>hybPOA F1:1</td>
<td>5.83</td>
<td>-8</td>
<td>10</td>
</tr>
</tbody>
</table>

As expected, this parameter doesn’t influence on large way the final properties of cured hybrid materials as no reaction is expected during this step. The slight increase of \( T_{E''_{\text{max}}} \) for hybPOA F1:1 could be explained by the fact that some hydrolysis and condensation reaction could occur during \( t_{\text{TEOS}} \) due to the presence of water in polyamidine which is highly hydrophilic and auto-catalyses the reactions.

B Influence of the time \( t_{\text{H2O}} \), for hydrolysis and condensation before curing

The water with acid (pH = 2) is introduced into POA F -TEOS mixture for a given time, \( t_{\text{H2O}} \) which was varied from 1 to 2 hours. As reported previously, the step concerns both hydrolysis and condensation reaction as at such pH (polyamidine induces basic conditions) both hydrolysis and condensation reaction are favoured and occur simultaneously[11].

Figure 21: Variation of storage modulus, \( E' \) and loss modulus, \( E'' \) as function of temperature: (a) \( E' \) hybPOA F1:1, (b) \( E' \) hybPOA F1:1 \( t_{\text{H2O/2}} \), (c) \( E'' \) hybPOA F1:1 and (d) \( E'' \) hybPOA F1:1 \( t_{\text{H2O/2}} \), (at 1 Hz)
Table 9: Transition temperatures obtained from DMA and DSC for POA F1:1 t_{H2O/2} and hybPOA F1:1

<table>
<thead>
<tr>
<th></th>
<th>Si (wt%)</th>
<th>T_{E''\text{max}}</th>
<th>T\alpha^a</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOA F1:1 t_{H2O/2}</td>
<td>4.9</td>
<td>-20</td>
<td>-9</td>
</tr>
<tr>
<td>hybPOA F1:1</td>
<td>5.83</td>
<td>-8</td>
<td>10</td>
</tr>
</tbody>
</table>

For the O/I hybrids denoted hybPOA F1:1 t_{H2O}, the time has been divided by two with respect to POA F1:1-based O/I hybrids. On the spectrum, two effects are observed: (i) a shift of the relaxation peak toward low temperature, (ii) a slight increase of the storage modulus at the glassy state as t_{H2O} decreases. As mentioned, time influences the sol-gel reactions but also polyamidine oligomers, which are sensitive to water. Nevertheless, the shape of the E’’ was not changed, i.e. a single relaxation peak is observed.

Thus, the POA F1:1-based O/I hybrid has a higher temperature of relaxation due to higher condensation state of the silanol species mixed with the POA chains but the potentially high condensation state did not modify the phase separation phenomenon occurring during the final curing/drying steps of processing.

C Influence of the curing time and temperature of O/I hybrid films

i - Influence of time

The time of curing for the final step of O/I materials films based on POA F1:1 polyamidines was varied from 24 to 72 hours at 80°C. The dynamic mechanical behaviour of O/I materials are reported in Figure 22.

![Figure 22: Variation of storage modulus, E’ and loss modulus, E’’ as function of temperature: (a) hybPOA F1:1, (b) E’ hybPOA F1:1_{t_{curing}}-3, (c) hybPOA F1:1 and (d) E’’ HYB POA F1:1_{t_{curing}}-3](image-url)
Table 10: Transition temperatures obtained from DMA and D.S.C. for hyb POA F1:1\textsubscript{t\text{curing}} and hybPOA F1:1

<table>
<thead>
<tr>
<th>Si (wt%)</th>
<th>$T_{E''_{\text{max}}}$ (°C)</th>
<th>$T_{\alpha}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOA F1:1\textsubscript{t\text{curing}}</td>
<td>5.45</td>
<td>-20</td>
</tr>
<tr>
<td>hybPOA F1:1</td>
<td>5.83</td>
<td>-8</td>
</tr>
</tbody>
</table>

The rubbery plateau observed for the hybPOA F1:1\textsubscript{t\text{curing}} indicates that the O/I material is condensed at a higher degree as the time of curing is extended. The relaxation peak is narrower and shifts to lower temperature which demonstrates that the organic phase is more pure. Nevertheless, a single relaxation peak is evidenced, i.e. the hybrid O/I system based on POA F1:1 seems to be based on a mixed organic-inorganic phase.

The SAXS profiles of the hybPOA F1:1 and hybPOA F1:1\textsubscript{t\text{curing}} are displayed in the figure 23.

![SAXS profiles of hybPOA F1:1 and hybPOA F1:1\textsubscript{t\text{curing}}](image)

**Figure 23: SAXS profiles of hybPOA F1:1 and hybPOA F1:1\textsubscript{t\text{curing}}**

For the POA F1:1-based materials cured during a longer time, the plateau gradually disappears. One can propose that the small particles within the larger domains gradually connect within the large aggregate to form internally more homogeneous structure.
ii - Influence of temperature
The curing time temperature was changed from 50 to 80°C in the following analysis of O/I hybrids. One can observe that 80°C is a temperature above the relaxation peak in the previous DMA analyses (part II.2.1). Thus, the curing at high temperature (80°C) allowed to do the condensation reaction in a higher mobility state which could explain a higher relaxation (or Tg) temperature of the final O/I materials.

Figure 24: Variation of storage modulus $E'$ and loss modulus $E''$ as function of temperature: (a) $E'$ hybPOAF1:1, (b) $E'$ hybPOAF1:1T$_{50}$°C, (c) $E''$ hybPOAF1:1 and (d) $E''$ hybPOAF1:1T$_{50}$°C

Table 11: Transition temperatures obtained from DMA and DSC for hybPOA F1:1T$_{50}$°C and hybPOAF1:1

<table>
<thead>
<tr>
<th></th>
<th>Si wt%</th>
<th>$T_{E''\text{max}}$</th>
<th>$T_{\alpha}$a</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOAF1:1T$_{50}$°C</td>
<td>5</td>
<td>-11</td>
<td>0.05</td>
</tr>
<tr>
<td>hybPOAF1:1</td>
<td>5.83</td>
<td>-8</td>
<td>10</td>
</tr>
</tbody>
</table>

The aim of this part was to show the influence of the process parameters which influence hydrolysis and condensation reactions on the thermo-mechanical property and on the morphology. The parameters were successively varied and the resulting hybrid compared to a reference hybPOA F1:1. All the hybrids are characterized by a single relaxation peaks which means the phase separation
phase is not modified; O/I materials are characterized by an O/I mixed characterized.
In summary, we studied:
Influence of $t_{\text{TEOS}}$: as expected it is not very significant. The condensation state seems to be slightly raised with the increase of this time: hydrolysis and condensation started during this step.
Influence of $t_{\text{H2O}}$: a better condensation is also observed at a higher extent than for the increase of $t_{\text{TEOS}}$.
Influence of $t_{\text{curing}}$: a longer curing time causes a higher cross-linking of inorganic phase and leads to more pure organic phase.
Influence of $T_{\text{curing}}$: a higher temperature of relaxation is observed for the material cured at higher temperature.
All the parameters do not influence the properties of the final O/I in the same way. The key parameters are the reaction time between silane and water and the time of curing.

II.2.2 Hybrid organic-inorganic materials from POC$_{20}$

II.2.2.a Influence of the structure of the polyamidine and of the functionalisation ratio: POC$_{20}$-based materials

A Dynamical mechanical analysis
The DMA spectra of two samples a hybPOC$_{20}$ F1:1 and hybPOC$_{20}$ F1:2 are given in Figure 25 and Figure 26.

![Figure 25: Comparison of storage modulus, $E'$ as a function of temperature for (a) hybPOC$_{20}$ F1:2 and (b) hybPOC$_{20}$ F1:1 (at 1Hz)](image-url)
The storage modulus is similar for the both types of hybrids. The functionalisation ratio, which corresponds to a higher ability to participate to silicon rich structures, seems to have no influence on the stiffness vs. temperature. Nevertheless, the two types of O/I hybrids exhibit two relaxation peaks ($E''$ or $\tan \delta$) which indicate that in both systems, a phase separation occurs during hydrolysis and condensation steps. For the higher functionality of triethoxysilane groups (hybPOC$_{20}$ F1:2), the two peaks are clearly separated and one shifts at a higher temperature (whereas the low temperature one remains at the same temperature as the low temperature peak of POC$_{20}$ F1:1-based hybrid). One can conclude that the low temperature one is associated with a POC$_{20}$-rich phase and the high temperature one to a silicon-rich phase. The Tg of starting polymers POC$_{20}$ F1:1 and POC$_{20}$ F1:2 are equal to Tg of 4.7 and 13.5 °C respectively. The Tg in the hybrid materials are lower than the Tg of the starting polyamidines.

Table 12: Transition temperatures obtained from DMA and DSC for hybPOC$_{20}$F1:1 and hybPOC$_{20}$F1:2

<table>
<thead>
<tr>
<th></th>
<th>Si (wt%)</th>
<th>$T_{E''\text{max}}$ (°C)</th>
<th>$T_\alpha^a$ peak (°C)</th>
<th>$T_\alpha^a$ 1$^{st}$ peak (°C)</th>
<th>$T_\alpha^a$ 2$^{nd}$ peak (°C)</th>
<th>$T_g^b$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOC$_{20}$F1:1</td>
<td>4.9</td>
<td>-10</td>
<td>8</td>
<td>24</td>
<td>-12</td>
<td></td>
</tr>
<tr>
<td>hybPOC$_{20}$F1:2</td>
<td>4.7</td>
<td>-4.5</td>
<td>6</td>
<td>39</td>
<td>-4</td>
<td></td>
</tr>
</tbody>
</table>
B Microscopy

The TEM micrographs of POC₂₀ F 1:1-based O/I materials show spherically shape domains with a diameter from 2 to 6 µm.

For POC₂₀ F 1:2-based O/I hybrid materials, the microstructure observed by TEM (Figure 28) is completely different. The two phases (POA rich and Si-rich ones) seem to be intimately “mixed”. Nevertheless, as observed from DMA analysis, two phases are present and the purity of the silicon-rich is higher than for the POC₂₀ F1:1-based materials.
In addition, structures with dimensions of 5-6 µm close and smaller particles of 1 µm are observed.

C Small Angle X-ray scattering

![SAXS profiles of hybPOC20F1:1 and hybPOC20F1:2](image)

Figure 28: T.E.M micrograph of hybPOC20 F 1:2

Figure 29: SAXS profiles of hybPOC20F1:1 and hybPOC20F1:2
The interference maximum for the sample hybPOC F1:2 exhibits well-ordered two-phase structures. The profiles of the hybPOC F1:1 indicates no or much less ordering. This observation was also done for the aliphatic polyamidine-based hybrid materials. The correlation distance is equal at 35 Å for hybPOC F1:2-based hybrid materials as for POA F1:2-based hybrid materials. The structures are quite compact as the slopes at low-q region are steep, χ=3.5.

D Wide Angle X-ray scattering
No ordering also is expected in these hybrid materials as the neat POC20 is amorphous as it is confirmed by WAXS analyses (Figure 2). As for POA (paragraph II.2.1.1.c) the appearance of diffraction peaks with respect to the neat polymers is obvious (Figure 30Figure 31). These peaks suggest the presence of an ordered phase. The crystallinity rates, calculated as explained in paragraph II.2.1.a.D, are reported in the Table 13:

<table>
<thead>
<tr>
<th>Hybrid materials</th>
<th>hybPOC20 F1:1</th>
<th>hybPOC20 F1:2</th>
</tr>
</thead>
<tbody>
<tr>
<td>χ (%)</td>
<td>2</td>
<td>7</td>
</tr>
</tbody>
</table>

Figure 30: X-ray diffraction, WAXS, pattern POC20F1:1
In this case also, the rates are very low but the existence of “organized” species is clearly stated.

E Thermal properties

Below 400°C the thermal stability of the oligomers is better but then the trend is reversed above this temperature for the O/I hybrid materials. The inorganic percentage of two types of hybrids differing from the degree of functionalisation of the POC oligomers is the same, in agreement with the value of silica content. Nevertheless, the thermal stability of the POC\textsubscript{20} F 1:2 -based hybrid materials is slightly better; such a phenomenon was already observed for POA-based hybrid materials. In this case, the two types of I/O hybrids display similar TGA traces.
II.2.2.b Influence synthesis conditions the dynamic mechanical behaviour of O/I hybrid materials

The influence of the curing time was also studied for O/I hybrids based on POC$_{20}$ F1:1, i.e. The curing time was of 72 hours for hybPOC$_{20}$ F1:1 $t_{\text{curing}}$ and 24 hours for hybPOC$_{20}$ F1:1.

![Graph](image)

Figure 33: Variation of storage modulus, E' and tan delta as function of temperature: (a) E' hybPOC$_{20}$ F1:1, (b) E' hybPOC$_{20}$ F1:1 $t_{\text{curing}}$, (c) tan delta F hybPOC$_{20}$ F1:1, (d) tan delta hybPOC$_{20}$ F1:1 $t_{\text{curing}}$

<table>
<thead>
<tr>
<th></th>
<th>Si (wt%)</th>
<th>$T_{\text{E''max}}$ (°C)</th>
<th>$T_{\alpha}$ (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>hybPOC$_{20}$ F1:1</td>
<td>4.9</td>
<td>-10</td>
<td>8</td>
</tr>
<tr>
<td>hybPOC$<em>{20}$ F1:1 $t</em>{\text{curing}}$</td>
<td>5.4</td>
<td>-1.04</td>
<td>14</td>
</tr>
</tbody>
</table>

O/I material cured for a longer time exhibits a rubbery plateau which was not clearly evidenced for the low curing time, i.e. the longer curing time induced a higher cross-linking density. This fact is confirmed by the increase of the $\alpha$ relaxation temperature.

In that case, as we proposed that these hybrids materials based on POC F are composed of two phases, the effect of curing time is expected to concern the inorganic-rich separated phase. Nevertheless, the extent of curing time increases
also the organic-rich phase indicating that one contains hydrolysed and condensed trialkoxysilane species.

As observed for the POA-based hybrid materials a higher functionalisation ratio leads to higher phase separation. Nevertheless, the TEM micrograph seems to show that the two phases are intimately mixed for the hybPOC\textsubscript{20} F1:2 while the large dark domain observed for hybPOC\textsubscript{20} F1:1 evidences a phase separation. The inference maximum which is observed on the SAXS profile of POC\textsubscript{20} F1:2 confirm that the material is organized in a two-phase structure. WAXS measurements also demonstrated the presence of organised domains for both hybPOC\textsubscript{20} F1:1 and hybPOC\textsubscript{20} F1:2. Characterization of thermal properties showed that the thermal stability is improved as the triethoxysilane functionalisation ratio of polyamidine is increased.

### III Conclusion

This part shows that free standing films from polyamidines with low DPn and low T\textsubscript{g} can be elaborated. Nevertheless, strong chemical bonds have to be developed between the organic and inorganic phase. The generated inorganic phase are mainly characterized in \textsuperscript{29}Si CP-MAS NMR by Q\textsuperscript{4} and T\textsuperscript{3} silicon species, although, because of the high noise to signal ratio, the absence of Q\textsuperscript{2} species is not totally confirmed, which means that the inorganic phase was designed as fully condensed.

Polyamidines, POA and POC\textsubscript{20} which are amorphous compounds as confirmed by X-ray diffraction and DSC present small organization in the corresponding hybrid materials as demonstrated by WAXS.

The properties of POA and POC\textsubscript{20}-based hybrid materials have been compared as a function of the triethoxysilane-functionalisation ratio.

Concerning the aliphatic polyamidines, a mono-functionalisation ratio leads to hybrid materials composed of zones with an intimate co-existence of O and I phases and others silica-rich zone. Then, silicon silicon can be found all over the specimen, the mapping of Si element showed.

On the opposite, POA F1:2-based hybrid materials are characterized by a more clear microphase separation with respect to the POA F1:1, as evidenced by dynamic mechanical analysis where two relaxations are observed. SAXS analyses which show an organised two-phase structure for hybPOA F1:2 confirm this more important phase separation. The increase of functionalisation leads to a purification of phase.

In addition of the functionalisation ratio the influence of the process parameters on a POA F1:1-based hybrid materials was investigated. While the reaction time between silane and water and the time of curing seems to be key
parameters, the mixing time with TEOS and the curing temperature less influence the final POA F1:1 hybrid materials.

The second part was devoted to the characterization of hybrid materials prepared from POC$_{20}$. The hybPOC$_{20}$ F1:1 shows a phase separation which is more pronounced than for the corresponding POA O/I materials. As explained, in the Chapter II, the POC$_{20}$ were functionalised only on amino chain ends in opposition to POA which was also functionalised along the chains. It could explained the more obvious phase separation. As observed for the POA-based hybrid materials, the dynamic mechanical analysis shows that a higher functionalisation ratio leads to higher phase separation. In the case of POC$_{20}$ the narrowness of the relaxation peak shows that the organic phase is enriched in polyamidine. Nevertheless, the TEM micrograph seems to show that the two phases are intimately mixed for the hybPOC$_{20}$ F1:2 while large dark domains observed for hybPOC$_{20}$ F1:1 evidence a phase separation. The interference maximum which is observed on the SAXS profile of POC$_{20}$F1:2 confirms that the material is organized in a two-phase structure.

The thermal properties of hybrid materials are better than the ones of the starting polyamidines. As the silica content is almost the same for all the O/I hybrid materials and as the POA F1:2 and POC$_{20}$ F1:2 shows better thermal stability than mono-functionalised polyamidines-based hybrid materials, it can be stated that the increase of functionalisation improve the thermal stability of hybrid materials.
REFERENCES

GENERAL CONCLUSION

This research work was aimed to process new innovative hybrid materials which could be used for coating applications. In such materials, in order to bring mechanical reinforcement an inorganic phase is introduced within an organic matrix chosen for its specific properties. As was mentioned, in the Chapter I dealing with bibliographic studies, polyamidines were considered in this work due to their ability to form ionic complexes and more specifically the aliphatic polyacylamidines. The inorganic phase was generated by means of the sol-gel process which allows designing different morphologies and developing chemical interactions as well as strong chemical bonds between both organic and inorganic phases. Our attention was focused on materials for which the inter phase between both components is generated from strong chemical bonds (I/O hybrid materials of class-II). Therefore previous functionlisation of oligomers by I/O alkoxyisilane precursors is required.

Chapter II of this manuscript was devoted to the synthesis, characterization and functionalisation of polyamidines. The first point concerns the synthesis of the starting polymers. As organic matrix, two types of polyamidines were synthesized and deeply characterized: Poly (1,8-octamethylacetamidine) and Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) copolymer. The characterization of molar masses showed that the Poly (1,8-octamethylacetamidine) oligomers synthesis needs to be controlled very precisely in order to be reproducible. As expected, oligomers with low molecular weight (3 < DPn < 8) and low glass transition temperature, Tg from -8°C to 8°C, were obtained. The catalyst, acetic acid, was not completely removed from the medium and the protonated amidine is in equilibrium with the unprotonated form.

The second organic matrix was the Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) copolymer with a cycloaliphatic/aliphatic ratio of 20:80. As expected, the introduction of cycloaliphatic monomer in the main chain of polyamidines increases the glass transition temperature at a value of 20°C; nevertheless oligomers with low DPn are also obtained. Amidine groups are mainly under non-protonated form.

With such low DP and Tg, poly (1,8-octamethylacetamidine) and poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) copolymer are not usable as materials.
The second point was the triethoxysilane functionalisation of polyamidines by \(\gamma\)-glycidoxypropyltriethoxysilane (GPTS) on the amino end groups of polyamidines, with a primary amine to epoxy ratio of 1:1 and 1:2.

For aliphatic polyamidines, as amino-acetamido and di-acetamido terminated oligomers are preferentially formed, all the macromolecular chains cannot be functionalised on chain ends. Nevertheless, the GPTS reacts also with the imino nitrogen of the amidine groups in the case of the aliphatic polyamidine; therefore the functionalisation degree can be increased by this way. For POC\(_{20}\), the functionalisation only occurred on amino terminal groups. The difference in the functionalisation site could come from the presence of acetic in POA, which could promote the reaction between the GPTS and the imino-nitrogen of amidine group.

These oligomers, POA and POC\(_{20}\), were successfully functionalised; GPTS is an appropriate organic/inorganic silane precursor for the grafting of triethoxysilane functions on the polyamidine considered.

Chapter III of this study was devoted to the processing and characterization of O/I hybrid materials obtained from triethoxysilane-functionalised polyamidines.

Free standing films from polyamidines were elaborated and the processing parameters were investigated. It was shown that the reaction time between silane and water and the time of curing appear as key parameters. The basicity of polyacetamidine determines the final morphology of the hybrid materials. The generated inorganic phase, studied through \(^{29}\)Si NMR, was designed as fully condensed, as could be expected since the polyamidines have a high pKa and induces a basic catalysis.

The morphologies of the materials was studied using a combination of techniques: electron microscopies, dynamic mechanical analysis, wide angle X-ray scattering and small angle X-ray scattering. The morphology depends on the interactions developed between the two phases and consequently on the functionalisation ratio of polyamidines.

For mono-functionalisation ratio, hybrid materials composed of areas with an intimate co-existence of O and I phases and silica-rich zone were obtained with aliphatic polyamidines. While, the cycloaliphatic-based hybrid materials show a phase separation which is more pronounced than for the corresponding aliphatic-based hybrid materials. This “higher” phase separation could come from the fact that the cycloaliphatic-based polyamidine was functionalised only on amino end-chains in opposition to aliphatic polyamidine which was also functionalised along the chains.

A higher functionalisation ratio led to an increased phase separation for both polyamidine-based hybrid materials and induced a purification of phase. SAXS analysis evidenced a well ordered two phase structure for a both materials.
Polyamidines are amorphous polymers, but surprisingly the hybrid O/I materials present small and ordered areas which correspond to small organised domain. This phenomenon could be induced by the anchoring of polymer chains to silica domain. Finally, an additional interest of these hybrid materials is that the thermal properties are enhanced as compared to the starting polyamidines.
**Annex A: Experimental protocols for the polymer synthesis and functionalisation**

I- Synthesis of the poly (1,8 octamethylacetamidine) POA [1]

A mixture of 0.2 mol of 1,8-diamino-octane, 0.21 mol of triethyl-orthoacetate and 0.168 mol of acetic acid was heated under nitrogen with a mechanical stirring and continuous removal of the resulting alcohol by distillation, at 80°C for 15 min and at 120°C for 235 additional minutes. Then the pressure was reduced at 3 mBar and the temperature was raised stepwise to 180°C within 45 min. After additional 135 min, the reaction was completed.

This very high temperature and vacuum were necessary to remove the acetic acid. We consider that the reactants were in equimolar ratio, the slight excess was just to compensate a removing of orthoester during the distillation of alcohol.

II- Synthesis of the Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) copolymers POC\textsubscript{20} and POC\textsubscript{80} [2]

A mixture of 52.5 mmol of amine monomers (1,8 diaminooctane: trans-1,4-diaminocyclohexane), 50 mmol triethyl orthoacetate and 40 mmol of phenol was heated under nitrogen with a mechanical stirring and continuous removal of the resulting alcohol by distillation, at 80°C for 15 min and at 120°C for 15 additional minutes. The temperature was kept at 120°C for 210 min. Then the pressure was reduced at 3 mBar and the temperature was raised stepwise to 180°C within 45 min. After additional 135 min, the reaction was completed.

This very high temperature and vacuum were necessary to remove the phenol. For the POC\textsubscript{20}, the 1,8 diaminooctane: trans-1,4-diaminocyclohexane molar ratio was equal of 80:20 and for the POC\textsubscript{80}, the 1,8 diaminooctane: trans-1,4-diaminocyclohexane molar ratio was equal of 20:80.

III- Synthesis of the model compound: decylamine-glycidoxypropyltriethoxysilane

The reagents, 1.4157 g (0.009 moles) of decylamine and 2.5 g (0.009 moles) glycidoxypropyltriethoxysilane were heated and stirred under nitrogen at 120°C for one hour.
IV-Synthesis of the model compound: N,N-dioctylacetamidine-glycidoxypropyltriethoxysilane

a- Synthesis of N,N’ dioctylacetamidine [3]
A mixture of 7.14 g (0.044 moles) of triethylorthoacetate, 10.34 g (0.08 moles) of octylamine and 1.92 g (0.032 moles) of acetic acid as catalyst was heated under nitrogen atmosphere at 80°C for two hours under reflux, then the mixture was heated for two additional hours and the resulting alcohol was continuously removed by distillation. After that, the temperature was raised at 120°C and the pressure reduced at 3mBar in order to remove the unreacted amine and triethylorthoacetate TEOA, distillation was stopped after for 30 min.

b-Functionalisation of N,N’ dioctylacetamidine
The N,N’ dioctylacetamidine (5.73 g: 0.02 moles) and the glycidoxypropyltriethoxysilane (5.66 g: 0.02 moles) were heated under nitrogen at 120°C for two hours.

V- Functionalisation of the poly (1,8 octamethylacetamidine) POA
When the polymerization of POA was completed the vacuum was stopped and replaced by a nitrogen stream and the temperature was decreased to 120°C. Then 0.028 moles of GPTS was added for a primary amine to epoxy molar ratio of 1:1 and 0.057 moles of GPTS in the case of a primary amine to epoxy ratio of 1:2. The mixture was stirred one hour at 120°C for the former, and for the latter, the temperature was gradually increased up to 155°C because of the higher viscosity of the mixture.

VI- Functionalisation the Poly (1,8-octamethyl-co-1,4-cyclohexylacetamidine) copolymers, POC

a- Functionalisation of POC20
For a primary amine to epoxy molar ratio of 1:1, 3.9 g of POC20 and 0.738 g (0.002652 moles) of GPTS were introduced in a Schlenk tube and after a repeated vacuum nitrogen purge, the mixture was heated up to 120°C under nitrogen. Then, the temperature was kept at 120°C for one hour under mechanical stirring.
For a primary amine to epoxy molar ratio of 1:2, 5 g of POC20 and 1.8933 g (0.0068 moles) of GPTS were introduced in a Schlenk tube and after a repeated vacuum nitrogen purge, the mixture was heated up to 120°C under nitrogen. Then, the temperature was gradually increased up to 135°C for one hour under mechanical stirring.
b-Functionalisation of POC₈₀
For a primary amine to epoxy molar ratio of 1:1, 8 g of POC₈₀ and 2.74 g (0.00984 moles) of GPTS were introduced in a Schlenk tube and after a repeated vacuum nitrogen purge, the mixture was heated up to a temperature of 160°C under nitrogen. The temperature was kept at 160°C for one hour under mechanical stirring.
For a primary amine to epoxy molar ratio of 1:2, 8 g of POC₂₀ and 5.48 g (0.01968 moles) of GPTS were introduced in a Schlenk tube and after a repeated vacuum nitrogen purge, the mixture was heated up to a temperature of 150°C under nitrogen. The temperature was kept at 150°C for one hour under mechanical stirring.
REFERENCES

Annex B: Investigation on PA-12 based hybrid materials

The polyamide is a non-widespread polymer and O/I hybrid materials was never been designed from polyamidines. As a consequence, a study was done on a reference system, i.e. a hybrid material from a well-documented polymer: an amino-terminated polyamide-12 was considered. This polymer was supplied by the Degussa AG (Germany). Due to the high melting temperature of the polyamide and its limited solubility the protocol of elaboration of films cannot be the same as the one used for polyamidines. This polyamide 12 is only soluble in solvents like hexafluoroisopropanol, trifluoroacetic acid, and m-cresol.

The supplier’s data are reported in the Table 1:

<table>
<thead>
<tr>
<th>Mn[^{a}]</th>
<th>[NH2]</th>
<th>[COOH]</th>
<th>Tg</th>
<th>Tm</th>
</tr>
</thead>
<tbody>
<tr>
<td>2000 g/mol</td>
<td>1000 mmol/kg</td>
<td>7 mmol/kg</td>
<td>31 °C</td>
<td>166 °C</td>
</tr>
</tbody>
</table>

\[^{a}\] controlled by 4,4’-diaminodicyclohexylmethane

I-Molar mass characterization

The molar mass has been investigated by GPC [1] and the authors obtained number-average molecular weight, Mn of 8500 g.mol\(^{-1}\) using a polystyrene calibration and a polydispersity index of 3.7.

In the frame of our study, the molecular weight was probed by MALDI-TOF. The spectrum shows that the polyamide-12 is composed of molecules having molar masses comprised between 394 and 3612 g.mol\(^{-1}\). The distribution is not Gaussian. The exact structure of PA-12 chains cannot be determined because it is a commercial product and the possibilities are numerous. As a consequence, the real polymerization degrees, DP cannot be calculated. The range of DP can be approximated by dividing the molar masses by the mass of a uniting repeat (197 g.mol\(^{-1}\)). The PA-12 should be composed of molecular chains with polymerization degrees comprised from 2 to 18.

II. Functionalisation of polyamide 12 and characterization by solid-state NMR

The functionalisation of the Polyamide 12 was carried in a micro-extruder (type «DSM Micro 15 Compounder») which is made of a heated cylinder, in which two screws can rotate to an adjustable speed (5-200 tr/min) at a
temperature of 180°C. The tetraethoxysilane and the
glycidoxypropyltriethoxysilane have boiling points of 169°C and 270°C.
An amount of 3.3 g of GPTS was added with a syringe in 12 g of melted
Polyamide-12, which correspond to a primary amine to epoxy molar ratio of
1:1. The batch is mixed for 30 min and a sample is taken for 13C NMR
analysis.

II.1 13C NMR characterization

Due to its lack of solubility, trialkoxysilane-functionalised polyamide-12
could only be analysed by 13C solid state-NMR. The 13C spectra of the
Polyamide 12 and functionalised Polyamide 12 were recorded both under
cross polarisation magic angle spinning (CP-MAS) and with simple
decoupling (HP-DEC).
The spectra of the neat Polyamide 12 and trialkoxysilane-functionalised
polyamide12, denoted as PA12 and PA12F, are reported in Figure 1.
On the neat PA12 spectrum, the following resonances were identified:
- δ = 30ppm: CH2 of the chain,
- δ = 172.5 ppm: C(O) amide,
- shoulder at 38 ppm should come from the CH2 of amino chain-end.

The 13C HP-Dec NMR spectrum of glycidoxypropyltriethoxysilane
(structure shown below) exhibits 8 peaks having the following assignments:
43 ppm (6e), 50.1 ppm (5e), 73.1 ppm (4e), 71.5 ppm(3e), 23 ppm (2e),
6.3(1e), 57.8 (7e) and at 17.9 ppm (8e).
The $^{13}$C HP-Dec of trialkoxysilane-functionalised polyamide-12 is reported in Figure 2.

Due to the weak resolution, it is not possible to conclude that the signals of epoxy ring (6e and 5e at 43 and 50 ppm respectively) disappeared. The PA12F spectrum shows weak resonances in a range of 50-80 ppm which are characteristics of alcohol and ether and which are not observed in the PA12 spectrum recorded in the same conditions. The opening of a epoxy ring by the amino group should cause a resonance at 70 ppm [2] for the CH-OH. The weak resolution of the signals does not allow concluding if this resonance is present. Moreover as on the neat PA12 spectrum the resonance of the Cα-NH$_2$ close to 40 ppm [3][4], is not well evidenced, and cannot be used to conclude to a possible amino-epoxy reaction. The analysis and comparison of the spectra of PA-12 and PA-12F do not allow giving definitive conclusion.

Figure 2: $^{13}$C HP-Dec of Polyamide 12-GPTS reaction product
II.2 Processing

The processing of the hybrid materials was carried out in the micro-extruder subsequently to the functionalisation of Polyamide 12. In the PA12-GPTS mixture (after 30 minutes of reaction), an amount of 3.12 g of tetraethoxysilane, TEOS was added with a syringe, followed by addition of 1g of water. The amount of GPTS and TEOS introduced correspond to a theoretical silica content of 6 wt%.

As the micro-extruder wall was at a temperature close to 180°C and as the reagents were at room temperature have a boiling lower than 180°C, a part was vaporized during the introduction in micro-extruder. The amount of TEOS and water added is not exact.

Consequently to the addition of TEOS and water the “strength” increased gradually from 4 Newton to 100 Newton, the mixture is then extruded. The resulting material is denoted as hybPA12F.

III. Thermal characterization

The PA12, PA12F and hybPA12F were analysed by thermogravimetric analysis, TGA and differential scanning calorimetry, DSC.

The TGA traces are displayed in Figure 3. The characteristic values are reported in the Table 2.

![Figure 3: TGA traces for (a) PA12, (b) PA12F and (c) hybPA12F](image-url)
The thermal stability of the polyamide is not modified and is not improved in the case of the O/I hybrid material. The slightly increasing amount of residues proves that an inorganic phase was incorporated. Nevertheless, according to the amount of GPTS and TEOS added the percentage of residues should be higher in the hybrid material as compared to PA12F. It is not the case so it demonstrates that a part of TEOS was not integrated. The silica essentially comes from GPTS. The silicon content determined by elemental analysis shows that 1.65 wt% of silicon was introduced in PA12F and 2.32 wt% in hybPOAF which confirms the results obtained by TGA.

Table 2: Characteristics temperature from TGA measurements

<table>
<thead>
<tr>
<th></th>
<th>PA12</th>
<th>PA12F</th>
<th>hybPA12F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_{5%}^a$ (°C)</td>
<td>411</td>
<td>302</td>
<td>257</td>
</tr>
<tr>
<td>$T_{\text{max}}^b$ (°C)</td>
<td>467</td>
<td>470</td>
<td>467</td>
</tr>
<tr>
<td>Residues (wt%)</td>
<td>0.15</td>
<td>2.86</td>
<td>3.14</td>
</tr>
</tbody>
</table>

\(^a\) temperature for which one the weight loss is of 5%  
\(^b\) the maximum temperature of the derivative weight loss curve

The unchanging values of $T_{\text{max}}$ confirm that the GPTS, the silica content and the process do not influence the thermal properties of the matrix. The values of the glass transition temperature and melting temperature for the three compounds are reported in the Table3.

Table 3: Values of $T_g$ and $T_m$ for PA12, PA12F and hybPA12F

<table>
<thead>
<tr>
<th></th>
<th>PA12</th>
<th>PA12F</th>
<th>hybPA12F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T_g$ (°C)</td>
<td>37</td>
<td>45</td>
<td>44</td>
</tr>
<tr>
<td>$T_m$ (°C)</td>
<td>166</td>
<td>163</td>
<td>162</td>
</tr>
</tbody>
</table>

PA12F and hybPA12F showed similar thermal behaviour which could be explain by their very close silica content.
IV Conclusion

The molar masses determined from MALDI spectroscopy are in agreement with the average-number molecular weight provided by the supplier Degussa. The thermal characterization showed that the glycidoxypropyltriethoxysilane was well incorporated. Nevertheless, from $^{13}$C NMR spectra, it is difficult to conclude on the grafting of glycidoxypropyltriethoxysilane on the polyamide. The hybrid materials cannot be characterized by dynamical mechanical analysis because of the difficulty of process this material as free-standing film.
REFERENCES

Annex C: Characterization techniques

I Liquid Nuclear Magnetic Resonance (NMR): $^{13}$C, $^1$H and $^{29}$Si

The NMR measurements were carried out by Fernande Boisson (Service de RMN du Réseau des Polyméristes Lyonnais à Solaize). Spectra were recorded on a Brucker DRX 400 spectrometer operating at 400 MHz for $^1$H, 100.6 MHz for $^{13}$C, 79.5 MHz for $^{29}$Si. Samples were analysed at room temperature using deuterated methanol as solvent and in presence of tetramethysilane as reference. For the recording of the $^{29}$Si spectra tris(acetylacetonato)chromium(III), Cr(acac)$_3$ was added in the solution in order to decrease the relaxation time.

II MALDI-TOF (Matrix-assisted laser desorption/ionization-Time of flight)

The MALDI-TOF measurements were carried out by Frédéric Delolme (Service Central d'Analyse du CNRS, Solaize). Both polyamidines and matrix (dithranol or α-Cyano-4-hydroxycinnamic acid (CHCA)) were dissolved in a chloroform/methanol mixture (50/50) at 10 g/l. 1µl of the matrix/sample (10/1, v/v) mixture was spotted on the MALDI sample plate and air-dried. Mass spectra were recorded on a Voyager DE-STR spectrometer (Applied Biosystems) equipped with a nitrogen laser emitting at 337 nm with a 4 ns pulse duration. The instrument was operated in reflection mode. For the polyamide 12 the protocol was the same, but the polymer and matrix (dithranol) were dissolved in HFIP (1,1,1,3,3,3 hexafluoro-2-propanol).

III Differential Scanning Calorimetry

The measurements were performed on a DSC TA Q10 at a heating rate of 10°C/min under nitrogen.

IV Thermogravimetric analysis

The measurements were performed on a TGA TA Q500 at a heating rate of 10°C/min under nitrogen.

III. $^{29}$Si and $^{13}$C solid-state NMR

Spectra were recorded on a Bruker DSX300 spectrometer equipped with a Bruker CPMAS 4 mm probe. The operating speed was 5 KHz for the silicium and 10 KHz for the carbon analyses.
V Dynamical mechanical analysis

The tests were performed on a dynamic mechanical analyzer Rheometrics Solid Analyser RSAII with frequency fixed at 1 Hz and heating rate of 2°C/min in a tension mode on rectangular samples.

VI. Microscopy

The observations were performed by Pierre Alcouffe (at ‘Centre technologique des microstructures’ – UCBL -Villeurbanne).

<table>
<thead>
<tr>
<th>Instruments</th>
<th>Manufacturer</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>T.E.M.</td>
<td>Philips accelerating voltage of 80kV.</td>
<td>CM120</td>
</tr>
<tr>
<td>T.E.M. EDX</td>
<td>JEOL with an accelerating voltage of 80kV</td>
<td>1200EX</td>
</tr>
<tr>
<td>S.E.M. E.D.X.</td>
<td>FEI</td>
<td>ESEM XL30</td>
</tr>
<tr>
<td>S.E.M</td>
<td>HITACHI with a accelerating voltage of 15KV</td>
<td>S800</td>
</tr>
</tbody>
</table>

Si-mapping was performed by SEM EDX in controlled pressure mode, this mode allows to avoid a preliminary metal-coating.

TEM-EDX: an electron beam bombards the sample and passes through the samples. This beam tears off electrons from the materials, called secondary electrons. The arrachement of these secondary electrons causes the reorganization of the electron cloud of the considered atom and the subsequent emission of photons. These photons are analysed by the semiconductor Si doped Li detector. The measurement of the energy of these photons allows the determination of the corresponding atom.

VII. Wide-angle X-ray scattering

Wide-angle X-ray scattering (WAXS) was performed using a diffractometer, Bruker D8 Advance, equipped with a goniometer at geometry BRAGG-BRENTANO by Ruben Vera (Centre de diffractometrie Henri Longchambon-UCBL-Villeurbanne). The measurements were directly performed on the films.
VII. Small-angle X-ray scattering

Small-angle X-ray scattering (SAXS) was performed using a pinhole camera (Molecular Metrology SAXS System) attached to a microfocused X-ray beam generator (Osmic MicroMax 002) operating at 45 kV and 0.66 mA (30 W). The camera was equipped with a multiwire, gas-filled area detector with an active area diameter of 20 cm (Gabriel design). Two experimental setups were used to cover the q range of 0.007 – 1.1 Å⁻¹ where q = (4π / λ)sin θ, (λ is the wavelength and 2θ is the scattering angle). The analysis was performed by Libor Matejka (Institute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague)