

Kinetics Study of Catio-Radically Polymerization of Aniline Catalyzed by Maghnite-Na⁺ Clay Catalyst Layered (Western Algeria)

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Abstract: The polymerization of aniline with oxidant (K₂S₂O₈) catalyzed by Maghnite-H⁺ in chloroform (CDCl₃) as solvent at 0°C was investigated. The effects of the amounts of Mag-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°C at T = 5°C. The reactions were monitored by gel permeation chromatography, ¹H-NMR spectroscopy and FTIR spectroscopy.

Key words: Polyaniline ¹H-NMR spectroscopy • Maghnite-H⁺ • Conductivity • Infra red

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 [1-2].

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 [3].

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 [4]. 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 [5]. 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 [6-7]. 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.

Table 1: The vibration frequencies of PANI-ES and PANI-EB

PANI-EB	PANI-ES	Vibration frequencies cm ⁻¹ Assignment
3631	3288	Asymmetric N-H stretching
155	1588	Asymmetric C-C stretching
1295	1293	C-C stretching of secondary aromatic amine
1174	1168	C-H in plane bending 1,4 disubstituted benzene
849	838	Out of plane C-H bending 1,4 disubstituted benzene ring

The greatest proton saturation of the <2 μm fractions of clay was obtained as follows. First, it was saturated with Na⁺ ions with a 1M NaCl solution and then the protonated forms of montmorillonite (Mag-H⁺) were prepared through the shaking of the clay in a solution of H₂SO₄(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 BaCl₂. Mag-H⁺ was isolated by filtration, dried at 105°C and then finely ground.

In present work, we have successfully prepared PANI/Mag-H⁺ nanoparticles composites by oxidative polymerization method. The product is characterized by using FTIR and ¹H-NMR spectroscopy, respectively. We report the effect of the amount of Mag-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.

MATERIALS AND METHODS

Preparation of Catalyst: (Maghnite-H⁺) were prepared by a method similar to that described by Belbachir *et al.* [8]. 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 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⁺.

Reagents: Aniline 99% (Aldrich), potassium persulphate 98% (Aldrich), hydrochloric acid (35%-38%), methanol and chloroform (CDCl₃) and ionized water (pH<7). MMT clay was obtained from ENOF Maghnia (Algeria). The MMT-H⁺ (Mag-H⁺) was prepared as described by Belbachir *et al.* [9], were used to synthesize émeraaldine salt (PANI-Mag-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) [10].

Instrumentation: The chemical structure of the products, ¹H-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, viscologic TI-1, version 3-1 Semantec, by the following Mark-Houwink equation:

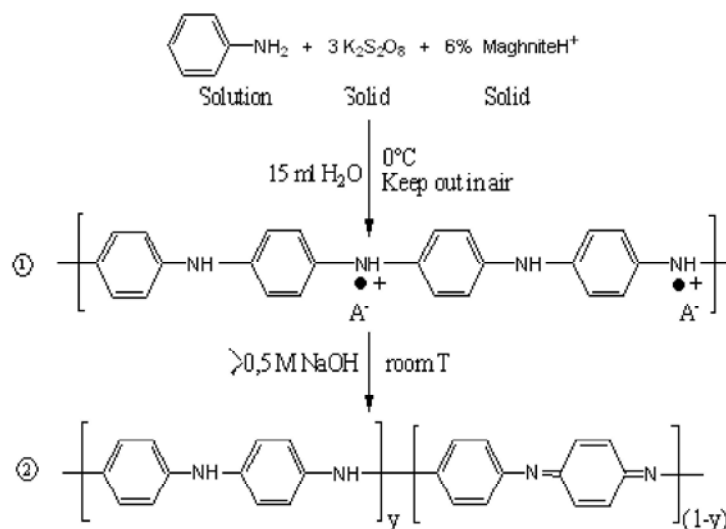
$$[\eta] = K (M_v)^a$$

Purification of the Products: The purification of polymers were carried out by dissolving the product in chloroform (CDCl₃) and filtering to eliminate the Mag-H⁺. Then, chloroform was removed by evaporation.

RESULTS AND DISCUSSION

Polymerization of Aniline by Mag-H⁺: The Aniline is well known to be polymerized by protonic acid such as chlorhydric acid (HCl) [11-12]. The cationic polymerization of ANI was examined in the presence of Mag-H⁺ powder in bulk at 0°C (Scheme 1). The proof for this polymerization obtained by ¹H-NMR spectroscopy (Bruker 300 AVANCE, solvent: CDCl₃), is shown in Fig. 3 and 4.

Structural Analysis: The FTIR spectra of the PANI-ES and PANI-EB under the same conditions were shown in Fig. 1 and 2. The FTIR spectroscopy evidence the formation of polyaniline structure containing 1,4-paradisubstituted 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 of aniline catalyzed by Mag-H⁺

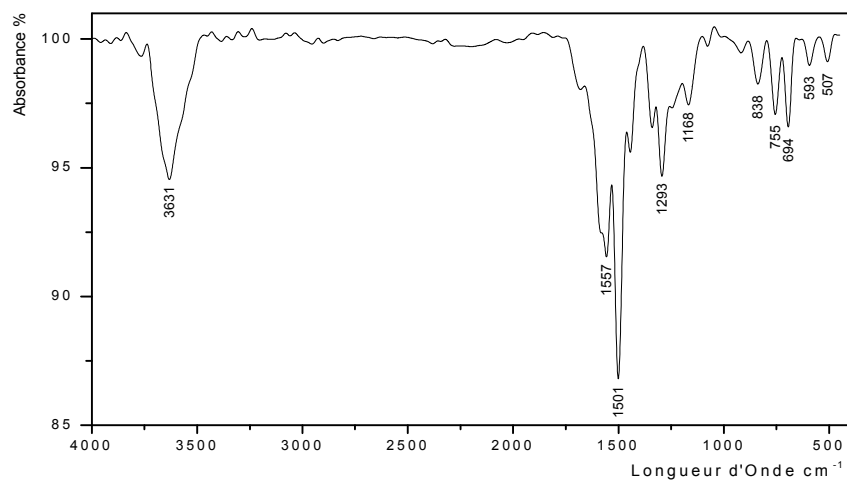


Fig. 1: FT-IR spectra of the polymer (PANI-ES) obtained by the persulfate oxidation method (emeraldine black) at 0°C.

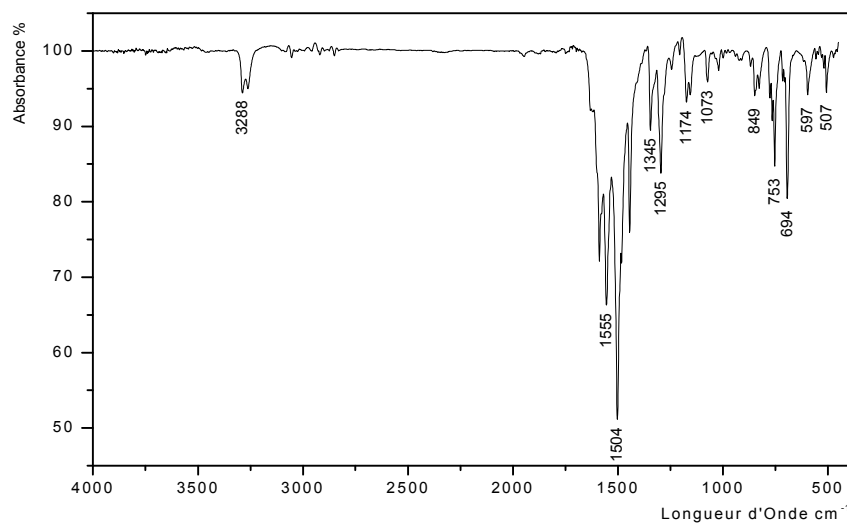


Fig. 2: FT-IR spectra of the reduced polymer (PANI-EB) prepared at 25°C.

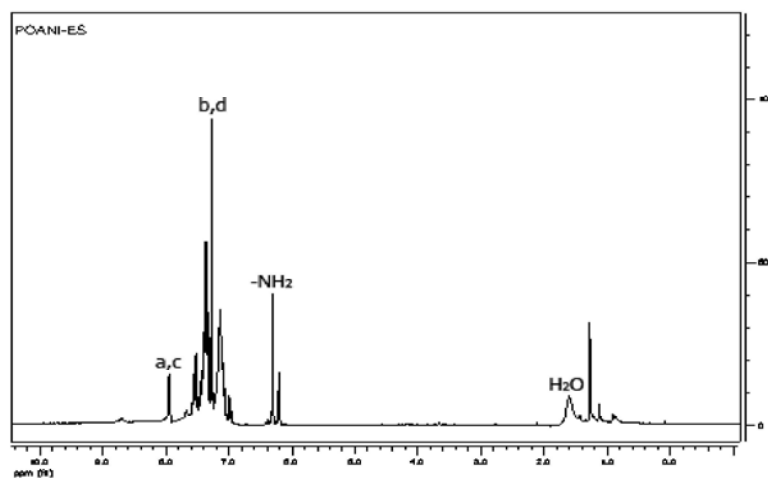


Fig. 3: ¹H NMR spectrum (300 MHz, CDCl₃, Tetramethylsilane (TMS) was used as the internal standard) of polyaniline (PANI-ES) obtained by the polymerization of aniline with Mag-H⁺ initiator system in CDCl₃ at 0°C.

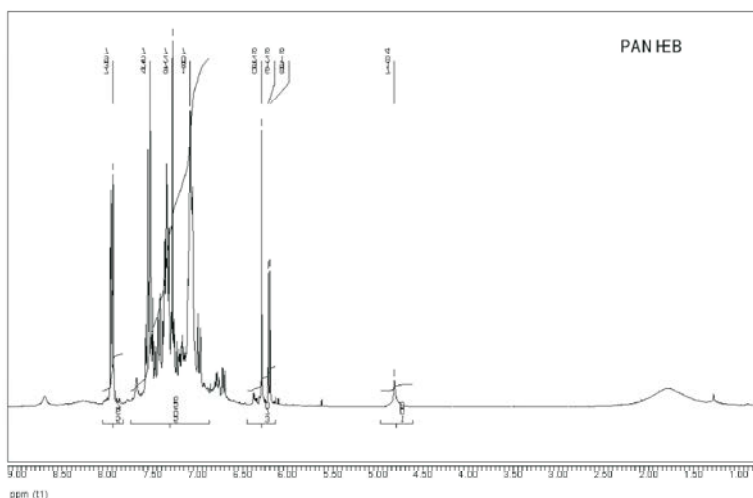


Fig. 4: ^1H NMR spectrum (300 MHz, CDCl_3 , Tetramethylsilane (TMS) was used as the internal standard) of polyaniline (PANI-EB) obtained by the polymerization of aniline with Mag- H^+ initiator system in CDCl_3 at 25°C .

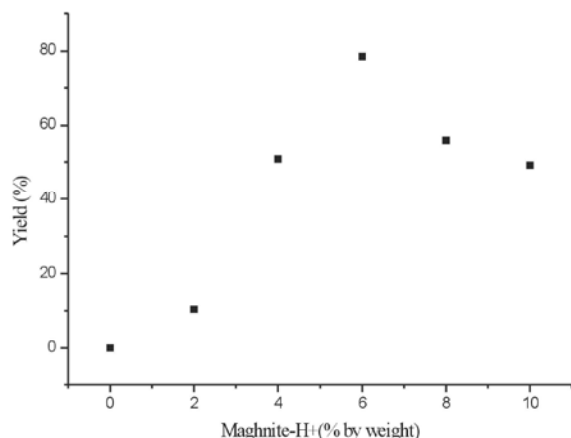


Fig. 5: Effect of the amount of Mag- H^+ on the yield of the polymerization.

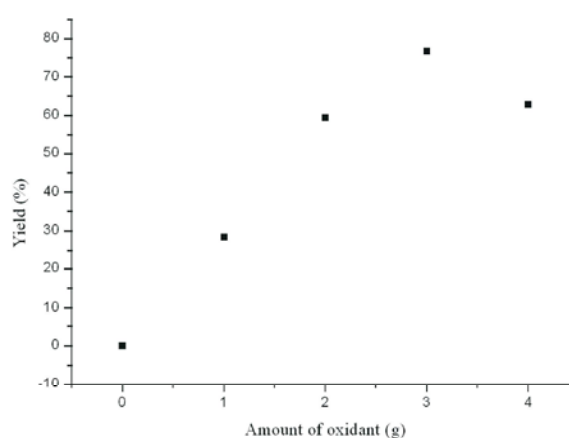


Fig. 6: Effect of the amount of oxidant on the yield of the polymerization.

The ^1H -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 (-NH-and-NH₂) end group respectively, another broad peaks centered at 1.78 ppm and 8 ppm may be due to the water protons bonded by (-NH-and-NH₂) groups and (H-N⁺) respectively, as show in Fig. 3 and 4 [13].

Effect of the Amount of Mag- H^+ on the Yield of Polymerization: Fig. 5 shows the effect of the amount of Mag- H^+ , expressed by using various weight ratios of Mag- H^+ / monomer on the polymerization rate. The polymerization was carried out in bulk. As shown in Fig. 5, a yield of 84,83 wt % was reached for 6 wt% of 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.* [14-15] in the polymerization of epichlorhydrin, propylene oxide and cyclohexene oxide by 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 $\text{K}_2\text{S}_2\text{O}_8$ 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 Fig. 6 (6 % of Maghnite- H^+ , 3g of oxidant, 3 hours of

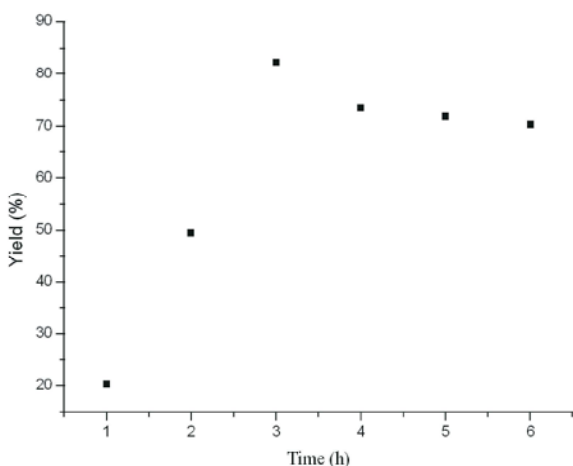


Fig. 7: Yield of polyaniline at Maghnite-H⁺ (5%), Aniline (0.055 mol).

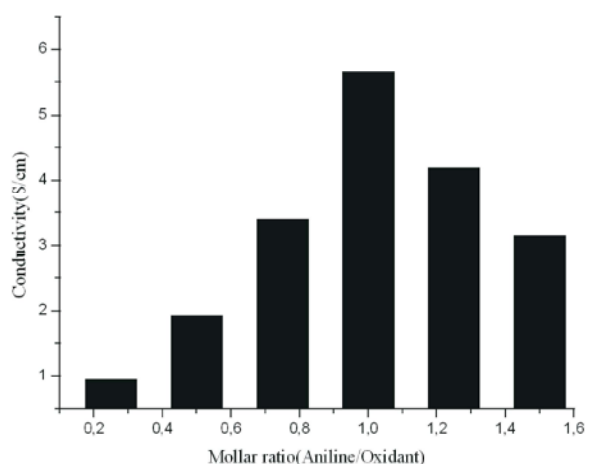


Fig. 9: Effect of the molar ratio (aniline/oxidant) on the yield of polymerization..

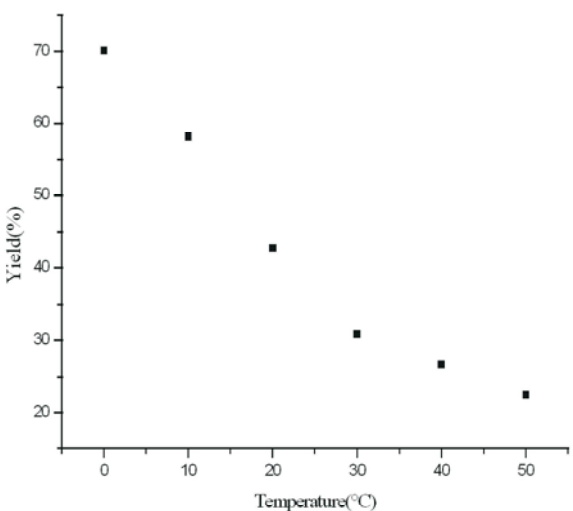


Fig. 8: Effect of the temperature on the yield of polyaniline (Maghnite-H⁺ = 6%, t=3h).

reaction time, 5 ml of Aniline, 15 ml of water, T=0°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 [16].

The Effect of Time on the Yield of the Polymerization:

Fig. 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 [17].

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 Fig. 8. The yield of polyaniline was found to increase with the temperature. The rate of polymerization at 0°C, however, was the small. A similar effect was shown in the polymerization of aniline initiated by chlorhydric acid [18].

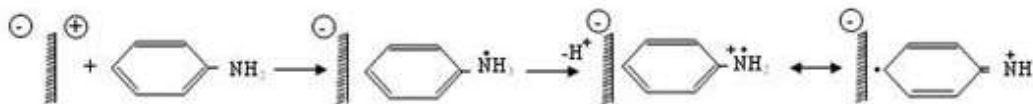
The Effect of Oxidant Content on the Conductivity of the Polymerization:

The PANI/Mag-H⁺ composite were prepared with K₂S₂O₈ as the oxidant and the relation between the content of oxidant and the conductivity was investigated. As shown in Fig. 9 (3 hr of reaction time, 0.334 g/5 ml An of Mag-H⁺, 15 ml of water and 0°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 [19].

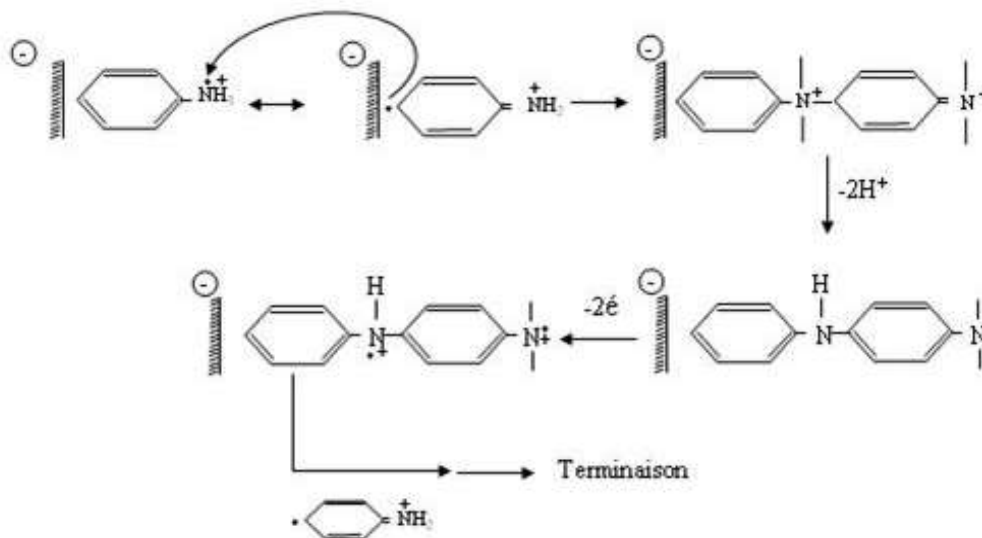
Proposed Mechanism of Polymerization:

In the present study, the process of synthesis of PANI/Mag-H⁺ composite can be divided into the following three steps:

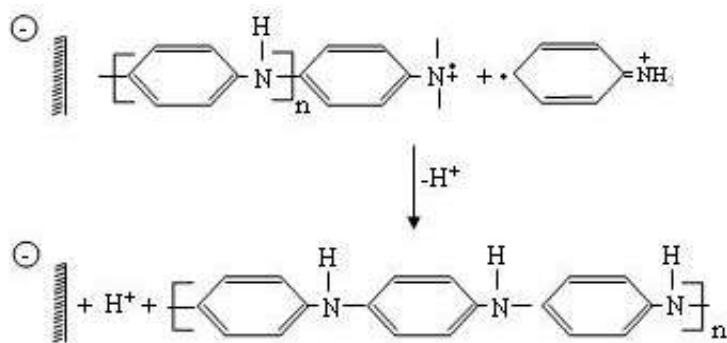
Initiation: The mechanism of the reaction occurs within the layers of the Maghnite exchanged by H^+ protons, which are capable of initiating cationic polymerization in the presence of the oxidant $K_2S_2O_8$.



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:

- Activation of Maghnite with H_2SO_4 can be done to increase the bentonite activity.
- Acid-exchanged Maghnite is effective as an acidic catalyst for the synthesis of polyaniline.

- 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^+ 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^+ , 3g (0,013 mol) of oxidant, 15 ml of water, $T=0^\circ C$ and reaction time 3 h.

Finally, it has been proved that Mag-H⁺ 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.

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