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Synthesis and Characterization of PANI and Block Copolymer PANI-b-PEO Catalyzed by Maghnite (Algerian MMT): Electrical and Electronic Domain

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Abstract

Polyaniline (PANI) and its block copolymer (PANI-PEO₂₀₀₀) has been prepared under effect of Maghnite-H⁺ (Algerian MMT) in different weight percentage (wt %) by cationic polymerization method. The structure of PANI and PANI-PEO₂₀₀₀ is predicted by the FT-IR and ¹HNMR spectra. The thermal stability of homopolymer and block copolymer is confirmed by difference scanning calorimetry and analysis thermogravimetry. So after this results we can suggest that our heterogeneous catalyst called maghnite (Algerian MMT) can modified the morphology and the physical chemical properties of polyaniline (PANI) and its homolog block polyaniline-b-poly ethylene oxide (PANI-b-PEO₂₀₀₀) in the mild conditions under microwave irradiation.

Keywords: ¹HNMR, green catalyst, green chemistry, conducting polymer, polyaniline, maghnite-H⁺, DSC, PEO

1. Introduction

Polyaniline (PANI) and its block copolymer (PANI-PEO) are the best promising material in conducting polymers, because of environmental stability, easy processing, and economical efficiency [1, 2]. PANI has been used for electrode of light emitting diode, Li ion rechargeable battery and corrosion protection [3, 4]. Nanocomposites (PANI-MMT) and (PANI-PEO-MMT) are interesting due to the special properties as abundance, low cost of MMT and attractive features such as a large surface area and ion-exchange properties [5, 6]. The clay is supplied by a local company known as ENOF Maghnia (Algeria) [7, 8]. Microwave heating has been found to be particularly advantageous for reactions under “dry” media [9, 10]. Microwave it’s rapidly method in modern chemistry because offer a certain number of advantage, that it can be completed in a few seconds or minutes and without a solvent [2, 11]. Absence of solvent reduces the risk of explosions when reaction takes place in a microwave oven [12, 13]. The absence of solvent reduces the risk of

explosions when the reaction takes place in a closed vessel in an oven [14, 15]. Aprotic dipolar solvents with high boiling points are expensive and difficult to remove from the reaction mixtures [16, 17]. The aim of this paper is to study the polymerization of aniline and its homolog block copolymer PANI-PEO catalyzed by Maghnite- H^+ under microwave irradiation [18]. This catalyst can be easily separated from the polymer product and regenerated by heating at a temperature above $100^\circ C$ [19, 20]. The kinetics studies of different synthesis are discussed together with the mechanism of polymerization.

2. Experimental

2.1 Microwave apparatus

The temperature was maintained at $160^\circ C$ in all experiments. Microwave irradiation was performed in a single mode focused CEM reactor (Model Discover, CEM Co., Matthew, NC) operating at 2.45 GHz with ability to control output power.

2.2 Materials and methods

MMT clay was obtained from ENOF Maghnia (Algeria). The MMT- H^+ (Mag- H^+) was prepared as described by Belbachir et al. and water ($pH < 7$) was used to synthesize emeraldine salt clay (PANI/Mag- H^+) by cationic polymerization [16]. Polyethylene oxide (relative molecular mass of $2 \cdot 10^3$) was obtained from Sigma Aldrich. Polyaniline (PANI) homopolymer was prepared in laboratory of polymers chemistry (Oran University, Algeria) by standard chemical intercalated method [21].

2.3 Measurements

1H nuclear magnetic resonance (NMR) measurements were carried out on a 300 MHz Bruker NMR Spectrometer equipped with a probe BB05 mm, in $CDCl_3$. Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm^{-1} on an ATI Matson FTIR No 9501165. Intrinsic viscosity, $[\eta]$, was measured at $30^\circ C$ in benzene. GPC measurements of the samples were carried out using a WISP 712, Waters Associates chromatograph. The purification of polymers were carried out by dissolving the product in chloroform ($CHCl_3$) and filtering to eliminate the Maghnite- H^+ . Then, chloroform was removed by evaporation [22, 23].

2.4 Preparation of (Maghnite- H^+) as catalyst

Catalyst called (maghnite- H^+) was prepared according to the process similar to that described by Belbachir et al. [24, 25]. The raw maghnite was placed in an erlenmeyer flask together with 100 ml of distilled water and a solution of sulfuric acid 0.25 M then stirred using a magnetic stirrer for 2 h at room temperature. After filtration up to pH 7, the activated maghnite- H^+ is dried in the stove for 24 hours at $105^\circ C$ for characterization [26].

2.5 Synthesis of polyaniline (PANI)

Into a flask with 100 mL and stirred to allow proper mixing was put a mixture of Maghnite- H^+ (5%) and solution of (H_2SO_4 0.25 M), adequate amount of aniline (0.05 mol) was added to a solution. The reaction mixture was then submitted to microwave irradiation at $160^\circ C$ for 4 minutes. Finally, the mixture was cooled at

room temperature, filtered and washed extensively with distilled water and methanol to remove catalyst and any unreacted aniline [27, 28].

2.6 Synthesis of block copolymer PANI-PEO

Copolymer PANI-PEO was synthesized via a cationic polymerization. To a (0.05 mol) of monomer aniline was added a solution of PEO (0.05 g in 25 mL of distilled water) and (5 wt %) of maghnite-H⁺ as an initiator. The mixture was stirred for 15 min. Then it is treated in a microwave oven at the power of 950 W, the temperature and viscosity of the reactive mixture increase fast and gelation point is reached after 4 min at 160°C. The mixture was cooled at room temperature, filtered and washed extensively with distilled water and methanol to remove impurity [16, 29].

3. Results and discussion

3.1 Spectroscopy characterization

Synthesized polyaniline was 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 and 838 cm⁻¹ for C–H vibration of Para coupling benzenoid and benzene rings. Finally, C–H bending at 694–593 cm⁻¹ corresponds to aromatic ring and 507 cm⁻¹ is stretching at out of the plane [30, 31].

As shown in (Figure 2), there are significant changes in both the intensities and the frequencies in the product (PANI-PEO₂₀₀₀). There are more pronounced between 690 and 1574 cm⁻¹, significant interaction between the oxygen of the ether group of PEO and the nitrogen in the PANI [32]. As shown in (Figure 1), polyethylene oxide (PEO₂₀₀₀) show a band of methylene group (CH₂) stretching between 2950 and 2840 cm⁻¹ and a large broad band appears centered at 3442 cm⁻¹ which confirms that PEO₂₀₀₀ is highly hydrophilic [9].

Polyaniline was successfully synthesized as show in (Figure 3) and the different hydrogen peaks are present. The strongest sharp peaks centered at 7 and 7.8 ppm due to protons from phenylene and disubstituted phenylene units and the weak peak at 4.81 ppm due to (–NH) group but the peak at 6.22 ppm due to (–NH₂) as end group [33, 34].

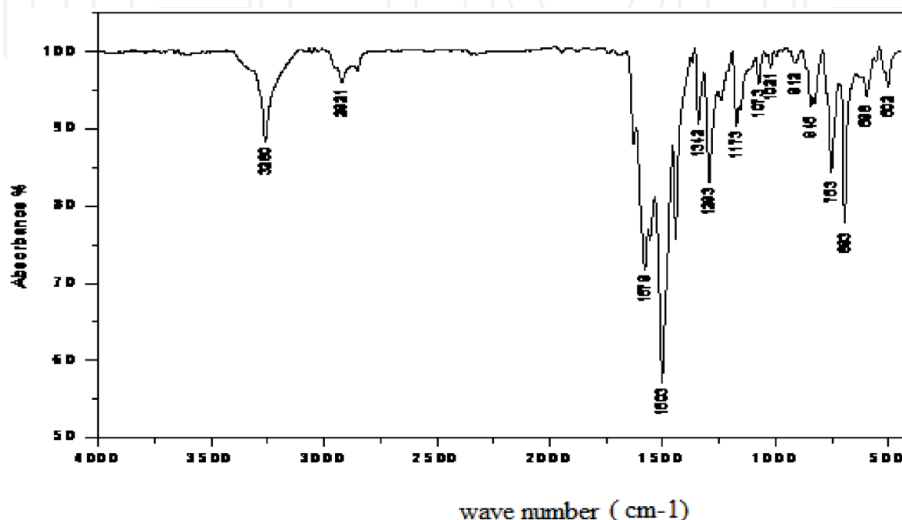


Figure 1.
 FT-IR spectra of polyaniline (PANI) catalyzed by maghnite-H⁺ under microwave irradiation.

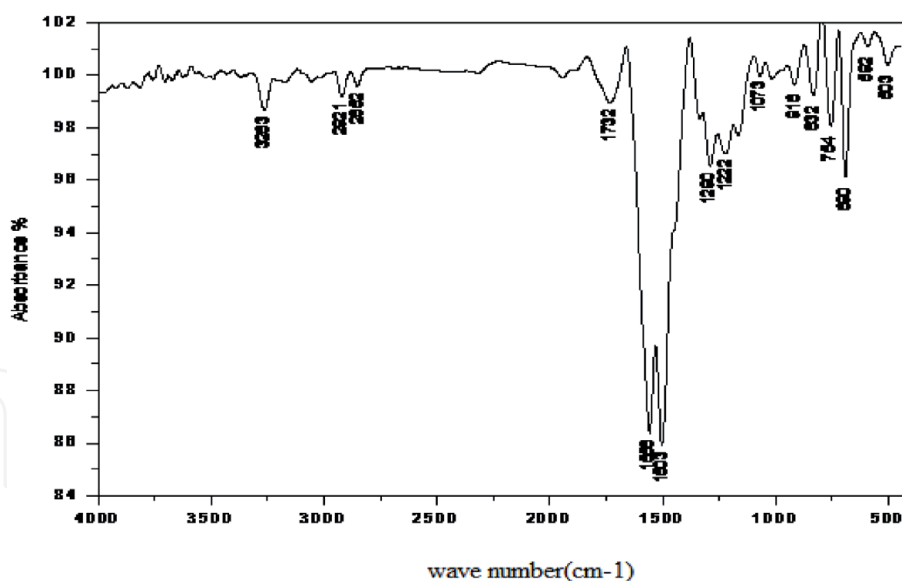


Figure 2.
FT-IR spectra of block copolymer (PANI-PEO₂₀₀₀) catalyzed by maghnite-H⁺ under microwave irradiation.

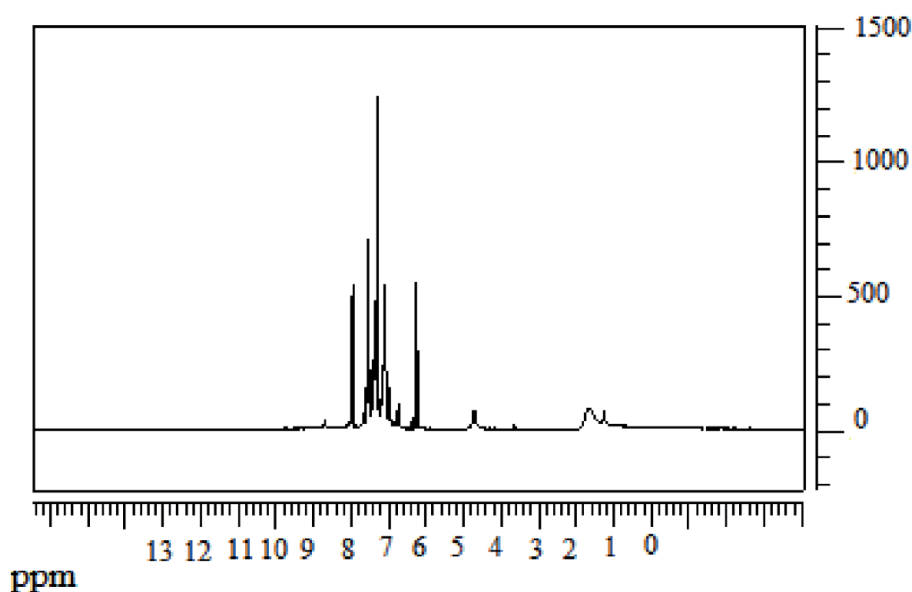


Figure 3.
Describes ¹H-NMR spectra of (PANI) catalyzed by maghnite-H⁺ under microwave irradiation.

¹H NMR spectroscopy at 300 MHz (Solvent CDCl₃) and according to the work published by Yahiaoui et al., (**Figure 4**) for pure PEO showed different peaks: (a) the methylene groups (CH₂-) at 2.6 ppm, and (b) the methylene (CH₂O⁻) at 3.7 ppm [35, 36].

The block copolymer (PANI-PEO₂₀₀₀) was confirmed by ¹H NMR spectrum as show in (**Figure 5**). The wide signal in the region of 6.8 to 8 ppm was assigned to benzenoid hydrogen of polyaniline. Signals at 3.25–3.75 ppm indicate peak of CH₂O⁻ and CH₂CH₂O⁻ hydrogen of polyethylene oxide reported [37]. Peak at 1.5–2 ppm is due to CH₂ hydrogen respectively [37, 38].

3.2 Optical properties

Conductive polymers synthesized PANI and PANI-PEO₂₀₀₀ has a conjugated system of double bonds in a backbone polymer. The UV-visible spectral peak in the

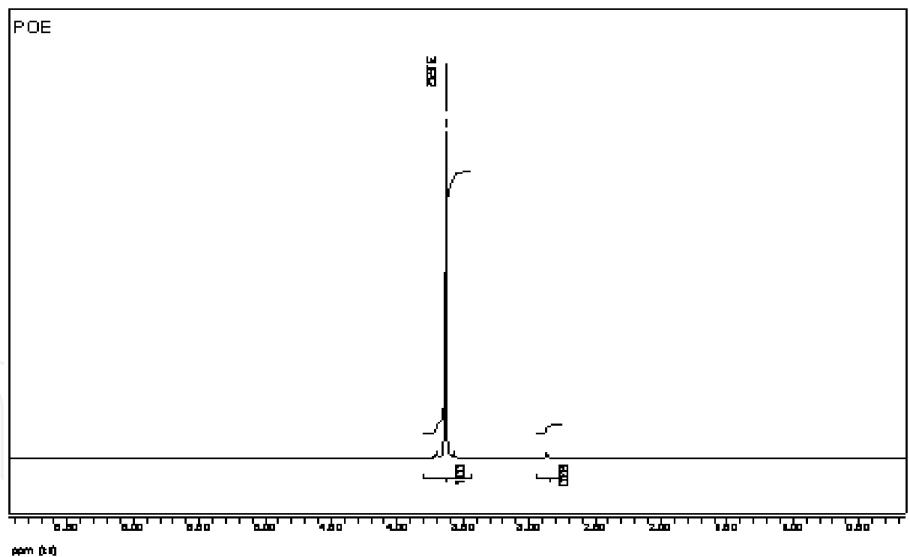


Figure 4.
Describes ¹H-NMR spectrum of poly ethylene oxide (PEO₂₀₀₀).

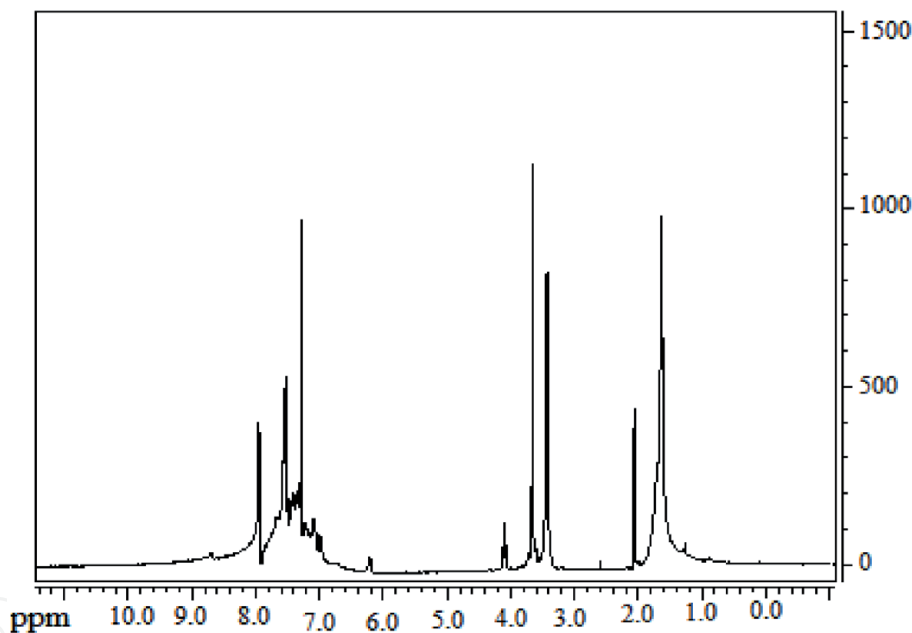


Figure 5.
Describes ¹H-NMR spectra of the copolymer (PANI-PEO₂₀₀₀) catalyzed by maghnite-H⁺ under microwave irradiation.

250–300 nm region is due to the aniline groups and $\pi \rightarrow \pi^*$ is a conjugated couple system of the benzoic states in the 350 to 400 nm regions (**Figure 6**) [39, 40].

3.3 Thermal properties

As shown in (**Figures 7 and 8**), the thermogram analysis of catalyst (maghnite-H⁺) shown two stages of weight loss. The weight loss in below 100°C is a result of free water and the weight loss around 600°C is associated with the dehydroxylation of silicate structure [37, 41].

For the thermogram analysis (TGA) of polyaniline (PANI), it can be found that the weight loss amounted 61, 17% at the temperature range of 187–600°C, which be

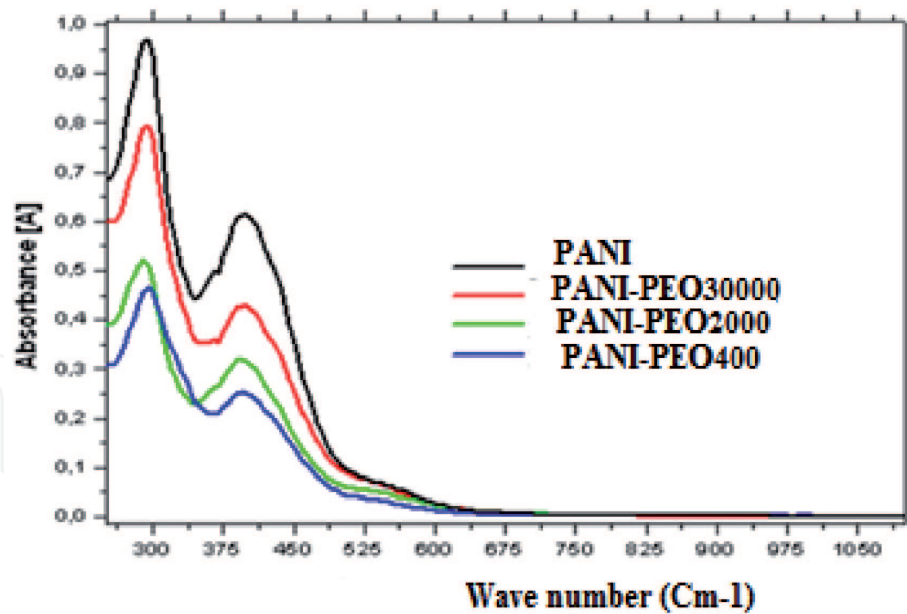


Figure 6.
UV spectral of the different form of (PANI-PEOs) catalyzed by maghnite-H+ under microwave irradiation.

true because polyaniline it is known a hygroscopic polymer as show in (Figure 9) [42, 43]. in the DSC thermogram of the PANI as show in (Figure 10), there were two endothermic peaks at 55.99 and 103.46°C. Therefore, these endothermic peaks were due to the evaporation of water, this is in agreement with the literature [44, 45]. The glass transition (T_g) appears at 74.06°C [46].

The curves of weight loss versus temperature showing the behavior of PANI-PEO₂₀₀₀ sample was presented in (Figure 11). The first significant weight loss occurs already at temperature between 50 and 100°C, that PANI-PEO₂₀₀₀ is hygroscopic and during the heating to 100°C the residual water evaporates [46]. Then the main mass loss, which corresponds to polymer degradation starts at about 200 and 500°C [47].

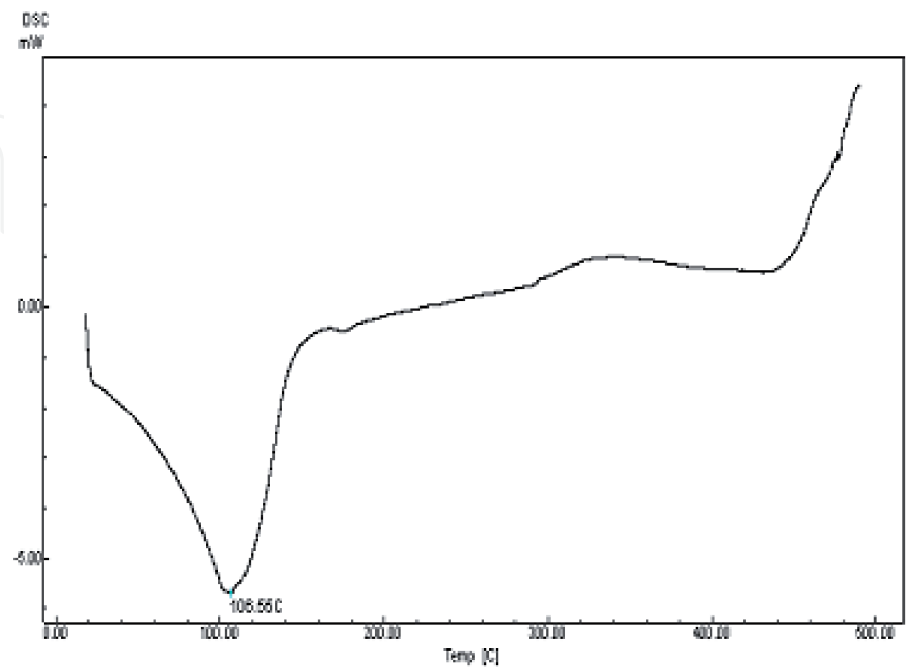


Figure 7.
Thermogram analysis measurements (DSC) of maghnite-H+ (heating rate 10°C/mn) catalyzed by maghnite-H+ under microwave irradiation.

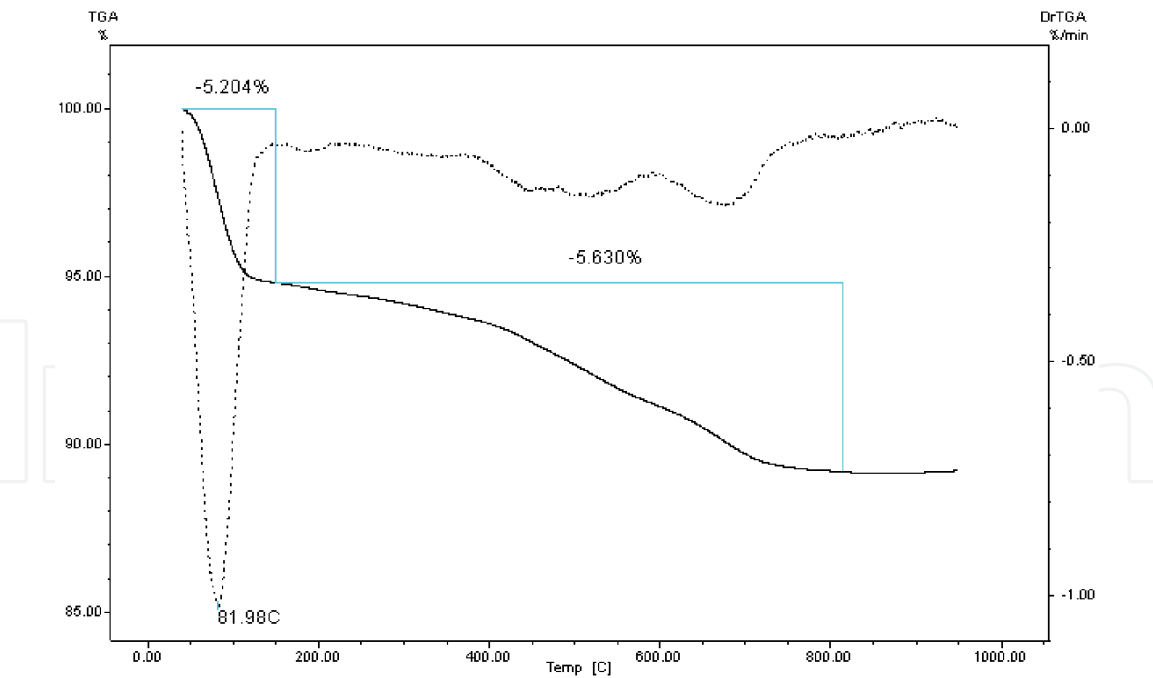


Figure 8.
Thermogram analysis (TGA) curves of a maghnite- H^+ obtained in nitrogen atmosphere at heating rate of $10^\circ\text{C}/\text{min}$.

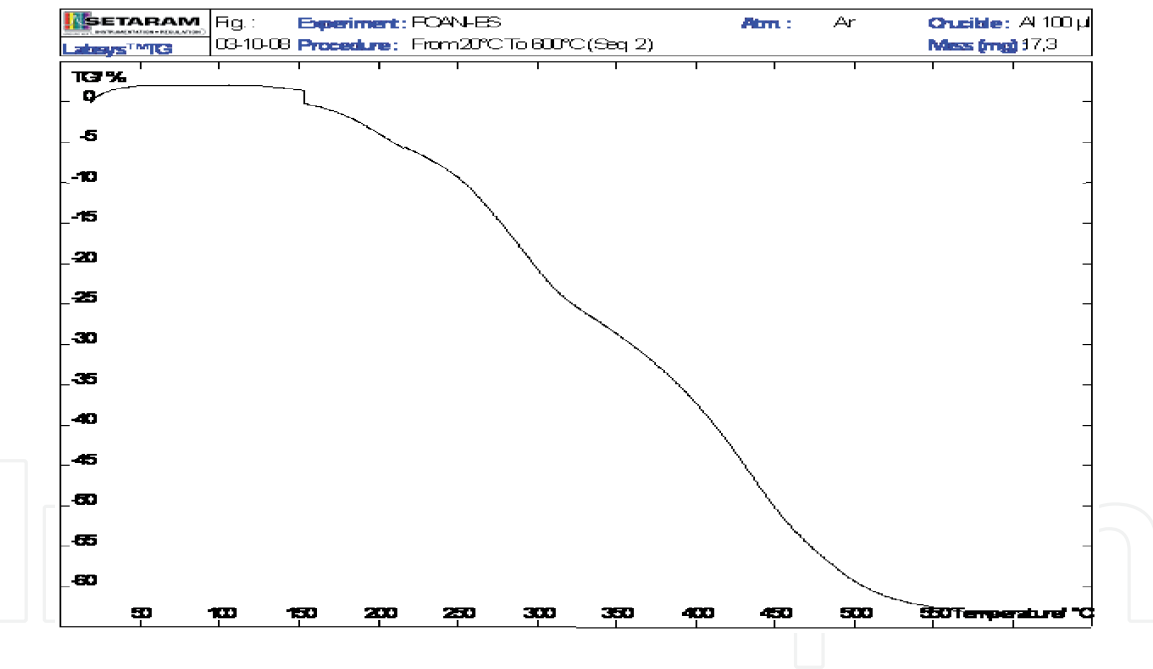


Figure 9.
Thermogram analysis (TGA) curves of PANI prepared in the presence of Maghnite- H^+ (0.25 M) under microwave irradiation.

In polyaniline (PANI) monomer and block copolymer (PANI-PEO2000) as show in (Figure 12). Firstly, we notice the presence of two endothermic peak at (68, 39 and 190, 09°C) it is associated respectively to the evaporation of water absorbed by the copolymer and melting POE2000 block [48, 49]. The glass transition temperature of block copolymer ($T_g = 16, 79^\circ\text{C}$) which is in agreement with the literature [50].

3.4 Gel permeation chromatography

Table 1 describes thermodynamics properties of PANI and its block PANI-PEO₂₀₀₀. Tables 2 and 3 describes the molecular weight distribution averages for the polymer

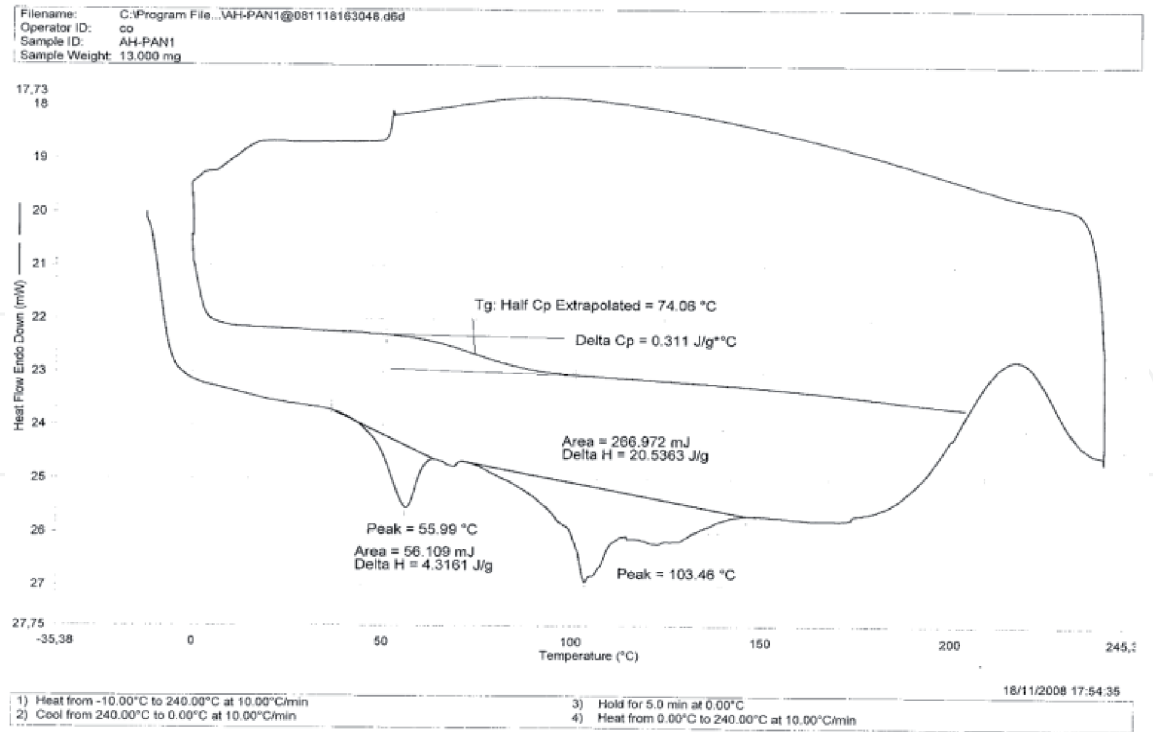


Figure 10.
Describes thermogram analysis (DSC) of PANI (heating rate 10°C/mn) catalyzed by maghnite-H+ under microwave irradiation.

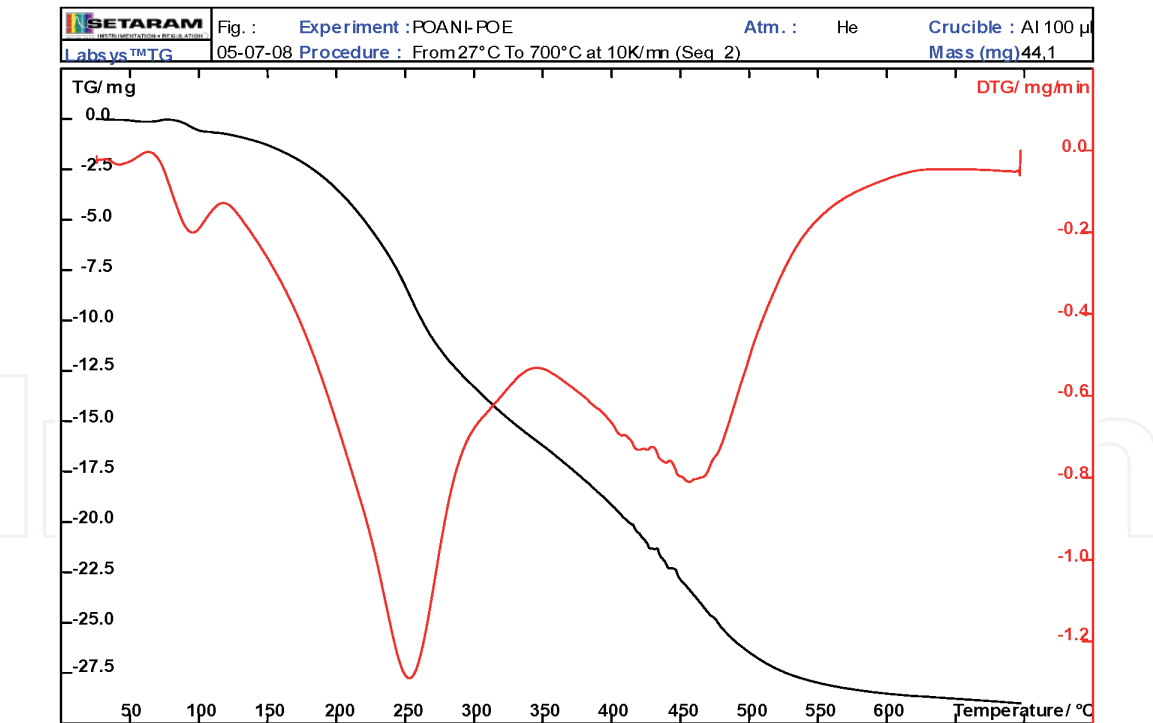


Figure 11.
Thermogram analysis (TGA) curves of PANI-PEO₂₀₀₀ prepared in the presence of maghnite-H+ (0.25 M) under micro wave irradiation.

and it's copolymer in the other hand (**Figures 13 and 14**) indicate a bimodal distribution. The macromolecular weight distribution of the obtained polymer and copolymer are narrow, this confirming the formation of the polymer PANI and the block copolymer PANI-PEO [51, 52].

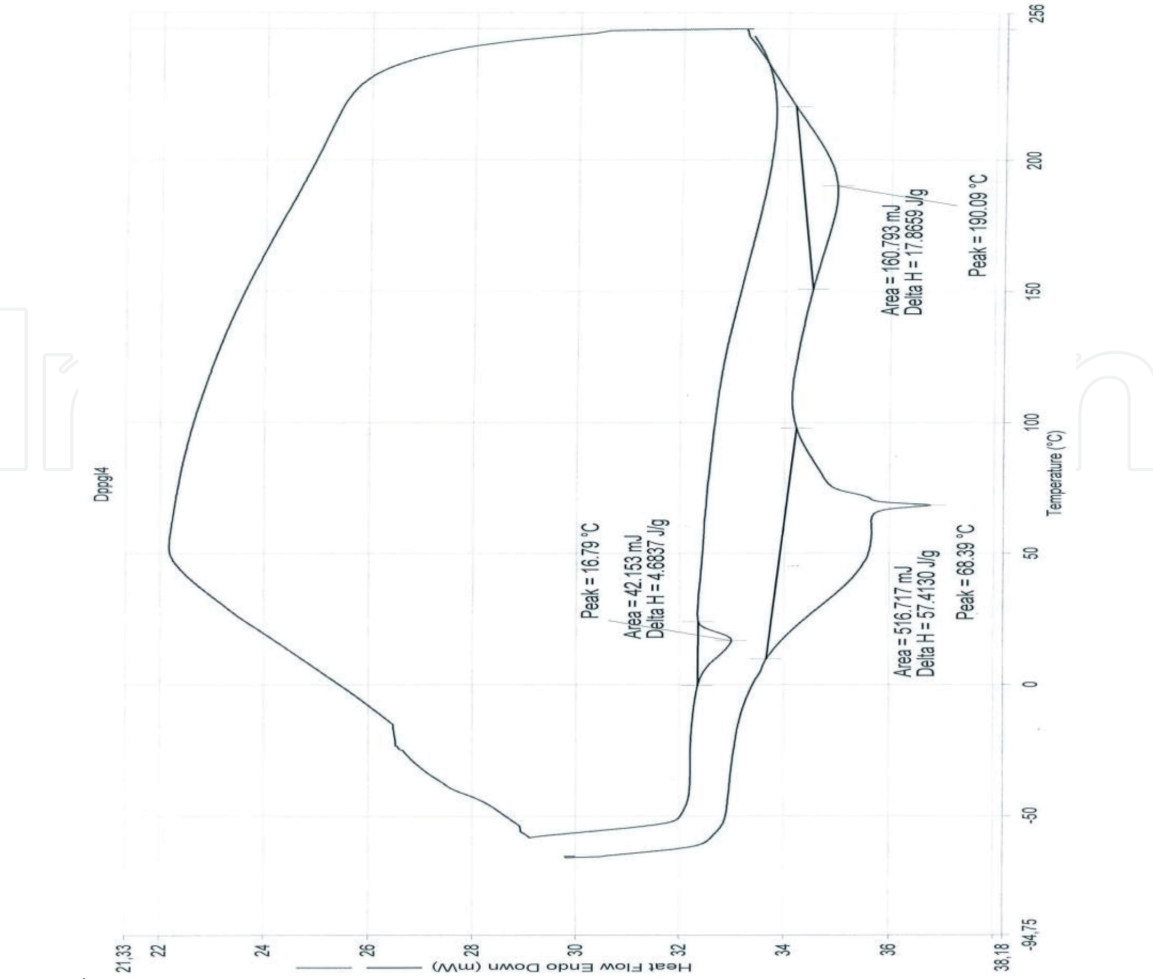


Figure 12.
Thermogram analysis (DSC) of PANI-PEO₂₀₀₀ (heating rate 10°C/mn) catalyzed by maghnite-H⁺ under microwave irradiation.

Sample	T ₁	T ₂	T ₃	T _g	ΔH ₁	ΔH ₂	ΔH ₃	ΔC _p
PANI	55.99	03.46	X	74.06	4.3161	20.5363	X	0.311
PANI-PEO ₂₀₀₀	68.39	190.09	X	16.79	57.4130	17.8659	X	4.6837

Table 1.
Describes thermodynamics properties of PANI and its block PANI-PEO₂₀₀₀.

Sample name	RT	Area	% Area	Mn	Mw	Polydispersity
PANI	17.973	1,318,425	6.01	644	746	1.15
	23.638	20,616,195	93.99	33	114	3.41

Table 2.
Gel permeation chromatograph of PANI composite in THF catalyzed by maghnite-H⁺ under microwave irradiation.

3.5 Electrical properties

The value of transverse strength and the electrical conductivity of the PANI and its block copolymer PANI-PEO2000 were calculated from Eqs. (1) and (2) as show in (Table 4) [53].

Sample name	RT	Area	% Area	Mn	Mw	Polydispersity
PANI-PEO ₂₀₀₀	17.917	130,748	1.30	2664	2701	1.013896
	23.032	9,960,549	98.70	50	264	5.342141

Table 3.
Gel permeation chromatograph of block copolymer PANI-PEO₂₀₀₀ composite in THF catalyzed by maghnite-H⁺ under microwave irradiation.

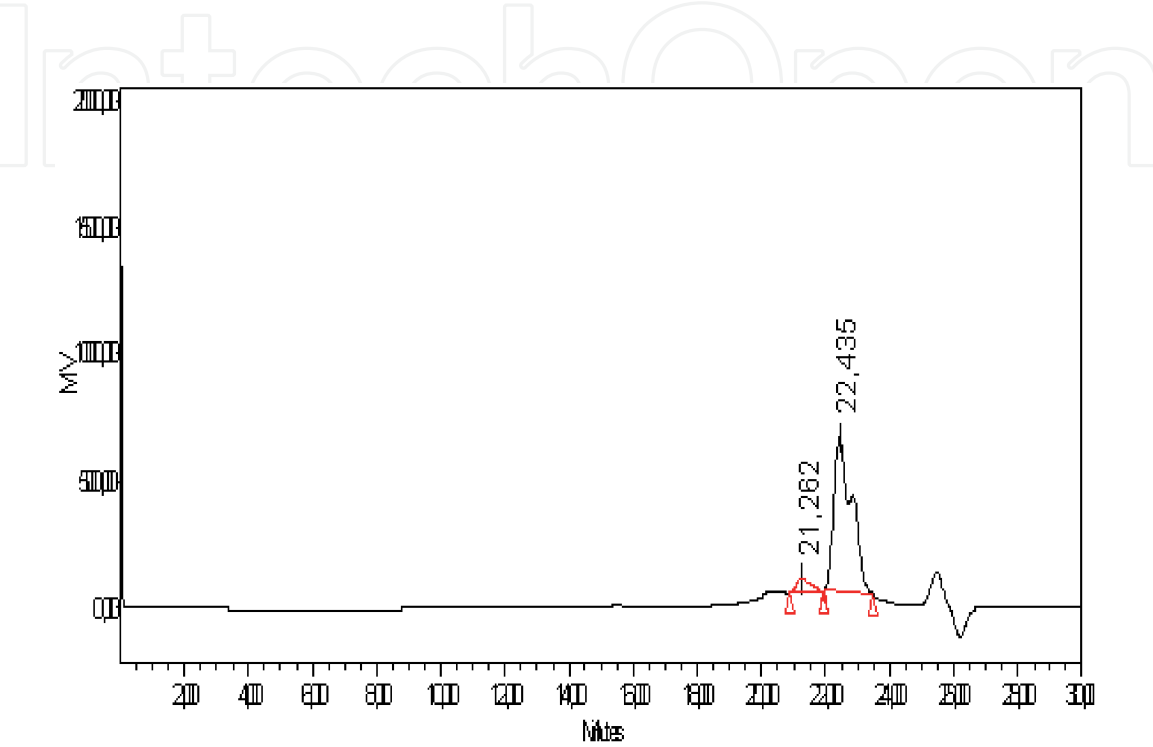


Figure 13.
Describes gel permeation chromatograph of PANI with 2% maghnite-H⁺ at 160°C for 4 min.

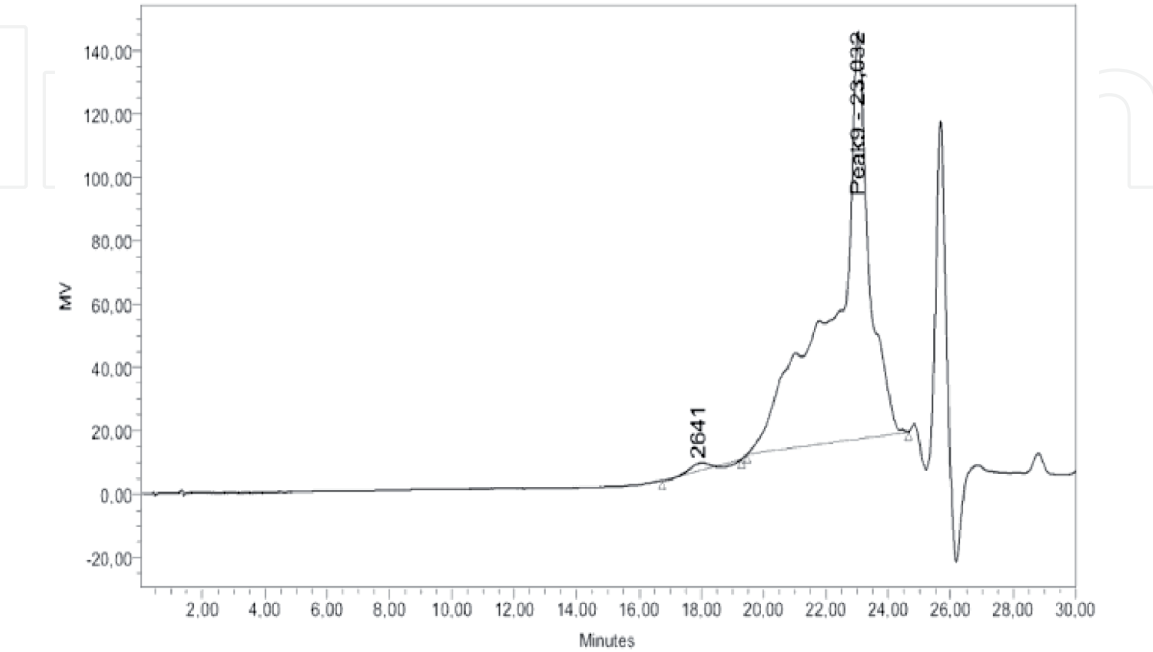


Figure 14.
Describes gel permeation chromatograph of PANI-PEO₂₀₀₀ with 2% maghnite-H⁺ at 160°C for 4 min.

$$\rho = R (\pi.r^2 / e) (\Omega.cm) \tag{1}$$

$$\sigma = 1 / \rho (S/cm) \tag{2}$$

3.6 Solubility of product

The polyaniline powder was added to 50 ml of different solvent (DMF, Acetonitrile, toluene, dichloromethane, THF, and chloroform). The dry weight of the filter paper was used to calculate the solubility of the composites. The best solvents for PANI and its block are determined to be DMF and Toluene as show in (Table 5) and (Figure 15). Finally, we can calculate the band of energy by equation (3) [54].

Sample	e (cm)	R(Ω)	ρ (Ω. cm)	σ (S/cm)
PANI	0.1	1.880	25.792	0.038
PANI-PEO ₂₀₀₀	0.1	0.976	0.163	6.134

Table 4.
Describes electrical properties of PANI and PANI-PEO catalyzed by maghnite-H⁺ under microwave irradiation.

Solvant	PANI	PANI-PEO ₂₀₀₀
DMF	0.55	1.6
Toluene	0.52	1.4
Chloroforme	0.47	1.05
Dichloromethane	0.39	0.95
Acetonitrile	0.20	0.79
THF	0.12	0.58

Table 5.
Describes solubility parameters of PANI and PANI-PEO₂₀₀₀ composites catalyzed by maghnite-H⁺ under microwave irradiation in different solvents (g/ml).

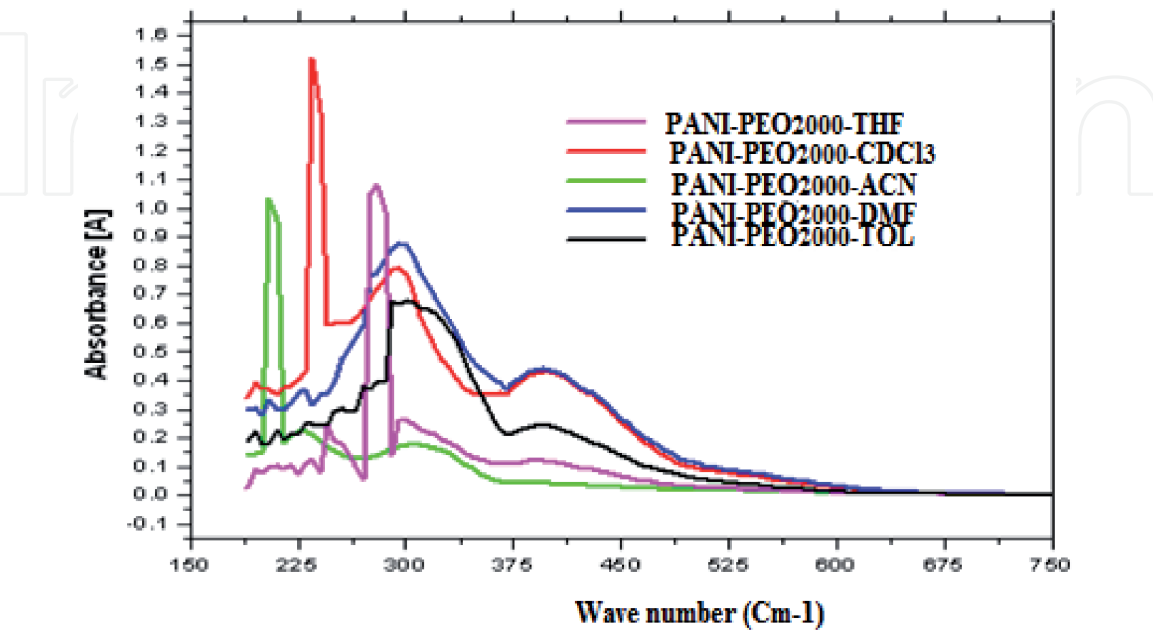


Figure 15.
Describes UV spectral of the copolymer (PANI-PEO₂₀₀₀) catalyzed by maghnite-H⁺ under microwave irradiation in different organic solvents.

Concentration	C	C ₁ =2C/3	C ₂ =C/2	C ₃ = C/3	C ₄ =C/4
Average	3.60	3.61	3.61	3.60	3.59
Cinema (cst)	0.61	0.61	0.61	0.60	0.6
Dynamic (cp)	0.91	0.90	0.92	0.89	0.89
Relative	1.00	1.01	1.01	1.01	1
Specific	0.00	0.01	0.00	0.00	0
Reduced	12.22	13.99	19.45	20.96	22.40
Inherent	12.10	13.90	19.45	20.90	22.41
Solomon	12.14	13.90	19.50	20.95	22.43
Visct. Intr (ml/g ⁻¹)	25.80		25.78		25.77

Table 6.
Describes viscosimertic properties of pure PANI catalyzed by maghnite-H+ under microwave irradiation.

Concentration	C	C ₁ =2C/3	C ₂ =C/2	C ₃ = C/3	C ₄ =C/4
Average	3.61	3.61	3.60	3.61	3.58
Cinema (cst)	0.61	0.60	0.61	0.61	0.61
Dynamic (cp)	0.91	0.91	0.91	0.88	0.90
Relative	1.00	1.00	1.01	1.01	1.01
Specific	0.00	0.01	0.01	0.01	0.00
Reduced	7.49	12.10	14.37	13.55	18.05
Inherent	7.40	12.05	14.31	13.50	17.99
Solomon	7.44	12.07	14.33	13.51	18.01
Visct. Intr (ml/g ⁻¹)	19.75		19.66		19.68

Table 7.
Describes viscosimertic properties of PANI-PEO₂₀₀₀ catalyzed by maghnite-H+ under microwave irradiation.

$$\Delta E = h\nu = h c / \lambda \tag{3}$$

The solubility parameter (δ) is usually calculate by equation (4) and expressed in (cal/cm³)^{1/2} or preferably (j/cm³)^{1/2} units for many compound is defined from Hildebrand-Scotchard Solution theory is:

$$\delta = (\Delta E / V)^{1/2} \tag{4}$$

3.7 Viscosimertic parameters of PANI and PANI-PEO

Tables 6 and 7 describe intrinsic viscosity and properties physics of (PANI) and block (PANI-PEO₂₀₀₀) according to the Mark-Houwink equation:

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

4. Kinetics studies

4.1 Effect of the amount of mag-H + on the yield of copolymerization

Figure 9 describe the effect of the amount of catalyst on the yield of this copolymerization (PANI-PEO). As can be seen in (Figure 16 and 19), the

copolymerization rate increased with the amount of Mag-H + and reaches a maximum at 160°C with (5% wt) of catalyst, above this temperature and percentage of catalyst, the yield decreases.

The increase in yield with temperature and molecular weight of catalyst is mainly due to the number of active sites in the catalyst responsible for initiating the reaction. Similar results are obtained by many research [55, 56].

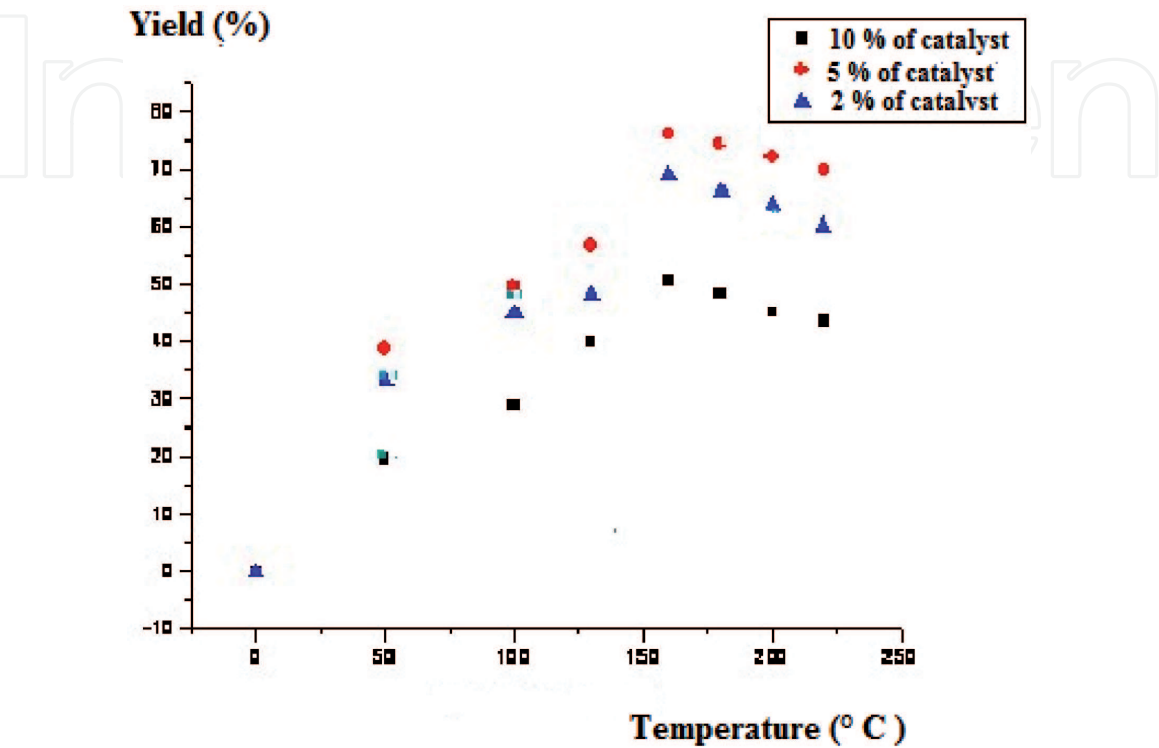


Figure 16.
Describes effect of the amount of mag-H+ (catalyst) on the yield of copolymerization.

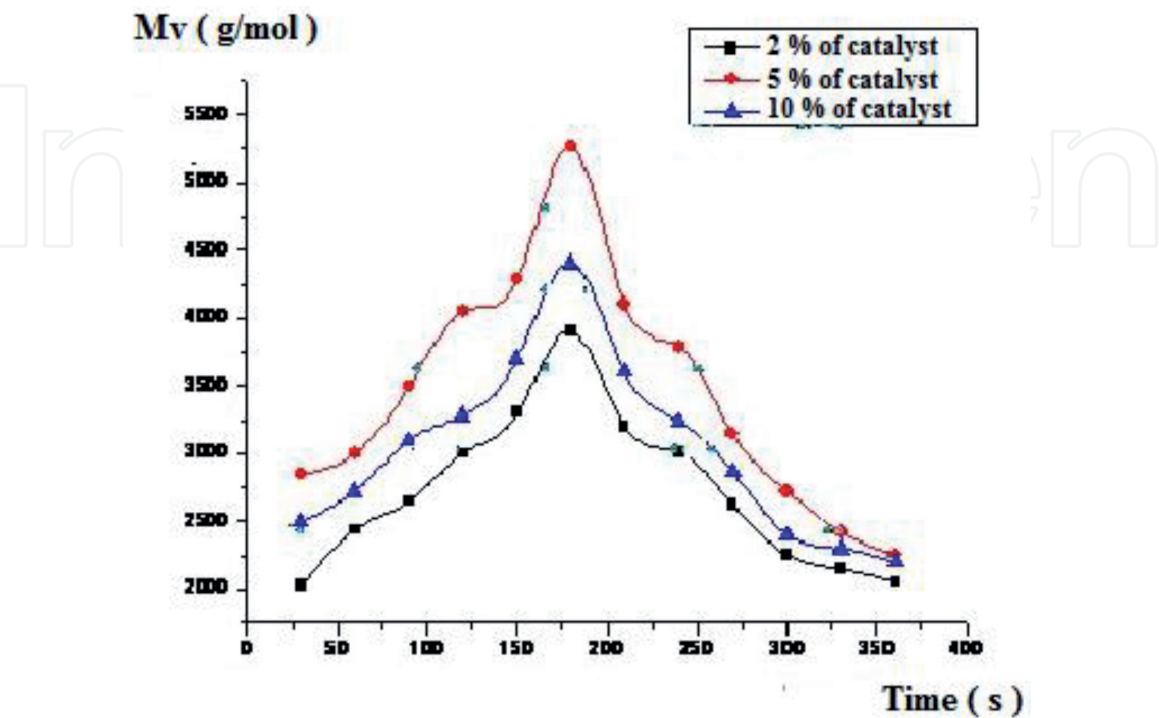


Figure 17.
Describes effect of the amount of mag-H + on the viscosimertic molecular weight of copolymerization.

4.2 Effect of the amount of Mag-H + on the molecular weight of copolymer

We have used (2%,5% and 10%) by weight as the amount maghnite and varying time after keeping the other parameters (the amount of monomers and the temperature). It is observed that the average molecular weight increases with time and reaches a maximum at 4 minutes of reaction and decrease after this time as show in (Figure 17) [57].

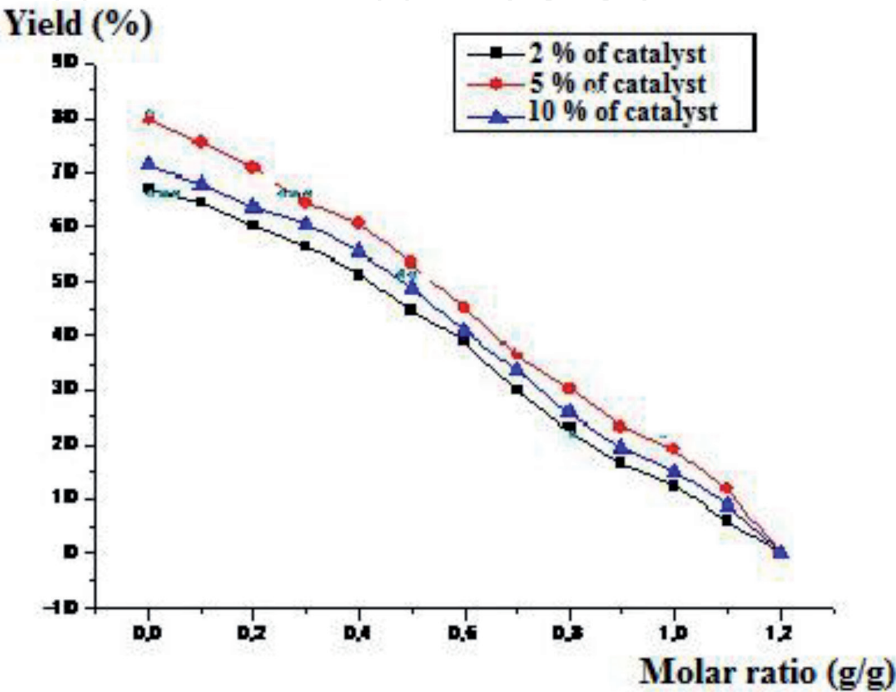


Figure 18.
Describes the effect of the molar ratio (ANI/PEO) upon the yield of copolymerization.

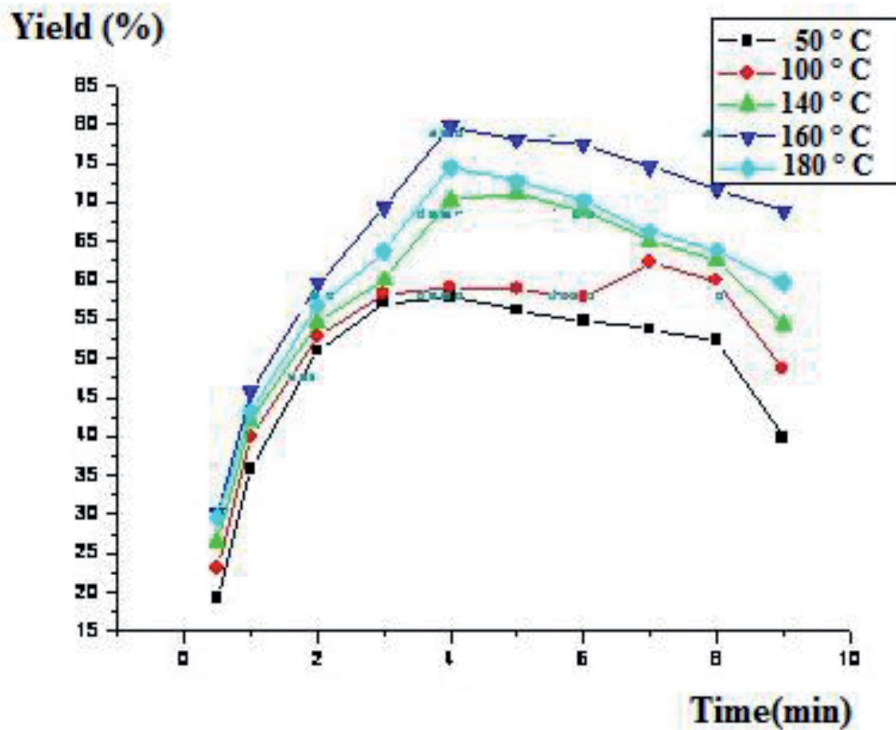


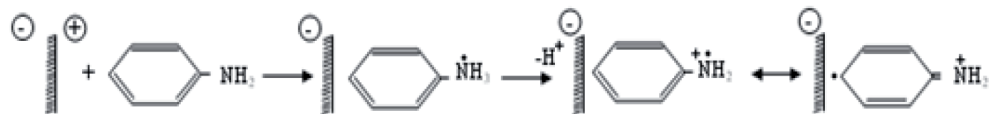
Figure 19.
Describes effect of temperature on the yield of copolymerization.

4.3 Effect of molar ratio aniline/PEO on the yield of copolymerization

We notice a significant change in the yield with increasing the amount ratio, in particular with increasing the amount of PEO used in this reaction processing. The (Figure 18.) below summarizes the influence of the molar ratio on Aniline/PEO upon

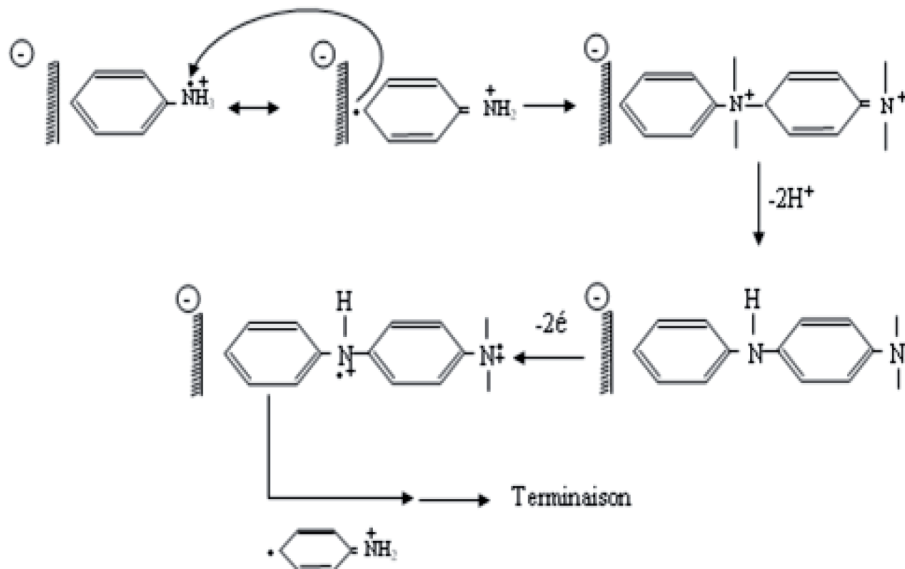
1-Initiation

The reaction occurs within the layers of the Maghnite exchanged by H⁺ protons, which are capable of initiating cationic polymerization.



2-Propagation

The successive addition of monomers on the chain macromere growing present propagation process.



3-Termination

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

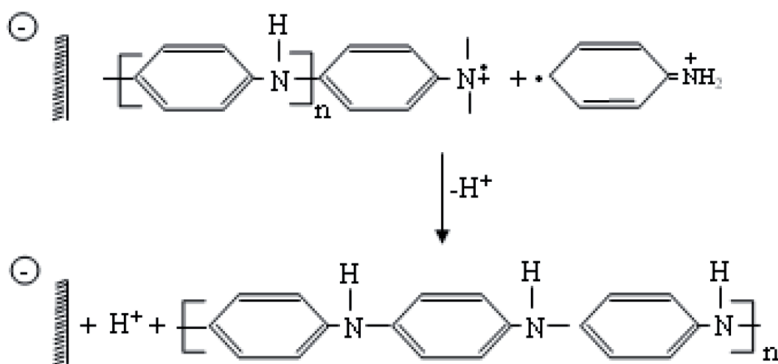
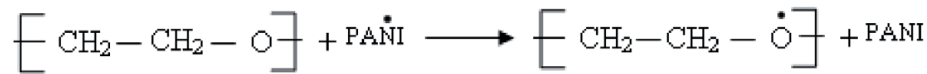
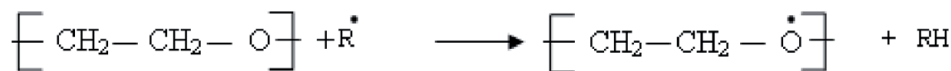
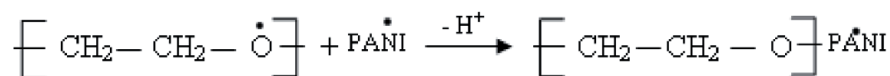


Figure 20.
Proposed mechanism of homopolymer (PANI) catalyzed by Maghnite-H⁺ under microwave irradiation.

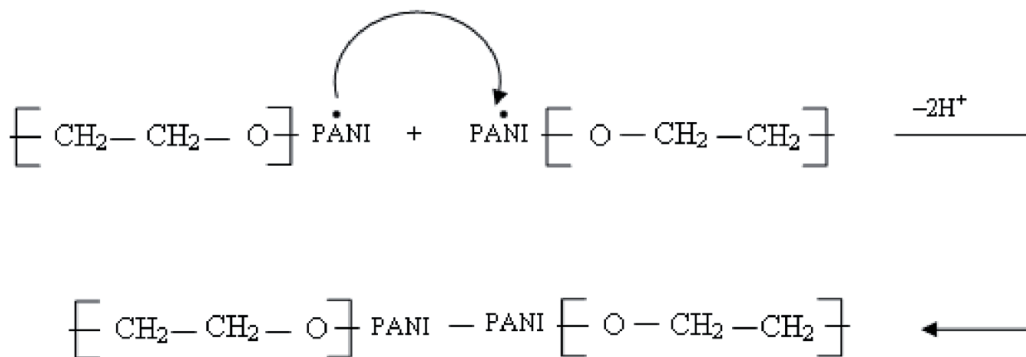
1-Initiation



2-Propagation



3-Terminaison

**Figure 21.**

Proposed mechanism of block copolymer (PANI-PEO₂₀₀₀) catalyzed by Maghnite-H⁺ under microwave irradiation.

the reaction yield. This phenomenon can explain by the high reactivity and solubility of the POE in water compared to the aniline in particular at high temperature [58].

5. Proposed mechanism of polymerization and copolymerization

As shows in (Figures 20 and 21), the process of synthesis of PANI-Maghnite-H⁺ and its homolog PANI-PEO₂₀₀₀-Maghnite-H⁺ composites can be divided into the following three steps [59–61].

6. Conclusion

Based on Maghnite-H⁺ (Algerian ecologic catalyst MMT) and under microwave irradiation our polymer (PANI) and block copolymer (PANI-b-PEO) were successfully synthesized and investigate. This product was prepared in order to combine the mechanical and physical properties of PEO₂₀₀₀ with conducting properties of PANI. A possible mechanism of this cationic polymerization is discussed based on the results of the ¹H NMR Spectroscopic analysis of these compounds. Thus all the two types of composites (PANI and PEO) provide opportunities and rewards creating new world wide interest in these new materials in electronics devises.

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