Structural investigations and characterization of hexa (diéthanolamino) cyclotriphosphazene induced by an evenerently catalyst layered called Maghnite-H⁺ (Algerian MMT) under suitable condition.

Lahouaria Medjdoub, Abdelkader Rahmouni and Mohammed Belbachir
Laboratory of Polymer Chemistry, Department of Chemistry, Faculty of Sciences, Oran University, BP 1524 El M’nouar. 31000 Oran, Algeria.

ABSTRACT
Cyclotriphosphazenes are prominent inorganic N-heterocycles. They consist of six-membered ring structures of alternating phosphorus and nitrogen atoms. The tetravalent phosphorus atoms carry two exocyclic substituents, which can be widely varied enabling fine-tuning of the size and shape of the molecular periphery. This study involved the synthesis and characterization of hexa (diethanolamino) cyclotriphosphazene by an evenerently and friendly system catalyst consist of clay layered called Maghnite-H⁺ (Algerian MMT) and diethyl ether. The effect of different synthesis parameters such as amount of catalyst, effect of time, temperature and solvent are discussed.

Introduction
Phosphazene are of interest due to their high degree of chemical stability. Many Phosphazene can be considered high performance polymers in that they are stable at temperatures as high as 300°C [1]. Cyclotriphosphazenes containing alternate phosphorus and nitrogen atoms in their non-delocalized cyclic skeletons are an important family of inorganic ring systems [2].

In the past few decades a rich variety of cyclotriphosphazenes with interesting properties and applications are synthesized by easily replacing the chloride of the chlorocyclotriphosphazene with various nucleophiles [3]. The properties of cyclotriphosphazenes depend on the inorganic (P-N) skeleton as well as on the nature of the substituent attached to the phosphorus atoms [4]. Phosphazene are inorganic heterocyclic ring systems in which phosphorus and nitrogen repeat units can form cyclic compounds or chains [5]. Cyclotriphosphazene are known as small cyclic Phosphazene and the derivatives of cyclotriphosphazene are usually prepared by nucleophilic displacement of reactive chlorines of hexachlorocyclotriphosphazene, N₃P₃Cl₆, with different ligands such as primary and secondary amines, diamines, polyamines [6], aliphatic and aromatic alcohols [7].

The clay layer is hydrophilic in nature and can be converted to organoclay surfactant to promote the wetting of the polymer molecule onto the clay surface [8]. By properly controlling the surface properties of the organoclay, various degrees of organoclay dispersion can be achieved to give: (a) conventional composites, (b) intercalated nanocomposites, (c) intercalated-exfoliated nanocomposites and (d) exfoliated nanocomposites [9]. The clay surface properties can be modified in various ways. One can use clay with a different layer charge density, control the surfactant surface coverage or vary the kind of intercalated surfactant [10].

MMT exhibit mechanical and thermal properties [11]. Due to their wide range of applications in nanotechnology, they have attracted attention in materials science, electronics, and biomedical devices [12]. Unfortunately, the key problem for the application of MMT in industry is still their poor dispersibility which reduces their great potential. The surface functionalization and modification of MMT, improve their dispersibility in liquids, which gave them new properties for different applications [13].

Recently, an Algerian montmorillonite called Maghnite-H⁺ was used as catalyst for a number of vinylic and heterocyclic monomers [14].

In the present paper, we present a simple and facile strategy of synthesis of organophosphazene in the presence of an evenerently and friendly catalyst layered called Maghnite-H⁺ (Algerian MMT).
Measurements

$^1$H nuclear magnetic resonance (NMR) measurements were carried out on a probe BB05 mm, in CDCl$_3$. Tetramethylsilane (TMS) was used as the internal standard in these cases. Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm$^{-1}$ on an ATI Matson FTIR No 9501165. Ten scans were averaged at a resolution of 4 cm$^{-1}$ for the solid tested samples of modified and unmodified montmorillonite prepared as KBr pellets (ca. 3% by mass in KBr). Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm$^{-1}$ on an ATI Matson FTIR No 9501165. Ten scans were averaged at a resolution of 4 cm$^{-1}$ for the solid tested samples of modified and unmodified montmorillonite prepared as KBr pellets (ca. 3% by mass in KBr). Viscosity measurements were carried out with an Ubbelhode Capillary Viscosimeter (viscologic T11, version 3–1 Semantec). Intrinsic viscosity $[\eta]$ was measured at 30°C in benzene.

Results and discussion

Preparation and chemical composition of catalyst “Maghnite-H$^+$” was prepared by a method similar to that described by Belbachir et al. [16]. Crude Maghnite (20g) was crushed for 20 min using a Prolabo ceramic ball grinder. It was then dried by baking at 105°C for 2 h. The maghnite was then weighed and placed in an Erlenmeyer flask together with distilled water (500 mL) and magnetically stirred maghnite/water mixture was combined with sulfuric acid until saturation was achieved. After 2 days at room temperature the mineral was washed with water until it became sulfate free and then dried at 150°C.

Table 1. Elemental compositions of Protons exchanged samples “Maghnite” (Compositions wt%). PF* : Pert in Fire

<table>
<thead>
<tr>
<th>Sample</th>
<th>SiO$_2$</th>
<th>Al$_2$O$_3$</th>
<th>Fe$_2$O$_3$</th>
<th>CaO</th>
<th>MgO</th>
<th>Na$_2$O</th>
<th>K$_2$O</th>
<th>TiO$_2$</th>
<th>SO$_3$</th>
<th>P$^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Raw-Mag</td>
<td>69.39</td>
<td>14.67</td>
<td>1.16</td>
<td>0.30</td>
<td>0.07</td>
<td>0.50</td>
<td>0.79</td>
<td>0.16</td>
<td>0.91</td>
<td>1</td>
</tr>
<tr>
<td>Mag-H+</td>
<td>71.70</td>
<td>14.04</td>
<td>0.71</td>
<td>0.28</td>
<td>0.80</td>
<td>0.21</td>
<td>0.77</td>
<td>0.15</td>
<td>0.34</td>
<td>1</td>
</tr>
</tbody>
</table>

Characterization of catalyst

The x-ray powder diffraction profiles (Figure 1) exhibited the presence of other crystalline phases such as quartz, feldspath and calcite in raw-Maghnite. Under acid treatment, all trace of calcite was removed in Maghnite-H$^+$. The increase in basal spacing from 12.5 Å in raw-Maghnite, characteristic of a single water layer between the sheets, to a 15.02 Å value in Maghnite-H$^+$ reflects the changes in interlayer cation and its associated hydration state as a result of the acid treatment [17].

Figure 1. X-ray powder diffraction of (a) “Raw-Maghnite” and (b) “H-Maghnite0.25M”

Experiments conditions and results:

Synthesis of Hexa (diethanolamino) cyclotriphosphazene was conducted from the hexa (chlorocyclotriphosphazene), diethanolamine as starting material, Maghnite-H$^+$ as catalyst and diethyl ether as solvent at room temperature in 12 hours. The substitution on the nucéophilic hexachlorocyclotriphosphazene ($N_3P_3Cl_6$) by diethanolamine was performed, as was described by Christoval et al [18]. Then, 3.03 ml of diethanolamine were diluted in 3.33 ml diethyl ether of and in the other hand, 1g (0.0028 mol) of $N_3P_3Cl_6$ and 5%wt of Maghnite-H$^+$ were dissolved in 5 ml of diethyl ether after these two solutions were mixed and left under stirring for 24h at room temperature. Whereas the Mag-H$^+$ was separated by filtration because it is insoluble in the solvents in which the product is soluble. The solvent was evaporated in a rot vapor, the resulting solid was extracted several times with diethyl ether and the product was then cooled to 20° C and recrystallized from cyclohexane. Material obtained as white crystal and in the yield was (77%). The product is characterized by $^1$H-NMR. The reaction conditions are described as following:

Table 2. Synthesis of Hexa (diethanolamino) cyclotriphosphazene in diethyl ether induced by Maghnite-H$^+$ (0.25M)

<table>
<thead>
<tr>
<th>Product</th>
<th>Catalyst (Maghnite-H$^+$)</th>
<th>Solvent</th>
<th>Yield (%)</th>
<th>Time (h)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Diethyl ether</td>
<td></td>
<td>77</td>
<td>2</td>
<td>20</td>
</tr>
</tbody>
</table>

Characterizations of product

The formation of the hexa (diethanolamino) cyclotriphosphazene was confirmed by 1HNMR spectroscopy at 300MHz (Figure 2) and the reaction taking place is shown in the following scheme:

Scheme 1. Representation schematic of the synthesis of hexa (diethanolamino) cyclotriphosphazene induced by Maghnite-H$^+$ (5% wt, 0.25M)

Table 3. Chemical shift of product protons

<table>
<thead>
<tr>
<th>$\delta$ (ppm)</th>
<th>Proton type</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.0</td>
<td>H$_3$</td>
</tr>
<tr>
<td>3.7</td>
<td>H$_b$</td>
</tr>
<tr>
<td>4.8</td>
<td>D$_2$O</td>
</tr>
</tbody>
</table>

According to the work published by Christoval et al [19], 1H NMR spectroscopy at 300 MHz (Solvent D$_2$O) (Fig. 2) showed different peaks: (a) the methylene groups (CH$_2$-) at 3.0 ppm, and (b) the methine groups (CH$_3$-O) at 3.7 ppm and (D$_2$O) at 4.8 ppm. Besides these well-known results, we note the absence of the peak (Hc) at 4.2 ppm attributed to the (NH) group, because it’s masked by the presence of D$_2$O solvent, this confirms the feasibility of the nucleophilic substitution on the hexachloro-cyclo-tri-phosphazene of diethanolamine.
Figure 2. $^1$HNMR (300MHz) spectrum of Hexa (diéthanolamino) cyclotriphosphazene generated by system catalyst diethyl ether/Maghnite-H$^+$ in D$_2$O

The FT-IR spectra of Hexa (diéthanolamino) cyclotriphosphazene generated by a system catalyst diethyl ether/Maghnite-H$^+$ in KBr are presented in Fig.3. The peak positions related to the corresponding chemical bonds are listed in the table 4 [20,21].

Table 4. Observed characteristic vibration from FT-IR

<table>
<thead>
<tr>
<th>References</th>
<th>Characteristic vibration</th>
</tr>
</thead>
<tbody>
<tr>
<td>3415 (forte)</td>
<td>OH(stretching)</td>
</tr>
<tr>
<td>1235 (faible)</td>
<td>P=N(stretching)</td>
</tr>
<tr>
<td>1068 (forte)</td>
<td>C-O(stretching)</td>
</tr>
<tr>
<td>1640</td>
<td>C-N(stretching)</td>
</tr>
</tbody>
</table>

Figure 3. IR Spectrum of Hexa (diéthanolamino) cyclotriphosphazene generated by system catalyst diethyl ether/Maghnite-H$^+$ in KBr

The chemical structure of hexa (diéthanolamino) cyclotriphosphazene was further supported by $^{31}$P-NMR spectra (see Fig.4 and 5). It is observed the presence two peak one at 0 ppm and another peak at 3.9 ppm this confirms that the substitution on the hexachlorocyclotriphosphazene of diethanolamine in presence of diethyl ether is a partial substitution [20]. In the other hand when we use (diethyl ether /Maghnite-H$^+$), it is observed the presence of one peak at 3.9 ppm this confirms that the substitution on the hexachlorocyclotriphosphazene of diethanolamine in presence of clay catalyst layered called maghnite (Algerian MMT) is a total substitution[21].

Figure 4. $^{31}$P-NMR Spectrum of Hexa (diéthanolamino) cyclotriphosphazene in presence of diethyl ether in D$_2$O

Figure 5. $^{31}$P-NMR Spectrum of hexa (diéthanolamino) cyclotriphosphazene in presence of diethyl ether /Maghnite-H$^+$ in D$_2$O

Conclusion

The present study shows that the synthesis of Hexa (diéthanolamino) cyclotriphosphazene can be induced in heterogeneous phase by a system catalyst between montmorillonite clay layered called Maghnite-H$^+$ (Algerian MMT) in diethyl ether. The catalytic activity of this catalyst depends on the amount of catalyst in the reaction medium. Through simple filtering the clay can be separated from the reaction mixtures. Moreover this acidic clay is inexpensive, stable and non corrosive. Hexa (diéthanolamino) cyclotriphosphazene was produced by simple procedure in presence of an enverement system catalyst consist of clay layered called Maghnite (Algerian MMT) and diethyl ether.

Acknowledgment

All our gratitude to the anonymous referees for their careful reading of the manuscript and valuable comments which helped in shaping this paper to the present form. We thank all laboratory staff of polymer chemistry from the University of Oran (Algeria) for their kind cooperation.

References


