

Chemical Transformation of Polyaniline Catalyzed by Maghnite-H⁺ (Algerian MMT) Under Microwave Irradiation.

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Abstract: In different weight percentages of our ecological and green catalyst called Maghnite-H⁺ (Algerian MMT) and a reactive polymer stabilizer such as poly (ethylene oxide) (PEO, Mn = 2000), the chemical transformation of polyaniline under effect of this green catalyst was investigated and discussed. The formation of the hydrogen bonding between PANI and PEO was predicted by the FT-IR and the ¹HNMR spectra. The glass transition temperature of pure PANI and pure PEO respectively (Tg=74°C and Tg= -65°C), in the other hand the DSC analysis showed only one (Tg=16.79°C) for the mixte product (PANI-PEO) implying compatibility of two components. Here we can suggest, that under suitable condition (the amount of catalyst, molecular weight and functionality of the reactive stabilizer (PEO) and molar ratio of PANI-PEO), our catalyst can improved the morphology, structure, stability and properties chemicals of polyaniline.

Keywords: Chemical transformation, Polyaniline, Maghnite-H⁺, DSC, ¹HNMR spectroscopy, PEO.

1 Introduction

The environmental protection and especially the sustainable development is one of the major challenges of the twenty-first century, the media make this title one of their most recurrent subjects. Green chemistry concept proposed there a decade by Anastas and Warner [1], is a community response chemists to try to minimize the impact of chemical products and processes on the environment and to counteract negative image exerted chemistry in the minds of people. Among the founding principles include limiting the quantities of solvents used, the less harmful chemical synthesis, improved energy efficiency, the use of raw material renewable and catalysis [2]. The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia (Western of Algeria) [3]. Its chemical composition is given in Table 1. The greatest proton saturation of the <2 mm fractions of clay were obtained by first saturating with Na⁺ ions using 1M NaCl solution, then the protonated forms of montmorillonite (Mag-H⁺) were prepared by shaking the clay in a solution of sulfuric acid 0.25M until saturation was achieved (normally after 2 days at room temperature) [4]. 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 present in the filtrate using BaCl₂. The Mag-H⁺ was then isolated by filtration,

dried at 105°C and then finely ground. The cation exchange capacity (CEC) and surface area of the clay was found to be 84 mEq (100 g)⁻¹ of dried clay and 786 m².g⁻¹ respectively [5].

Our catalyst is a solid that has the property of accelerating the reaction rate of a chemical transformation thermodynamically possible [6]. The catalyst covered in principle unaltered at the end of the reaction [7]. If it is a solid, it is then able to create active intermediaries of a different type adsorbed species (adsorption of reagents to the surface) [8]. Heterogeneous catalysis is essentially a surface phenomenon [9]. The reaction taking place not in the whole volume of a fluid phase, but at the solid / fluid interface, training of active adsorbed species involves transport of molecules to the surface, followed by adsorption [10]. The surface reaction gives products that must first be desorbed the solid, and then migrate into the fluid phase [11].

Polyaniline (PANI), one of the most important conducting polymers, has received considerable attention due to its ease of synthesis [12], environmental stability [13], and unique acid/base doping/dedoping and oxidation/reduction chemistry [14]. Nanostructured PANI offers an opportunity to applications on sensors, actuators, supercapacitors, etc., due to its large specific surface area [15]. Many methods,

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including hard template, soft template and template-free methods, have been used to prepare nanostructured PANI as yet [16]. On the other hand, self-assembly of block copolymers is an effective method to synthesize various polymer or metal nanostructures because its morphology can be conveniently tuned into various nanostructures such as spheres, cylinders, tubules, and vesicles [17]. So, it is expected that various PANI structures could be produced by self-assembling of block copolymers containing PANI block [18]. Poly (ethylene oxide) (PEO) has been one of the most extensively studied synthetic polymers, because of not only its unique behaviors in solution but also its wide applications [19]. In particular is an exceptional polymer which dissolves with concentrations of a wide variety of salts to form polymer electrolytes [20]. Polymer electrolytes consist of polar polymer and ionizable salts. PEO is the most popular polymer used, due to its high solvating power with metal ions and outstanding mechanical properties [21]. In this present work authors have carried out the green chemical transformation of polyaniline by poly (ethylene oxide) based on Maghnite-H⁺ (Algerian ecologic catalyst MMT). It is found that the chemicals and physical properties of PANI transformed is more than pure PANI. This transformation was prepared in order to combine the mechanical and physical properties of PEO with conducting properties of PANI.

2 Experimental

2.1 Materials And Methods

Polyaniline (PANI) was prepared in our laboratory (laboratory of polymers chemistry, oran university, Algeria) by standard chemical intercalated method [22]. Polyethylene oxide (relative molecular mass of 2.103) was obtained from Sigma Aldrich, Potassium persulphate K₂S₂O₈ was analytical grade from Sigma Aldrich and dried under vacuum at 120°C for 24 h to remove water from the crystal, hydrochloric acid (35%–38%), MMT clay was obtained from ENOF Maghnia (Algeria). The MMT-H⁺ (Mag-H⁺) was prepared as described by Belbachir et al [23], and water (pH<7) was used to synthesize emeraldine salt clay (PANI-ES / Mag-H⁺) by emulsion polymerization [24]. Some of the emeraldine base (PANI-EB), non-conducting form of polyaniline, was prepared by de-protonating PANI-ES in NaOH Solution (0.5M) [25]. A doping EB was carried out in aqueous medium of hydrochloric acid (1M) [26]. The emeraldine base (50 mg) to dope it and dissolving it in (100 ml) of (2M) HCl. For two hour and the same time (PEO) 10 mg dissolving matrix (PEO) with (PANI) thin films of conducting polymer alloys PANI-PEO prepared by mixed different volume ratio of PANI with PEO [27].

2.2. Measurements

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. Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm⁻¹ on an ATI Matson FTIR No 9501165. Ten scans were averaged at a resolution of 4 cm⁻¹ for the solid tested samples of modified and unmodified montmorillonite prepared as KBr pellets (ca. 3% by mass in KBr). Viscosity measurements were carried out with an Ubbelohde Capillary Viscosimeter (viscologic TI1, version 3–1 Semantec). Intrinsic viscosity, [η], was measured at 30°C in benzene. GPC measurements of the samples were carried out using a WISP 712, Waters Associates chromatograph, THF was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. The flow rate of tetrahydrofuran was 10 ml/min. intrinsic viscosity measurements were performed on SEMATECH Viscologic TI 1 apparatus at 25°C using THF as solvent. The purification of polymers were carried out by dissolving the product in chloroform (CHCl₃) and filtering to eliminate the Mag-H⁺. Then, chloroform was removed by evaporation.

2.3 Synthesis Of Product

free solvent, a solution of 5.1g of aniline, 0.05g of PEO and (5%) of maghnite-H⁺ (Alerian MMT) was then added. The mixture was put into a flask with 100 mL and stirred to allow proper mixing. The mixture was subjected to several short burst of microwave irradiation using a microwave oven at frequency of 2.45 GHz at power output of 200 W. The reaction mixture was then submitted to microwave irradiation at 180°C and for 3 min. The mixture was cooled (5-10 min at room temperature), filtered and washed extensively with distilled water, chloridric acid and methanol to remove any unreacted aniline and PEO until the washing solution became neutral and air dried.

3 Results and Discussion

3.1 Spectroscopy Characterization

Fig1. Shows the FTIR spectra of pure polyaniline (PANI). The formation of polyaniline is confirmed by noticing the predominant peaks at the wave numbers of 1501 cm⁻¹ corresponding to C=C stretching of quinine ring, 1557 cm⁻¹ for C=C stretching of benzenoid ring, 1293 cm⁻¹ for C-N stretching, 755 cm⁻¹ and 838 cm⁻¹ for C-H vibration of Para coupling benzenoid and benzene rings, C-H bending is at 694 - 593 cm⁻¹ is corresponds to aromatic ring and 507 cm⁻¹ is stretching at out of the plane. In pure PEO Spectrum a large broad band appears centered at 3442 cm⁻¹ which is due to the hydration of PEO which confirms that PEO is highly hydrophilic and gets hydrated. Thus pure PEO shows a large broad band of CH₂ stretchings between 2950 -2840 cm⁻¹. It is also been

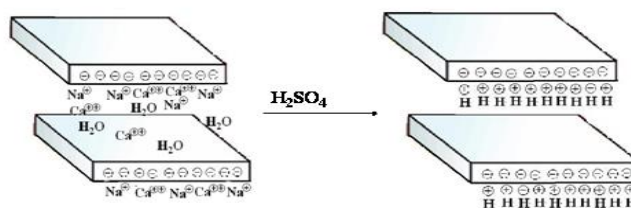
observed that CH_2 vibrational modes appear in PEO at 1467 cm^{-1} which corresponds to asymmetric CH_2 bending and 1344 cm^{-1} which corresponds to symmetric CH_2 wagging [28].

The infra-red spectra for PANI-PEO mixte is also shown in Fig.2. There are significant changes in both the intensities and the frequencies in the product (PANI-PEO). There are more pronounced between 690 and 1574 cm^{-1} . The bonds also show doublet and triplets. This may indicate that there is significant interaction between the oxygen of the ether group of polyethylene oxide and the nitrogen in the aniline of polyaniline [29].

As show in (Fig 3.), the down field signals centered at 7.2 ppm to 7.5 ppm are due to four aromatic protons of the pure reduced form (leucoemeraldine base). Integral ratio of the NH proton signal appeared at 3.55 ppm. Whereas non-reduced form of the product (Emeraldine base) gave a ^1H -An investigation was devoted to the analysis of the polyethylene oxide (PEO) by ^1H NMR spectroscopy at 300 MHz (Fig. 4). According to the work published by Yahiaoui et al [31], ^1H NMR spectroscopy at 300 MHz

(Solvent CDCl_3) (Fig. 4) showed different peaks: (a) the methylene groups (CH_2 -) at 2.6 ppm, and (b) the methylene (CH_2O -) at 3.7 ppm .

In the ^1H NMR spectra of the product mixte (PANI-PEO), a wide signal in the region of 6.8 to 8 ppm was assigned to benzenoid hydrogen of polyaniline already reported by MacDiarmide et al [32]. Three peaks in these region was assigned to para position of polyaniline is linked for the polymerization. Signals at 3.25 to 3.75 ppm indicate peak of CH_2O - and $\text{CH}_2\text{CH}_2\text{O}$ - hydrogen of polyethylene oxid reported by Yahiaoui et al [33]. Peak at 1.5 to 2 ppm is due to CH_2 hydrogen respectively. The shift of the CH_2 peak to highly shielded region is due to polymerization. Integral ratio of the NH proton signal of polyaniline in PANI-PEO appeared at 4.25 ppm, to note that the chemical displacement of this peak was changed from polyaniline (4.81 ppm) to PANI-PEO copolymer (4.25 ppm) which shows the modification of PANI by the PEO.



Scheme 1. Activated form of maghnite under sulfuric acid (H_2SO_4 , 0.25 M)

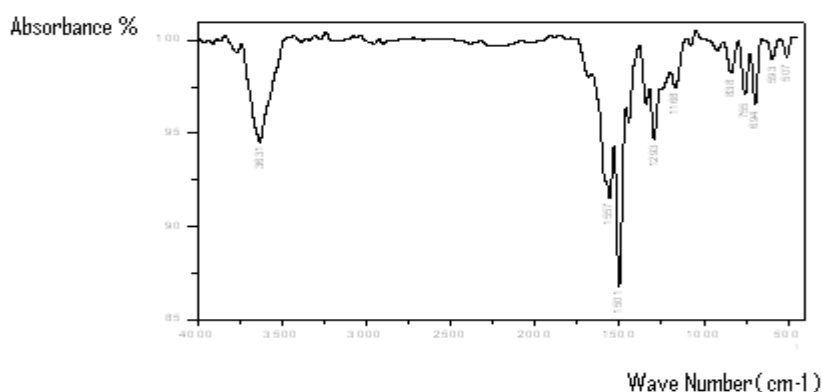


Fig 1. FT-IR spectra of polyaniline (PANI-EB) obtained by the intercalated method between Aniline and Maghnite- H^+ (black powder) at 0°C .

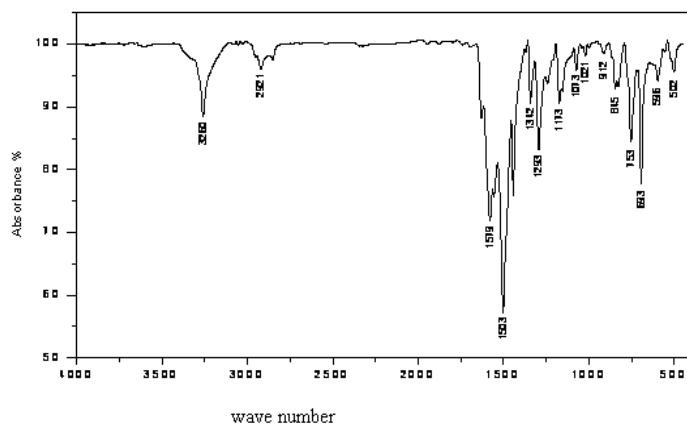


Fig 2. FT-IR spectra of block copolymer polyaniline-polyethylene oxide (PANI-PEO) obtained by the intercalated method between Aniline, polyethylene oxide and Maghnite-H⁺ (black powder) at 70°C.

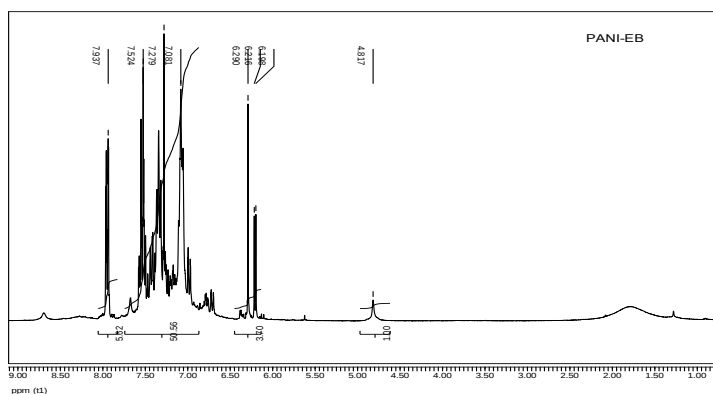


Fig 3. ¹H-NMR spectra of the polyaniline (PANI) obtained by the intercalated method between Aniline and Maghnite-H⁺ (black powder) at 0°C.

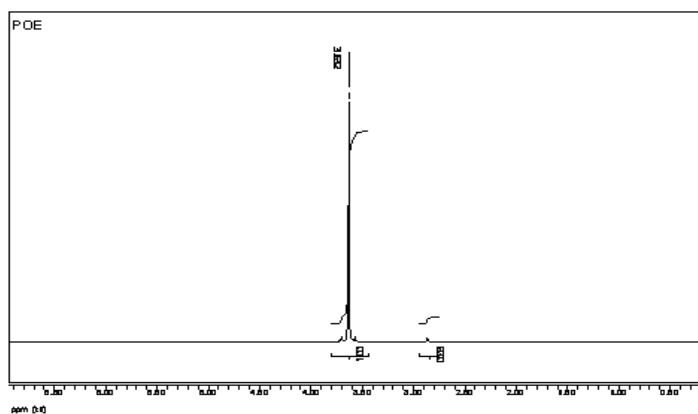


Fig 4. ¹H-NMR spectra of pure poly ethylene oxide (PEO)

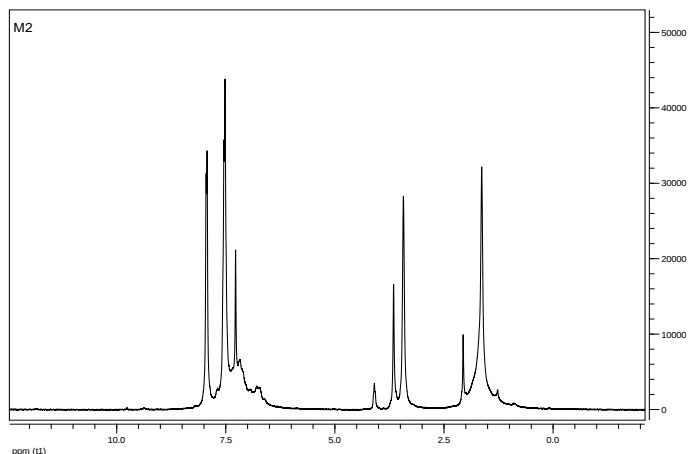


Fig 5. ^1H -NMR spectra of the product polyaniline-co-poly (ethylene oxide) (PANI-PEO) obtained by the intercalated method between Aniline, poly (ethylene oxide) and Maghnite- H^+ (black powder) at 70°C .

3.2 Thermophysical Properties

The thermophysical properties of PANI-PEO were studied by TGA, TDA and DSC. The weight loss (%) was recorded as function of temperature for both PANI-PEO using TGA (SDT Q600 V20.9 Build 20). The samples weighing about 2.0 mg were scanned in the temperature range of 0 – 800°C under nitrogen atmosphere at a heating rate of $10^\circ\text{C}/\text{min}$. The curves of weight loss versus temperature showing the behaviour of PANI-PEO sample was presented in Fig 6. The first significant weight loss occurs already at temperature between 50°C and 100°C . It is known, that PANI-PEO is hygroscopic and during the heating to 100°C the residual water evaporates. Then the main mass loss, which corresponds to polymer degradation starts at about 200°C and 500°C [34].

Thermal behavior of pure PANI and PANI-POE were also verified by differential scanning calorimetry in which the first and second scan is shown in (Fig 6.7). The first scan gives very little information on the thermal behavior of the product. First we notice the presence of an endothermic effect ($68, 39^\circ\text{C}$ and $190, 09^\circ\text{C}$) the first is associated to the evaporation of water absorbed by the copolymer and the second for melting POE block. The second scanning, will foresee it no effect on this temperature range, because the product was heated to 280°C , which facilitates the onset of glass transition temperature ($T_g=16, 79^\circ\text{C}$) which is in agreement with the literature [35].

3.3 Kinetics Studies

After having good knowledge of the physicals and chemical properties of our product, we made a fairly detailed kinetic study of which we have followed the influence of the amount of catalyst, the amount of the oxidant, temperature, volume water, the time and the

monomer ratio in the reaction yield, the intrinsic viscosity of the product, and their average molecular weights.

3.3.1. Effect of The Amount Of Mag-H+ On The Yield Transformation

We used different amounts of Maghnite- H^+ and we have maintained the same time: the monomer ratio, the amount of the oxidant and the volume of water. This series of reaction was carried out at a temperature (70°C) for 2 hours and 30 minutes. The results obtained were summarized in Fig8. It is observed that the increase in the catalyst leads to a percentage steady increase in yield and there after increased monomer conversion but a lower average molecular weight. This result shows the cationic nature of the mechanism involved. Similar results were observed with other reactions catalyzed by Maghnite- H^+ . The increase in yield with time is mainly due to the number of active sites in the catalyst responsible for initiating the reaction of transformation. The latter is proportional to the amount of the Maghnite- H^+ used in the reaction. Indeed, the more available active sites, there are more opportunities to contact with the monomer, up to a maximum amount of the catalyst from which the performance is unchanged. [36]

3.3.2 Effect Of The Amount Of Mag-H+ On The Molecular Weight

Several reactions have summers made to follow the influence of the amount of catalyst on the performance of the reaction. We have used (5% and 10%) by weight as the amount Maghnite and varying time after keeping the other parameters (amount of the oxidizing $\text{K}_2\text{S}_2\text{O}_8$, the volume of water, the amount of monomers and the temperature). The percentage by weight Maghnite- H^+ /Monomer is 10%. It is observed that the average molecular weight increases

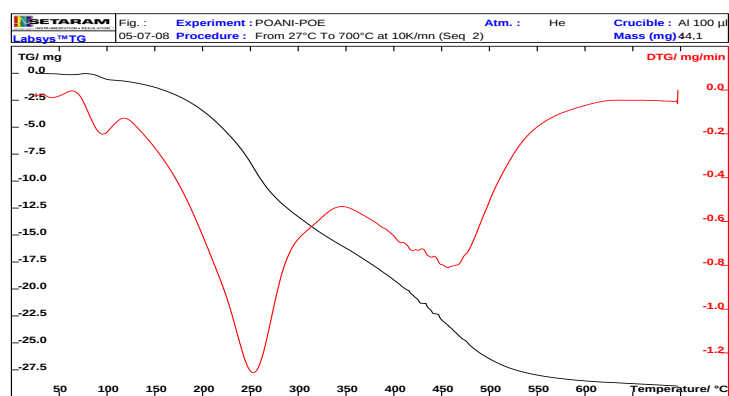


Fig 6. TGA curves of PANI-PEO prepared in the presence of Maghnite-H⁺ (25M).

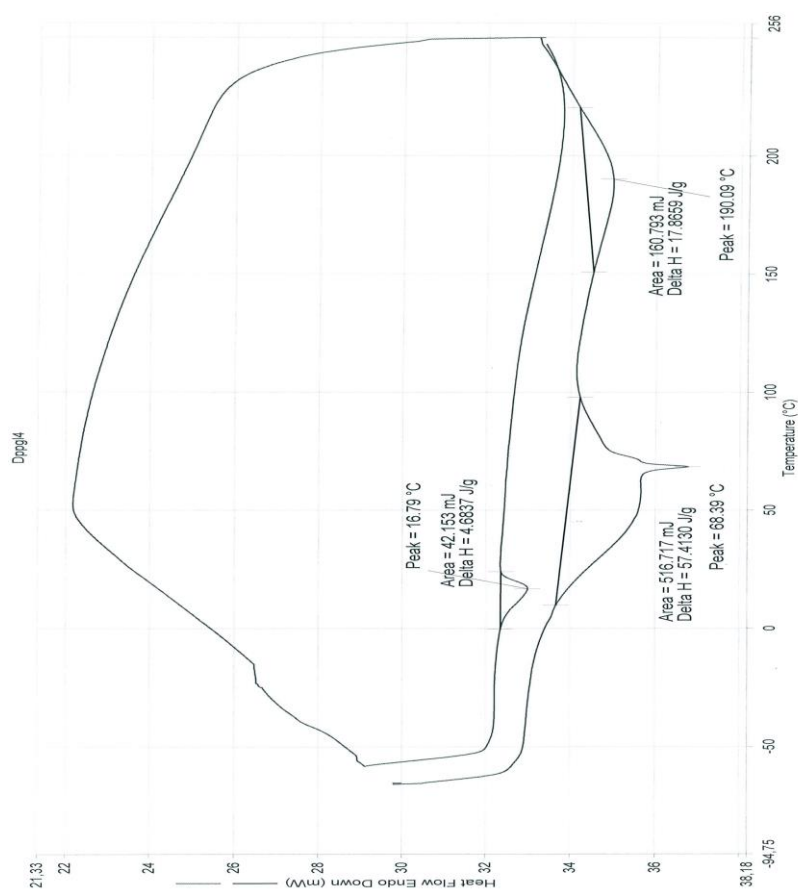


Fig 7. DSC measurements of PANI-POE (heating rate 10 °C/mn)

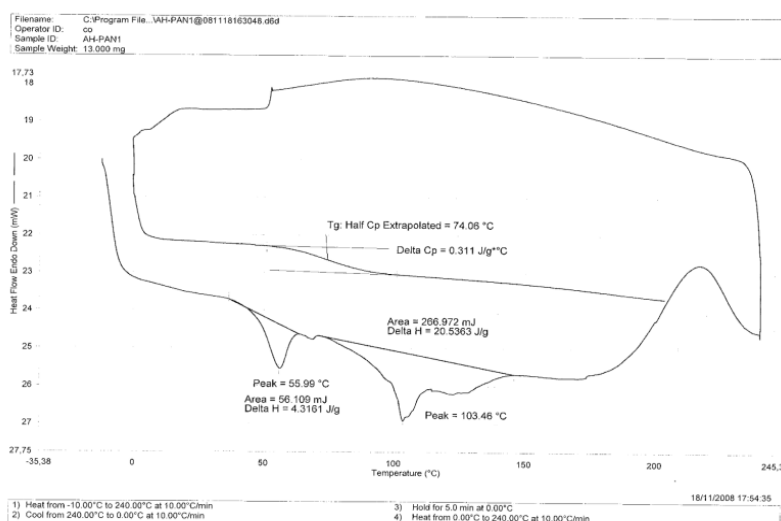


Fig 8. DSC measurements of PANI-POE(heating rate 10 °C/mn)

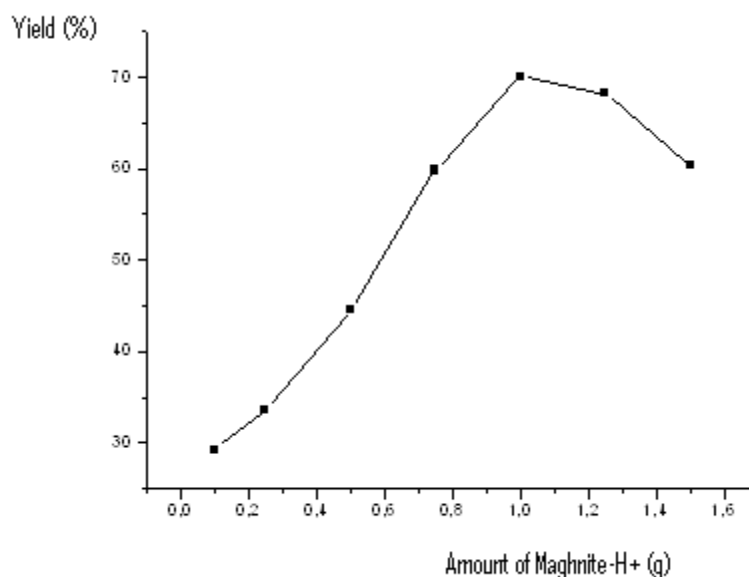


Fig 9.Effect of the amount of Mag-H⁺ on the yield of transformation

with time and reaches a maximum after 5 hours of reaction. There is also a steady increase in molecular weight, between 4-6 h and a decrease from 7 h. We deduce that at sufficiently long periods, degradation reactions, are becoming more frequent and cause the formation of oligomers of low molecular weights. This explains the decrease in molecular weight to longer reaction times. [37]

3.3.3. Effect of the amount of oxidant on the yield of transformation

To know the influence of the amount of the oxidizing performance of the reaction, we conducted a series of experiments starting from different quantities and types of oxidant and we kept the ratio of the two monomers (50/50), the amount of Mag-H⁺ (5) and the

volume of water. The influence of the oxidizing amount ($K_2S_2O_8$) on the reaction yield was below shows in Fig 10.

In remarks that there is a proportionality between the amount of oxidant and performance more than increasing the amount of more oxidant than the yield increases, these may be due to the birth of more number of active site because of the rapid oxidation of aniline, which are sensitized to produce the long chain of the copolymer as a measure with increasing the amount of oxidant that this is in agreement with the literature [38].

3.3.4. Effect Of Rapport PANI/ PEO On The Yield Of Transformation

Several reactions have been made starting different ratios of monomers (Aniline / PEO), maintaining the amount of the Mag-H + (5%wt), and the amount of the oxidant (3g) and the volume of water (15ml). All reactions were held in a temperature (70°C). The (Fig 11.) below summarizes the influence of the ratio of the two monomers in the reaction yield. It notices a significant change in performance as a measure with increasing the amount of monomer ratio, specifically with increasing the amount of PEO used in this transformation. As can explain this phenomenon by the high reactivity of the POE compared to aniline especially at high temperature [39].

3.3.5. Effect of Temperature On The Yield Of Transformation

Results presented (Fig 12.) allows us to say that there is an effect of temperature on the reaction yield. This phenomenon can be explained by the reactivity of the aniline and the PEO at high temperature and their miscibility with water to 70° C after this temperature the product will be degraded, so that the transformation reaction was carried out at 70°C is almost the melting temperature of the PEO ($T_c = 65^\circ$) [40]. On the other hand, it is observed that temperatures above 80°C, there is an increase in monomer conversion and subsequently the reaction yield and the average molecular weight, was also observed, the molecular weight distributions (M_w / M_n) much wider beyond 100°C. This is reflected by the manifestation of chain transfer reactions and degradation reactions at higher temperatures [41].

3.3.6 Effect Of Solvent

To check the influence of different solvents on the

copolymerization reaction was carried out a series of reactions at room temperature. The results are summarized in the (table1.) below: The effect of different solvents on the aniline transformation reaction, and poly (ethylene oxide) catalyzed by Mag-H + / $K_2S_2O_8$ is summarized in the table above. Note the influence of the solvent on the polarity conversion of the monomers and on the average molecular weights of the copolymer. It is observed that the monomer conversion and number average molecular weight of the polymer resulting from the copolymerization of aniline with PEO effected in non-polar solvents (toluene), are more significant than those from the reaction carried out in solvents polar (chloroform, dichloromethane, THF). This result is related to the nature of the catalyst. Like any clay material, the Maghnite-H + has an affinity towards all polar particle. Polar solvent molecules are adsorbed on the catalyst surface and reduce, consequently, the contact between the monomer and the active sites responsible for the initiation of the polymerization. This results in low conversions of monomer and thereafter low reaction yields [42].

3.4 Electrical Properties

The (table3.) below summarizes the values of electrical conductivity measured for three products with different molar ratio (Aniline / PEO). From these results it is noted that the electrical conductivity increases significantly with increasing aniline ratio in the product, this is due to the good conductivity of anilines. What do the units present in the product (since it is known that the PANI is a polymer having good electrical properties with the regularity of the electronic structure in molecules). Alternatively, the inclusion of a large number of PEO units in the polymer chain causes a decrease in electrical conductivity; this decrease is due to the decrease of the structural regularity and degree of conjugation of the product chains due to the presence of groups (CH_2O -) [43].

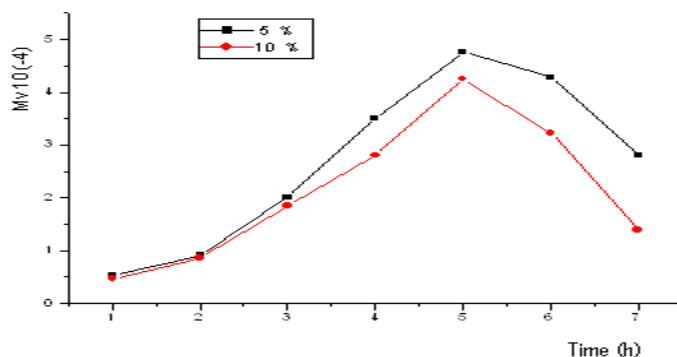


Fig 10. Effect of the amount of Mag-H⁺ on the molecular weight of transformation

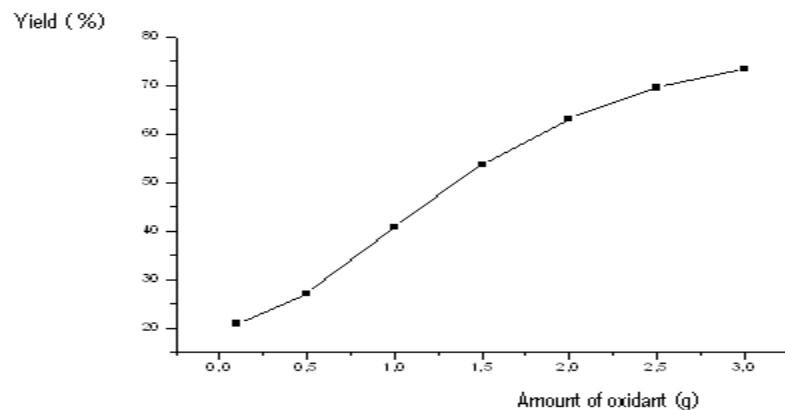


Fig 11.Effect of the amount of oxidant on the yield of transformation

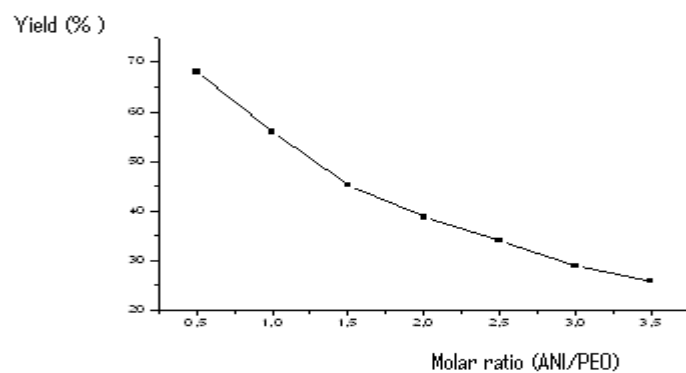


Fig 12.Effect of molar ratio (ANI /PEO) on the yield of transformation

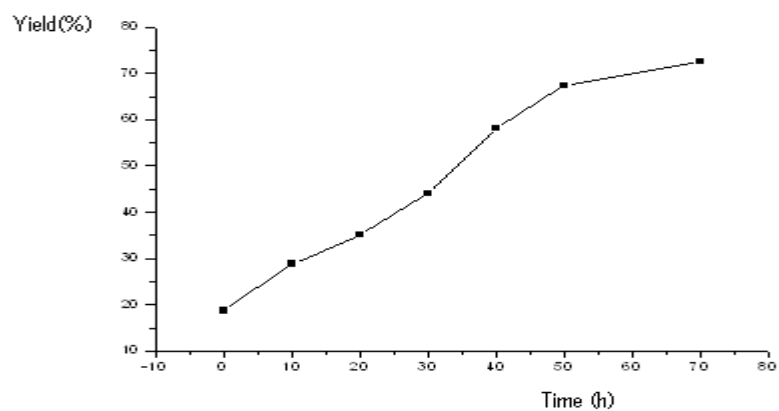


Fig 13. Effect of temperature on the yield on the yield of transformation

Table 1. Effect of solvent on yield of transformation

Solvent	Yield (%)
Toluene	73,95 %
DMF	65,57 %
CHCL ₃	60,83 %
CH ₂ CL ₂	51,12 %
THF	32,6 %
Acetonitrile	28,71 %

Table 2. Effect of rapport (Aniline/POE) electrical Conductivity

Aniline / PEO	Electrical Conductivity (Scm ⁻¹)
10/90	4,5. 10 ⁻⁵
50/50	6,8. 10 ⁻⁵
90/10	8,8. 10 ⁻⁵

4 Conclusions

In this present work authors have carried out the green chemical transformation of polyaniline by poly (ethylene oxid) based on Maghnite-H⁺ (Algerian ecologic catalyst MMT). Several main advantages were shown in the transformation system, the product was produced by a very simple procedure, just by filtering, the clay can be separated from the reaction mixtures, modified clay is inexpensive, stable, non corrosive and the polyaniline modified was found many more than pure polyaniline .

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