



# Structural investigations and characterization of hexa (diéthanolamino) cyclotriphosphazene induced by an enveremently catalyst layered called Maghnite-H<sup>+</sup> (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.

## ARTICLE INFO

### Article history:

Received: 11 June 2014;

Received in revised form:

19 November 2014;

Accepted: 29 November 2014;

### Keywords

Phosphazene,  
1H-NMR spectroscopy,  
Maghnite-H<sup>+</sup>,  
cyclotriphosphazene,  
diethanolamine.

## 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 enveremently and friendly system catalyst consist of clay layered called Maghnite-H<sup>+</sup> (Algerian MMT) and diethyl ether. The effect of different synthesis parameters such as amount of catalyst, effect of time, temperature and solvent are discussed.

© 2014 Elixir All rights reserved

## 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]. Cyclophosphazenes 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 cyclophosphazenes with interesting properties and applications are synthesized by easily replacing the chlorine of the chlorocyclotriphosphazene with various nucleophiles [3]. The properties of cyclophosphazenes 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, N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>, 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<sup>+</sup> 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 enveremently and friendly catalyst layered called Maghnite-H<sup>+</sup> (Algerian MMT).

## Materials and methods

HDCTP was synthesized through the aminolysis of (NPCl<sub>2</sub>)<sub>3</sub> with excess allylamine as describe. Diethanolamine and diethyl ether (Aldrich 99%) was purified by fractional distillation under reduced pressure, was used as received.

Maghnite-H<sup>+</sup> was prepared according to the process reported by Belbachir *et al* [15]. Raw-Maghnite (20g) was crushed for 20 mn using a prolabo ceramic balls grinder. It was then dried for 2 h at 105°C. The Maghnite was placed in an Erlenmeyer flask together with 500 mL of distilled water. The Maghnite/water mixture was stirred using a magnetic stirrer and combined with 0.25M sulfuric acid solution, until neutralization was achieved over 2 day at room temperature, the mineral was then washed with distilled water to become sulfate free and then dried at 105°C.

### Measurements

<sup>1</sup>H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl<sub>3</sub>. Tetramethylsilane (TMS) was used as the internal standard in these cases. Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm<sup>-1</sup> on an ATI Matson FTIR No 9501165. Ten scans were averaged at a resolution of 4 cm<sup>-1</sup> 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 4000cm<sup>-1</sup> on an ATI Mattson FTIR no. 9501165. Ten scans were averaged at a resolution of 4cm<sup>-1</sup> 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 Ubbelohde Capillary Viscosimeter (viscologic T11, version 3-1 Semantec). Intrinsic viscosity [η] was measured at 30°C in benzene.

### Results and discussion

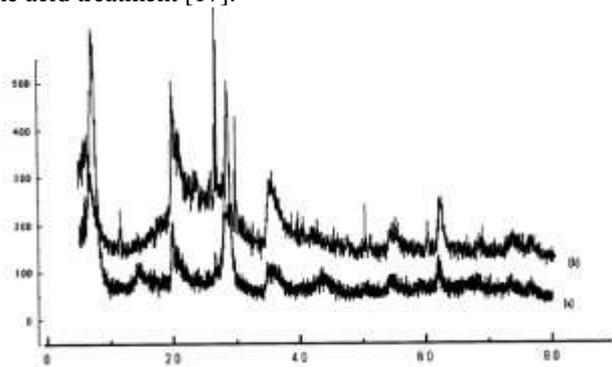
Preparation and chemical composition of catalyst "Maghnite-H<sup>+</sup>" was prepared by a method similar to that described by Belbachir *et al.* [16]. Crude Maghnite (20g) was crushed for 20 min using a Prolabo ceramic ball grinder. It was then dried by baking at 105°C for 2 h. The maghnite was then 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. Elementary compositions of Protons exchanged samples "Maghnite" (Compositions wt%). PF\* : Pert in Fire**

Sample	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	Na <sub>2</sub> O	K <sub>2</sub> O	TiO <sub>2</sub>	SO <sub>3</sub>	PF*
Raw-Mag	69.39	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91	11
Mag-H+	71.70	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34	11

### 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<sup>+</sup>. 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<sup>+</sup> for two interlamellar water layers 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:

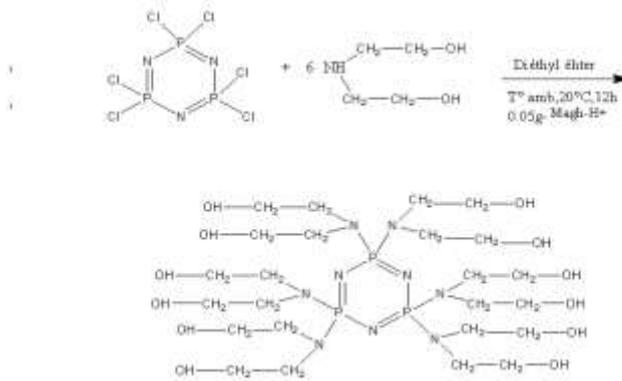
Synthesis of Hexa (diéthanolamino) cyclotriphosphazene was conducted from the hexa (chlorocyclotriphosphazene), diethanolamine as starting material, Maghnite-H<sup>+</sup> as catalyst and diethyl ether as solvent at room temperature in 12 hours. The substitution on the nucleophilic hexachlorocyclotriphosphazene (N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>) 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<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub> and 5%wt of Maghnite-H<sup>+</sup> 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: <sup>1</sup>H-NMR. The reaction conditions are described as following:

**Table 2. Synthesis of Hexa (diéthanolamino) cyclotriphosphazene in diethyl ether induced by Maghnite-H<sup>+</sup> (0.25M)**

Product	Catalyst (Maghnite-H <sup>+</sup> )	Solvent	Yield	Time (h)	Temperature (°C)
1	5%	Diethyl ether	77%	12	20

### Characterizations of product

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

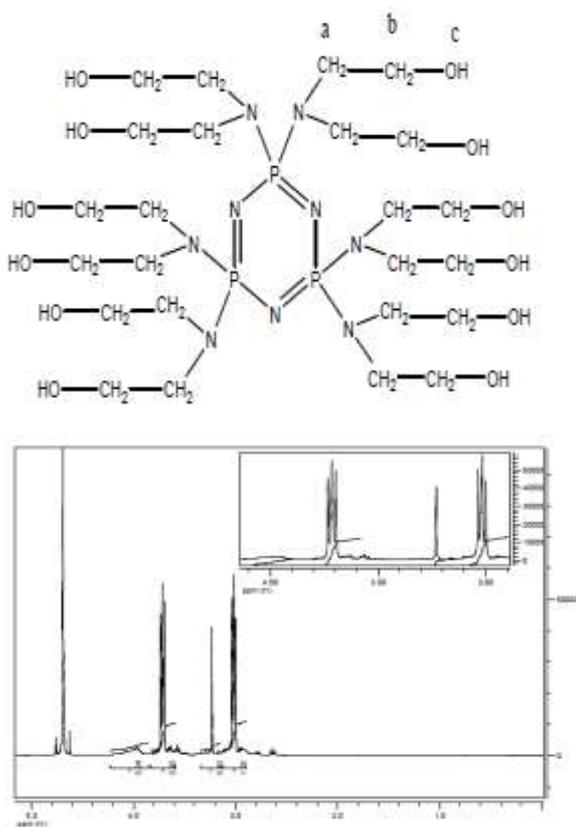


**Scheme 1. Representation schematic of the synthesis of hexa (diethanolamino) cyclotriphosphazene induced by Maghnite-H<sup>+</sup> (5%wt, 0.25M)**

**Table 3. Chemical shift of product protons**

δ (ppm)	Proton type
3.0	H <sub>a</sub>
3.7	H <sub>b</sub>
4.8	D <sub>2</sub> O

According to the work published by Christoval *et al* [19], <sup>1</sup>H NMR spectroscopy at 300 MHz (Solvent D<sub>2</sub>O) (Fig. 2) showed different peaks: (a) the methylene groups (CH<sub>2</sub>-) at 3.0 ppm, and (b) the methine groups (CH<sub>2</sub>-O) at 3.7ppm and (D<sub>2</sub>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<sub>2</sub>O solvent, this confirms the feasibility of the nucleophilic substitution on the hexachloro-cyclo-tri-phosphazene of diethanolamine.

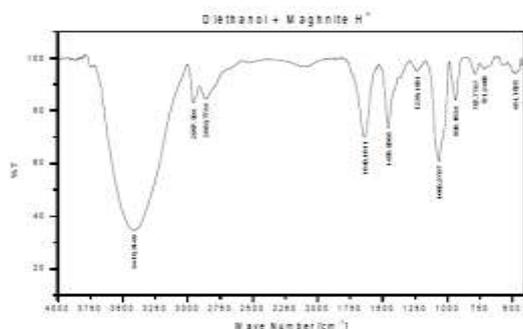


**Figure 2 .  $^1\text{H}$ -NMR (300MHz) spectrum of Hexa (diéthanolamino) cyclotriphosphazene generated by system catalyst diethyl ether/Maghnite- $\text{H}^+$  in  $\text{D}_2\text{O}$**

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

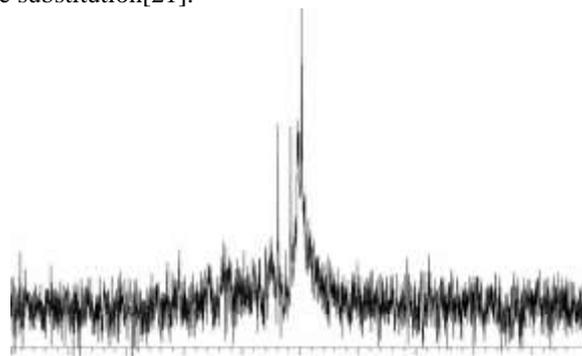
**Table 4. Observed characteristic vibration from FT-IR**

References	Characteristic vibration
3415 (forte)	OH(stretching)
1235 (faible)	P=N(stretching)
1068 (forte)	C-O(stretching)
1640	C-N(stretching)

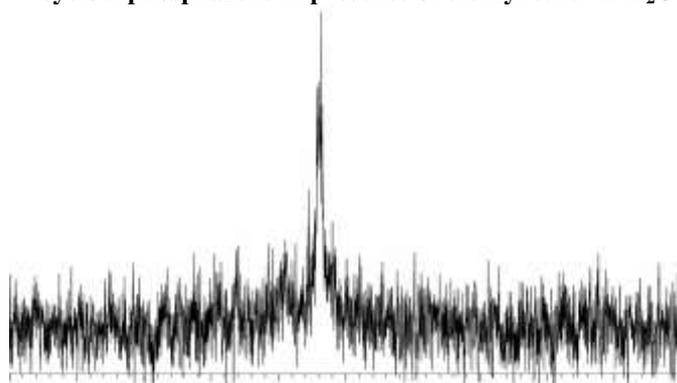


**Figure 3 .IR Spectrum of Hexa (diéthanolamino) cyclotriphosphazene generated by system catalyst diethyl ether/Maghnite- $\text{H}^+$  in KBr** The chemical structure of hexa (diéthanolamino) cyclotriphosphazene was further supported by  $^{31}\text{P}$ -NMR spectra (see Fig.4 and 5).It is observed the presence two peak one at 0 ppm and another peak at 3.9 ppm this confirms that the substitution on the hexachloro-cyclotriphosphazene of diethanolamine in presence of diethyl ether is a partial substitution [20].In the other hand when we use (diethyl ether /Maghnite- $\text{H}^+$ ),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 totale substitution[21].



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



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

### Conclusion

The present study shows that the synthesis of Hexa (diéthanolamino) cyclotriphosphazene can be induced in heterogenous phase by an system catalyst between montmorillonite clay layered called Maghnite- $\text{H}^+$  (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 everemently system catalyst consist of clay layered called Maghnite (AlgerianMMT) 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

- [1].N. Higashi, T. Koga, N. Niwa, and M. Niwa, Chem. Commun., 5, 361 (2000).
- [2].K. Inoue, A. Miyahara, and T. Itaya, J. Am. Chem. Soc., 119, 6191 (1997).
- [3].M. Mutter, K. H. Altmann, G. G. Tuchscherer, and S. Vuilleumier, Tetrahedron, 44, 771 (1988).
- [4].Brown DE.,Ramachandra K.,Carter KR.,Allen CW.,Macromolecules, 34-2870,2001.
- [5].K. Inoue, H. Sakai, A. Ochi, T. Itaya, and T. Tanigaki, J. Am. Chem. Soc., 116, 10783 (1994).

- [6]. Labarre, J.F., natural polyaminelinked cyclophosphazenes. attempt at the production of antitumore selective antitumorals. *Top curr chem* 129 ;173-260,1985
- [7]. Caminade, A.M.; Turrin, C.-O.; Laurent, R.; Ouali, A.; Delavaux-Nicot, B., Eds. *Dendrimers: Towards Catalytic, Material and Biomedical Uses*; John Wiley & Sons: Chichester, U.K., 2011.
- [8]. Rahmouni A, Harrane A, Belbachir M (2013). 1H-NMR Spectra of Conductive, Anticorrosive and Soluble Polyaniline Exchanged by an Eco-Catalyst Layered (Maghnite-H+). *wod J. Chem.*, 8(1): 20-26.
- [9]. Rahmouni A, Harrane A, Belbachir M (2013). Maghnite-H+, an eco-catalyst layered (Algerian Montmorillonite) for synthesis of polyaniline/Maghnite clay nano-composites. *Int. J. Chem. Mater. Sci.*, 1(6): 175-181.
- [10]. Gao, L.; Song, Q.; Huang, X.; Huang, J. *J. Colloid Interface Sci.* 2008, 323, 420–425.
- [11]. Chen Yang YW, Lee HF, Yuan CY, *J. Polym. Sci., Polym. Chem.*, 38-972, 2000.
- [12]. Dez I., De Jaeger R., *J. Appl. Polym. Sci.*, 89-1925, 2003.
- [13] Belbachir M., Yahiaoui A., Hachemaoui A. *International Journal of Molecular Sciences*, 2003, 4, 548–561.
- [14] Belbachir M, Bensaoula A (2001). “Composition and method for catalysis using bentonites,” United States Patent Number: 6274527 B1.
- [15]. Belbachir, M ; Bensaoula, A, Composition and method for catalysis using bentonites, US patent, No7, 094-823 B2, 2006.
- [16]. Belbachir M, Bensaoula A (2001). “Composition and method for catalysis using bentonites,” United States Patent Number: 6274527 B1.
- [17]. Yahiaoui A., et al., An acid exchanged montmorillonite clay catalyst synthesis of poly ephloridrin, *Int. J. Mol. Sci.*, 4:548-561, 2003.
- [18,19]. Christova D., et al. *Designed Monomers and Polym*, 6, 11-21. (2003).
- [20]. Vögtle, F., Gestermann, S.; Kauffmann, C.; Ceroni, P.; Vicinelli, V.; Balzani, V. *J. Am. Chem. Soc.* 2000, 122, 10398–10404.
- [21] N. Hasegawa, H. Okamoto, M. Kawasumi, M. Kato, A. Tsukigase, and A. “Usuki. Polyolefin–clay hybrids based on modified polyolefins and organoclay”. *Macromol. Mater. Engng.*, Vol. 280/281, pp. 76–79, 2000