



## Kinetics Study of Catio-radically Polymerization of Aniline Catalyzed by Maghnite- $\text{Na}^+$ Clay Catalyst Layered (Western Algeria)

Rahmouni Abdelkader\*, Harrane Amine, Belbachir Mohammed

Université d'Oran Es-senia, Département de chimie, Faculté des sciences, BP 1524.El M'nouar 31000 Oran ALGERIA

Available online at: [www.isca.in](http://www.isca.in)

Received 14<sup>th</sup> November 2012, revised 25<sup>th</sup> January 2012, accepted 28<sup>th</sup> April 2013

### Abstract

The polymerization of aniline with oxidant ( $\text{K}_2\text{S}_2\text{O}_8$ ) catalyzed by Maghnite- $\text{H}^+$  in chloroform ( $\text{CDCl}_3$ ) as solvent at  $0^\circ\text{C}$  was investigated. The effects of the amounts of Mag- $\text{H}^+$ , agent oxidant, water and temperature on the polymerization of aniline were studied. The polymerization yield increased as the proportions of catalyst and oxidant were increased in temperature range  $T = 0^\circ\text{C}$  at  $T = 5^\circ\text{C}$ . The reactions were monitored by gel permeation chromatography,  $^1\text{H}$ -NMR spectroscopy and FTIR spectroscopy.

**Keywords:** Polyaniline,  $^1\text{H}$ -NMR spectroscopy, Maghnite- $\text{H}^+$ , Conductivity and infra red spectroscopy.

### Introduction

The discovery of electrical conductivity of organic conjugated polymers has opened a novel and very important field of modern functional material science. In the past few years, a conducting polyaniline PANI has been the center of great interest because of its high electrical conductivity and chemical stability<sup>1-2</sup>.

The molecular chain structure polyaniline are very complex. Polyanilines do not dissolve in water and most organic solvents. They decompose before reaching the melting temperature. Also, it is difficult to determine their structures experimentally. As a result, there is still a lot of disagreement about the structures and conducting mechanism of Polyanilines<sup>3</sup>.

One way to improve PANI bulk properties is the confinement into nanoscale porous materials, due to the organization of the polymeric chains in the confined environment<sup>4</sup>. Clay montmorillonite is a layered silicate possessing ion exchange ability. The acid property of montmorillonite can be easily altered by replacing of the crystalline structure<sup>5</sup>. It has been reported that aluminium, iron and tin ion exchanged montmorillonite are strongly acidic and efficient for several acid-catalyzed organic reactions, such as aldol and Michael reactions<sup>6-7</sup>. The clay, which was used as a catalyst, was supplied by a local company known as ENOF Maghnia (Western Algeria). Its chemical composition is given in table-1. The greatest proton saturation of the  $<2\ \mu\text{m}$  fractions of clay was obtained as follows. First, it was saturated with  $\text{Na}^+$  ions with a 1M NaCl solution, and then the protonated forms of montmorillonite (Mag- $\text{H}^+$ ) were prepared through the shaking of the clay in a solution of  $\text{H}_2\text{SO}_4$  (0.25M) until saturation was achieved (normally after 2 days at room temperature). The cation-exchanged clay was then recovered by filtration and again suspended in deionized water. This process was repeated until no sulfate ions were indicated in the filtrate with  $\text{BaCl}_2$ . Mag- $\text{H}^+$  was isolated by filtration, dried at  $105^\circ\text{C}$ , and then finely ground.

In present work, we have successfully prepared PANI/Mag- $\text{H}^+$  nanoparticles composites by oxidative polymerization method. The product is characterized by using FTIR and  $^1\text{H}$ -NMR spectroscopy, respectively. We report the effect of the amount of Mag- $\text{H}^+$ /oxidant on the yield of the reaction and the effect of time and temperature on the yield of the reaction. The potential formation mechanism is also discussed and suggested.

### Material and Methods

**Preparation of Catalyst:** (Maghnite- $\text{H}^+$ ) were prepared by a method similar to that described by Belbachir et al.<sup>8</sup>. Raw maghnite (20 g) was crushed for 20 min using a Prolabo ceramic ball grinder. It was then dried by baking at  $105^\circ\text{C}$  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  $\text{H}_2\text{SO}_4$  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  $150^\circ\text{C}$ .  $\text{H}_2\text{SO}_4$  solutions of 0.25M concentration was used to prepare Maghnite- $\text{H}^+$ .

**Reagents:** Aniline 99% (Aldrich), potassium persulphate 98% (Aldrich), hydrochloric acid (35%–38%), methanol and chloroform ( $\text{CDCl}_3$ ) and ionized water ( $\text{pH}<7$ ). MMT clay was obtained from ENOF Maghnia (Algeria). The MMT- $\text{H}^+$  (Mag- $\text{H}^+$ ) was prepared as described by Belbachir et al.<sup>9</sup>, were used to synthesize émeraaldine salt (PANI-Mag- $\text{H}^+$ ) by emulsion polymerization. Some of the emeraldine base (PANI-EB), non-conducting form of polyaniline was prepared by de-protonating PANI-ES in NaOH Solution (0, 5 M). A doping EB was carried out in aqueous medium of HCl (1M)<sup>10</sup>.

**Instrumentation:** The chemical structure of the products,  $^1\text{H}$ -NMR was used (BRUKER 300 AVANCE) with Tetramethylsilane as the internal reference. The viscosimetric

molecular weight  $M_v$  was also calculated from the intrinsic viscosity measured in acetone at 25°C, with capillary Viscosimeter, viscolytic TI-1, version 3-1 Sematec, by the following Mark-Houwink equation:  $[\eta] = K (M_v)^a$

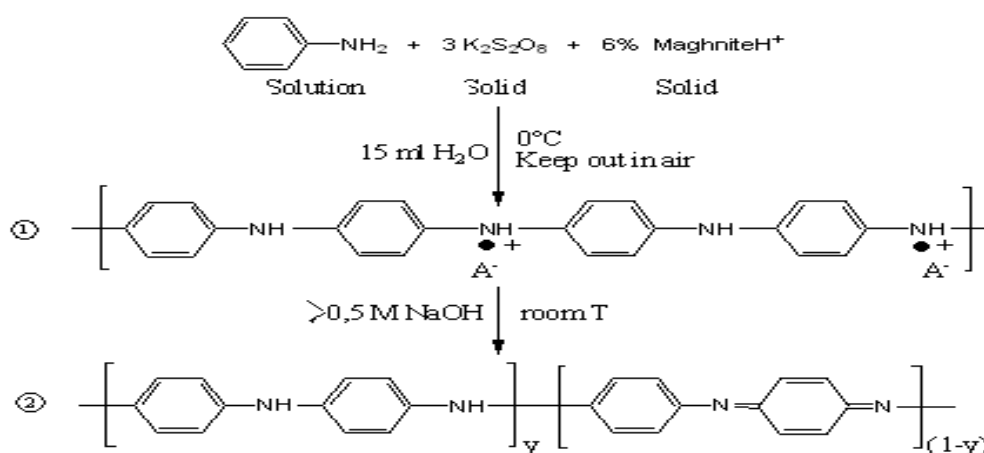
**Purification of the products:** The purification of polymers were carried out by dissolving the product in chloroform ( $\text{CDCl}_3$ ) and filtering to eliminate the Mag-H<sup>+</sup>. Then, chloroform was removed by evaporation.

## Results and Discussion

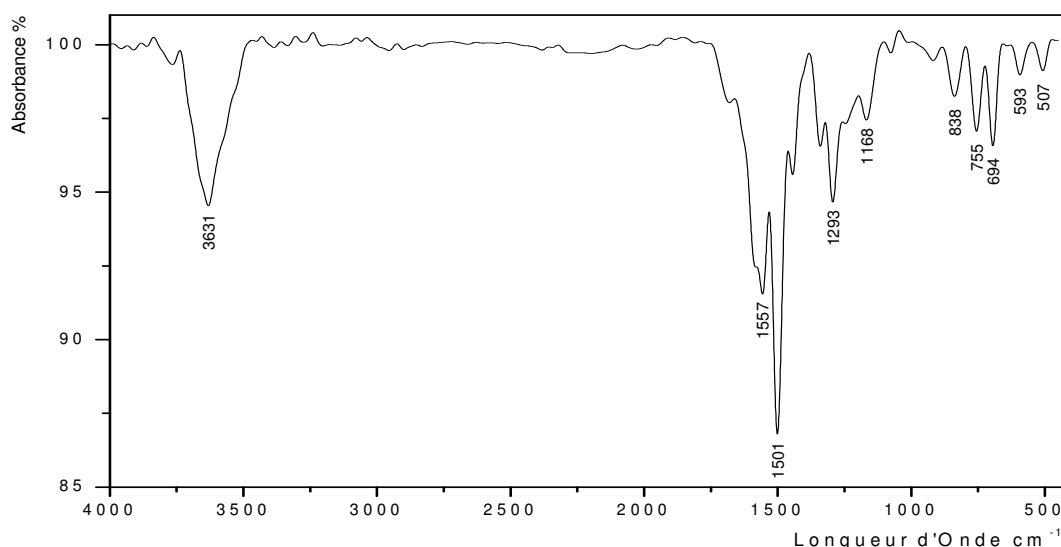
**Polymerization of Aniline by Mag-H<sup>+</sup>:** The Aniline is well known to be polymerized by protonic acid such as chlorhydric

acid ( $\text{HCl}$ )<sup>11-12</sup>. The cationic polymerization of ANI was examined in the presence of Mag-H<sup>+</sup> powder in bulk at 0°C (Scheme-1). The proof for this polymerization obtained by <sup>1</sup>H-NMR spectroscopy (Bruker 300 AVANCE, solvent:  $\text{CDCl}_3$ ), is shown in figure. 3 and 4.

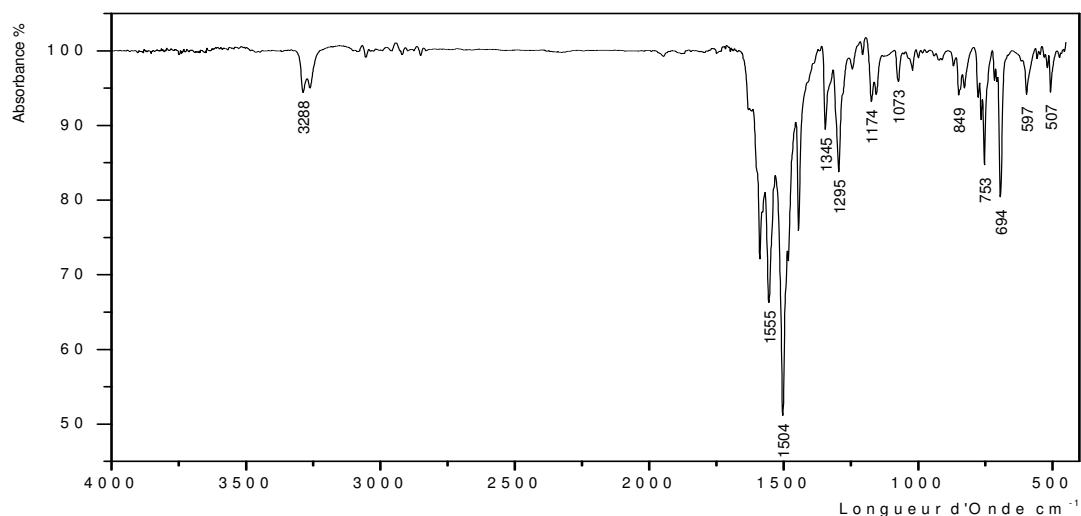
**Structural Analysis:** The FTIR spectra of the PANI-ES and PANI-EB under the same conditions were shown in Figure.1 and 2. The FTIR spectroscopy evidence the formation of polyaniline structure containing 1,4-para-disubstituted linear chain. The vibration frequencies of the major infrared bands and their assignment for polyaniline PANI-ES and PANI-EB are summarized in table 1.



**Scheme-1**  
**Polymerization process of aniline catalyzed by Mag-H<sup>+</sup>**



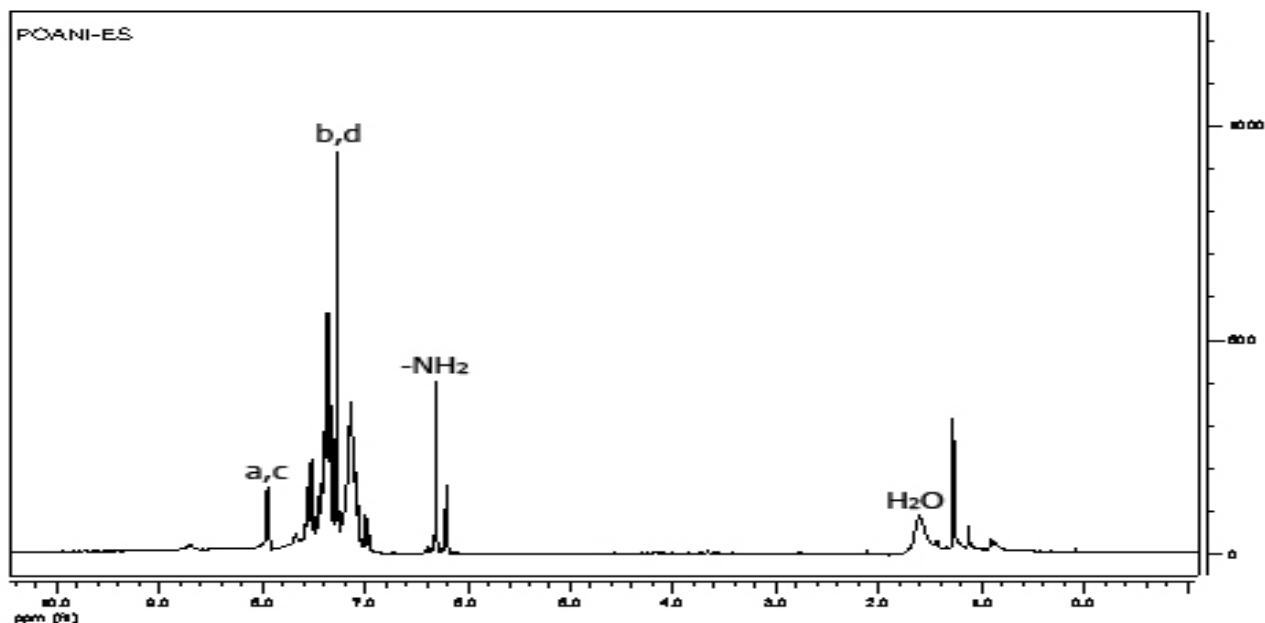
**Figure-1**  
**FT-IR spectra of the polymer (PANI-ES) obtained by the persulfate oxidation method (emeraldine black) at 0°C.**



**Figure-2**  
FT-IR spectra of the reduced polymer (PANI-EB) prepared at 25°C

**Table-1**  
The vibration frequencies (cm-1) of PANI-ES and PANI-EB synthesized by Mag-H<sup>+</sup>

PANI-ES	PANI-EB	Assignement
3631	3288	Asymmetric N-H stretching
1555	1557	Aromatic C-C stretching
1295	1293	C-N stretching of secondary aromatic amine
1174	1168	C-H in plane bending 1,4 disubstuted benzene
849	838	Out of plane C-H bending 1,4 disubstuted benzene ring



**Figure-3**  
1H NMR spectrum (300 MHz, CDCl<sub>3</sub>, Tetramethylsilane (TMS) was used as the internal standard) of polyaniline (PANI-ES) obtained by the polymerization of aniline with Mag-H<sup>+</sup> initiator system in CDCl<sub>3</sub> at 0°C

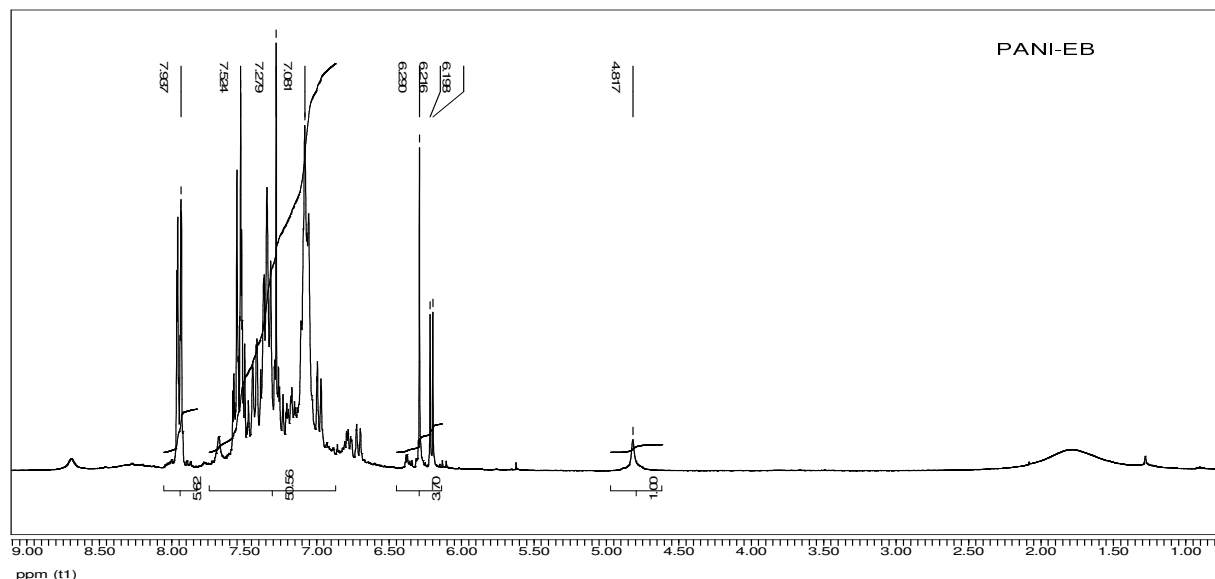


Figure-4

$^1\text{H}$  NMR spectrum (300 MHz,  $\text{CDCl}_3$ , Tetramethylsilane (TMS) was used as the internal standard) of polyaniline (PANI-EB) obtained by the polymerization of aniline with  $\text{Mag-H}^+$  initiator system in  $\text{CDCl}_3$  at  $25^\circ\text{C}$

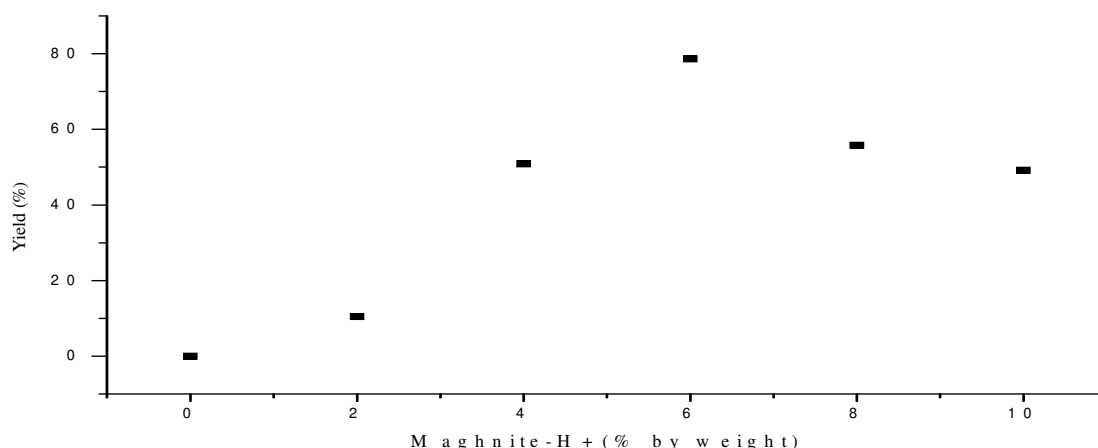


Figure-5

Effect of the amount of  $\text{Mag-H}^+$  on the yield of the polymerization

The  $^1\text{H}$ -NMR spectra of the PANI-ES and PANI-EB polymers exhibit strongest sharp peak centered at 7 ppm and 7.8 ppm due to protons on phenylene and disubstituted phenylene units, the weak peak at 4.81 ppm and medium broad peak at 6.22 ppm due to  $(-\text{NH}-$  and  $-\text{NH}_2)$  end group respectively, another broad peaks centered at 1.78 ppm and 8 ppm may be due to the water protons bonded by  $(-\text{NH}-$  and  $-\text{NH}_2)$  groups and  $(\text{H-N}^+)$  respectively, as show in figure 3 and 4<sup>13</sup>.

**Effect of the Amount of  $\text{Mag-H}^+$  on the Yield of Polymerization:** Figure. 5 shows the effect of the amount of

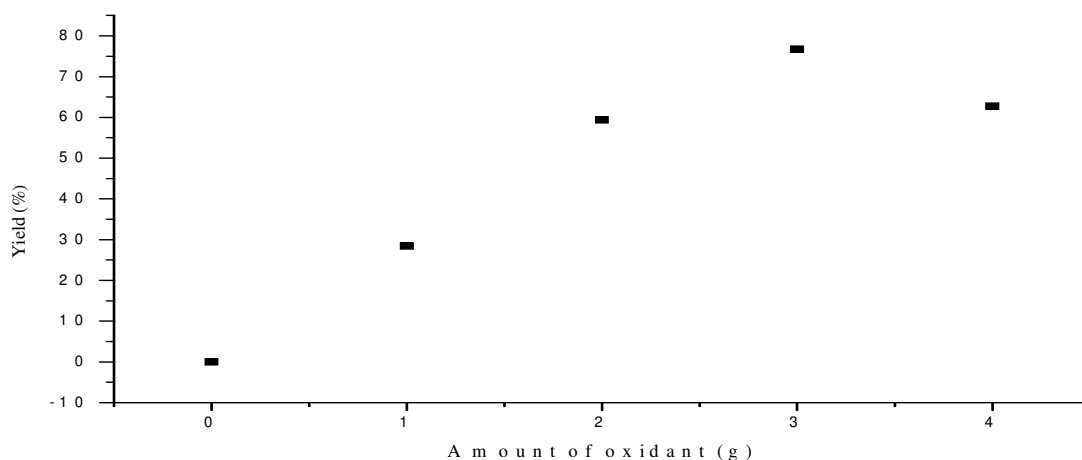
$\text{Mag-H}^+$ , expressed by using various weight ratios of  $\text{Mag-H}^+$ /monomer on the polymerization rate. The polymerization was carried out in bulk. As shown in figure 5, a yield of 84, 83 wt % was reached for 6 wt% of  $\text{Mag-H}^+$ , and the use of a lower or higher amount of clay caused a decrease of the yield of the reaction. Similar results are obtained by Yahiaoui et al.<sup>14-15</sup> in the polymerization of epichlorhydrin, propylene oxide and cyclohexene oxide by  $\text{Mag-H}^+$  and the polymerization of styrene by montmorillonite, respectively. This phenomenon is probably the result of the number of initiating active sites

responsible of inducing polymerization; this number is prorating to the catalyst amount used in reaction.

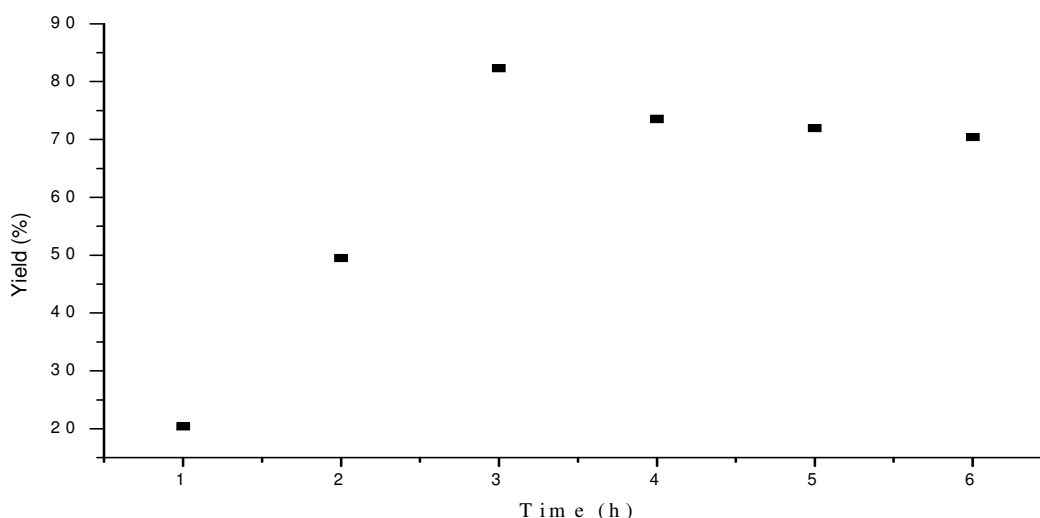
**The Effect of Oxidant Content on the Yield of the Polymerization:** In the present study, the PANI/Mag was prepared with  $K_2S_2O_8$  as the oxidant, Maghnite- $H^+$  as a catalyst and the relation between the content of oxidant and the yield of the reaction was investigated. As shown in Figure. 6 (6 % of Maghnite- $H^+$ , 3g of oxidant, 3 hours of reaction time, 5 ml of Aniline, 15 ml of water,  $T=0^\circ C$ ), the yield of the product is largest when the molar ratio of aniline and oxidant is near 0.58, when it is less than the value, the yield of the reaction increases significantly with the addition of oxidant; when it is 1:1, the

yield reached a maximum 84,83% and then it decreased. This is because polyaniline could further oxidize under the excessive oxidant and cracked into other compounds of lower molecular weight<sup>16</sup>.

**The Effect of Time on the Yield of the Polymerization:** Figure 7 shows the yield of polymer versus time for polymerization of aniline using Mag- $H^+$  as catalyst. As the figure shows, polymerization takes place rapidly and smoothly, reaching a yield of 82.30% after 3h. The polymerization yield became constant at that time; this is probably the result of an increase in the medium viscosity<sup>17</sup>.



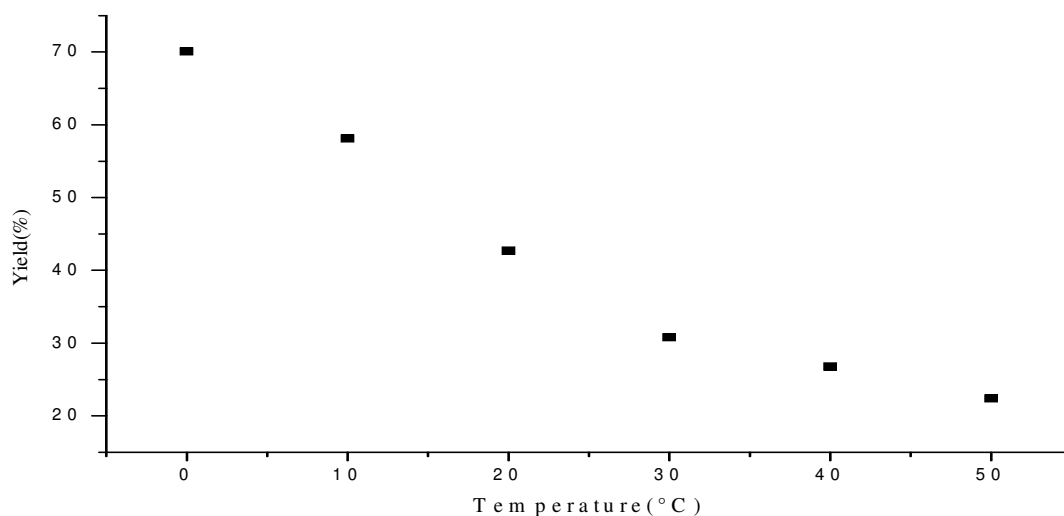
**Figure-6**  
Effect of the amount of oxidant on the yield of the polymerization.



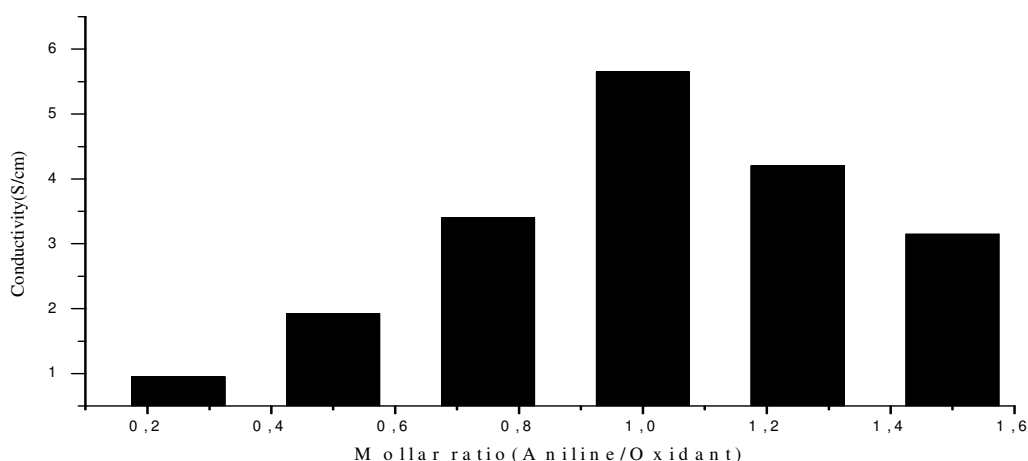
**Figure-7**  
Yield of polyaniline at Maghnite- $H^+$ (6%), Aniline (0.055 mol)

**The Effect of Temperature on the Yield of the Polymerization:** In the presence of Maghnite- $H^+$  at various weight ratios Maghnite- $H^+$ /monomer, the polymerization of aniline was carried out for 3 hours. The reaction was induced at different temperatures and the effect of temperature on polymerization was studied. The results are shown in Figure. 8. The yield of polyaniline was found to increase with the temperature. The rate of polymerization at  $0^\circ C$ , however, was the small. A similar effect was shown in the polymerization of aniline initiated by chlorhydric acid<sup>18</sup>.

**The Effect of Oxidant Content on the Conductivity of the Polymerization:** The PANI/Mag- $H^+$  composite were prepared with  $K_2S_2O_8$  as the oxidant and the relation between the content of oxidant and the conductivity was investigated. As shown in figure 9 (3 hr of reaction time, 0.334 g/5 ml An of Mag- $H^+$ , 15 ml of water and  $0^\circ C$  of temperature), the conductivity of the product is largest when the molar ratio of aniline and oxidant is near 1:1, when it is less than the value, the conductivity increases significantly with the addition of oxidant, when it is 1:1, the conductivity reached a maximum 5.65 S/cm and then it decreased. This is because polyaniline could further oxidize under the excessive oxidant<sup>19</sup>.



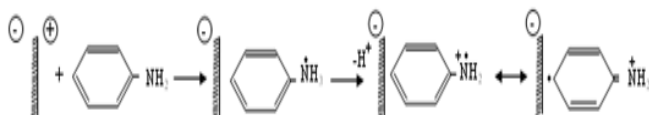
**Figure-8**  
Effect of the temperature on the yield of polyaniline (Maghnite- $H^+ = 6\%$ ,  $t=3h$ ).



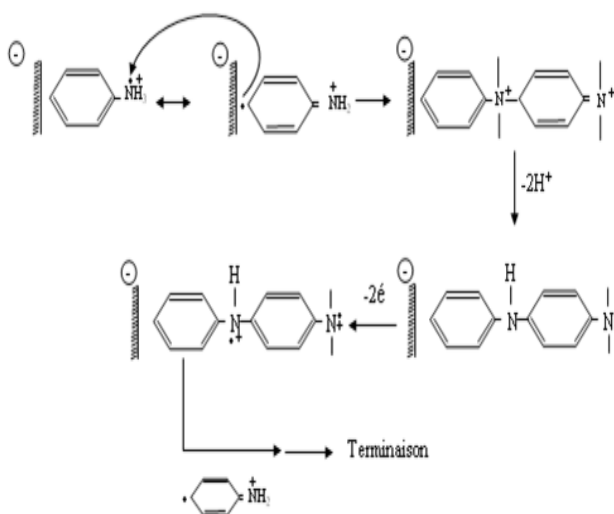
**Figure-9**  
Effect of the molar ratio (aniline/oxidant) on the conductivity

**Proposed Mechanism of Polymerization:** In the present study, the process of synthesis of PANI/Mag-H<sup>+</sup> composite can be divided into the following three steps:

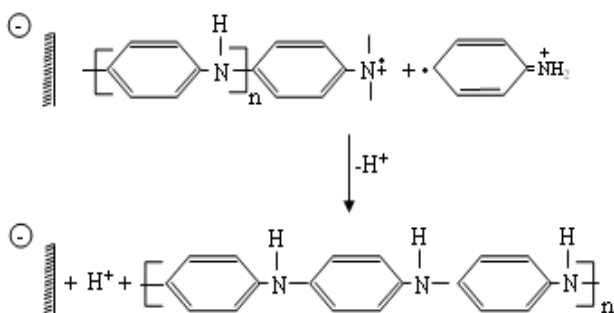
**Initiation:** The mechanism of the reaction occurs within the layers of the Maghnite exchanged by H<sup>+</sup> protons, which are capable of initiating cationic polymerization in the presence of the oxidant K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>.



**Propagation:** Propagation is by the successive addition of monomers on the chain macromere growing.



**Termination:** The termination takes place during the recombination of two radical ions giving rise to the final polymer.



## Conclusion

On the basis of the results obtained during this investigation, the following conclusions have been drawn: i. Activation of Maghnite with H<sub>2</sub>SO<sub>4</sub> can be done to increase the bentonite

activity. ii. Acid-exchanged Maghnite is effective as an acidic catalyst for the synthesis of polyaniline. iii. We investigated the reaction conditions for polymerization of polyaniline. The yield, the solubility, the electrical conductivity and the thermal stability of the synthesized polyaniline depend on both the amount of Mag-H<sup>+</sup> and water used, the reaction time and the temperature. The optimum reaction conditions for the synthesis of polyaniline were defined as: 6 wt % of Mag-H<sup>+</sup>, 3g (0,013 mol) of oxidant, 15 ml of water, T=0°C and reaction time 3 h.

Finally, it has been proved that Mag-H<sup>+</sup> can be used to induce the polymerization of aniline, and this offers new possibilities for the selective study of montmorillonite as catalysts and for the synthesis of polymers conductors soluble in various organics solvent.

## References

1. Kim B.H., Jung J.H., Kim J.W., Choi H.J. and Joo j, *Synth Met*, **117**, 115 (2001)
2. Arsalani N and Hayatifar N., *Polym Int*, **54**, 933 (2005)
3. Asturias G.E., MacDiarmid A.G., McCall R.P. and Epstein A.J., *Synth. Met*, **29**, E157 (1989)
4. Chuang T.H., Guo W., Cheng K.C., Chen SW., Wang H.T. and Yen Y.Y., *J Polym Res*, **11**, 169 (2004)
5. Kannan C., Devi M.R., Muthuraja K., Esaivani K. and Sudalai Vadivoo V. Green catalytic Polymerization of Styrene in the Vapor phase over Alumina, *Res.J.chem.sci.*, **2**(7), 27-35 (2012)
6. Shukur Majid M., Kadhim. F. Al-Sultani and Hassan Mohammed N. Preparation of Alkali Lead Glass and Glass Ceramic Compositions as Electrical Insulators., *Res.J.chem.sci.*, **2**(2), 28-34 (2012)
7. Sanchez C., Soler-Illia J.A., Ribot F., Lalot T., Mayer C.R. and Cabuil V., Designed hybrid Organic-inorganic nanocomposites from functional nanobuilding blocks, *Chem Mater*, **13**(10), 3061-3083(2001)
8. Belbachir M. and Bensaoula A, *U.S. Pat.* 6, 274, 527B (2001)
9. Harrane A., Meghabar R and Belbachir M, *Int J Mol Sci*; **3**, 790 (2002)
10. Joel O.F., Durueke U.J., Kinigoma B.S. and Nwokoye C.U., Evaluation of Effect of Different Concentrations of Shale on Rheological Properties of Water-Based Mud , *Res. J. Chem. Sci.*, **2**(10), 13-19 (2012)
11. Epstein J., McCall R.P., Ginder J.M and MacDiarmid A.G., in: R.J.H.Clark (Ed.), *Spectro. of adv. Materials*, Wiley, Chichester,UK, 305-319(1991)
12. Yildirim K., Altun S. and Ulcay Y. DSC Analysis of Partially Oriented (Poy) and Textured Poly (Ethylene Terephthalate) Yarns, *Res.J.chem.sci.*, **1**(9), 57-66(2011)

13. Bıçak N., Filiz S and enkal E.S., *Synthetic Metals*, **155**, 105–109 (2005)
14. Yahiaoui A and Belbachir M., Ring-opening Polymerization of Styrene oxide with  $\text{Mg-H}^+$  as eco-catalyst, *Journal of Applied Polymer Science*, **100**, 1681–1687(2006)
15. Yahiaoui A., et al., An acid exchanged montmorillonite clay-catalyzed synthesis of poly- Epichlorhydrin; *Int. J. Mol.Sci.*, **4**, 548-561 (2003)
16. Bangale Sachin and Bamane Sambaji. Synthesis, Characterization and Hydrophilic Properties of Nanocrystalline  $\text{ZnFe}_2\text{O}_4$  Oxide, *Res. J. Recent Sci.*, **1(ISC-2011)**, 202-206 (2012)
17. Rasika D., Wang X., Gamini R.M., Elsenbauer R.L., *Chem Commun.*, 976 ( 2006)
18. Cao Y., Smith P. and Heeger A.J., Spectroscopic studies of polyaniline in solution and in spin-cast films, *Synth. Met.*, **32**, 263 (1989)
19. Shinde Santosh S. and Jachak Madhukar N.Synthesis and fluorescent behavior of Pyran and Pyridine-3, 5-dicarbonitrile derivatives, *Res. J. Recent Sci.*, **1(ISC-2011)**, 67-72 (2012)