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By Medjdoub Lahouaria, Rahmouni Abdelkader & Belbachir Mohammed

Oran University, Algeria

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New Approach for Synthesis of Hexa (Allylamino) Cyclotriphosphazene Catalysed by an Ecologic and Friendly Catalyst Layered Called Maghnite-H⁺ (Algerian MMT)

Medjdoub Lahouaria ^α, Rahmouni Abdelkader ^σ & Belbachir Mohammed ^ρ

Abstract- Cyclic and linear phosphazenes are characterized by a repeating unit $[-N=PR_2]_n$ 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" a montmorillonite sheet silicate clay, exchanged with protons to produce "H-Maghnite" is an efficient catalyst for cationic polymerisation of many heterocyclic and vinylic monomers [1]. The structural compositions of "Maghnite" have already been determined. A phosphazenes derivative, hexa-allylamino-cyclotriphosphazene (HACTP) reaction was performed under optimum conditions at 20°C. Experiments revealed that the reaction induced by "H-Maghnite" proceeds in bulk.

The prepared samples were subsequently characterized by FTIR spectroscopy, ¹H-NMR spectroscopy and. It should be noted that the product coating containing 1wt. %, 3wt. % and 5wt. % of clay loading was found to exhibit an observable structure, physicochemical properties and controlled molecular weight.

Keywords: ¹H-NMR spectroscopy, dsc, nucleophilic substitution, cyclic structure, maghnite-h⁺, phosphazene, hexa-allylamino-cyclotriphosphazene, allylamine, maldi-tof.

I. INTRODUCTION

Phosphazenes (or phosphonitrile or azaphosphorine) are compounds inorganics substances which belong to the most important class of cyclic or linear structure general formula $(R_2P=N)_n$. The degree of polymerization may vary from 3 to more thousands and (R) may be halogen, alkyl, aryl, amino, alkoxy and other groups[2]. Most of the structures of phosphazenes are easily synthesized by aminolysis of phosphorus pentachloride, PCl_5 . The chlorophosphazenes $(Cl_2P=N)_n$ are the starting compounds for the preparation of almost wholes phosphazenes. Christova *et al* [3] have prepared cyclophosphazènes allyl-substituted for use as cross linking agents in the polymerization of 2-hydroxyethyl methacrylate (HEMA) or in the synthesis of composites

with good optical transparency and good flame resistance, compared to poly (dichlorophosphazene). A phosphazenes derivative, hexa-allylamino-cyclotriphosphazene (HACTP) was synthesized through the aminolysis of hexa-chloro-cyclo-triphosphazene with excess allylamine [4]. Their potential applications included polymer electrolytes [5], biodegradable materials [6].

Montmorillonite have both Bronsted and Lewis acid sites and when es the catalytic activity of Algerian proton exchanged montmorillonite clay (Maghnite-exchanged with cations having a high charge density, as protons, they produce highly active catalysts for acid-catalysed reactions[7]. It has been demonstrated that intercalated organic molecules on the surface of Montmorillonite are mobile and can be highly polarize when situated in the space between the charged clay layers [8-9]). This study examinH⁺). It was demonstrated that there is an excellent correlation between the acid treatment and the catalytic activity of Maghnite) [10].

The originality of this study is to obtain organophosphazenes compounds under very mild operating conditions using an ecologic and friendly catalyst layered called Maghnite-H⁺ (Algerian MMT). Hesa (hallylamino) cyclotriphosphazene was prepared in the first place by the monomers organophosphazènes nucleophilic substitution on hexa-chloro-cyclo-phosphazène by the allylamine using the same method as that used by D.Christova *et al*. [11] , secondly this monomer was prepared by a new method using Maghnite-H⁺ and changing the solvent benzene with diethyl ether.

II. MATERIALS AND TESTING METHODS

a) Materials

Maghnite (MMT) 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 production of nonferrous products and useful substances). Allylamine $CH_2=CH-CH_2NH_2$ (98 %) GC, laboratory FLUKA AG (Buchs) SG. Benzene (99%), boiling point: 80°C, mp: 5.50°C.

Author ^σ : Laboratory of Polymer Chemistry, Département of Chemistry, Faculty of Sciences, Oran University, BP 1524.El M'nouar, Oran, Algeria. e-mail: ramaek23@yahoo.fr

b) Testing methods

¹H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl₃. Tetramethylsilane (TMS) was used as the internal standard in these cases.

The thermo grams obtained have been made in the laboratory institute molecular chemistry, university of Burgundy (ICMUB) DIJON 1 option unit 500 MT GATM Hi ResTM 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 during 5 min then cooled to 25°C at 20°C/mn. The tests were performed on a TA instrument (TGA Q500) by heating the samples from 20 to 550°C at 20°C/mn. DTG thermo grams gave the variations of the weight loss derivative as a function of temperature.

The MALDI-TOF spectra have been carried out in a Bruker Ultra flex; the samples were prepared in methanol with DHBA as matrix or with CHCl₃ Ditranol as template.

c) Preparation of catalyst

Maghnite-H⁺ were prepared by a method similar to that described by Belbachir et al [12]. 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 (500mL) and magnetically stirred maghnite/water mixture was combined with H₂SO₄ 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. H₂SO₄ solutions of 0.25M concentration was used to prepare Maghnite-H⁺.

d) Thermal stability of Catalyst

The thermal characterizations of the composites include thermo gravimetric analysis TGA. Figure-2. Show 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 Na⁺ Mag below 100 °C is a result of the release of free water. The second weight loss around 600 °C is associated with the dehydroxylation of silicate structure [13-14]. The total weight loss is only 13.94% up to 800 °C. As can be expected, Maghnite-Na⁺ shows a

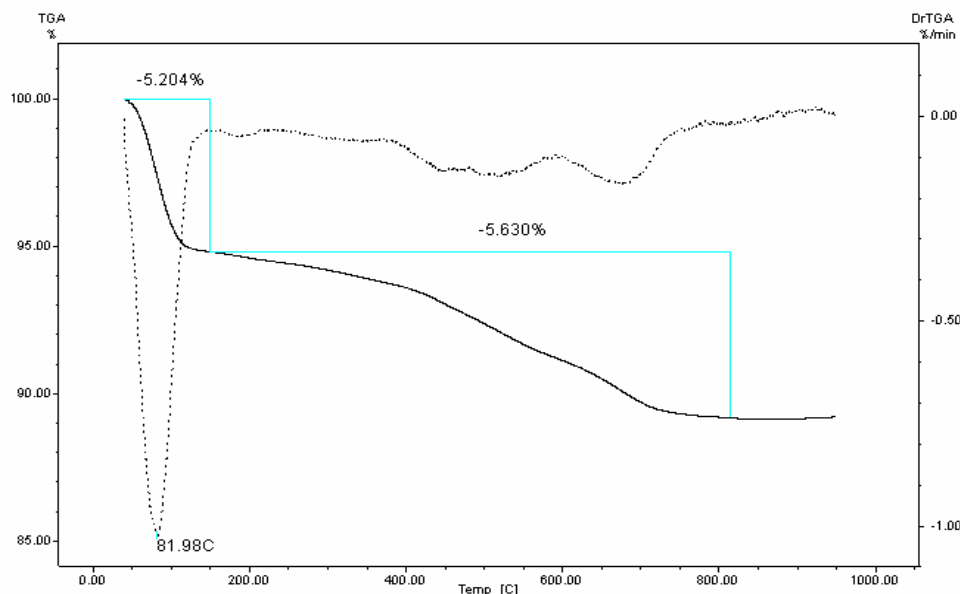


Figure 1 : TGA curves of a Maghnite-Na⁺ obtained in nitrogen atmosphere at heating rate of 10 °C/min

e) Procedures of synthesis

Synthesis of hexa (allylamino) cyclotriphosphazene was conducted from the hexa (chlorocyclotriphosphazene) and allylamine as starting material and use benzene as solvent at 20° C and in 24 hours. The substitution on the nucleophilic hexachlorocyclotriphosphazene (N₃P₃Cl₆) by allylamine (NH₂-CH₂ CH = CH₂) was performed, as was described by Christoval et al [15]:

3.03 ml of allylamine were diluted in 3.33 ml of benzene and in the other hand, 1g (0.0028 mol) of

N₃P₃Cl₆ was dissolved in 5 ml of benzene after these two solutions were mixed and left under stirring for 24h at room temperature. 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 (64%). The product is characterized by: ¹H-NMR: 3.5 ppm (CH₂-NH), 5.8 ppm (CH = CH₂), 5.0, 5.1 ppm (CH = CH₂), IR: 3232 cm⁻¹ (NH), 1248 cm⁻¹ (P = N), 1644 cm⁻¹ (C = C). The reaction conditions are described as following:

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

Product	Catalyst (Mag-H ⁺)	solvent	yield	Time(h)	Temperature (°C)
1	–	Benzène	64%	24	20

Another synthesis of hexa (allylamino) cyclotriphosphazene was carried out by a new method: from the hexachlorocyclotriphosphazene of allylamine at 20°C using diethyl ether as solvent and a Mag-H⁺ (5%) an ecologic catalyst layered (Algerian MMT), finally the reaction lasted for 12 hours. Nucleophilic substitution on the allylamine by hexachlorocyclotriphosphazene was performed according to the same procedure as that used for precedent reaction except that we added (0.05 g) Mag-H⁺ clay catalyst layered and the solvent used is

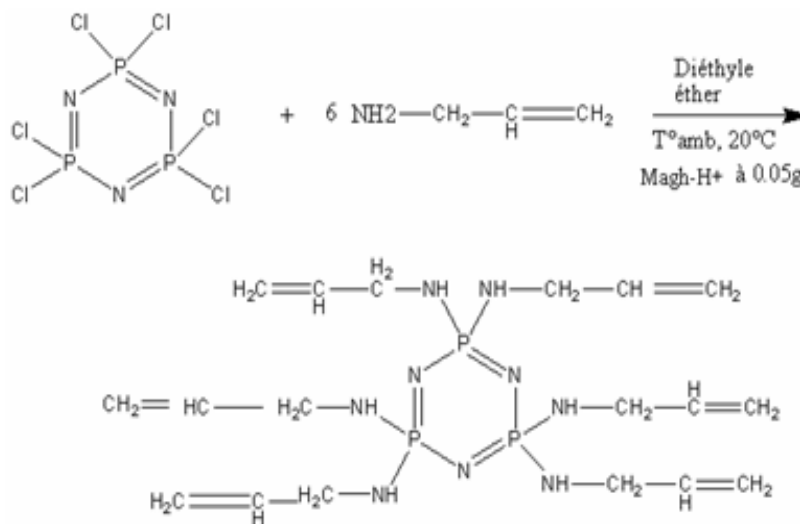
diethyl ether, the reaction time was reduced to 12 h, the solution was then filtered after adding CDCl₃ and recovered Mag-H⁺, then the filtration was purified as for the precedent product, the product obtained is white crystals in the yield was 74%. Finally, the product is characterized by: ¹H-NMR: 1.2 ppm (NH), 3.5 ppm (CH₂-NH), 5.8 ppm (CH = CH₂), 5.1, 5.0 ppm (CH = CH₂), IR: 3450 cm⁻¹ (NH), 1254 cm⁻¹ (P = N), 1644 cm⁻¹ (C = C), RMN ³¹P: 12 ppm (three phosphors). MALDI TOF: 471g/mol.

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

Product	Catalyst (Mag-H ⁺)	solvent	yield	Time (h)	Temperature (°C)
2	5%	Diethyl ether	74%	12	20

To complete the synthesis of hexa (allylamino) cyclotriphosphazene, can be avoided hazards of benzene (carcirogen solvent), using his place diethyl

ether in the presence of Maghnite-H⁺ where achieving this synthesis under conditions sweet. The reaction taking place is shown in the following scheme:



Scheme 1 : Representation schematic of the synthesis of hexa (allylamino) cyclotriphosphazene catalysed by Maghnite-H⁺ (0.25M).

III. RESULTS AND DISCUSSION

Figure 2. Shows the FTIR spectra of HACTP. The characteristic IR peaks of the resulting HACTP has characteristic peaks appear edat 3194.32 cm⁻¹ for NOH groups, and at 1642.28 and 909.38 cm⁻¹ for CAC bonds. The IR peak of PAN bonds were shifted to 1176.19 cm⁻¹ as shown in Figure2.

230-320°C was proceeded by 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 [16].

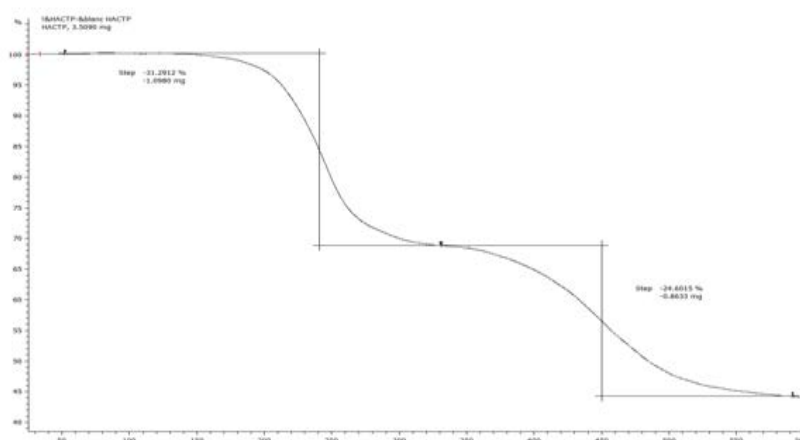


Figure 5 : TGA curves of hexa (allylamino) cyclotriphosphazene obtained in nitrogen atmosphere at heating rate of 10 °C/min

The molecular weight of HACTP determined from the mass spectrometry is 701 (see Fig. 4). Other significant observation on the mass spectrum of HACTP is its fragmentation to 488, 486, 472, and 461. The major

peaks are contributed by the sequential cleavages of allylamine groups from HACTP and were contributed by the former fragments plus one $[-NH]^+$ group [17].

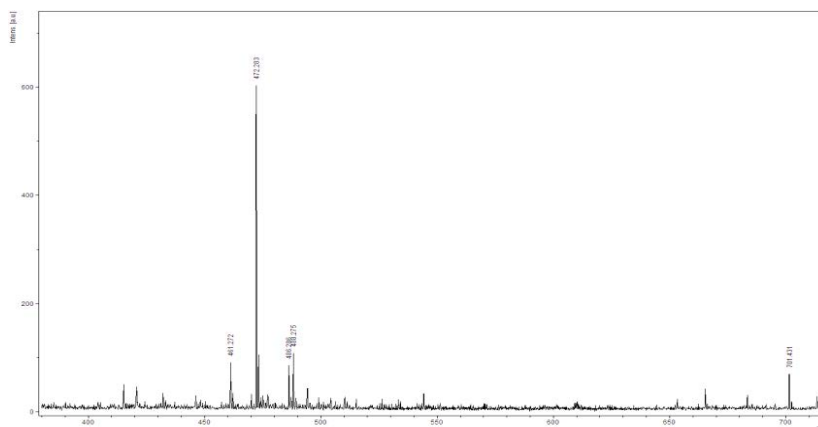


Figure 6 : Mass spectrum of hexa (allylamino) cyclotriphosphazene (HACTP) induced by Maghnite-H⁺(0.25M).

The DSC result shown in Figure 6 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 [18].

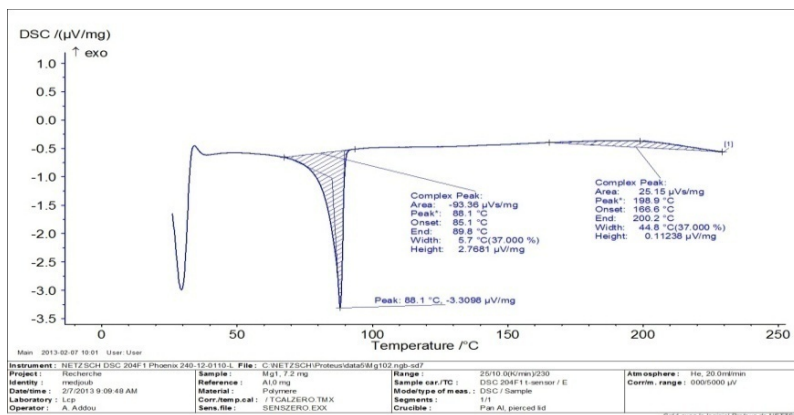


Figure 7 : DSC curves of obtained in nitrogen atmosphere at heating rate of 10 °C/min

IV. CONCLUSION

We have developed a new synthetic method to produce hexa allylamino cyclotriphosphazene, which does not use inorganic acid but friendly, green, ecologic and non toxic catalyst clay as proton source. To complete the synthesis of hexa (allylamino) cyclotriphosphazene, can be avoided hazards of benzene (carci- nogen solvent), using his place diethyl ether in the presence of Maghnite-H⁺ where achieving this synthesis under conditions sweet. The simplicity of the methods, good properties catalytic of the support catalyst solid super acid (Maghnite-H⁺) and non toxic solvent make this an attractive method for the synthesis of hexa (allyl- amino) cyclotriphosphazene.

REFERENCES RÉFÉRENCES REFERENCIAS

1. Belbachir M, Bensaoula A (2001). "Composition and method for catalysis using bentonites," United States Patent Number: 6274527 B1.
2. Yi-Zhong Cai, Mei Sun, Jie Xing, Qiong Luo, Harold Corke. Structure-radical scavenging activity relationships of phenolic compounds from traditional Chinese medicinal plants. *Life Sciences* 2006, 78(25), 2872-2888.
3. D. Christova et al. Designed Monomers and Polym, 6, 11-21. (2003).
4. D. Christova et al. Designed Monomers Polym, 6, 11-21.(2003)
5. Nakamura Y., Watanabe S., Miyake N., Kohno H., Osawa T. Dihydrochalcones: evaluation as novel radical scavenging antioxidants. *Journal of Agriculture Food Chemistry* 2003, 51, 309-3312.
6. Bindzus W., Livings S.J., Gloria-Hernandez H., Fayard G., van Lengerich B. and Meuser F. Glass transition of extruded wheat, corn and rice starch. *Starch* 2002, 54, 393-398.
7. Belbachir M., Yahiaoui A., Hachemaoui A. *International Journal of Molecular Sciences*, 2003 4, 548-561.
8. Ray S, Okamoto M (2003). "Polymer/Layered Silicate Nano composites: A Review from Preparation to Processing." *Prog. Polym. Sci.*, 28(11): 1539-1641.
9. 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, 200.
10. Belbachir, M; Bensaoula, A, Composition and method for catalysis using bentonites, US patent, No7, 094-823 B2, 2006.
11. D. Christova et al. Designed Monomers and Polym, 6, 11-21. (2003).
12. Belbachir M., Yahiaoui A., Hachemaoui A. *International Journal of Molecular Sciences*, 2003 4, 548-561.
13. 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.
14. 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.
15. S.D. Johnson, J.M. Anderson, R.E. Marchant, Biocompatibility studies on plasma polymerized interf- ace materials encompassing both hydrophobic and hydrophilic surfaces, *J. Biomed. Mater. Res.* 26 (1992) 915- 935.
16. Ray S, Okamoto M (2003). "Polymer/Layered Silicate Nano composites: A Review from Preparation to Processing." *Prog. Polym. Sci.*, 28(11): 1539-1641.
17. Mahesh DB, Basavaraja S, Balaji DS, Shivkumar V, Arunkumar A, Venkataraman L (2009). Preparation and characterization of Pani and Pani-Ag nanocomposites via interfacial polymerization". *Polym. Composit*, 30(11): 1668-1677.
18. Fukuoka et al .US patent no 7,317, 046, (2008).