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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°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°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 2.10³) 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 CDCl₃. Fourier transform infrared spectroscopy (FTIR) spectra were obtained between 900 and 4000 cm⁻¹ on an ATI Matson FTIR No 9501165. 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. The purification of polymers were carried out by dissolving the product in chloroform (CHCl₃) 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°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 (H₂SO₄ 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°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 $694\text{--}593\text{ cm}^{-1}$ 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].

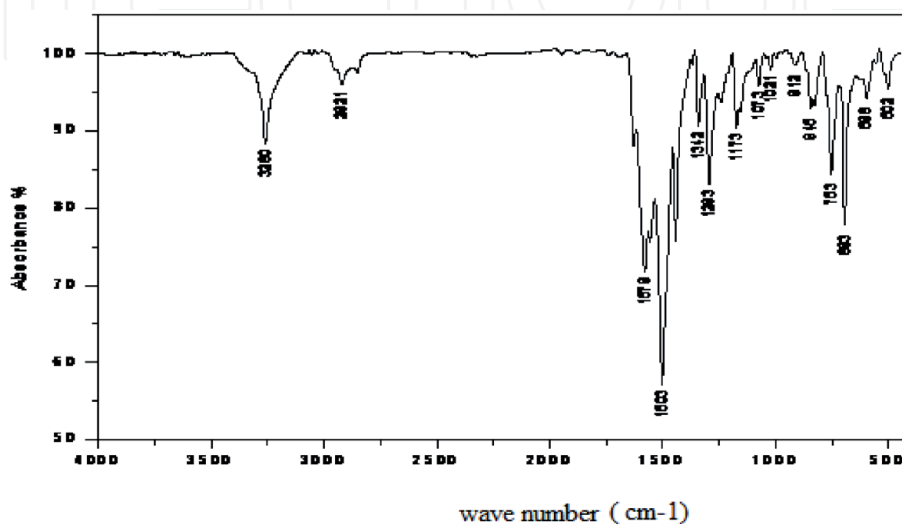


Figure 1.
FT-IR spectra of polyaniline (PANI) catalyzed by maghnite- H^+ under microwave irradiation.

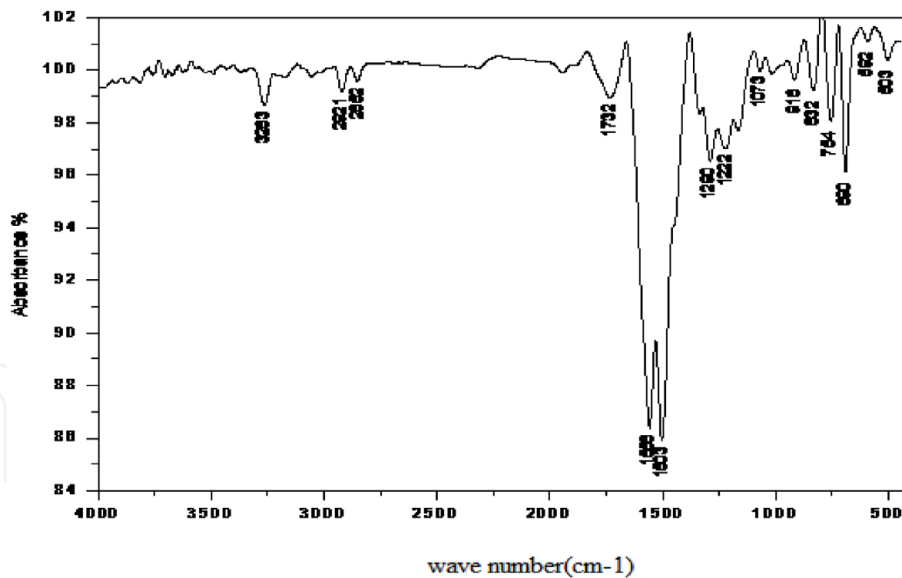


Figure 2.
FT-IR spectra of block copolymer (PANI-PEO₂₀₀₀) catalyzed by maghnite-H⁺ under microwave irradiation.

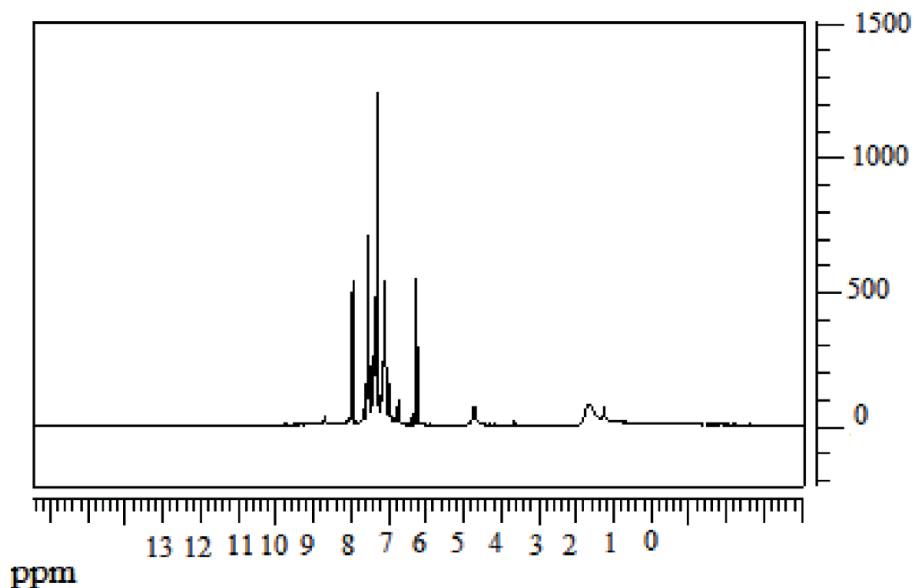


Figure 3.
Describes ¹H-NMR spectra of (PANI) catalyzed by maghnite-H⁺ under microwave irradiation.

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

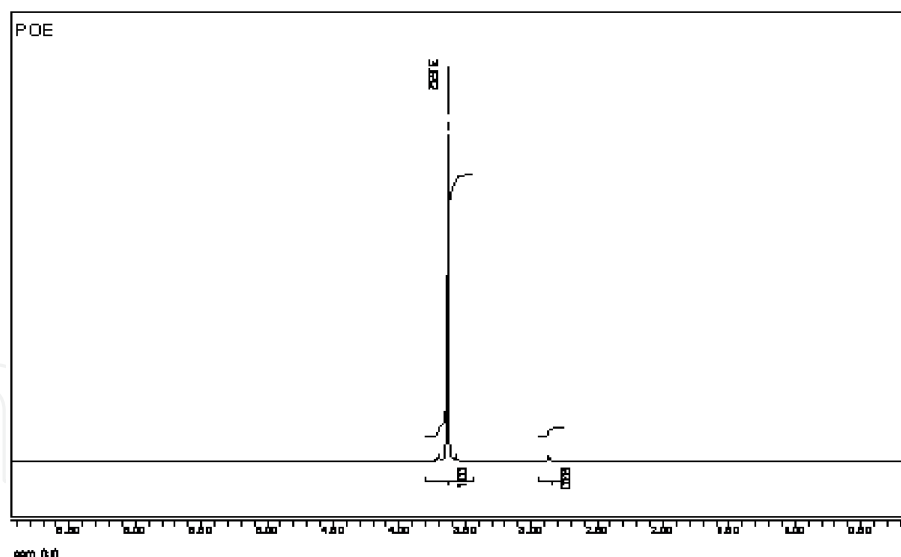


Figure 4.
Describes ^1H -NMR spectrum of poly ethylene oxide (PEO_{2000}).

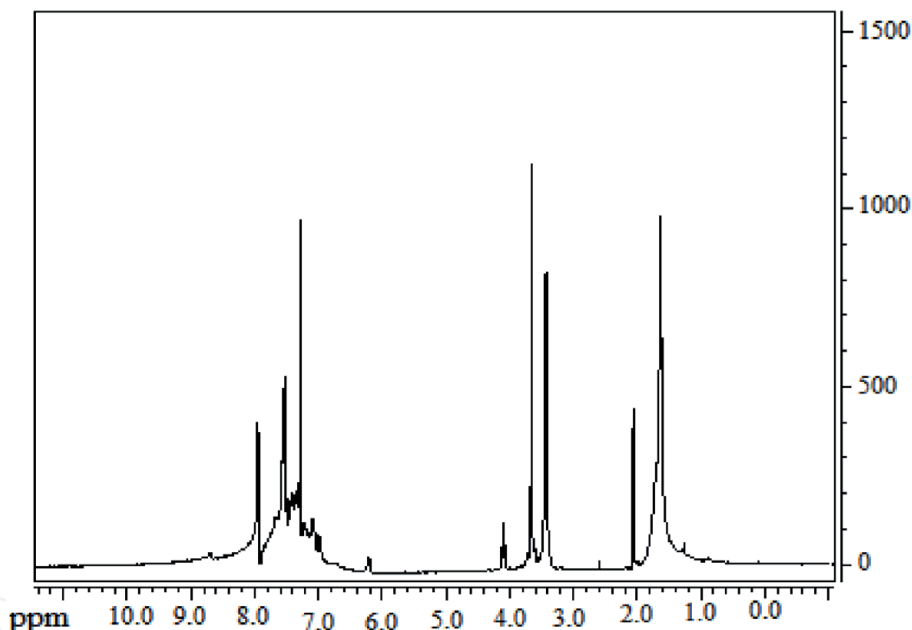


Figure 5.
Describes ^1H -NMR spectra of the copolymer (PANI-PEO_{2000}) catalyzed by maghnite- H^+ under microwave irradiation.

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 $187\text{--}600^\circ\text{C}$, which be

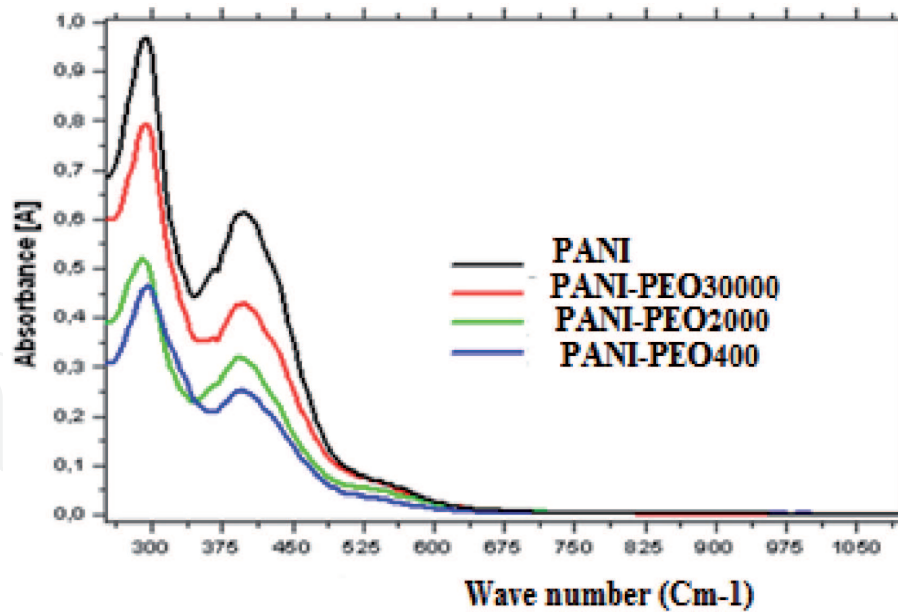


Figure 6.
UV spectral of the different form of (PANI-PEOs) catalyzed by maghnite-H⁺ under microwave irradiation.

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

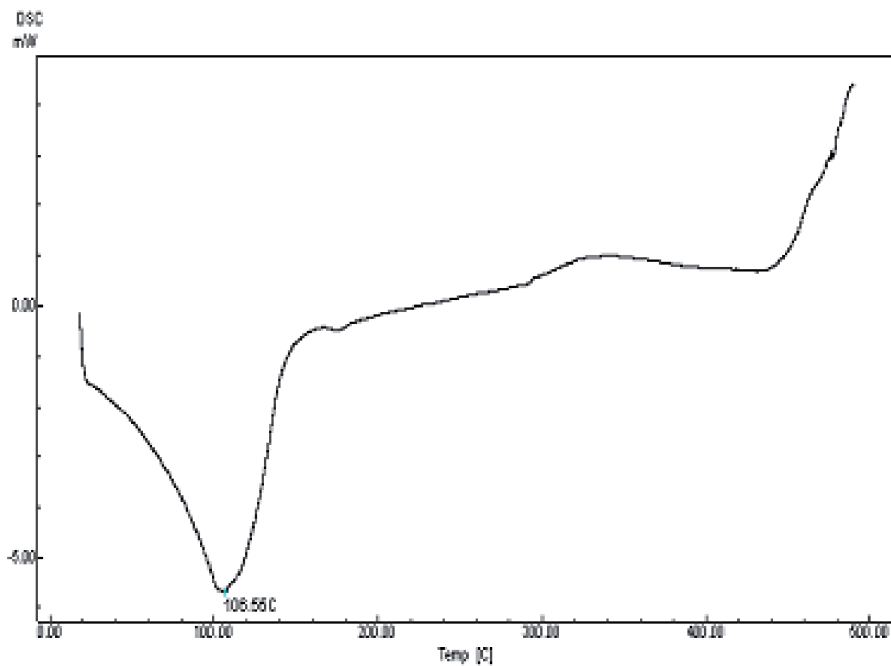


Figure 7.
Thermogram analysis measurements (DSC) of maghnite-H⁺ (heating rate 10°C/min) catalyzed by maghnite-H⁺ under microwave irradiation.

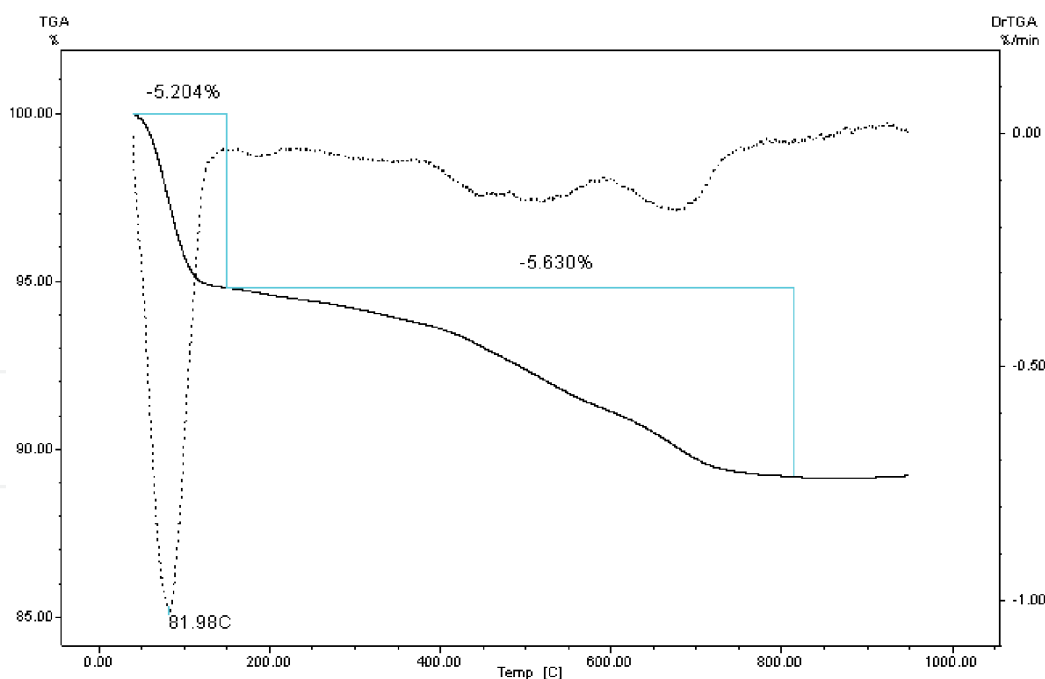


Figure 8.
 Thermogram analysis (TGA) curves of a maghnite- H^+ obtained in nitrogen atmosphere at heating rate of $10^\circ C/min$.

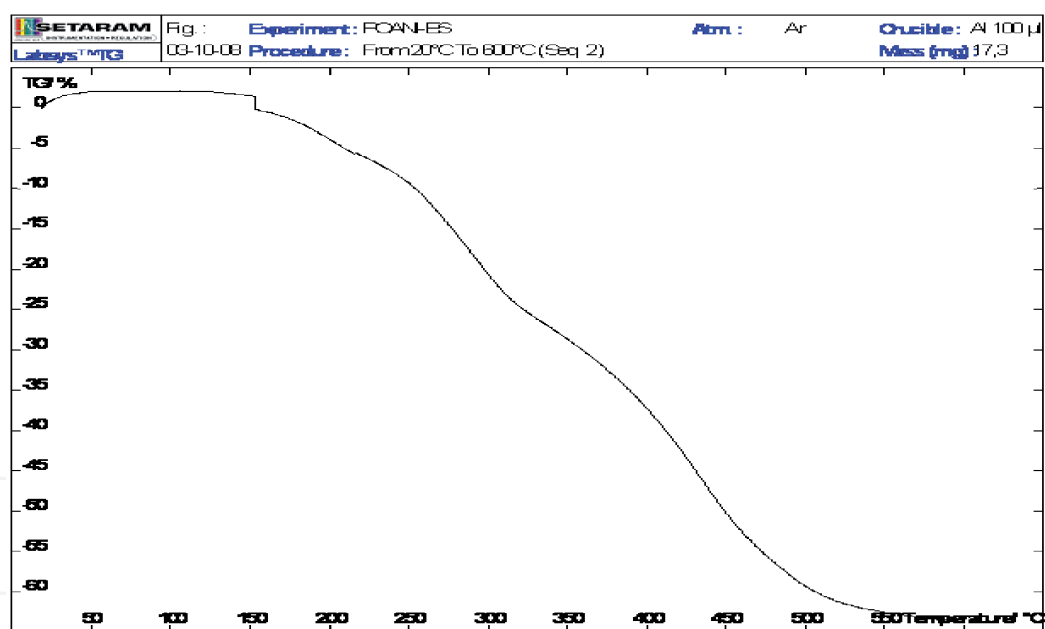


Figure 9.
 Thermogram analysis (TGA) curves of PANI prepared in the presence of Maghnite- H^+ (0.25 M) under microwave irradiation.

the main mass loss, which corresponds to polymer degradation starts at about 200 and $500^\circ C$ [47].

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 ($T_g = 16, 79^\circ C$) which is in agreement with the literature [50].

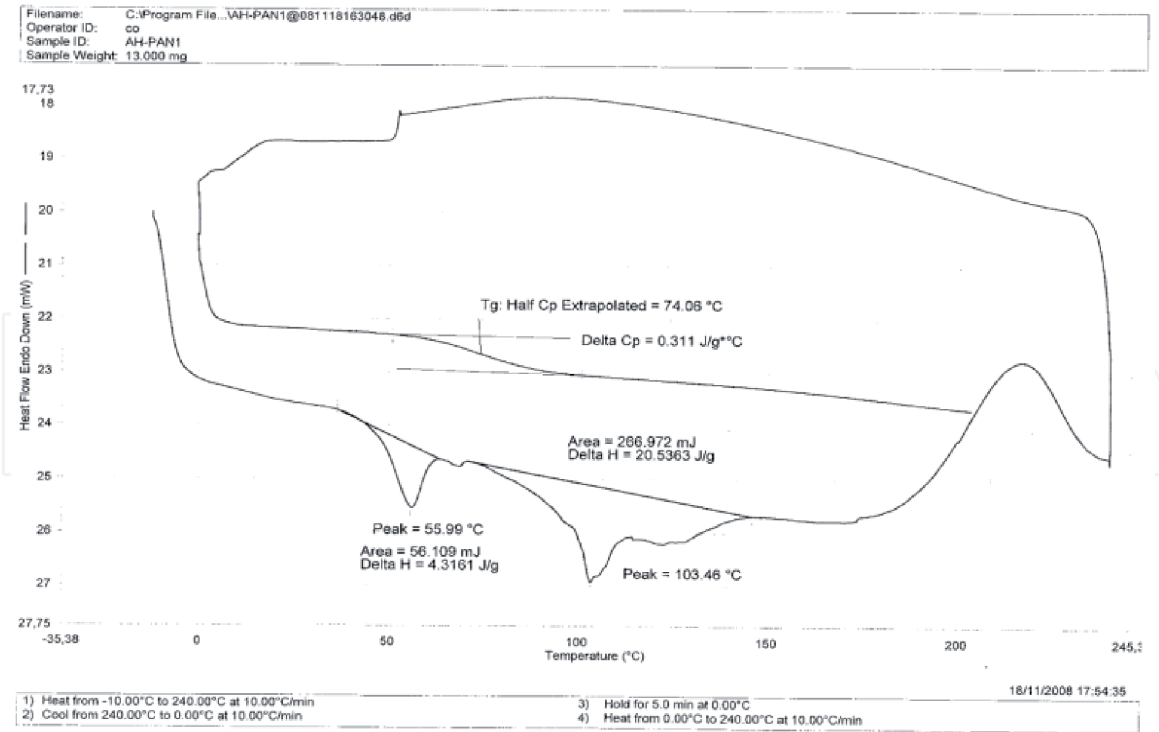


Figure 10. Describes thermogram analysis (DSC) of PANI (heating rate 10°C/mn) catalyzed by maghnite-H+ under microwave irradiation.

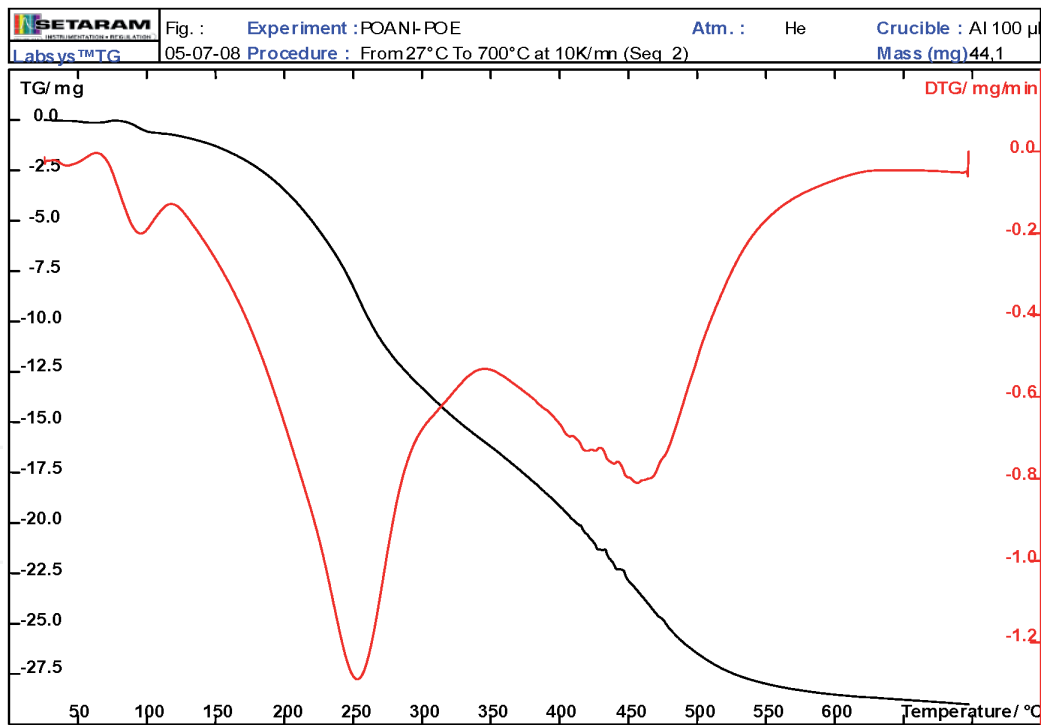


Figure 11. Thermogram analysis (TGA) curves of PANI-PEO₂₀₀₀ prepared in the presence of maghnite-H+ (0.25 M) under micro wave irradiation.

3.4 Gel permeation chromatography

Tables 2 and 3 describes the molecular weight distribution averages for the polymer 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].

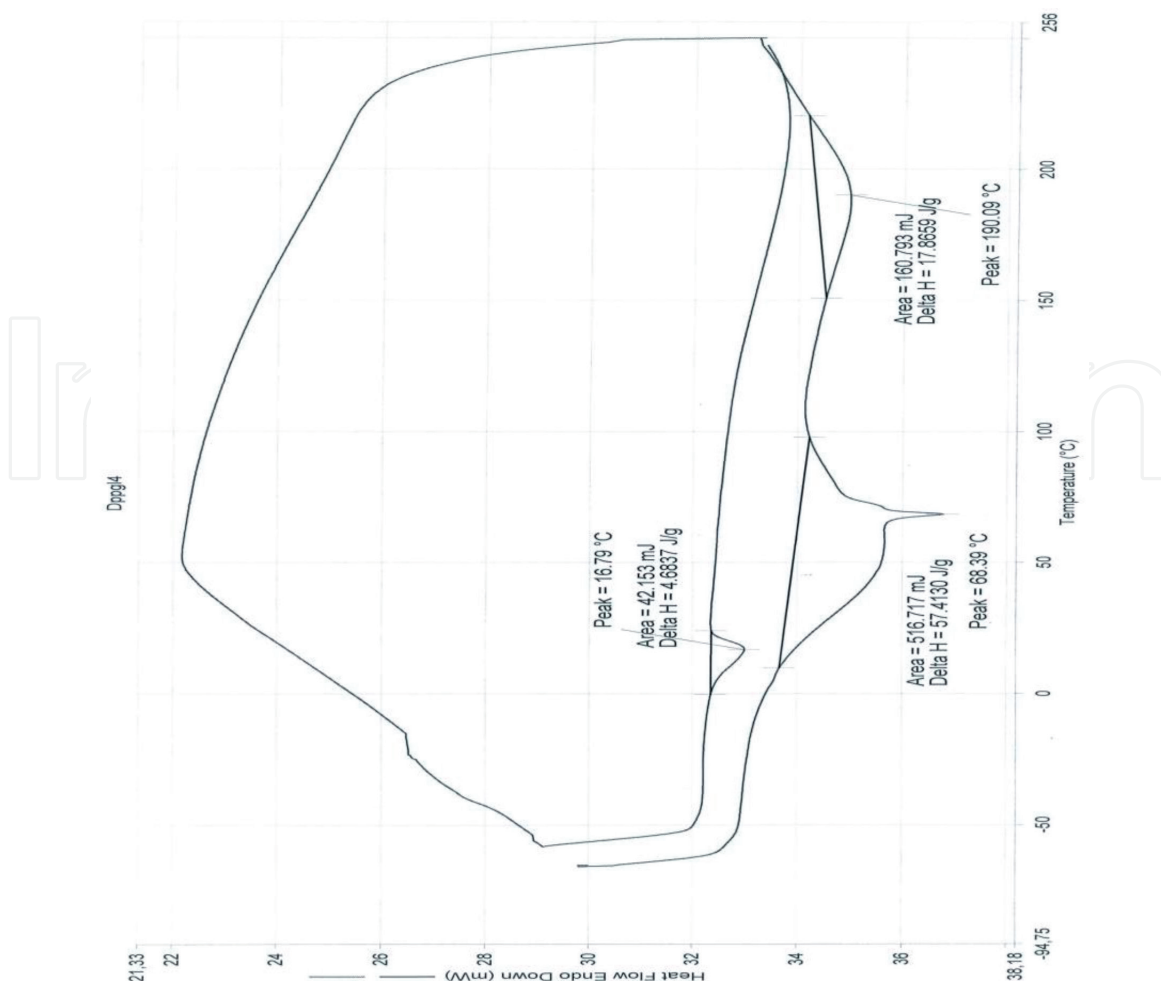


Figure 12. Thermogram analysis (DSC) of PANI-PEO₂₀₀₀ (heating rate 10°C/mn) catalyzed by maghnite-H⁺ under microwave irradiation.

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.

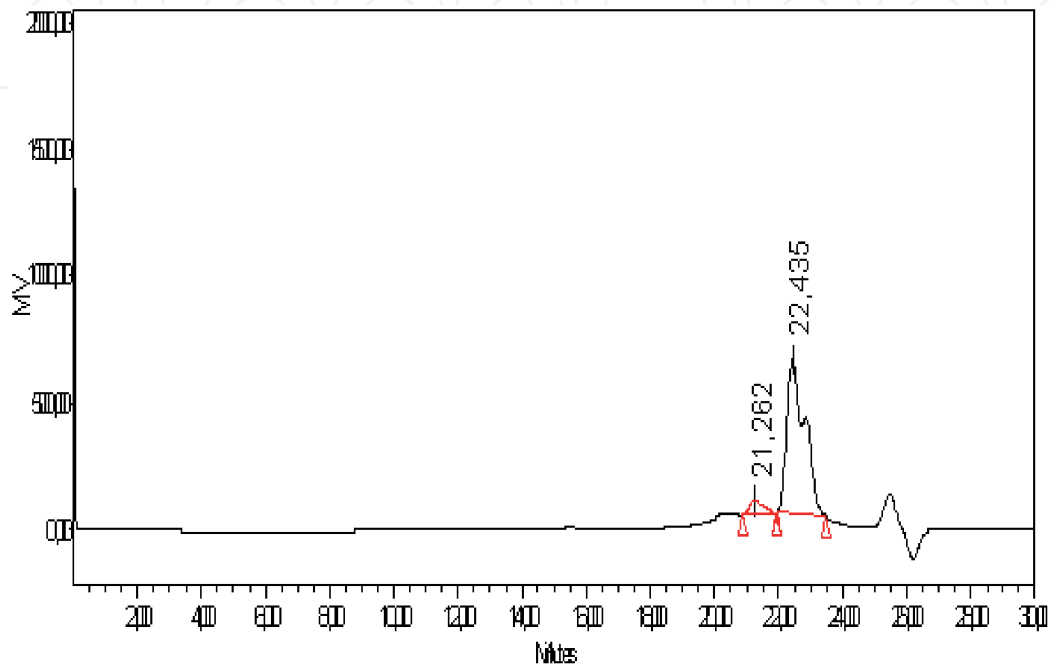


Figure 13.
Describes gel permeation chromatograph of PANI with 2% maghnite-H⁺ at 160°C for 4 min.

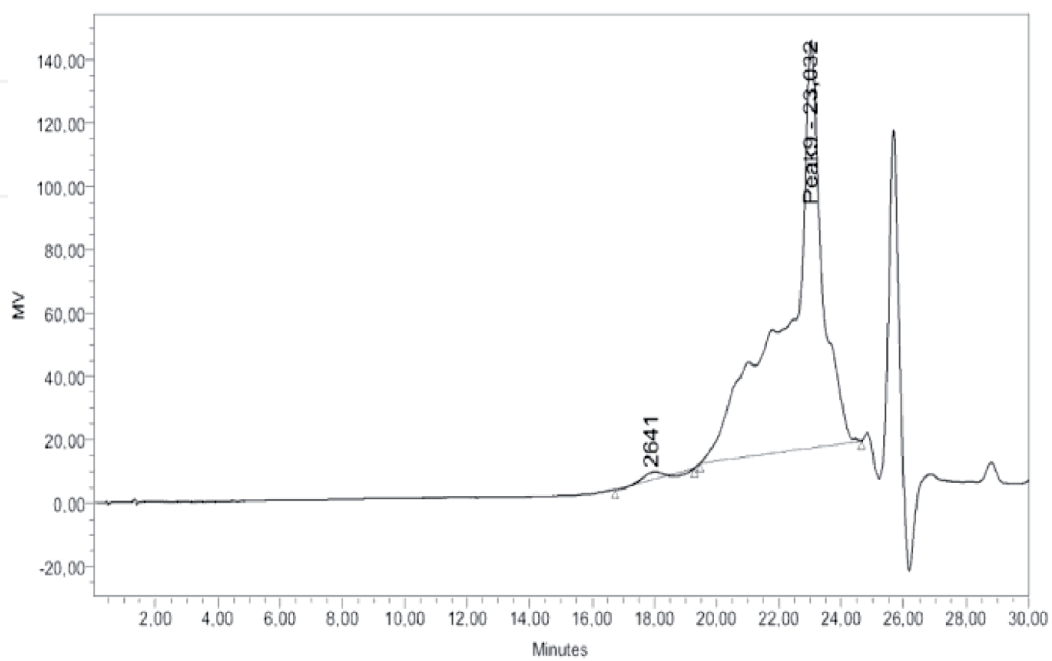


Figure 14.
Describes gel permeation chromatograph of PANI-PEO₂₀₀₀ with 2% maghnite-H⁺ at 160°C for 4 min.

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

$$\sigma = 1/\rho (S/cm) \quad (2)$$

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).

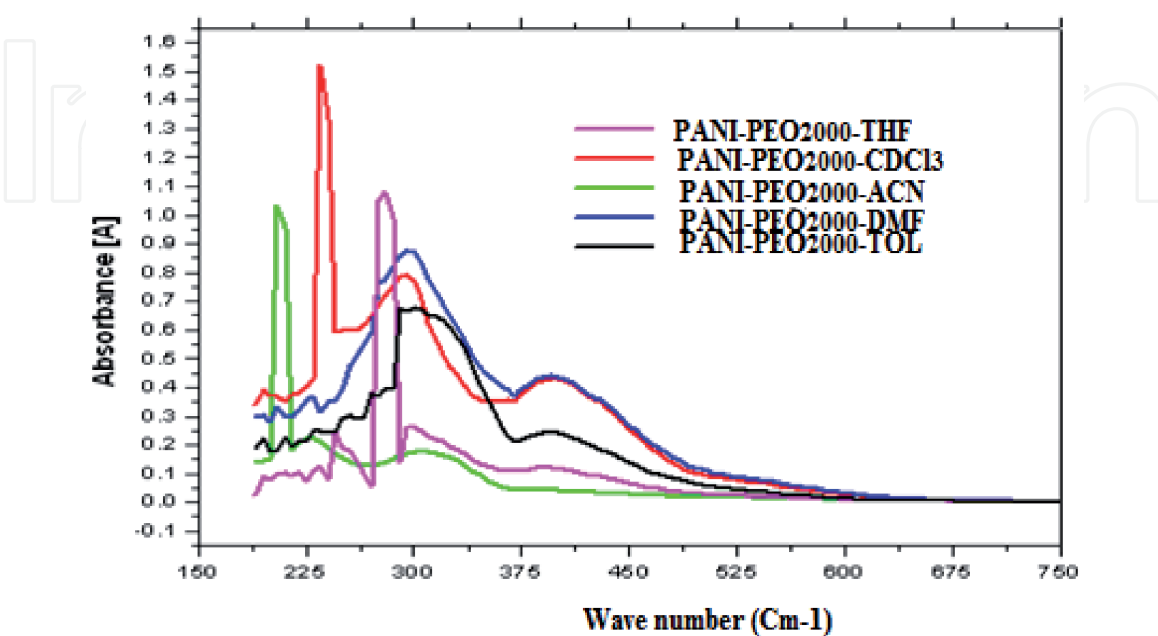


Figure 15.
 Describes UV spectral of the copolymer (PANI-PEO₂₀₀₀) catalyzed by maghnite-H⁺ under microwave irradiation in different organic solvents.

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.

$$\Delta E = hv = h c/\lambda \quad (3)$$

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:

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

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].

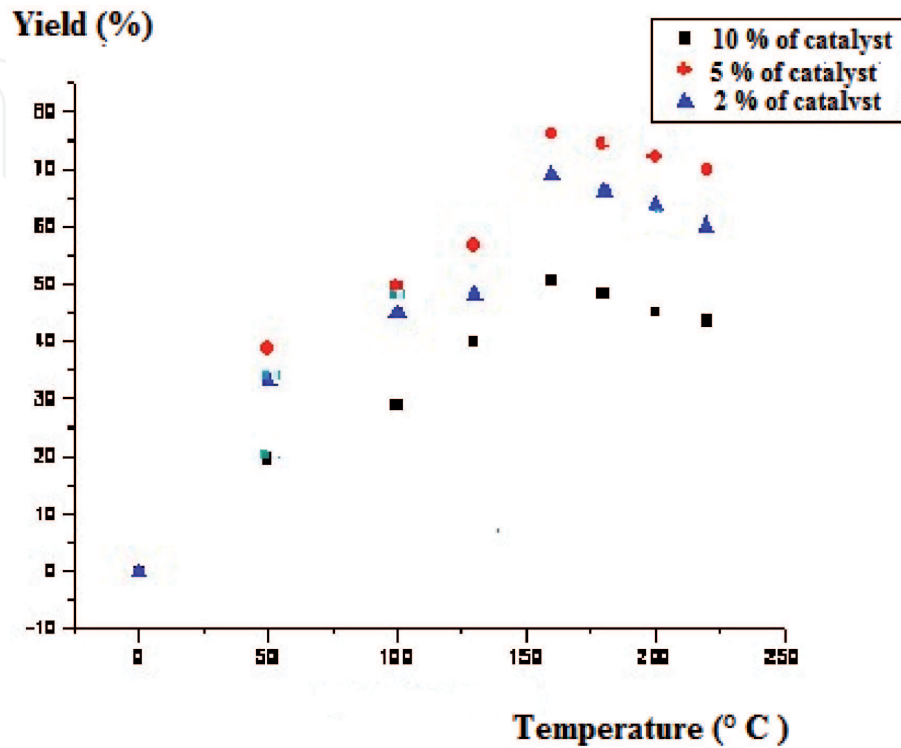


Figure 16. Describes effect of the amount of mag-H+ (catalyst) on the yield of copolymerization.

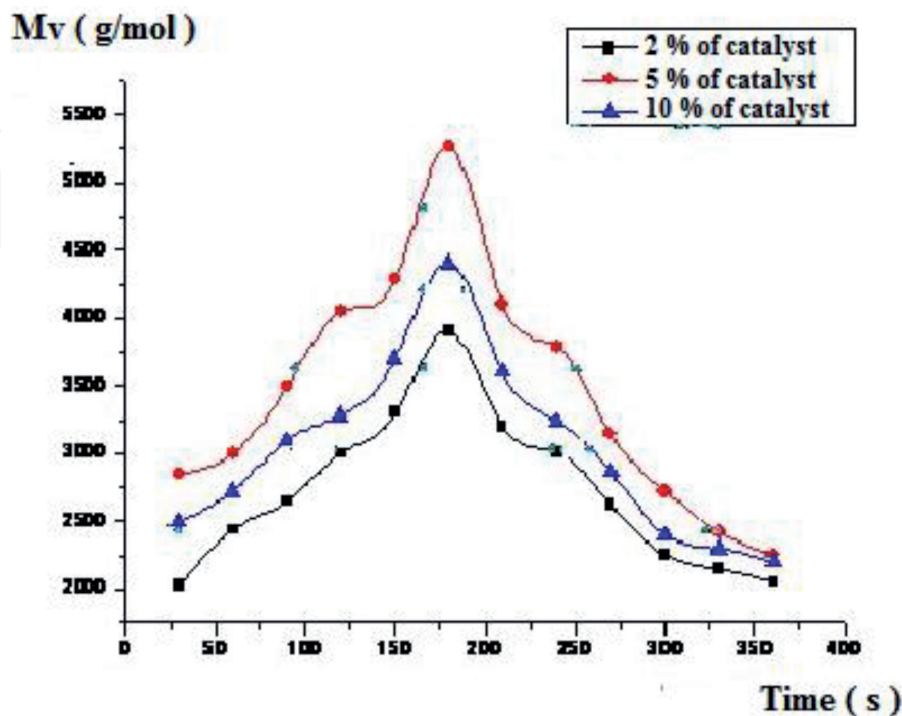


Figure 17. Describes effect of the amount of mag-H + on the viscosimetric molecular weight of copolymerization.

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].

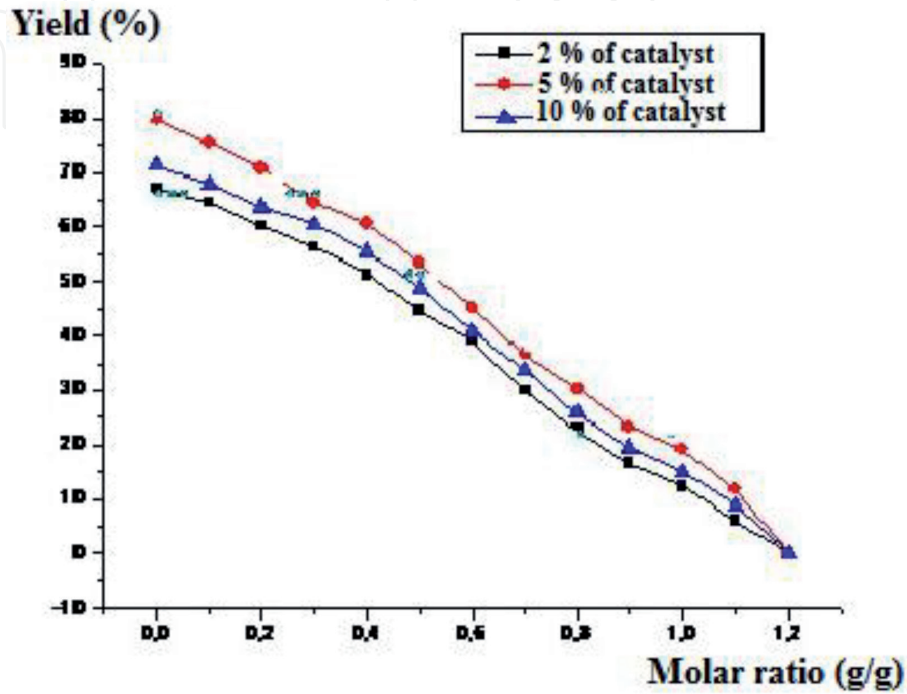


Figure 18. Describes the effect of the molar ratio (ANI/PEO) upon the yield of copolymerization.

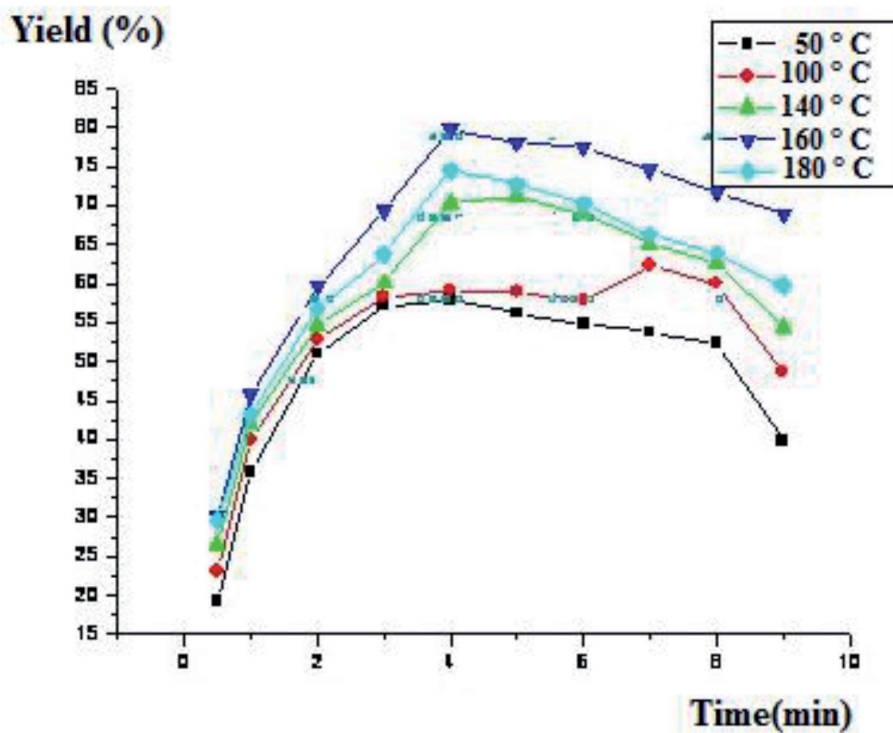


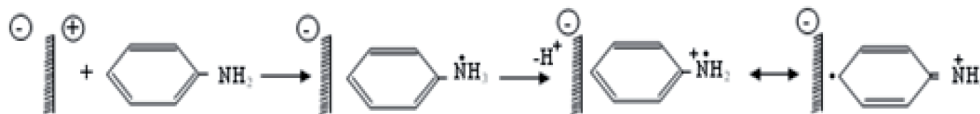
Figure 19. Describes effect of temperature on the yield of copolymerization.

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

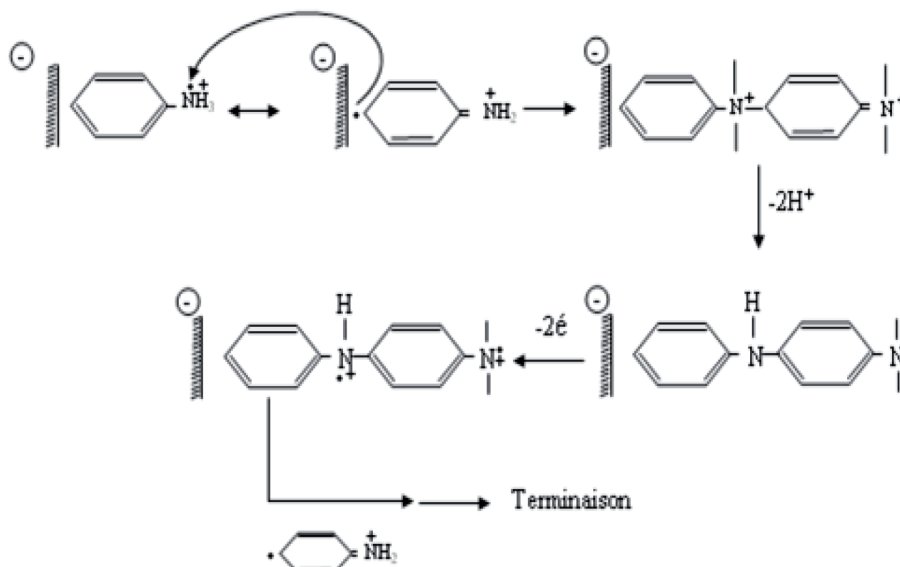
1-Initiation

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.

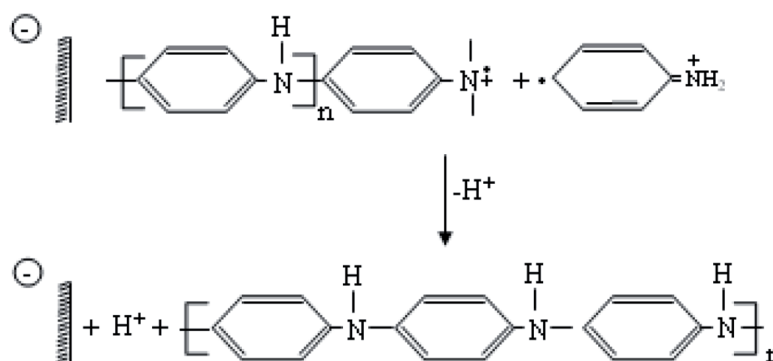
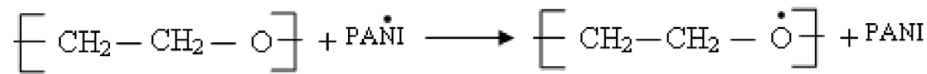
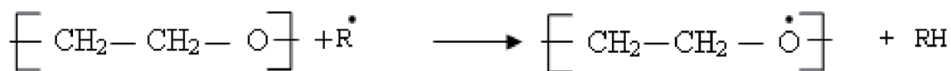
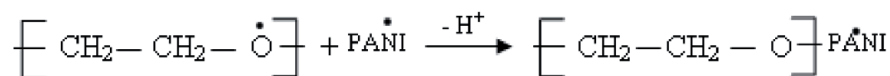


Figure 20.
 Proposed mechanism of homopolymer (PANI) catalyzed by Maghnite-H⁺ under microwave irradiation.

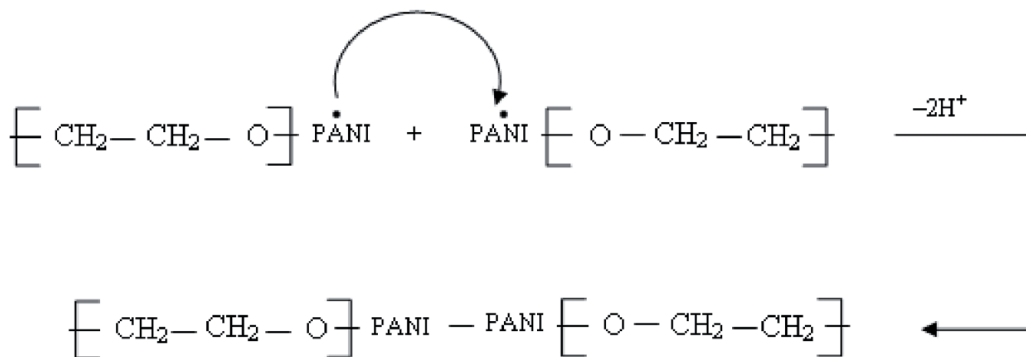
1-Initiation



2-Propagation



3-Termination

**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.

Acknowledgements

All work was supported by the DGRSDT of Algeria republic and was performed using the equipment of the center of research scientific and technics in analysis chemical and physical (CRAPC)-Tipaza-Algeria.

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References

- [1] Carini GD, Angelo G, Tripodo G, Bartolotta A, Di Marco G. Low temperature excess specific heat and fragility in semicrystalline polymers. *Physical Review B*. 1996;**54**:15056-15063
- [2] Brune DA, Bicerano J. Micromechanics of nanocomposites comparison of tensile and compressive elastic moduli, and prediction of effects of incomplete exfoliation and imperfect alignment on modulus. *Polymer*. 2002;**43**(2):369-387
- [3] Mac Diarmid A. Synthetic metals: a novel role for organic polymers. *Angewandte Chemie, International Edition*. 2001;**40**:2581-2590
- [4] Rajesh AT, Kumar D. Recent progress in the development of nanostructured conducting polymers/nanocomposites for sensor applications. *Sensors and Actuators B: Chemical*. 2009;**136**:275-286
- [5] Zhang LJ, Long YZ, Chen ZJ, Wan MX. The effect of hydrogen bonding on self assembled polyaniline nanostructures. *Advanced Functional Materials*. 2004;**14**:693-698
- [6] Park S, Chung SW, Mirkin CA. Hybrid organic-inorganic, rod-shaped nanoresistors and diodes. *Journal of the American Chemical Society*. 2004;**126**:11772-11773
- [7] Jaroslav S, Irina S, Miroslava T. Polyaniline nanostructures and the role of aniline oligomers in their formation. *Progress in Polymer Science*. 2010;**35**:1420
- [8] Zhang XY, Manohar SK. Polyaniline nanofibers: Chemical synthesis using surfactants. *Chemical Communications*. pubs.rsc.org. 2004:2360-2361
- [9] Ray S, Okamoto M. Polymer/layered silicate nanocomposites: A review from preparation to processing. *Progress in Polymer Science*. 2003;**28**(11):1539-1641
- [10] Rahmouni A, Harrane A, Belbachir M. ¹H-NMR spectra of conductive, anticorrosive and Soluble polyaniline exchanged by an eco-catalyst layered (Maghnite-H⁺). *wod. Journal of Chemistry*. 2013;**8**(1):20-26
- [11] Jang J. Conducting polymer nonmaterials and their applications. *Advances in Polymer Science*. 2006;**199**:189-259
- [12] Li X, Tian SJ, Ping Y, Kim DH, Knoll W. One-step route to the fabrication of highly porous polyaniline nanofiber films by using PS-b-PVP diblock copolymers. As templates. *Langmuir*. 2005;**21**:9393-9397
- [13] Long YZ, Duvail JL, Wang QT, Li MM, Gu CZ. Electronic transport through crossed conducting polymer nanowires. *Journal of Materials Research*. 2009;**24**:3018-3022
- [14] Johnson SD, Anderson JM, Marchant RE. Biocompatibility studies on plasma polymerized interface materials encompassing both hydrophobic and hydrophilic surfaces. *Journal of Biomedical Materials Research*. 1992;**26**:915-935
- [15] Raghunathan A, Kahol PK, Ho JC, Chen YY, Yao YD, Lin YS, et al. Low temperature heat capacities of polyaniline and polyaniline polymethylmethacrylate blends. *Physical Review B* 1998;**58**:15955-15958
- [16] Belbachir M, Bensaoula A. Composition and Method for Catalysis Using Bentonites. United States Patent Number: 6274527 B1. 2001
- [17] Belbachir M, Yahiaoui A, Hachemaoui A. An acid exchanged montmorillonite clay-catalyzed

synthesis of polyepichlorhydrin.
International Journal of Molecular
Sciences. 2003;**4**:548-561

[18] Kumar KV, Rao UVS. Thin solid electrolyte systems based on PEO and their application as an electrochemical cell. In: Proceedings of 2nd International Conference on Ionic Devices, 28-30th November. Chennai, India; 2003

[19] Choi HJ, Kim JW, Joo J, Kim BH. Synthesis and electrorheology of emulsion intercalated PANI-clay nanocomposite. Synthetic Metals. 2001;**121**(1-3):1325-1326

[20] Kuilla T, Bhadra S, Yao DH, Kim NH, Bose S, Lee JH. Recent advances in graphene based polymer composites. Progress in Polymer Science. 2010;**35**:1350-1375

[21] Spitalsky Z, Tasis D, Papagelis K, Galiotis C. Carbon nanotube polymer composites: Chemistry, processing, mechanical and electrical properties. Progress in Polymer Science. 2010;**35**:357-401

[22] Shin MK, Kim YJ, Kim SI, Kim SK, Lee H, Spinks GM, et al. Enhanced conductivity of aligned PANi/PEO/MWNT nanofibers by electro-spinning. Sensors and Actuators B: Chemical. 2008;**134**:122-126

[23] Pinto NJ, Johnson AT, Mueller CH, Theofylaktos N, Robinson DC, Miranda FA. Electrospun polyaniline/polyethylene oxide nanofiber field-effect transistor. Applied Physics Letters. 2003;**83**:4244-4246

[24] Yang R, Shichao Z, Lan Z, Wenbo L. Electrical properties of composite polymer electrolytes based on PEO-SN-LiCF₃SO₃. International Journal of Electrochemical Science. 2013;**8**:10163

[25] Devindrappa HU, Subba R, Ambika P. Study of dc conductivity and battery application of PEO/PANI

Composites. Journal of Power Sources. 2006;**155**:3689

[26] Kunteppa H et al. AC conductivity and battery application of polyethylene oxide/PANI/ sodium chlorate composites. Advanced Materials Letters. 2013;**11**:856

[27] Gray KB, Rodrigues SJ. Poly (ethyleneoxide)-based composite electrolytes: Crystalline amorphous transition. Journal of the Electrochemical Society. 2001;**148**:1336

[28] Sujeet KC, Rajendra KS. Electrical conductivity studies on composite polymer electrolyte based on ionic liquid. Phase Transitions. 2010;**83**:457

[29] Rahmouni A, Harrane A, Belbachir M. Thermally stable forms of pure polyaniline catalyzed by an acid-exchanged MMT clay called maghnite-H⁺ as an effective catalyst. International Journal of Polymer Science. 2012;**2012**:846710, 7 p. DOI: 10.1155/2012/846710,2012

[30] Belbachir M, Bensaoula A. Composition and method for catalysis using bentonites. US Patent No. 7, 094-823 B2. 2006

[31] Megherbi A, Meghabar R, Belbachir M. Preparation and characterization of clay (Maghnite-H)/ poly (3,4-ethylenedioxythiophene) composites. Journal of Surface Engineering Materials and Advanced Technology. 2013;**3**:21-27

[32] Olad A, Rashidzadeh A. Preparation and anticorrosive properties of PANI/Na-MMT and PANI/OMMT nanocomposites. Progress in Organic Coating. 2008;**622**:93

[33] Norris ID, Shaker MM, Ko FK, Macdiarmid AG. Electrostatic fabrication of ultrafine conducting fibers: Polyaniline/polyethylene

oxide blends. *Synthetic Metals*. 2000;**114**(2):109-114

[34] Yahiaoui A, Hachemaoui A, Belbachir M. Synthesis and structural analyses of poly (1, 2-cyclohexene oxide) over solid acid catalyst. *International Journal of Molecular Sciences*. 2003;**4**:548-561

[35] Yahiaoui A, Belbachir M, Hachemaoui A. *International Journal of Molecular Sciences*. 2003;**4**:548-561

[36] Li Q, Cruz L, Phillips P. Granular-rod model for electronic conduction in polyaniline. *Physical Review B*. 1993;**47**:1840-1845

[37] Wright PV. Electrical conductivity in ionic complexes of poly(ethylene oxide). *British Polymer Journal*. 1975;**7**:319

[38] Kherroub DE, Belbachir M, Lamouri S. Nylon 6/clay nanocomposites prepared with Algerian modified clay (12-maghnite). *Research on Chemical Intermediates*. 2015;**41**:5217-5228

[39] Nascimento GM, Temperini ML. Structure of polyaniline formed in different inorganic porous materials: A spectroscopic study. *European Polymer Journal*. 2008;**44**:3501

[40] Zhang L, Zujovic ZD, Peng H, Bowmaker GA, Kilmartin PA, Travas-Sejdic J. Structural characteristics of polyaniline nanotubes synthesized from different buffer solutions. *Macromolecules*. 2008;**41**:8877-8884

[41] Rahmouni A, Harrane A, Belbachir M. Kinetics study of cationic polymerization of aniline catalyzed by Maghnite-Na clay catalyst layered (Western Algeria). *World Journal of Nano Science & Technology*. 2012;**1**(2):26-32

[42] Ayat M, Rahmouni A, Belbachir M. Methyl methacrylate and alpha-methyl styrene: New strategy for synthesis of bloc copolymers for use in potential biomedical applications generated by an ecologic catalyst called maghnite (Algerian MMT). *Bulletin of Chemical Reaction Engineering and Catalysis*. 2016;**11**:316-329

[43] Rahmouni A, Belbachir M. Green synthesis of cationic polyacrylamide composite catalyzed by an ecologically catalyst clay called maghnite-H⁺ (Algerian MMT) under microwave irradiation. *Bulletin of Chemical Reaction Engineering and Catalysis*. 2016;**11**:170-175

[44] Kao HM, Tsai YY, Chao SW. Functionalized mesoporous silica MCM-41 in poly (ethyleneoxide)-based polymer electrolytes: NMR and conductivity study. *Solid State Ionics*. 2005;**176**:1261-1270

[45] Xia JY, Qiu XP, Ma XM, Cui MZ, Yang J, Tang XZ, et al. Composite polymer electrolyte doped with mesoporous silica SBA-15 for lithium polymer battery. *Solid State Ionics*. 2005;**176**:1249-1260

[46] Xi JY, Tang XJ. Enhanced lithium ion transfer number and ionic conductivity of composite polymer electrolyte doped with inorganic-inorganic hybrid P123@SBA-15. *Chemical Physics Letters*. 2004;**400**:68-73

[47] Tominaga Y, Hong IC, Asai S, Sumita M. Proton conduction in Nafion composite membranes filled with mesoporous silica. *Journal of Power Sources*. 2007;**171**:530-534

[48] Gao Q, Xu Y, Wu D, Sun Y, Li XA. PH-responsive drug release from polymer-coated mesoporous silica spheres. *Journal of Physical Chemistry C*. 2009;**113**:12753-12758

[49] Chu HQ, Yu C, Wan Y, Zhao DY. Synthesis of ordered mesoporous

- bifunctional TiO₂- SiO₂-polymer nanocomposites. *Journal of Materials Chemistry*. 2009;**19**:8610-8618
- [50] Praveen S, Sun ZF, Xu JG, Patel A, Wei Y, Ranade R, et al. Compression and aging properties of experimental dental composites containing mesoporous silica as fillers. *Molecular Crystals and Liquid Crystals*. 2006;**448**:223-231
- [51] Jiao J, Sun X, Pinnavaia TJ. Reinforcement of a rubbery epoxy polymer by meso structured silica and organo silica with wormhole framework structures. *Advanced Functional Materials*. 2008;**18**:1067-1074
- [52] Gayon E, Debleds O, Nicouveau M, Lamaty F, Van der Lee A, Vrancken E, et al. Transition-metal-catalyzed uninterrupted four-step sequence to access trisubstituted isoxazoles. *The Journal of Organic Chemistry*. 2010;**75**:6050
- [53] Fioravanit S, Morreale A, Pellacani L, Tardella PA. *Tetrahedron Letters*. 2003;**44**:3031
- [54] Chakraborty B, Sharma PK, Chhetri MS. *Journal of Heterocyclic Chemistry*. 2012;**49**(5):1260
- [55] De Vitis L, Florio S, Granito C, Ronzini L, Troisi L, Capriati V, et al. Experimental Crystal Structure determination. *Tetrahedron*. 2004;**60**:1175
- [56] Padwa A. In: Katritzky AR, editor. *Comprehensive Heterocyclic Chemistry*. Vol. III. Amsterdam: Elsevier; 2008. pp. 1-97
- [57] Bergmeier SC, Katz SJ, Huang J, McPherson H, Donoghue PJ, Reed DD. *Tetrahedron Letters*. 2004;**45**:5011
- [58] Hodgson DM, Stefane B, Miles TJ, Witherington J. Unsaturated 1,2-amino alcohols and ethers from aziridines and organolithiums. *Journal of the Chemical Society, Chemical Communications*. 2004:2234
- [59] Pourjavadi A, Soleyman R, Bardajee GR. Novel superabsorbent Hydrogel Based on natural hybrid backbone: Optimized synthesis and its swelling behavior. *Bulletin of the Korean Chemical Society*. 2009;**30**:2680-2686
- [60] Danks TN. Microwave assisted synthesis of pyrroles. *Tetrahedron Letters*. 1999;**40**:3957-3960
- [61] Ganji F, Vasheghani-Farahani S, Vasheghani-Farahani E. Theoretical description of hydrogel swelling: A review. *Iranian Polymer Journal*. 2010;**19**:375-398