Correlation between the acid treatment and the catalytic activity of Maghnite-H+

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Abstract

Cyclic and linear phosphazenes are characterized by a repeating unit $[-N=PR_1R_{2}-]_n$ in which nitrogen is trivalent and phosphorus pentavalent. Ring sizes for the cyclic derivatives vary from three to about forty repeating units whereas for the linear polyphosphazenes derivatives are known which contain up to 15000 repeating units. Algerien (MMT) called "Maghnite-H^+" has been a sheet silicate clay, exchanged with protons to produce "H-Maghnite" shown to be an efficient catalyst for cationic polymerisation of many heterocyclic and vinylic monomers. The structural compositions of "Maghnite" have already been determined. The synthesis of a phosphazenes derivative, hexa-allylamino-cyclotriphosphazene (HACTP) induced by Maghnite was performed under optimum conditions at 20°C in bulk. Experiments revealed that the reaction induced by "H-Maghnite" proceeds in bulk. The prepared samples were subsequently characterized by FTIR spectroscopy, and 1H-NMR spectroscopy. It should be noted that the product coating containing 1wt. %, 3wt. % and 5wt. % of clay loading were found to exhibit an observable structure, physicochemical properties and controlled molecular weight.

Key words:

1H-NMR spectroscopy, DSC, nucleophilic substitution, cyclic structure, Maghnite-H^+, phosphazenes, hexa-allylamino-cyclotriphosphazene, allylamine, MALDI-TOF
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sites and when exchanged with cations having a high charge density, as protons, they produce highly active catalysts for acid-catalysed reactions (Belbachir et al., 2003: 4: 548-561). It has been demonstrated that intercalated organic molecules on the surface of montmorillonite are mobile and can be highly polarized; if intercalated they are in the space between the charged clay layers (Ray and Okamoto, 2003; Hasegawa et al., 2000). This study examines the catalytic activity of Algerian proton exchanged montmorillonite clay (Maghnite-H^+). It was demonstrated that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite-H^+ (Belbachir and Bensaoula, 2006).

It was possible to obtain organophosphazenes compounds under very mild operating conditions using this ecologic and friendly catalyst layer called Maghnite- H^+ (Algerian MMT). HACTP was prepared from organophophazènes monomers nucleophilic substitution on hexachlorocyclophosphazène by allylamine using a method previously described by Christova et al. (2003) 18(12): 1067 - 1073). Secondly, this monomer was prepared by a new method using Maghnite-H^+ and changing the solvent from benzene to diethyl ether.

MATERIALS AND METHODS

Materials

The maghnite (MMT) used in this work came from a quarry located in Maghnia (North West of Algeria) and was supplied by the company “ENOF” (Algerian manufacture specialized in the production of nonferric products and useful substances). Allylamine CH_2 = CH-CH_2NH_2 (98%) GC was obtained from laboratory FLUKA AG (Buchs) SG. Benzene (99%), boiling point: 80°C, mp: 5.50°C was obtained from Sigma Aldrich.

Testing methods

^{1}H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer (Germany) in CDCl3. Tetramethylsilane (TMS) was used as the internal standard in these cases.

The thermograms obtained have been made in a laboratory of the Molecular Chemistry, University of Burgundy (ICMUB) DIJON 1 option unit 500 MT GA^{TM} Hi-Res^{TM} MFC STD. DSC measurements were carried out on a TA Instrument, according to the following program: the specimens were first heated from ambient temperature to 250°C at 10°C/mn maintained at this temperature for 5 min and then cooled to 25°C at 20°C/mn. The thermal stability tests were performed on a TA Instrument (TGA Q500) by heating the samples from 20 to 550°C at 20°C/mn. DTG thermograms gave the variations of the weight loss derivative as a function of temperature.

The MALDI-TOF spectra were obtained in a Bruker Ultra flex (Germany); the samples were prepared in methanol with DHBA as matrix or with $CHCl_3$ as template.

Preparation of the catalyst

Maghnite-H^+ were prepared by a method similar to that described by Belbachir et al. (2003), 4(11): 572-585). Raw maghnite (20 g) 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. The maghnite/water mixture was combined with H_2SO_4 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. H_2SO_4 solutions of 0.25 M concentration was used to prepare Maghnite-H^+.

Thermal stability of the catalyst

The thermal characterizations of the heading show that the catalyst was conducted by a thermogravimetric analysis TGA. Figure 2 shows the weight losses (%) versus temperature (°C) curves for pure Maghnite-Na.
The TGA of pure Maghnite-Na^+ show two stages of weight loss. The first weight loss in maghnite-Na^+ below 100°C was the result of the release of free water. The second weight loss around 600°C is associated with the dehydroxylation of the silicate structure (Rahmouni et al., 2013: 1(6): 175-181; Rahmouni et al., 2013: 8(1): 20-26). The total weight loss is only 14.3% up to 150°C. As can be expected, Maghnite-Na+ shows a high thermal stability (Figure 1).

Procedures of synthesis

Synthesis of HACTP was conducted from the hexa (chlorocyclotriphosphazene) and allylamine as starting materials with benzene as solvent at 20°C for 24 h. The substitution on the nucéophilic hexa chlorocyclotriphosphazene ($N_3P_3Cl_6$) by allylamine (NH_2-CH_2 CH = CH_2) was performed, as was described by Johnson et al. (1992): 915-935):

As shown by the chemistry, 3.03 ml of allylamine were diluted in 3.33 ml of benzene and on the other hand, 1 g (0.0028 mol) of $N_3P_3Cl_6$ was dissolved in 5 ml of benzene. Afterwards, these two solutions were mixed and left under stirring for 24 h at room temperature. The solvent was evaporated in a rot vapor, the resulting solid was extracted several times with diethyl ether at 20°C and the product was then cooled to 20°C and recrystallized from cyclohexane. The material was obtained as white crystals with a yield of (64%). The product was characterized by: ^{1}H-NMR: 3.5 ppm (CH_2-NH), 5.8 ppm (CH = CH_2), 5.0, 5.1 ppm (CH = CH_2), IR: 3232 cm^{-1} (NH), 1248 cm^{-1} (P = N), 1644 cm^{-1} (C = C).

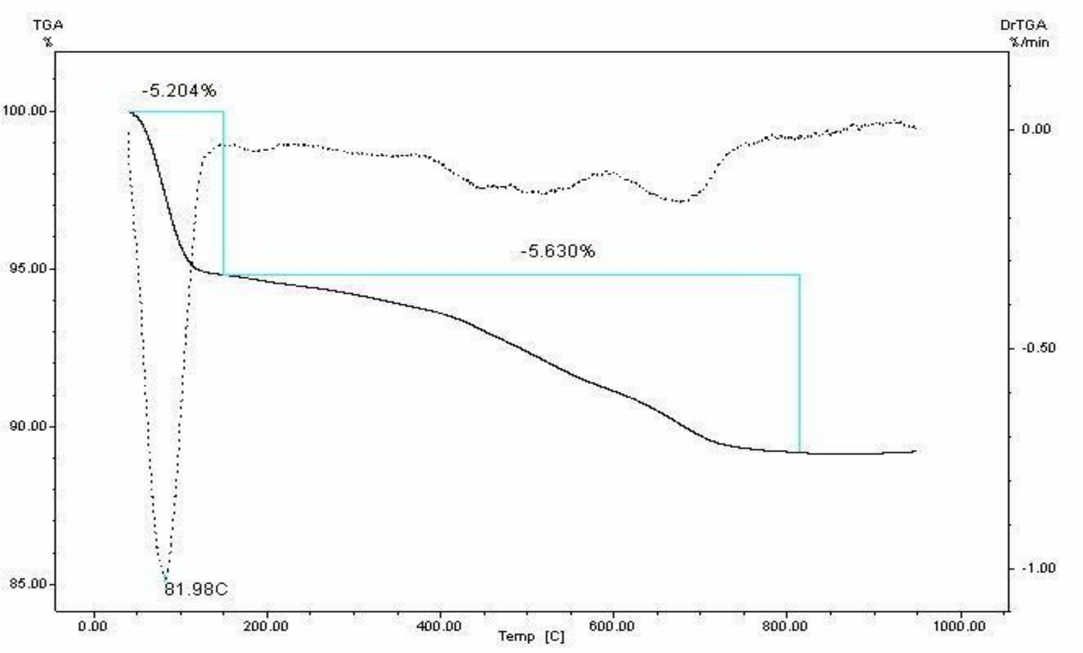


Figure 1. TGA curves of a Maghnite-Na^+ obtained in nitrogen atmosphere at heating rate of 10°C/min.

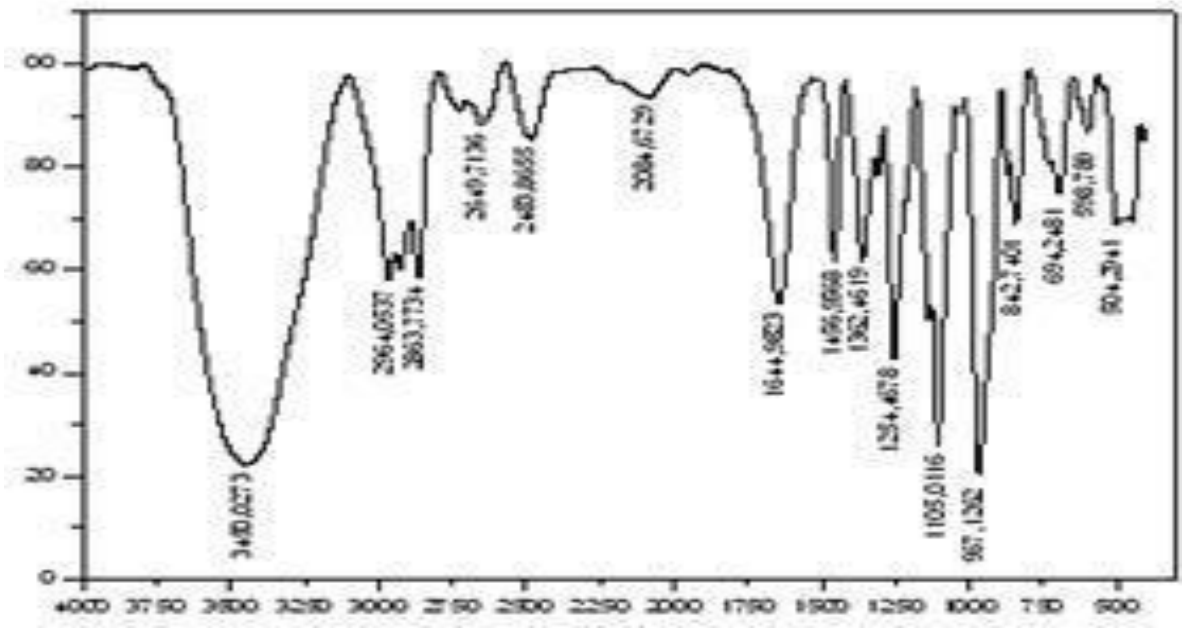


Figure 2. FTIR spectrum of HACTP induced by Maghnite-H^+ (0.25 M) at room temperature.

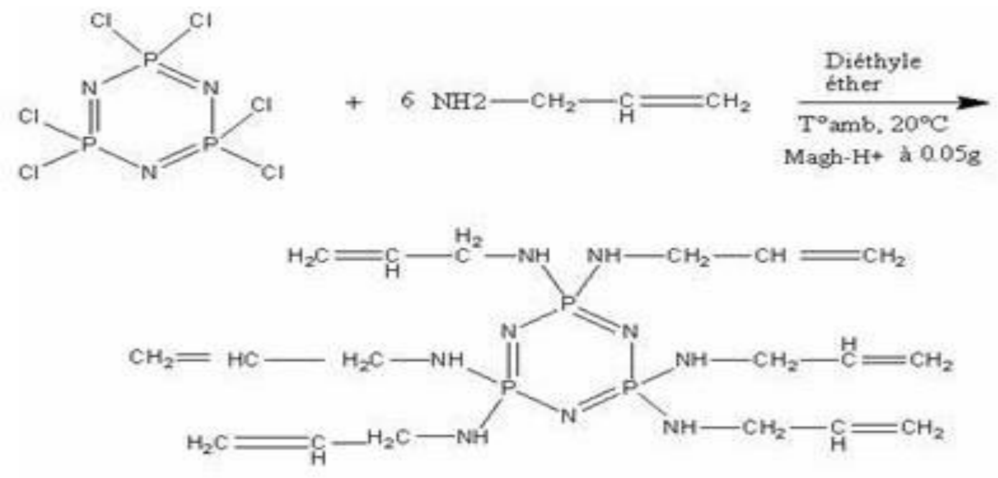
The reaction conditions were described in Table 1. Another synthesis of HACTP was carried out by a new method: from the hexa chlorocyclotriphosphazene and allylamine at 20°C using diethyl ether as solvent and a Mag-H^+ (5%). Finally, the reaction lasted for 12 h. Nucéophilic substitution on the allylamine by hexa chlorocyclotriphosphazene was performed according to the same procedure as that used for the preceding reaction except that (0.05 g) Mag-H^+ was added and the solvent used was diethyl ether. The reaction time was reduced to 12 h. The solution was then filtered after adding $CDCl_3$ and Mag-H^+ was recovered. Then the

Table 1. Synthesis of hexa (allylamino) cyclotriphosphazene in benzene induced by Maghnite-H$^+$ (0.25 M).

Product	Catalyst (Mag-H)$^+$	Solvent	Yield	Time (h)	Temperature (°C)
1	5%	Benzène	64%	24	20

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

Product	Catalyst (Mag-H)$^+$	Solvent	Yield	Time (h)	Temperature (°C)
2	5%	Diethyl ether	74%	12	20



Scheme 1. Schematic representations of the synthesis of HACTP catalyzed by Maghnite-H$^+$ (0.25 M).

filtrate was purified as for the preceding product, the product was white crystals with a yield of 74%. The product was also characterized by: ^{1}H-NMR: 1.2 ppm (NH), 3.5 ppm (CH2-NH), 5.8 ppm (CH = CH_2), 5.1, 5.0 ppm (CH = CH_2), IR: 3450 cm-1 (NH), 1254 cm-1 (P = N), 1644 cm-1 (C = C), RMN ^{31}P: 12 ppm (three phosphors). MALDI-TOF: 471 g/mol (Table 2).

In the synthesis of HACTP, due to the hazards of benzene (carcirogen solvent), diethyl ether was used in the presence of Maghnite-H$^+$ in achieving this synthesis under environmentally safe conditions. The reaction that took place is shown in Scheme 1:

RESULTS AND DISCUSSION

Figure 2 shows the FTIR spectra of HACTP. The characteristic IR peaks appeared at 3194.32 cm^{-1} for NOH groups, and at 1642.28 and 909.38 cm^{-1} for CAC bonds. The IR peak of the PAN bonds was shifted to 1176.19 cm^{-1} as shown in Figure 2.

The ^{1}H-NMR spectra at 300 MHz (solvent $CDCl_3$) (Figure 3) was complicated, but the integrated ratios of aliphatic to aromatic protons were consistent with the structure of HACTP. The different peaks of HACTP were at ^{1}H-NMR: 1.2 (s, H_a), 3.4 (s, H_b), 5.8 (m, H_c, J_{dc}=17.1, $J_{d'c}$=10.1, J $_{cb}$=4.8), 5.1, 5.2 (d, H_d, J $_{dd'}$=1.5, $J_{d'c}$=10.1), 7.2 (s, $CDCl_3$).

The chemical structure of HACTP was further supported by ^{13}C-NMR. The ^{13}C-NMR spectrum clearly shows three resonance peaks with their carbons assigned in Figure 4. The TGA data of HACTP shown in Figure 5 indicate a two-stage degradation behavior. By comparing to the mass spectrometry of HACTP, we suggest that the first stage of degradation at around 230- 320°C was due to the cleavage of two allylamine groups remaining 56.89 wt % residue, and then proceeded with the cleavage of another two allylamine groups after 450°C (Ray and Okamoto, 2003).

The molecular weight of HACTP determined from the mass spectrometry is 925.335 (Figure 6). Another

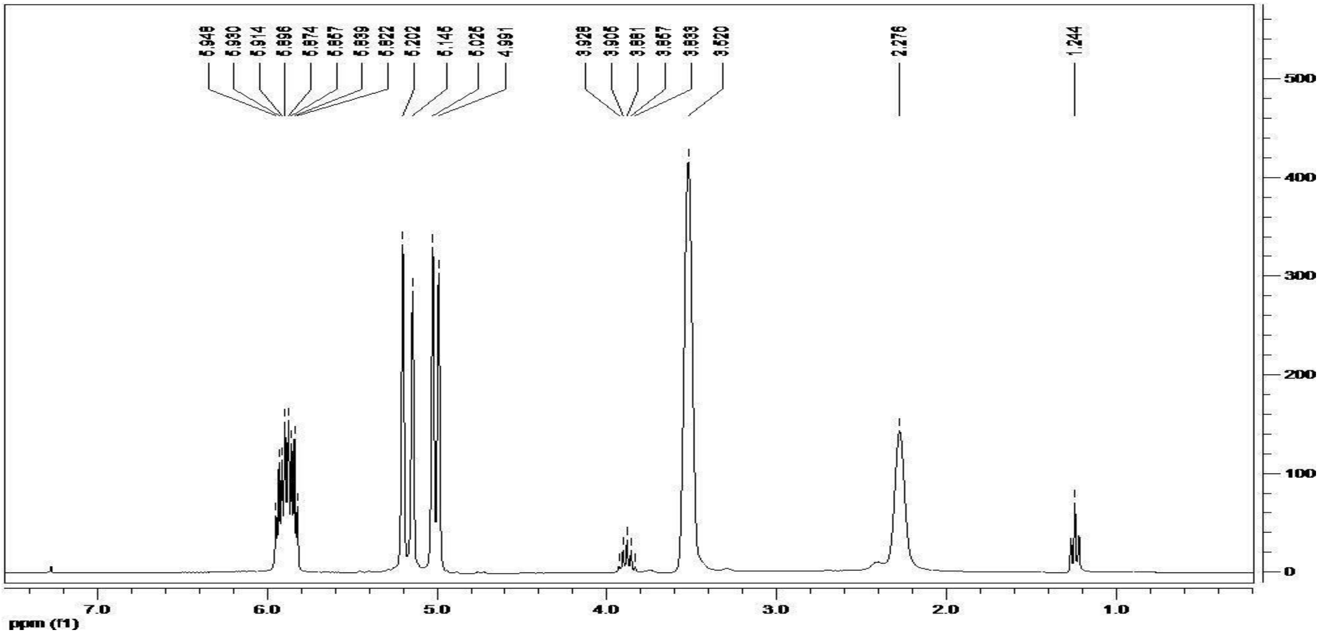


Figure 3. ^{1}H-NMR spectrum of HACTP induced by Maghnite-H^{+} at room temperature in CDCl$_3$.

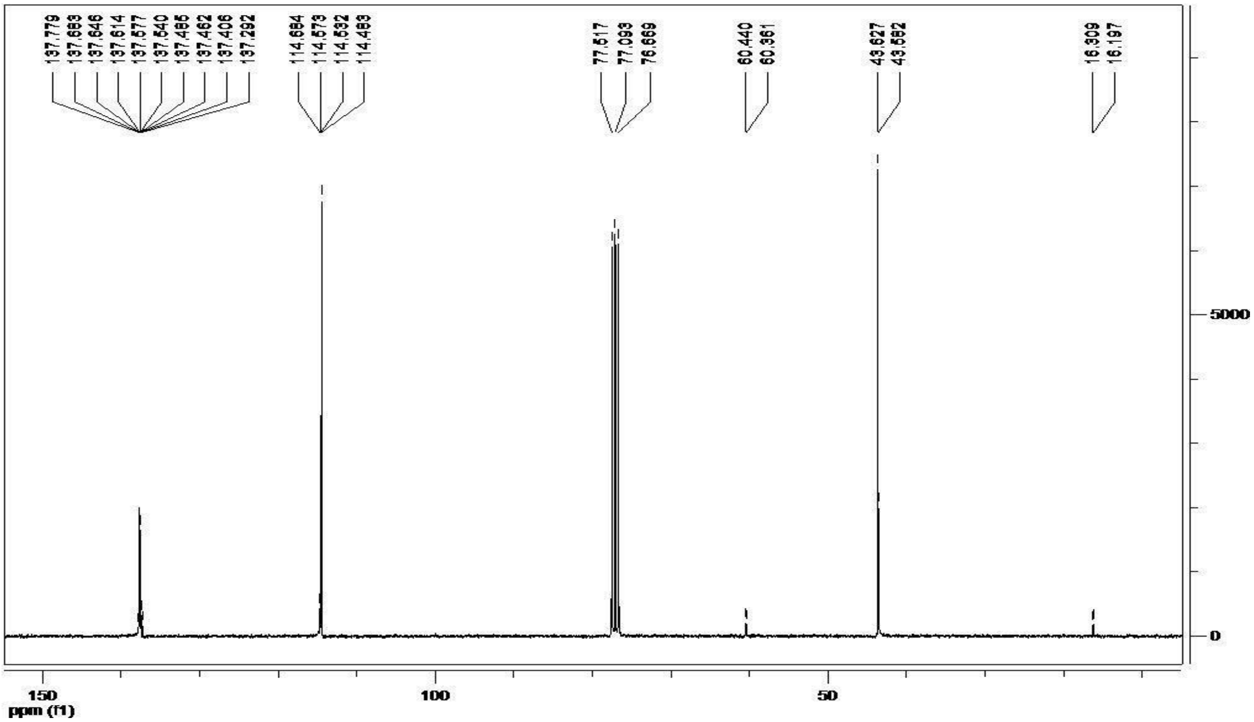


Figure 4. ^{13}C-NMR spectrum of hexa (allylamino) cyclotriphosphazene (HACTP) induced by Maghnite-H^{+} (0.25 M).

significant observation on the mass spectrum of HACTP is its fragmentation to *m/e* 799.394, 696.042, 640.99, 582.987, 505.935 and 471.925. The major peaks at *m/e* 505.935, 471.925, 422.346 and 226.643 are contributed by the sequential cleavages of allylamine groups from HACTP and were contributed by the former fragments plus one [-NH]$^{+}$ group (Mahesh et al., 2009). The DSC result shown in Figure 7 indicates that HACTP was a highly crystalline material with a melting temperature of 88.1°C. It was mildly reactive after being melted with the maximum reaction temperature at 198.9°C (Fukuoka et al., 2008).

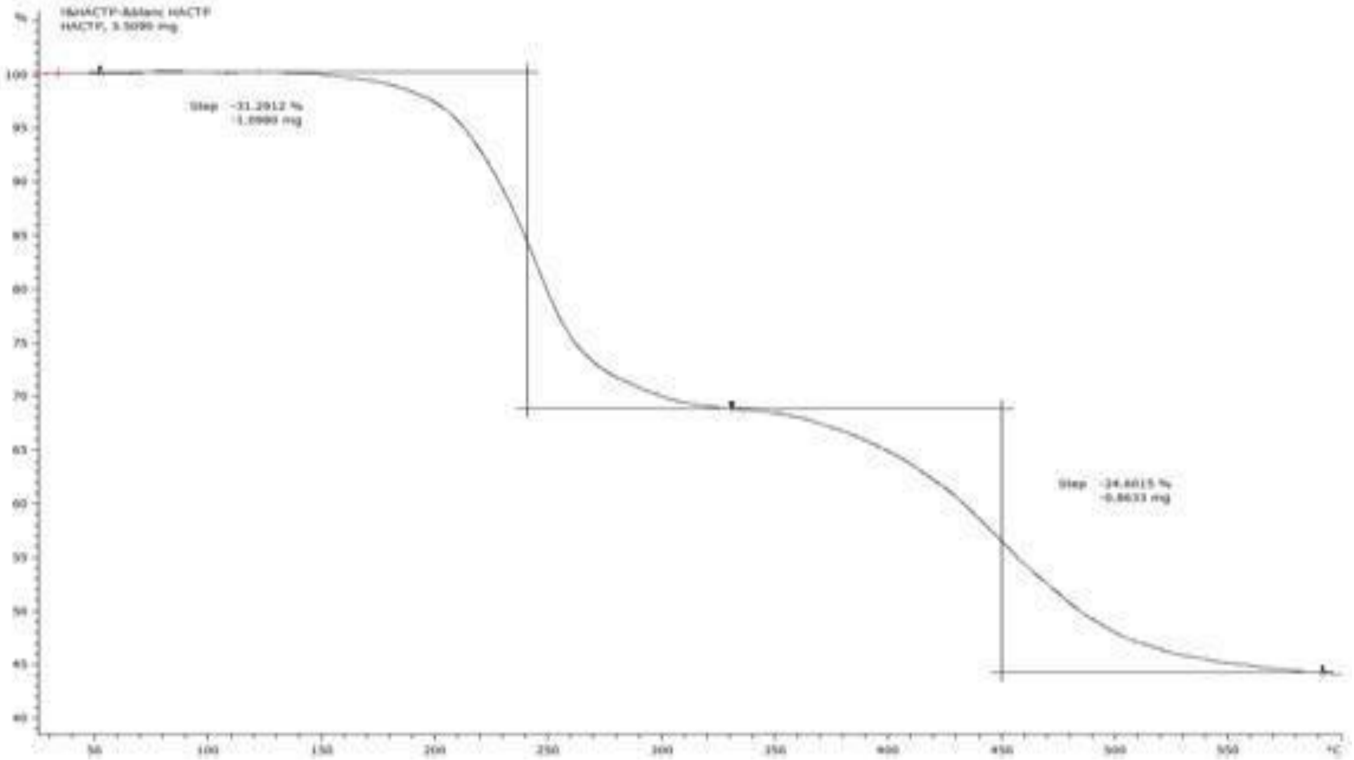


Figure 5. TGA curves of HACTP obtained in nitrogen atmosphere at heating rate of 10°C/min**.**

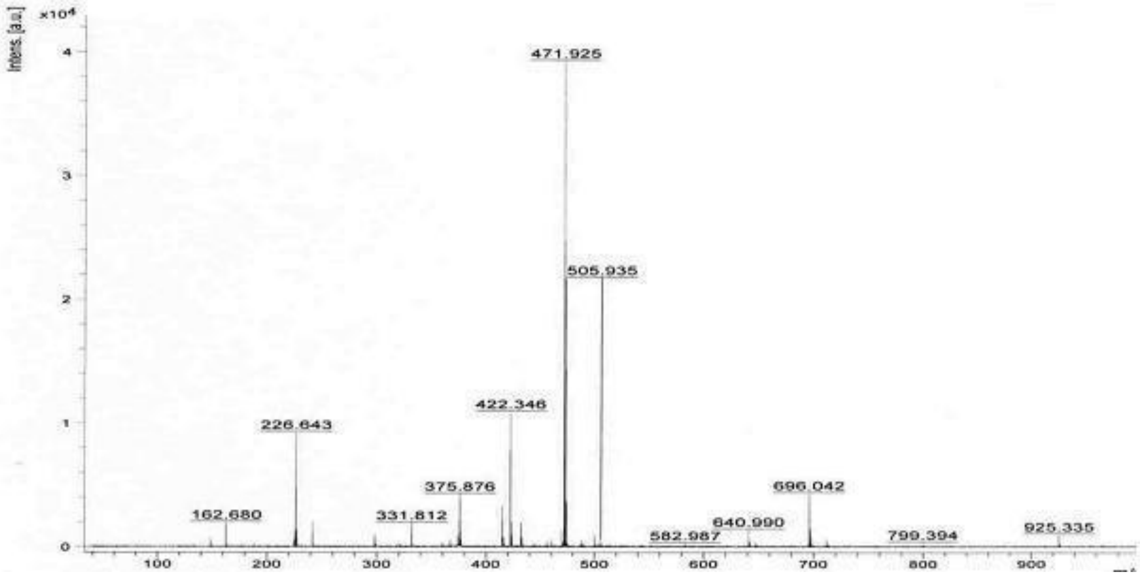
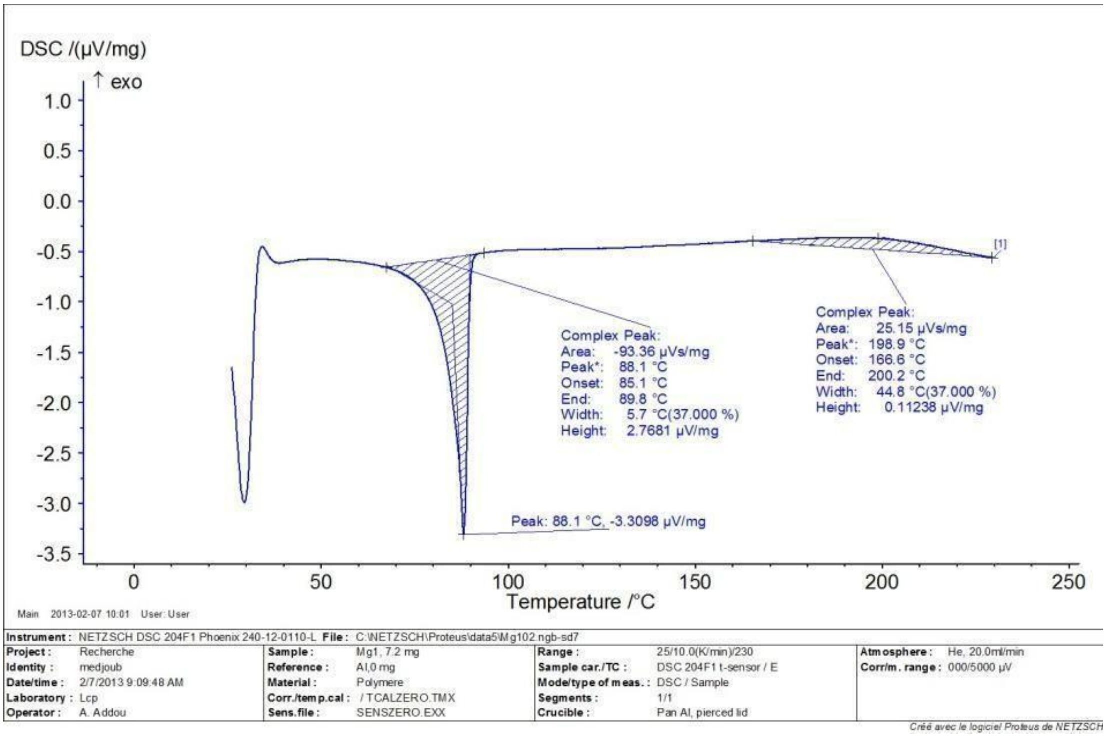


Figure 6. Mass spectrum of hexa (allylamino) cyclotriphosphazene (HACTP) induced by Maghnite-H^+ (0.25 M).

Conclusion

We have developed a new synthetic method to produce HACTP, which does not use inorganic acid but instead uses an ecologic and non toxic catalyst clay as the proton source. This synthesis of HACTP avoids the hazards of benzene (carcinogenic solvent), using in its place diethyl ether in the presence of Maghnite-H^+ where this synthesis



Instrument : NETZSCH DSC 204F1 Phoenix 240-12-0110-L **File :** C:\NETZSCH\Proteus\data5\Mg102.ngb-sd7

Project :	Recherche	**Sample :**	Mg1, 7.2 mg	**Range :**	25/10.0(K/min)/230	**Atmosphere :**	He, 20.0ml/min
Identity :	medjoub	**Reference :**	Al,0 mg	**Sample car./TC :**	DSC 204F1 t-sensor / E	**Corr/m. range :**	000/5000 µV
Date/time :	2/7/2013 9:09:48 AM	**Material :**	Polymere	**Mode/type of meas. :**	DSC / Sample		
Laboratory :	Lcp	**Corr./temp.cal :**	/ TCALZERO.TMX	**Segments :**	1/1		
Operator :	A. Addou	**Sens.file :**	SENSZERO.EXX	**Crucible :**	Pan Al, pierced lid		

Figure 7. DSC curves of HACTP obtained in nitrogen atmosphere at a heating rate of 10°C/min.

was achieved under good conditions. The simplicity of the methods, good properties catalytic of the support catalyst (Maghnite-H^+) and non toxic solvent make this an attractive method for the synthesis of HACTP.

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