

Research Article

# New Method for Nucleophilic Substitution on Hexachlorocyclotriphosphazene by Allylamine Using an Algerian Proton Exchanged Montmorillonite Clay (Maghnite-H<sup>+</sup>) as a Green Solid Catalyst

Lahouaria Medjdoub\*, Belbachir Mohammed

Laboratory of Polymer Chemistry, Department of Chemistry, Faculty of Exact and Applied Sciences, University of Oran1 Ahmed BenBella, BP 1524 El M'Naouar, 31000 Oran, Algeria

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## Abstract

Nucleophilic substitution on hexachlorocyclotriphosphazene (HCCTP) with allylamine in order to give hexa(allylamino)cyclotriphosphazene (HACTP) is performed for the first time under mild conditions by using diethylether as solvent to replace benzene due to its toxicity. The reaction time is reduced to half and also performed at room temperature but especially in the presence of an eco-catalyst called Maghnite-H<sup>+</sup>. This catalyst has a significant role in the industrial scale. In fact, the use of Maghnite is preferred for its many advantages: a very low purchase price compared to other catalysts, the easy removal of the reaction mixture. Then, Maghnite-H<sup>+</sup> is became an excellent catalyst for many chemical reactions. The structure of HACTP synthesized in the presence of Maghnite-H<sup>+</sup> to 5% by weight is confirmed by <sup>1</sup>H-NMR, <sup>13</sup>C-NMR, <sup>31</sup>P-NMR (Nuclear magnetic resonance) and FTIR (Fourier Transform Infrared spectroscopy). MALDI-TOF (Matrix-Assisted Laser Desorption/Ionisation-time-of-flight mass spectrometry) is used to establish the molecular weight of HACTP which is 471 g/mol. DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) show that HACTP is a crystalline product with a melting point of 88 °C. It is reactive after melting but is degraded from 230 °C. Copyright © 2016 BCREC GROUP. All rights reserved

**Keywords:** Hexachlorocyclotriphosphazene; Allylamine; Nucleophilic substitution; Maghnite-H<sup>+</sup>; NMR spectroscopy; Thermal properties

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## 1. Introduction

Phosphazenes are inorganic compounds which belong to the most important class of cy-

clie or linear structure of general formula (R<sub>2</sub>P=N)<sub>n</sub>. The degree of polymerization "n" may vary from 3 to more thousand. R can be a halogen, alkyl, aryl, amine, alkoxy, and other groups. Cyclophosphazenes are cyclic trimers (R<sub>2</sub>P=N)<sub>3</sub> and when R represents halogen Cl, there will be formation of hexachlorocyclotriphosphazene (HCCTP) (N=Cl<sub>2</sub>P)<sub>3</sub>

\* Corresponding Author.

E-mail: [houariamejdoub@yahoo.fr](mailto:houariamejdoub@yahoo.fr) (L. Medjdoub),  
Telp: (+213)778256833

(Figure 1). HCCTP is prepared from ammonium chloride and pentachloride phosphorus. It is an inorganic compound which has a basic character [1, 2]. The physical properties of HCCTP are summarized in Table 1.

Nucleophilic substitution on HCCTP is the main way to the synthesis of hybrid compounds (organic-inorganic) called organophosphazenes [3-5]. The choice of the monomer organophosphazene is justified by the importance of its use in the production of toric joint, gas pipes and a variety of joints, for storing and transferring oils and fuels. Some derivatives compounds are microcrystalline (influence of R) and can be used in the production of flexible films and fibers [6,7]. Many derivatives are biocompatible, biodegradable and some of them are bioactive and are studied for their potential medical applications [8-10]. There are also polymers synthesized from organophosphazenes monomers [11-13] which have exceptional elastomers properties [14] and are used as solid electrolytes in the production of rechargeable batteries of low weight [15-17].

These organophosphazenes have a great importance by their many applications, so a particular interest is given to nucleophilic substitution on hexachlorocyclophosphazene (HCCTP) by allylamine according to the method of Christova *et al.* [18] to give hexa(allylamino)cyclotriphosphazene (HACTP) but operating under milder process conditions. In fact, the originality of this work consists in the synthesis of HACTP using a clay called "Maghnite-H+" as a catalyst [19]. It is very ecological, economic and regenerable by simple filtration. The synthesis method of Christova *et al.* [18] is also modified by replacing benzene, which is carcinogenic, by diethylether as solvent.

## 2. Materials and Methods

### 2.1. Materials

Maghnite used in this work comes from a quarry located in Maghnia (North West of Algeria) and was supplied by company "ENOF" (Algerian manufacture specialized in the pro-

duction of nonferric products and useful substances). Hexachlorocyclotriphosphazene (HCCTP) (Sigma Aldrich, 99%) (Figure 1 and Table 1), allylamine (Fluka, 98%), benzene (Fluka, 99%) and diethylether (Sigma Aldrich, 99,5%) were purchased without further purification.

### 2.2. Preparation of Maghnite-H+

The preparation of Maghnite-H+ was carried out by using a method similar to that described by Belbachir and coworkers [20]. In an Erlenmeyer flask of 500 mL, 30 g of crushed and dried raw-maghnite were dispersed in 120 mL of distilled water, the mixture was stirred for 2 hours. After this time, 100 mL of 2.5 M sulfuric acid solution was added, the solution thus obtained was kept under stirring for two days at room temperature. Then, the product was filtered and washed with distilled water until complete disappearance of traces of acid. Once purified clay, it was dried overnight in an oven at 105 °C, and then stored in vials well saddled against moisture and any impurity.

### 2.3. Synthesis of hexa(allylamino)cyclotriphosphazene

Nucleophilic substitution on HCCTP (N<sub>3</sub>P<sub>3</sub>Cl<sub>6</sub>) by allylamine (NH<sub>2</sub>-CH<sub>2</sub>-CH=CH<sub>2</sub>) is performed as is described by Christova *et al.* [18]. To a stirred solution of 3 mL (0.040 mol) of allylamine in 3.33 mL of benzene, 1 g (0.0028 mol) of HCCTP dissolved in 5 mL of benzene was added dropwisely. The reaction mixture was stirred for 24 hours at room temperature. The volatile solvents were removed in a rotary evaporator and the remaining solid was ex-

Figure 1. Structure formula of HCCTP

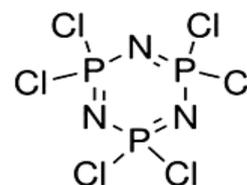


Table 1. Physical Properties of HCCTP

Appearance	Fw (g/mol)	Mp °C (lit.)	Bp °C (13 mmHg)	D (g/mL) at 25 °C (lit.)	CAS
White crystalline powder	347.66	112-115	127	1.98	[940-71-6]

tracted with several portions of diethylether. The crystallized product thus obtained was recrystallized from cyclohexane and the yield was 64%.

#### 2.4. Synthesis of hexa(allylamino) cyclotriphosphazene using Maghnite-H+

The synthesis of HACTP was conducted from HCCTP and allylamine as starting materials with the addition of a catalyst which was Maghnite-H<sup>+</sup> at 5% by weight and using diethylether as solvent to replace benzene. The reaction time was reduced to 12 h. At the end of the reaction, chloroform was added to the solution and then filtered to separate the product from Maghnite-H<sup>+</sup>. Then, the final product was purified by recrystallization. The yield was 74%. Operating conditions of the synthesis of HACTP, according to the method of CHRISTOVA and in the presence of Maghnite-H<sup>+</sup>, were summarized in Table 2.

#### 2.5. Characterization of products

<sup>1</sup>H-NMR, <sup>13</sup>C-NMR and <sup>31</sup>P-NMR spectra were recorded in CDCl<sub>3</sub> solution under room temperature on an AM 300 FT Bruker spectrometer using tetramethylsilane as internal standard. FTIR absorption spectra were recorded on an MATTSON GENESIS II FT-IR spectrometer using the KBr pressed disc technique. Thermogravimetric analyzes were recorded on a SETARAM Labsys TG-DTA/DSC (room temperature - 1600 °C) with a nitrogen sweep of 200 mL/min at a heating rate of 10 °C/min. DSC measurements were carried out on a TA instrument (TGA Q500), according to

the following program: products were first heated from ambient temperature to 250 °C at 10 °C/min maintained at this temperature during 5 min then cooled to 25 °C at 20 °C/min. The MALDI-TOF spectra have been carried out in a Bruker microflex, the samples were prepared in CHCl<sub>3</sub> with Dithranol as matrix.

### 3. Results and Discussion

#### 3.1. Characterization of the catalyst (Maghnite-H<sup>+</sup>)

Table 3 shows the variation of the elementary chemical composition of the Raw-Maghnite before and after its activation with 2.5 M sulfuric acid solution. It is observed that the acid treatment leads to a decrease in Al<sub>2</sub>O<sub>3</sub> and an increased percentage of SiO<sub>2</sub> in the material.

The X-ray powder diffraction profiles (Figure 2) exhibit the increase in basal spacing from 12.5 Å in the 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 reflecting the changes in interlayer cation and its associated hydration state as a result of the acid treatment.

The FTIR spectra of the treated Maghnite (Figure 3) confirmed the montmorillonite structure of the Maghnite-H<sup>+</sup>. The characteristic absorption of the OH groups linked to the octahedral aluminum is observed by a broad band between 3200 cm<sup>-1</sup> and 3400 cm<sup>-1</sup>. The strong band at 1007 cm<sup>-1</sup> corresponds to the Si-O stretching vibration in the tetrahedral layer. Angular deformation bands at 518 and 449 cm<sup>-1</sup> are assigned to the type links of Si-OM smectites, M may be Mg, Al or Fe.

**Table 2.** Synthesis of HACTP in diethylether catalyzed by Maghnite-H<sup>+</sup>

Product	Catalyst	Solvent	Time (h)	Temperature (°C)	Yield (%)
HACTP <sup>(1)</sup>	---	Benzene	24	20	64
HACTP <sup>(2)</sup>	Maghnite-H <sup>+</sup> (5%w)	Diethylether	12	20	74

(1) HACTP synthesized according to the method of Christova [18].

(2) HACTP synthesized in the presence of Maghnite-H<sup>+</sup> as catalyst

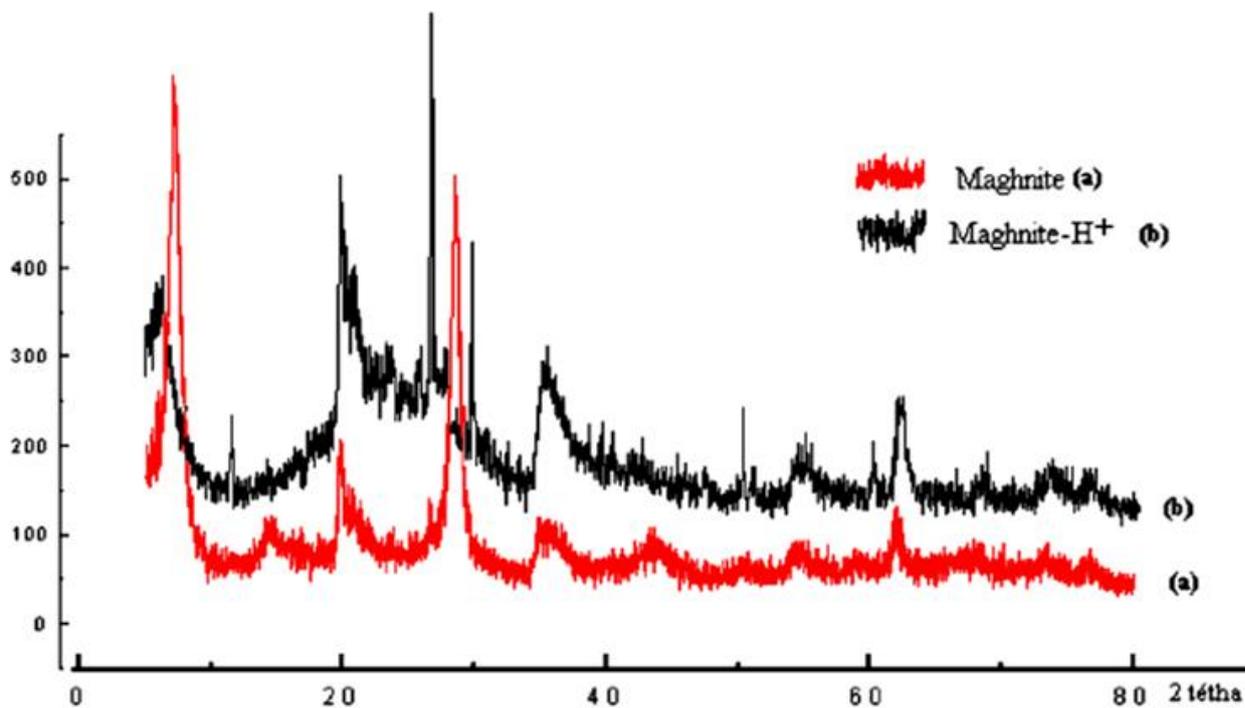
**Table 3.** Chemical composition of Protons exchanged sample "Maghnite-H<sup>+</sup>" (composition wt%).

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>
Raw-Maghnite	69.3	14.67	1.16	0.30	1.07	0.50	0.79	0.16	0.91
Maghnite-H <sup>+</sup>	71.7	14.03	0.71	0.28	0.80	0.21	0.77	0.15	0.34

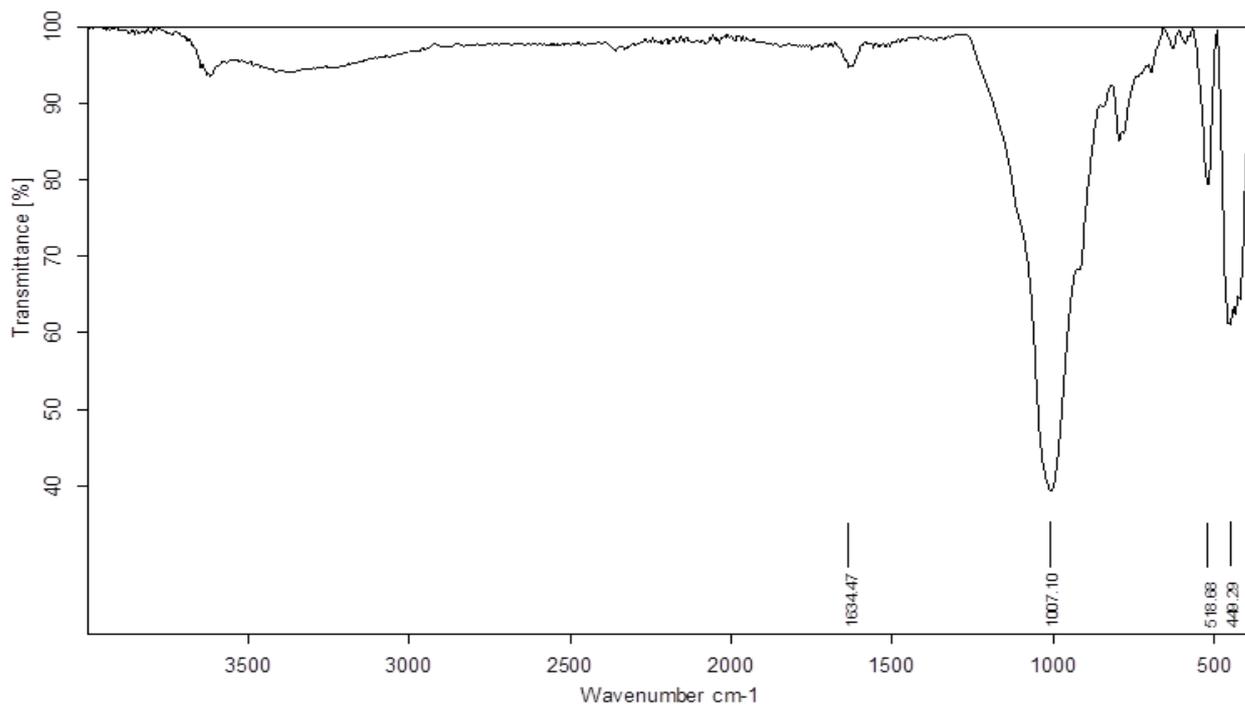
**3.2. Characterization of HATCP catalysed by Maghnite-H<sup>+</sup>**

Figure 4 shows that the most characteristic bond in the FTIR spectrum of HCCTP is the band of N=P group degenerated in the area of 1200 cm<sup>-1</sup>. This frequency is not only influenced

by single and double bond, but also by the electronegativity of the groups linked to phosphorus. The characteristic peaks appeared at 505 and 594 cm<sup>-1</sup> are assigned to two P-Cl bonds. When the Chloro groups of HCCTP are substituted with allylamine, the resulting HACTP has



**Figure 2.** X-ray powder diffraction of (a) “Raw-Maghnite” and (b) “Maghnite-H<sup>+</sup>”



**Figure 3.** FTIR spectrum of Maghnite-H<sup>+</sup>

FTIR spectrum shown in Figure 5. The spectrum shows characteristic peaks at 3450  $\text{cm}^{-1}$  corresponding to N-H groups, and at 1644 and 967  $\text{cm}^{-1}$  for C=C bonds. The absorption band at 1204  $\text{cm}^{-1}$  assigned to N=P group in the starting material becomes 1254  $\text{cm}^{-1}$  in HACTP, confirming that Cl atom attached to phosphorus has been substituted by another electron-donating group, which explains the increase in the value of the absorption band assigned to the group P=N.

The chemical structure of HATCP is further

supported by  $^1\text{H-NMR}$ ,  $^{13}\text{C-NMR}$  and  $^{31}\text{P-NMR}$  spectra. The different signals observed in the  $^1\text{H-NMR}$  spectrum of Figure 6 and which are summarized in Table 4, correspond to the groups shown in the structural formula of HACTP catalyzed by Maghnite- $\text{H}^+$  at 5%wt. The resonance peak at 2.276 ppm is assigned to proton linked to Nitrogen (N-H<sub>A</sub>). This peak confirms that nucleophilic substitution on HCCTP has been occurred. The  $^{13}\text{C-NMR}$  spectrum clearly shows three resonance peaks with their carbons assigned in Figure 7. In the  $^{31}\text{P-}$

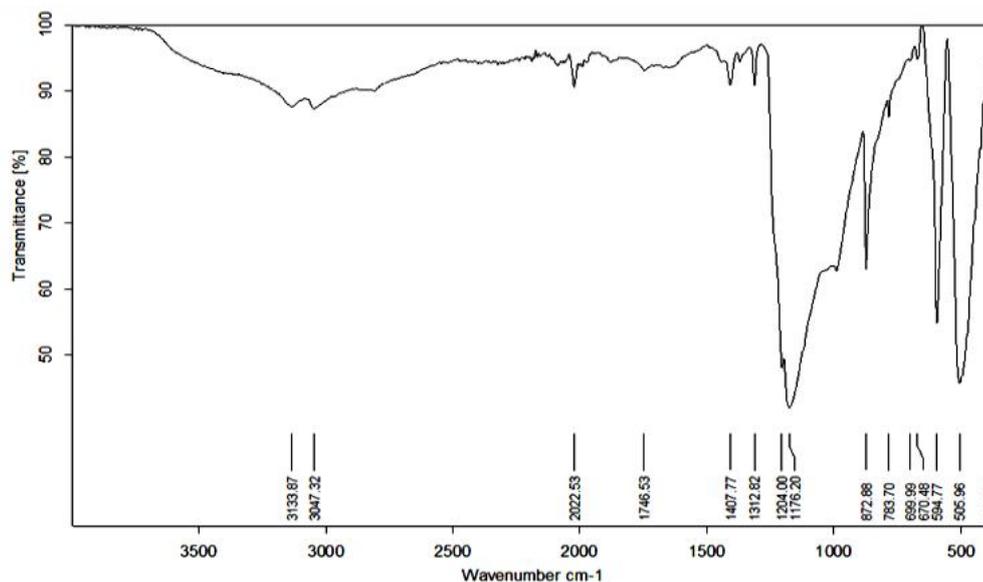


Figure 4. FTIR spectrum of HCCTP

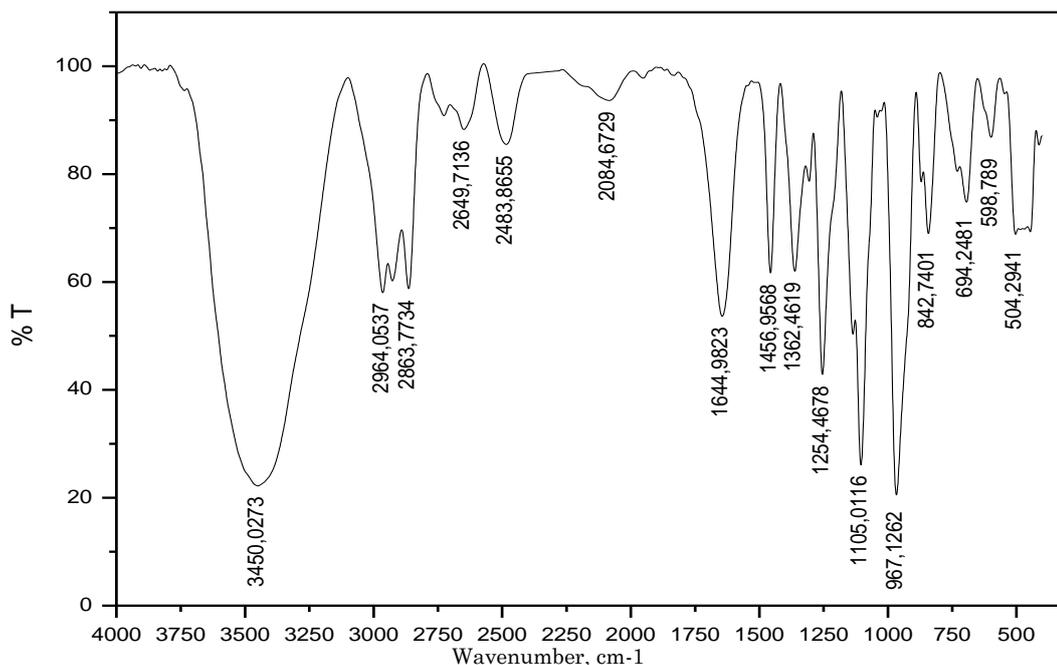


Figure 5. FTIR spectrum of HACTP catalyzed by Maghnite- $\text{H}^+$  (5 wt%)

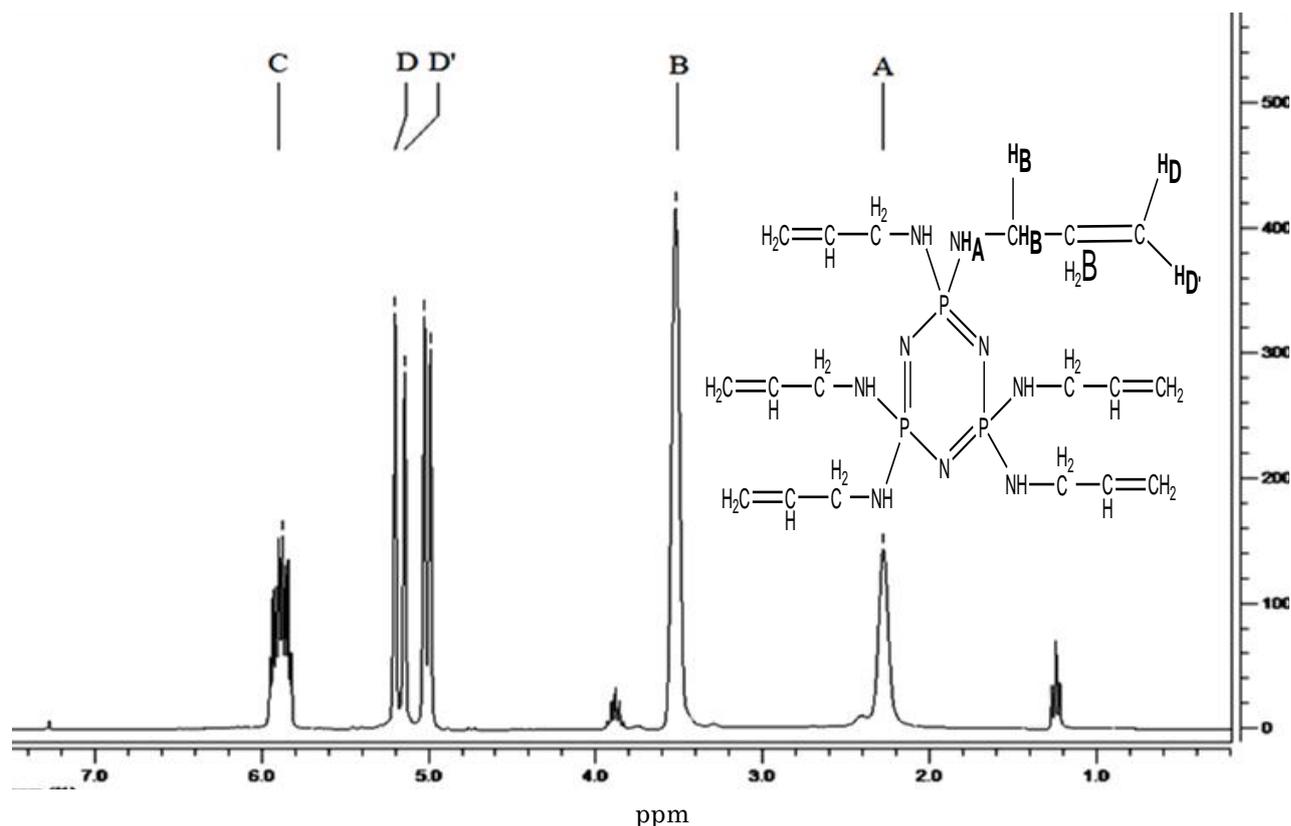


Figure 6.  $^1\text{H-NMR}$  spectrum of HACTP catalysed by Maghnite-H+ (5 %wt) in  $\text{CDCl}_3$

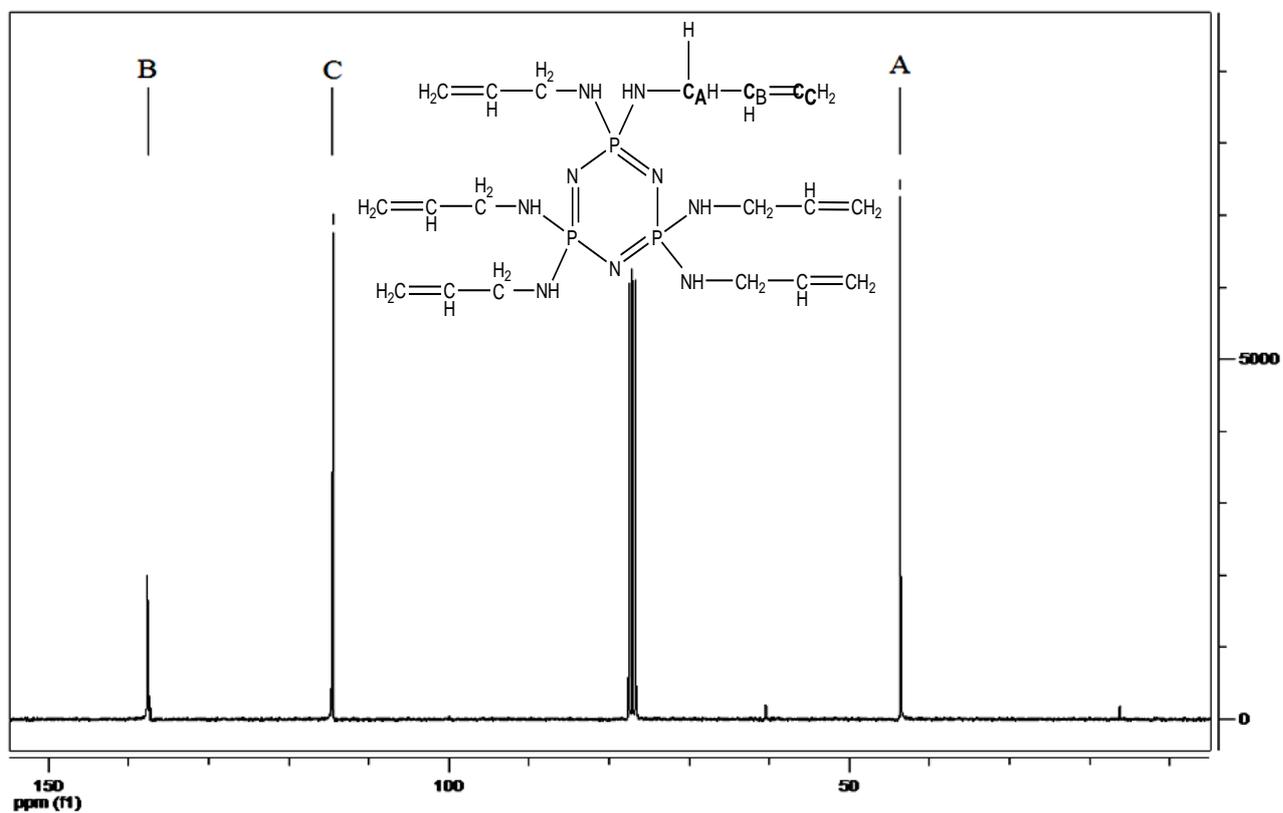


Figure 7.  $^{13}\text{C-NMR}$  spectrum of HACTP catalysed by Maghnite-H+ (5 %wt) in  $\text{CDCl}_3$

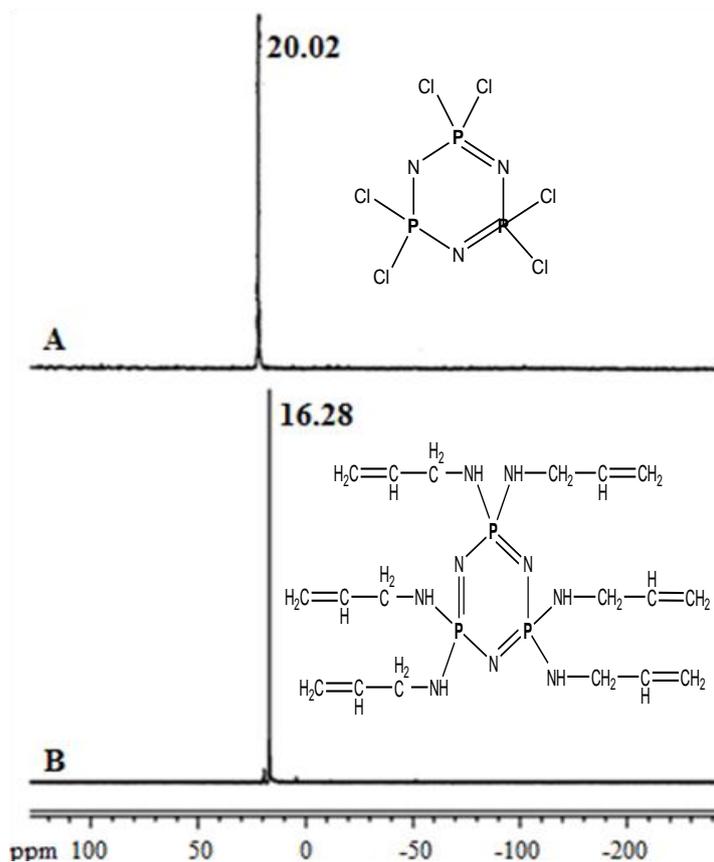


Figure 8.  $^{31}\text{P}$ -NMR spectrum of A) HCCTP [21], B) HACTP catalysed by Maghnite-H+ (5 %wt) in  $\text{CDCl}_3$

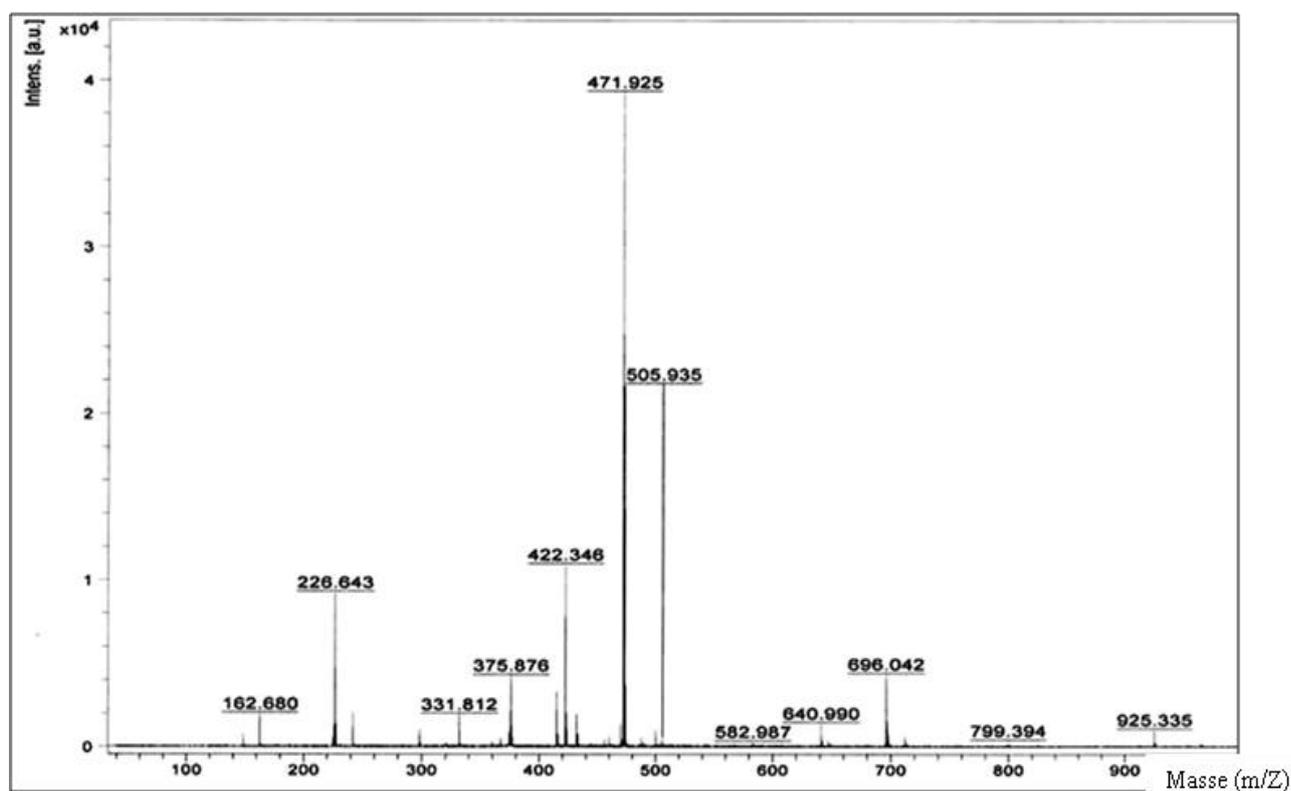


Figure 9. Mass spectrum of HACTP catalyzed by Maghnite-H+ (5%wt)

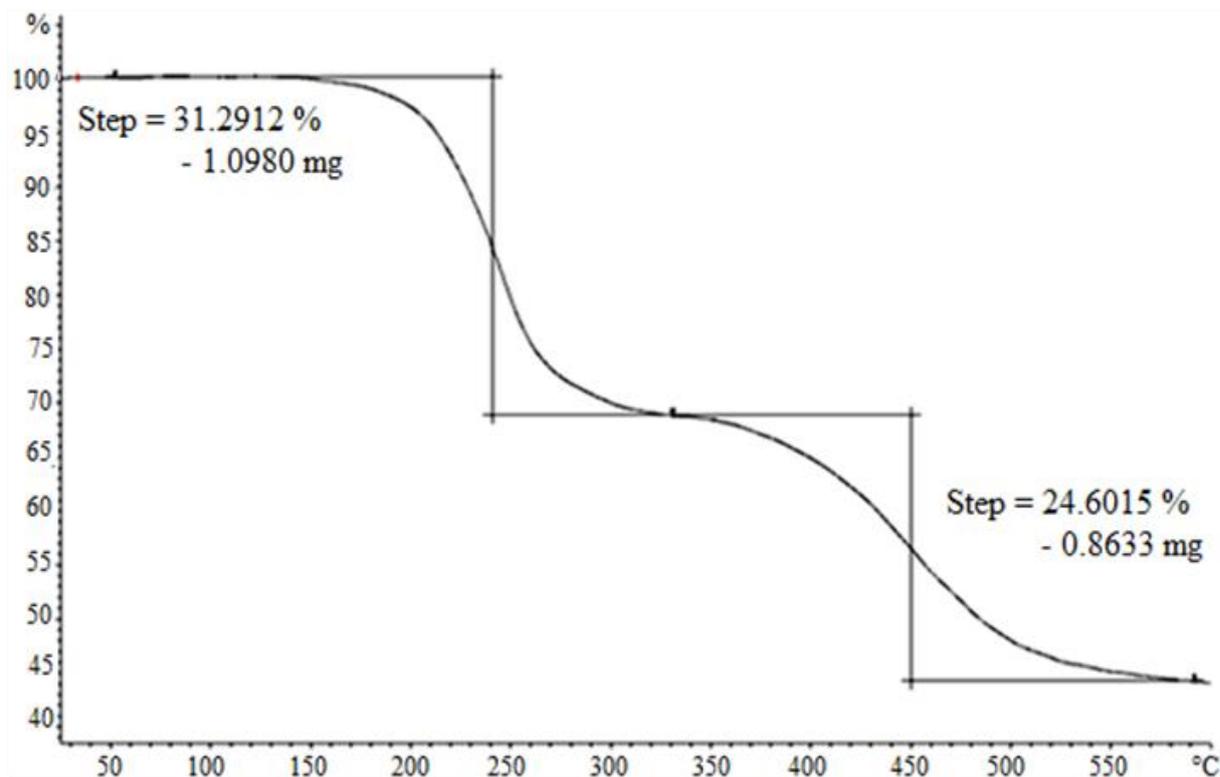


Figure 10. TGA thermogram of HACTP catalyzed by Maghnite-H+ (5 %wt) obtained in Nitrogen atmosphere at heating rate of 10 °C/min

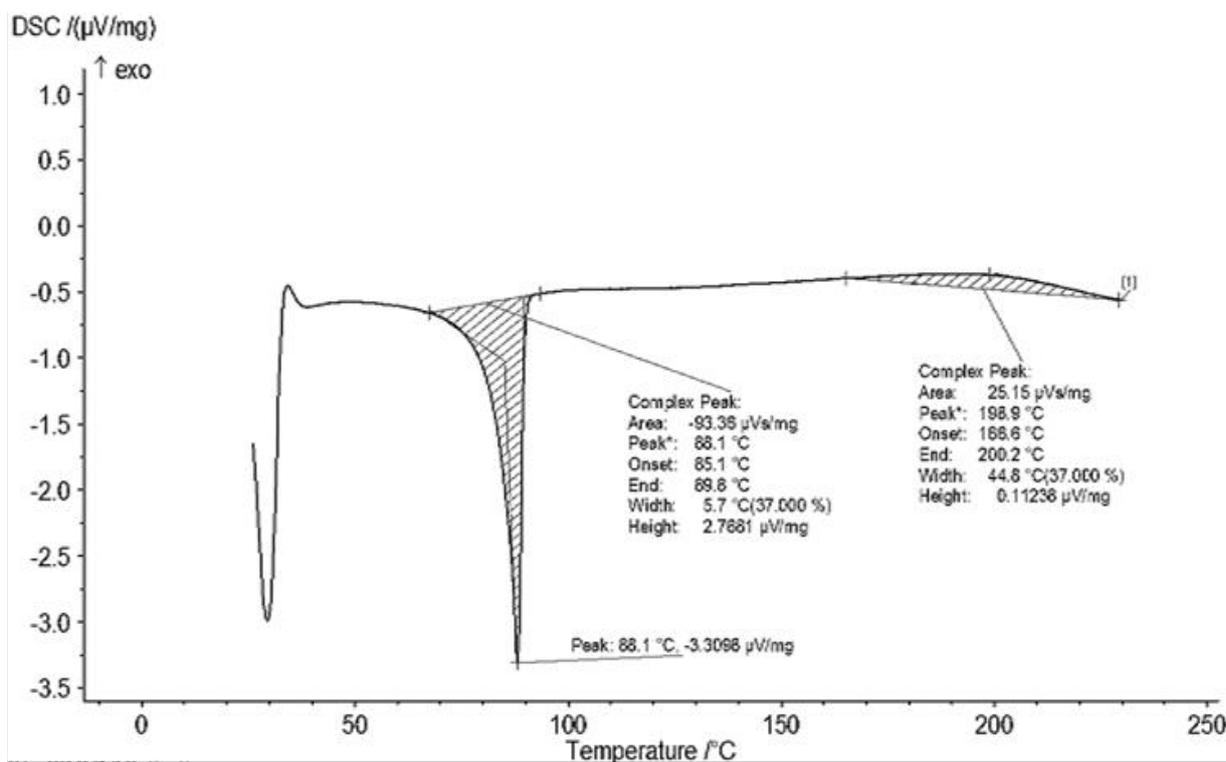


Figure 11. DSC thermogram of HACTP catalyzed by Maghnite-H+ (5 %wt) obtained in Nitrogen atmosphere at heating rate of 10 °C/min

NMR spectrum of HACTP (Figure 8-A), there is one peak appeared at 16 ppm. For comparison, the  $^{31}\text{P}$ -NMR of HCCTP [21], also in Figure 8-B, has resonance peak located at 20 ppm. The molecular weight of HACTP determined from the mass spectrometry is 471 (Figure 9). Other significant observation on the mass spectrum of HACTP is its fragmentation to  $m/e$  422, 375, 331, and 226.

The TGA data of HACTP shown in Figure 10 indicates a two-stage degradation behavior. The first stage of degradation at around 230-320 °C. It is proceeded by the cleavage of two allylamine groups remaining 31.29 wt% residue, and then proceeded with the cleavage of another two allylamine groups after 400 °C. The DSC result shown in Figure 11 indicates that HACTP is a highly crystalline material with a melting temperature of 88.1 °C. It is mildly reactive after melt with the maximum reaction temperature at 198.9 °C.

#### 4. Conclusions

In this work, a new synthetic method was developed to produce HACTP using friendly, green, ecologic and non toxic catalyst clay as proton source avoiding the use of benzene as a solvent because it is carcinogenic, so it is replaced by diethyl ether which is less toxic. The synthesis of HACTP is also carried out at room temperature with a halving of reaction time from 24 to 12 h which is very attractive from an industrial point of view. The simplicity of the synthesis method, good catalytic properties of the support catalyst Maghnite- $\text{H}^+$  and the use of non toxic solvent make this an attractive way for the synthesis of hexa(allylamino)cyclotriphosphazene.

**Table 4.** Different signals of Protons of HACTP catalyzed by Maghnite- $\text{H}^+$  (5 %wt).

Resonance peaks (ppm)	Attribution
2.276	HA
3.520	HB
5.896	HC
5.145, 5.202	HD
7.2	$\text{CDCl}_3$

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