

¹H-NMR Spectra of Conductive, Anticorrosive and Soluble Polyaniline Exchanged by an Eco-Catalyst Layered (Maghnite-H⁺)

Rahmouni Abdelkader, Harrane Amine and Belbachir Mohammed

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

Abstract: Polyaniline PANI is one of the important classes of conjugated polymers that proceed excellent electronic, optical and environmental stability. The chemical oxidative polymerization of a partially aniline solution results in the formation of PANI which is highly soluble in common solvents. This work focuses on the preparation and characterization of intercalated polyaniline and Na-Maghnite clay eco-catalyst (Western Algerian). In spite of the extensive studies on the chemical and physical properties of polyaniline, clear assignment of ¹H-NMR signals of the polyaniline has not been made presumably due to the low solubility of the polymers in usual ¹H-NMR solvents and overlapping of the signals of (NH) and aromatic protons. The aim of this work as the preparation and characterization of polyaniline/montmorillonite nanocomposite using Na-Maghnite as catalyst in order to improve its solubility and discuss ¹H-NMR signals of different forms of polyaniline when we improve the influence of water and NaOH solute on properties physico-chemicals of polyaniline.

Key words: Polyaniline • Maghnite-H⁺ • ¹H-NMR spectroscopy • Conducting polymers • PANI-ES

INTRODUCTION

The development of polymers with high electrical conductivity has attracted significant research interest in the last decade due to the possibility of a new application [1]. Recently a considerable research attention was paid to the synthesis and properties of conductive polymers / clay nanocomposites such as polypyrrole PPY and polythiophene PTP. Among conducting polymers, polyaniline PANI is a potential material for various commercial application and has been studied more than other conducting polymers because of its high electrical conductivity, environmental stability, ease of preparation in large quantities and low cost [2]. Research has demonstrated that the introduction of only a small amount of clay into the polymers structure of PANI can lead to a significant enhancement of its properties. Clearly, the ratio of MMT to aniline in the initial mixture will influence the degree of cross-linking and the spacing between polyaniline chains [3]. These changes will in turn alter the molecular weight, the thermal stability, solubility and the conductivity of the resulting polymers. In spite of the extensive studies on the chemical and physical properties

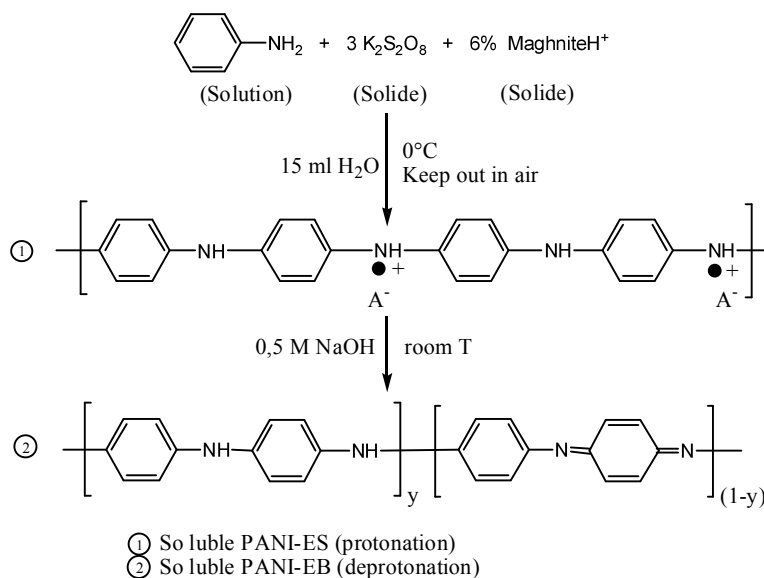
of polyaniline, clear assignment of ¹H-NMR signals of the polyaniline has not been made presumably due to the low solubility of the polymers in usual ¹H-NMR solvents and overlapping of the signals of (NH) and aromatic protons [4].

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 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 sulfuric acid (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 deionised 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.

Here, we reported a preliminary chemical study of conducting polymers created using non-toxic cationic catalyst, known-as Maghnite-H⁺ (Mag-H⁺) [5].

Table 1: Show composition of Mag-H+(catalyst)

Sample	Chemical Composition									
	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	Na ₂ O	K ₂ O	TiO ₂	SO ₃	As
Maghnite raw	69.3	14.67	1.16	0.3	1.07	0.5	0.79	0.16	0.91	0.05
Maghnite H ⁺	71.7	14.03	0.71	0.28	0.8	0.21	0.77	0.15	0.34	0.01



Chemical Structure of PANI-ES and PANI-EB

The properties of different forms of polyaniline (PANI-ES and PANI-EB) have been discussed. That acid-exchanged montmorillonite (Mag-H⁺) is a novel, efficient solid catalyst for the Catio-radically polymerization of aniline (ANI) to produce PANI-EB (Schema-1). Additionally, the NMR spectra of PANI-ES, PANI-EB₁ and PANI-EB shows a peak at 8 ppm may be due to the water protons bonded by (H-N⁺). The NMR spectrum also has peaks at 6.2 ppm corresponding to the primary amine, attached to a benzene ring which is adjacent to a secondary amine attached to another benzene ring. The peak at 6.4 ppm corresponds to the primary amine, attached to a benzene ring adjacent to imine nitrogen attached to a quinoid ring. The broad peak at 7.0 ppm is due to the protons on the benzene ring and the multiplet at 7.2-7.8 ppm is due to the quinoid ring protons. The ratio of benzenoid to quinoid protons peak area indicates that there are three benzene rings for one quinoid ring. The ratio of benzenoid plus quinoid protons peak area to that of the sum of the two primary amines indicates that the average chain length for PANI is 6 units corresponding to Mn of 519.

MATERIALS AND METHODS

Aniline 99%, potassium persulphate 98% (Aldrich), hydrochloric acid (35%-38%), Montmorillonite clay was obtained from ENOF Maghnia (Algeria). The MMT-H⁺ (Mag-H⁺) was prepared as described by Yahiaoui *et al.*, [6] and water (pH < 7) were used to synthesis emeraldine salt (PANI-Mag-H⁺) by in situ polymerization.

The clay, which was used as a catalyst, was supplied by a local company known as ENOF Maghnia (Western Algeria). The greatest proton saturation <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 sulfuric acid (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 deionised 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.

^1H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in CDCl_3 . Tetramethylsilane (TMS) was used as the internal standard in these cases. Average molecular weights and molecular weight distributions of the different polymers were measured using size exclusion chromatography (SEC) on a system equipped with a Spectra SYSTEM AS1000 auto-sampler, with a guard column (Polymer Laboratories, PL gel 5 μm Guard, 50 \times 7.5 mm) followed by 2 columns (Polymer Laboratories, 2 PL gel 5 μm MIXED-D columns, 2 \times 300 \times 7.5 mm), with a Spectra SYSTEM RI-150 and a Spectra SYSTEM UV2000 detectors. The eluent used is THF at a flow rate of 1 mL min^{-1} at 35 $^\circ\text{C}$. Polystyrene standards (580-483 10^3 g mol^{-1}) were used to calibrate the SEC.

Viscosity measurements were carried out with an Ubbelohde Capillary Viscosimeter (viscologic T11, version 3-1 Sematec). Intrinsic viscosity $[\eta]$, was measured at 30 $^\circ\text{C}$ in benzene. Viscosity-average molecular weight M_v was calculated according to the equation:

$$[\eta] (\text{mg.l}^{-1}) = K [M_v]^a$$

Gel permeation chromatography (GPC) was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastaygel 10 3 , 10 4 , 10 5 , 10 $^6\text{A}^\circ$, tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights.

RESULTS AND DISCUSSION

The ^1H -NMR spectra of the PANI-ES polymer exhibit strongest sharp peak centered at 7 ppm and 7, 8 ppm due to protons on phenylene and disubstituted phenylene units, the medium broad peak at 6.2 and 6.4 ppm due to (-NH $_2$) end group, another broad peaks centered at 1,78 ppm and 8 ppm may be due to the water protons bonded by (-NH $_2$) groups and (H-N $^+$) respectively, as show in Fig. 1 [7].

The leuco-emeraldine base (PANI-EB $_1$) it's obtained by deal treatment of polyaniline salt (PANI-ES) with a solution of dilute NaOH (0,5 M). Then, the prepared ES-form PANI was converted to EB-form PANI by stirring with 200 ml of 0,5 M NaOH dilute solution at room temperature for 5 to 10 hours. At the end of the stirring, the PANI-EB $_1$ was filtered, washed with water and methanol several times and dried under vacuum at 60 $^\circ\text{C}$ for 48 hours by characterization. Finally, 1,53g of the dark black EB $_1$ -form PANI powder was obtained (84, 14% yield) [8].

Fig. 2 shows the ^1H -NMR spectrum of leuco-emeraldine base (PANI-EB $_1$) in CDCl_3 which contains a small amount of water and 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 peaks at 6.2 and 6.4 ppm due to (-NH-and-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 (-NH-and-NH $_2$) groups and (H-N $^+$) respectively. Chen and Jenekhe [9]

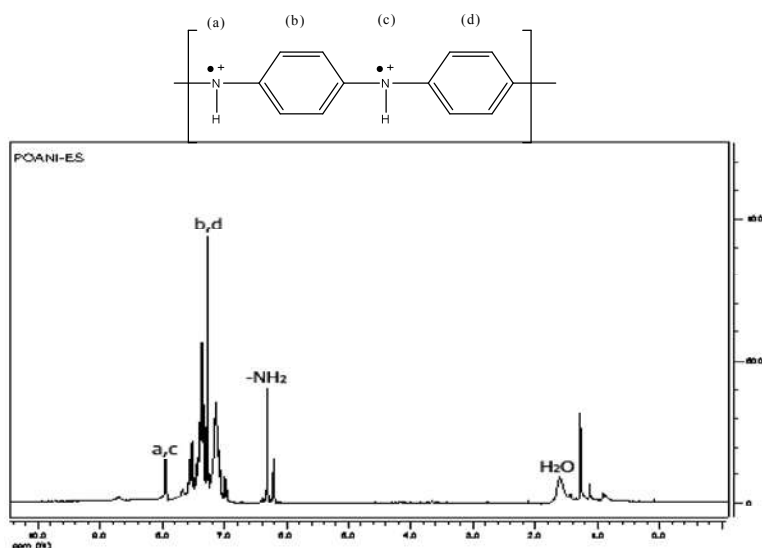


Fig. 1: ^1H NMR spectrum of the synthesized polymer (PANI-ES) obtained by the persulfate oxidation method (emeraldine black) in CDCl_3 at 0 $^\circ\text{C}$

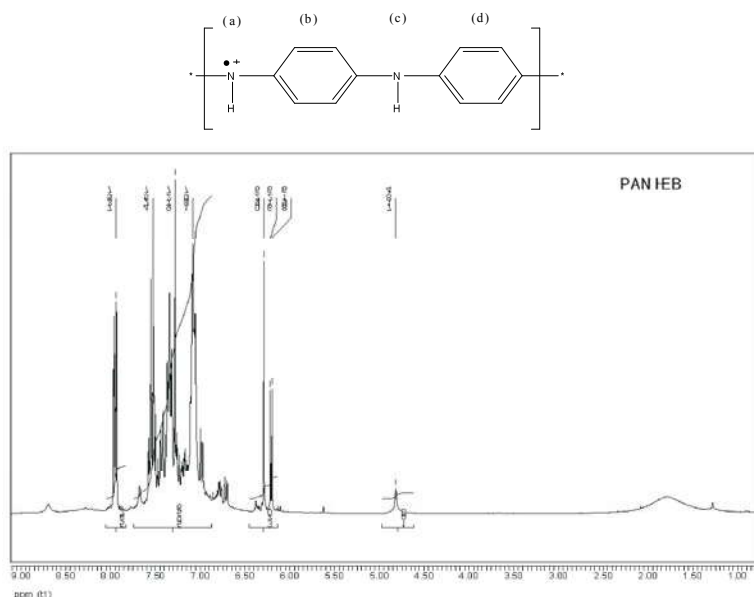


Fig. 2: ¹H-NMR spectrum of fully reduced PANI-EB₁ (obtained by the reduction of the sample) with 0.5M of NaOH in CDCl₃

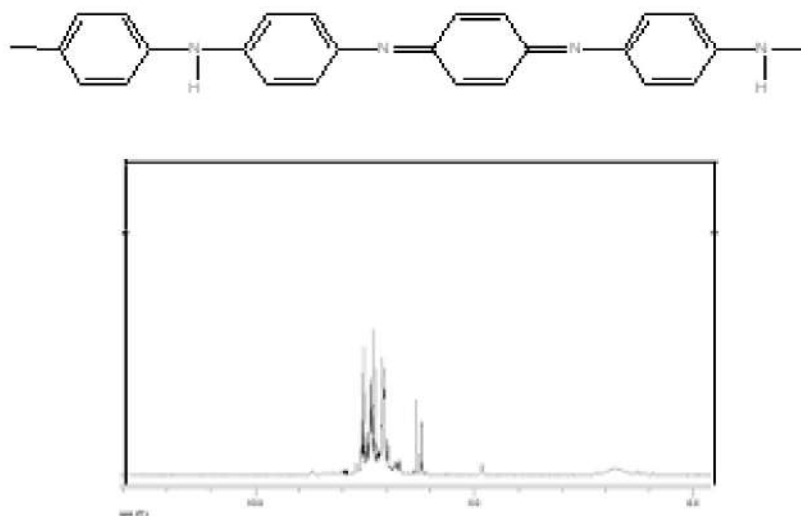


Fig. 3: ¹H-NMR spectrum of fully reduced PANI-EB (obtained by the reduction of the sample) with 5M of NaOH in CDCl₃

took ¹H-NMR spectra of analogues of this polymer in DMSO and assigned signals in the range $\delta = 4, 88-5, 66$ ppm to the-NH-protons of the polymer.

Additionally, the NMR spectrum (Fig. 1, 2, 3) shows a peak at 8 ppm may be due to the water protons bonded by (H-N⁺). The NMR spectrum also has peaks at 6.2 ppm corresponding to the primary amine, attached to a benzene ring which is adjacent to a secondary amine attached to another benzene ring. The peak at 6.4 ppm corresponds to the primary amine, attached to a benzene ring adjacent to imine nitrogen attached to a quinoid ring.

The broad peak at 7.0 ppm is due to the protons on the benzene ring and the multiplet at 7.2-7.8 ppm is due to the quinoid ring protons. The ratio of benzenoid to quinoid protons peak area indicates that there are three benzene rings for one quinoid ring. The ratio of benzenoid plus quinoid protons peak area to that of the sum of the two primary amines indicate that the average chain length for PANI is 6 units corresponding to an Mn of 519 [10, 11].

The ¹H-NMR spectra of PANI-ES and PANI-EB₁ shows broad peaks at 8 ppm assigned to the H-N⁺ hydrogen which disappear on the exchange with solute of

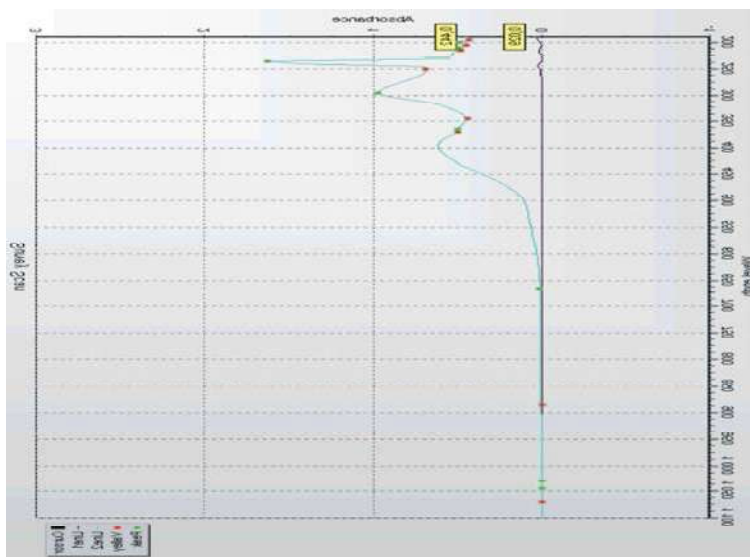


Fig. 4: UV spectra of the synthesized polymer (PANI-ES) obtained by the persulfate oxidation method (emeraldine black)

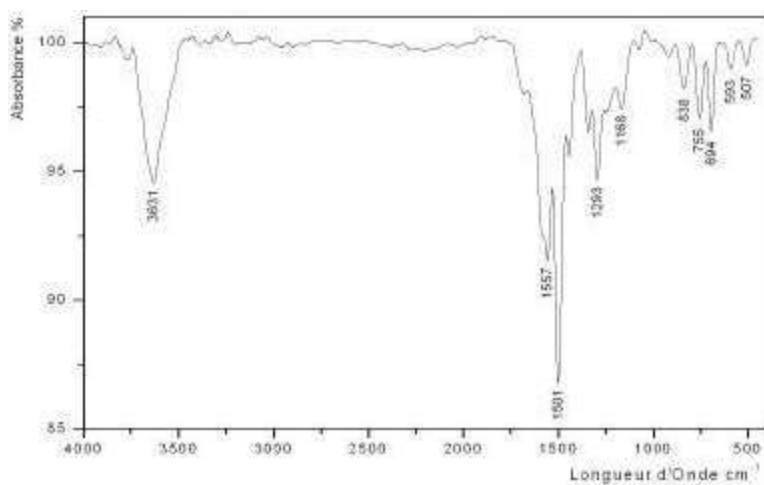


Fig. 5: FTIR spectra of the synthesized polymer (PANI-ES) obtained by the persulfate oxidation method (emeraldine black)

2NaOH (C > 0.5M) and reappearance of broad peak at 4.81ppm assigned to the NH hydrogen. Finally, it has become possible to assign the signal of the NH hydrogen of PANI-EB₁ and PANI-EB by using the highly soluble polyaniline and highly concentration of NaOH solute [12, 13].

Viscosity measurements were carried out with an Ubbelohde Capillary Viscosimeter (viscolytic T11, version 3-1 Semantec). Intrinsic viscosity $[\eta]$, was measured at 30 °C in benzene. Viscosity-average molecular weight M_v was calculated according to the equation:

$$[\eta] (\text{mg.l}^{-1}) = K [M_v]^a$$

Viscosity of the polymer is slightly higher (25.79 ml g⁻¹) than that of PANI (19 ml g⁻¹) obtained in aqueous solution for 24 h. Viscosity intrinsic and properties physics of PANI-ES are showed in Table 2.

Conductive polymers have a conjugated system of double bonds in a backbone polymer. These polymers show some conventional transitions in the UV region, such as $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$. The $\pi \rightarrow \pi^*$ transitions of conjugated double bonds are close to the visible region, associated with polaron and bipolaron states as well as solution conductive polymers [14]. The UV-visible spectral peak in the 250-300nm region is due to the aniline groups and $\pi \rightarrow \pi^*$ is a conjugated couple system of the benzoic states in the 350-400 nm regions (Fig. 4).

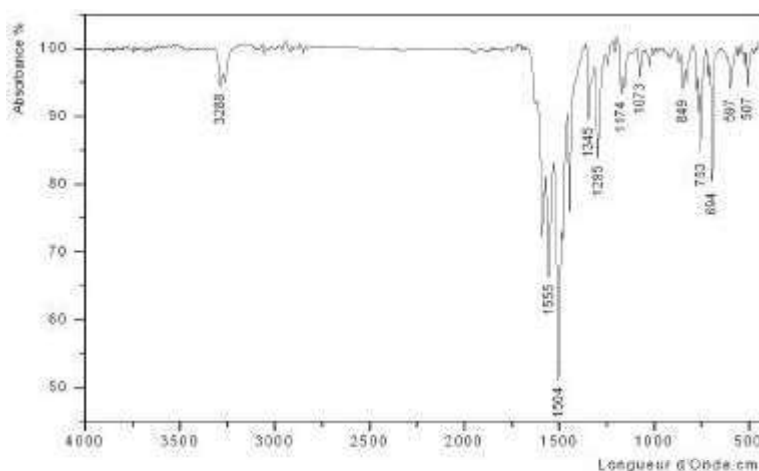


Fig. 6: FTIR spectra of the prepared polymer (PANI-EB) obtained by the reduction method with NaOH solution (emeraldine black dark)

Table 2: Show properties viscosimetrics of PANI-ES

Concentration	C(0) 2C/3	C/2 C/3	C/4
Moyenne	3,60 3.60	3.60 3.60	3.59
Cinema (cst)	0,61 0.60	0.60 0.60	0.6
Dynamique (cp)	0.90 0.90	0.90 0.89	0.89
Relative	1.01 1.00	1.01 1.00	1
Spécifique	0.01 0.00	0.01 0.00	0
Réduite	12.20 13.98	19.46 20.95	22.43
Inhérente	12.13 13.91	19.46 20.95	22.43
Salomon	12.15 13.93	19.49 20.97	22.45
Intr(g.ml ⁻¹)	25.83	25,76	25.78

Table 3: The conductivity values of PANI-Mag

Content of Maghnite-H+(%)	Conductivity(S/cm)
10	2,0.10 ⁻⁴
50	3,1.10 ⁻⁴
100	3,9.10 ⁻⁴

The FTIR spectra of the PANI-ES and PANI-EB under the same conditions were shown in Fig. 5 and 6. It was found that PANI had characteristic peaks at around 3631 cm⁻¹ and 3288 cm⁻¹ due to the characteristic free N-H stretching vibration suggests the presence of primary and secondary amino group (-NH-and-NH₂), 1557 cm⁻¹, 1501cm⁻¹ (C-C stretching deformation of quinoide and benzenoide ring respectively), 1293 cm⁻¹ (C-N stretching of secondary aromatic amine), 1168 cm⁻¹ and 838 cm⁻¹ (out-of-plane deformation of C-H in the 1,4-disubstituted benzene ring), which was similar with that of PANI sample without HCl under the same conditions. All of these peaks were identical to those of PANI synthesized by a common method [15, 16].

The conductivity of PANI-Mag depends on the molecular weight, oxidation state, interactions intrachain, degree of doping, ratio of oxidant/ monomer, content of catalyst (Mag-H⁺) and nature of (oxidant, solvent, dopant) etc [17-19].

In the present study, the PANI-Mag composite was prepared with K₂S₂O₈ as the oxidant, aniline as monomer and Mag-H⁺ as a catalyst. The relation between the content of catalyst and the conductivity was investigated. As shown in Table 3, the conductivity of the polymer is largest when ratio of oxidant/monomer = 0,58 and increases significantly with the addition of content of catalyst, the dc conductivity of PANI-Mag composite measured through a two probe method is 3.9 10⁻⁴ S/cm, same method shows conductivity in the range 10⁻⁶ only [20, 21], which proves the superiority of present method.

CONCLUSIONS

This work focuses on the preparation, characterization and behavior properties and physico-chemicals of intercalated polyaniline/Na-maghnite. These materials consisting of polyaniline and Na-maghnite were prepared by oxidative polymerization. Here we report influence of different parameter on properties of prepared soluble polyaniline such as temperature, water and concentration of NaOH. The ¹H-NMR spectra of PANI-ES and PANI-EB, shows broad peaks at 8 ppm assigned to the H-N⁺ hydrogen which disappear on the exchange with solute of NaOH (C > 0.5M) and reappearance of broad peak at 4.81ppm assigned to the NH hydrogen. Finally, it has become possible to assign the signal of the NH

hydrogen of PANI-EB, and PANI-EB by using the highly soluble polyaniline and highly concentration of NaOH solution.

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