Molecular structure of PANI and its homologue PANI–PEO₂₀₀₀ catalyzed by Maghnite-H⁺ (Algerian MMT): synthesis, characterization and physical and chemical properties

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Abstract

The homopolymer (PANI) and its homologue PANI–PEO₂₀₀₀ copolymer have been prepared under effect of Maghnite-H⁺ (Algerian MMT) in different weight percentages (wt%) by cationic polymerization method. The formation of the hydrogen bonding between PANI and PEO₂₀₀₀ and structure of PANI are predicted by the FT-IR and ¹HNMR spectra. Glass transition temperature of pure PANI and pure PEO₂₀₀₀ are, respectively, $T_g = 74\text{ }^{\circ}\text{C}$ and $T_g = 65\text{ }^{\circ}\text{C}$, but DSC analysis for the copolymer (PANI–PEO₂₀₀₀) showed only one ($T_g = 16.79\text{ }^{\circ}\text{C}$) implying compatibility of PANI and PEO₂₀₀₀. Here we can suggest that under suitable condition (the amount of catalyst, molecular weight and functionality of the reactive stabilizer (PEO₂₀₀₀) and molar ratio of (PANI/PEO₂₀₀₀), our catalyst can improve the morphology, structure and chemical properties of PANI and its homologue PANI–PEO₂₀₀₀.

Keywords Green catalyst · Conducting polymer · Polyaniline · Maghnite-H⁺ · DSC · ¹HNMR spectroscopy · PEO · GPC

Introduction

Clay minerals especially the members of smectite group are the most suitable candidates for synthesis of polymer nanocomposites [1], because these possess a unique structure and reactivity together with high strength [2]. In general, the structures of polymer/clay nanocomposites are classified according to the level of intercalation and exfoliation of polymer chains into the clay galleries [3]. Various parameters including clay nature, organic modifier and polymer matrix and preparation method

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are affective on the intercalation and exfoliation level [4]. Therefore, depending on the nature and properties of clay and polymer as well as preparation methodology of nanocomposites, different composite microstructures can be obtained [5]. For commercial applications, PANI homopolymer and its homologue (PANI-PEO) are the best promising materials in conducting polymers, because of environmental stability [6], easy processing [7] and economical efficiency [8]. PANI has been used for electrode of light emitting diode [9], Li-ion rechargeable battery [10] and corrosion protection [2]. Polymer electrolytes have received considerable attention due to their potential uses in solid-state electrochemical devices and particularly in lithium batteries [11]. Nowadays the efforts are on the addition of plasticizers to the polymer electrolytes for improving their ionic conductivity [12]. In some cases, a large amount of plasticizers is required to dissolve the salts, and the materials are referred to as polymer gel electrolytes [13]. Among organic–inorganic nanocomposites, PANI–MMT and PANI–PEO–MMT nanocomposites are the most prevalent and interesting due to the special properties as well as wide uses of polyaniline [14], the nature, abundance, low cost of MMT and attractive features such as a large surface area and ion-exchange properties [15]. The clay, which has been used as catalyst, is supplied by a local company known as ENOF Maghnia (Western of Algeria) [16]. The greatest proton saturation of the <2 mm fractions of clay was obtained by first saturating with Na⁺ ions using 1 M NaCl solution, then the protonated forms of montmorillonite (Mag-H⁺) were prepared by shaking the clay in a solution of sulfuric acid 0.25 M until saturation was achieved (normally after 2 days at room temperature) [17]. 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 and 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 were found to be 84 mEq (100 g⁻¹) of dried clay and 786 m² g⁻¹, respectively [18].

However, traditional polymerization techniques show some practical disadvantages (e.g., requirement for extremely pure reagents, low functional group tolerance, limited combination with other monomers or polymer segments). It has long been known that molecules undergo excitation with electromagnetic radiation. This effect is utilized in household microwave ovens to heat up food. However, chemists have only been using microwaves as a reaction methodology for a few years. Some of the first examples gave amazing results, which led to a flood of interest in microwave-accelerated synthesis. Microwave heating has been found to be particularly advantageous for reactions under “dry” media. Enormous accelerations in reaction time can be obtained if overheating is carried out in closed containers under high pressure; a reaction which takes several hours under conventional conditions can be completed in a few minutes; in addition in the absence of solvent on a solid support with or without a catalyst, it offers a certain number of advantages: the solvents are often expensive, toxic and difficult in the case of high-boiling aprotic solvents [19]. Moreover, the absence of solvent reduces the risk of explosions when reaction takes place in a microwave oven [20]. Reactions under “dry” conditions were originally developed in the late eighties [21]. Synthesis without solvents under microwave irradiation offers several advantages [22]. The absence of solvent reduces the

risk of explosions when the reaction takes place in a closed vessel in an oven [23]. Moreover, aprotic dipolar solvents with high boiling points are expensive and difficult to remove from the reaction mixtures [24]. During microwave induction of reactions under dry conditions, the reactants are adsorbed on the surface of alumina, silica gel and clay [25]. Consequently, such supported reagents efficiently induce reactions under safe and simple conditions with domestic microwave ovens instead of specialized expensive commercial microwave systems [26]. Many researchers have studied cationic polymerization of polyaniline using “H₂O”/KPS initiator system and CH₂Cl₂ solvent [27, 28]. Frequently, these initiators require the use of very high or very low temperature and high pressures during the polymerization reaction. The separation of the initiators from the polymer is not always possible. Therefore, the presence of toxic initiators presents problems in the manufacture of polymers used especially in medical and veterinary procedures. The purpose of this paper is to study the polymerization of aniline and its homologue block copolymer PANI–PEO catalyzed by Maghnite-H⁺ as proton exchanged montmorillonite clay under microwave irradiation. This new non-toxic cationic catalyst has exhibited higher efficiency via the polymerization of vinylic and heterocyclic monomers [29, 30]. This catalyst can be easily separated from the polymer product and regenerated by heating at a temperature above 100 °C [9]. The effects of different synthesis parameters, such as the amount of Maghnite-H⁺, the molar ratio (aniline/PEO) and reaction time, on the yield of polymerization are discussed together with the mechanism of polymerization.

Experimental

Microwave apparatus

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. Temperature in the system was measured by a fiber optic temperature sensor preventing interaction with MWs and influence on the temperature reading. The heat capacity *C_p* of the solution was approximated as the heat capacity of water. All experiments were done under the same conditions by keeping constant irradiation power, temperature and the initial reaction mixture volume (12 mL). With the experimental design that was used, the temperature was maintained at 160 °C in all experiments.

Materials and methods

Polyaniline (PANI) was prepared in our laboratory (laboratory of polymers chemistry, Oran University, Algeria) by standard chemical intercalated method [31]. Polyethylene oxide (relative molecular mass of 2×10^3) was obtained from Sigma Aldrich. MMT clay was obtained from ENOF Maghnia (Algeria). The MMT-H⁺ (Mag-H⁺) was prepared as described by Belbachir et al. [32], and water (pH < 7) was used to

synthesize emeraldine salt clay (PANI/Mag-H+) by cationic polymerization. Some of the emeraldine base (PANI-EB), non-conducting form of polyaniline, was prepared by de-protonating PANI-ES in NaOH solution (0.5 M). A doping EB was carried out in aqueous medium of hydrochloric acid (1 M). The emeraldine base (50 mg) is doped and dissolved in (100 ml) of (2 M) HCl. For 2 h and the same time (PEO), 10 mg dissolving matrix (PEO) with (PANI) thin films of conducting polymer alloys PANI-PEO₂₀₀₀ is prepared by mixed different volume ratio of PANI with PEO₂₀₀₀ [33].

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 (FT-IR) spectra were obtained between 900 and 4000 cm⁻¹ on an ATI Matson FT-IR 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 Semantic). 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 was carried out by dissolving the product in chloroform (CHCl₃) and filtering to eliminate the Maghnite-H+. Then, chloroform was removed by evaporation.

Preparation of catalyst (Maghnite-Na+)

The montmorillonite used in this work came from a quarry located in Maghnia (North West of Algeria) and was supplied by company “ENOF” (an Algerian manufacture specialized in the production of nonferrous products and useful substances). The different chemical elements of the native montmorillonite were transformed into oxides and analyzed by FT-IR and X-ray fluorescence (experiment carried out at ENOF). These results confirm that the maghnite used consists essentially of montmorillonite (MMT) and has been prepared in laboratory chemistry of polymers in ORAN University (LCPO), and this clay is purified by separation of the argillaceous phase and the coarse phases. Rough clay is put in suspension in distilled water. In the suspension, the solid/liquid report/ratio is approximately 1/10. The suspension is then filtered on a sieve 0.02 mm in diameter of pores to eliminate the coarse matter and stones. It then versed in test tubes and is left at rest during 2 h. The separation of the argillaceous phase of the coarse fraction which remains at the bottom is made by siphonage. The recovered suspension is then centrifuged with 4500 tr/min during

20 min. Recovered clay is treated with a solution 1 M of sodium hexametaphosphate ($\text{NaPO}_3)_6$ (clay 20 g in 100 ml), by maintaining agitation, during 3 h. The suspension is versed then in the test tubes of separation and Na-montmorillonite is to separate while exploiting its falling speed, MMT crosses with 20 °C, a distance of 10 cm each 8 h. Therefore, Na-montmorillonite is recovered by siphonage at a distance of 20 cm after 16 h of decantation. One adds water distilled to the test tubes. After each siphonage, one agitates during 15 min and one lets the suspension be elutriated before proceeding to new a siphonage. MMT is then recovered by centrifugation with 4500 tr/min during 1 h. With the end, it is washed with distilled water (on several occasions), filtered using one sintered of porosity 3 (maximum diameter of pores from 16 to 40 μm), dried in the drying oven with 105 °C, crushed using a mortar and kept in a desiccators [33, 34].

Preparation of catalyst (Maghnite-H⁺)

The Maghnite-H⁺ was prepared according to the process similar to that described by Belbachir et al. [29, 35]. 30 g of raw maghnite was crushed for 20 min using a pro-labo ceramic balls grinder. The maghnite was placed in an Erlenmeyer flask together with 100 ml of distilled water and then stirred using a magnetic stirrer for 2 h at room temperature, a solution of sulfuric acid 0.25 M was added to the mixture and stirred over 2 days at room temperature until saturation was achieved, the mineral was then washed with distilled water up to pH 7. After filtration, the activated maghnite is dried in the stove for 24 h at 105 °C.

Synthesis of PANI composite

A solution of 0.25 M of sulfuric acid (H_2SO_4) was prepared and (5 wt%) of Maghnite-Na⁺ (Algerian MMT) was then added. The mixture of (Maghnite-Na⁺ and H_2SO_4) was put into a flask with 100 mL and stirred to allow proper mixing. To this end, adequate amount of aniline (ranging from 0.05 mol) was added to a solution of maghnite and sulfuric acid (0.25 M in 25 mL of distilled water) under vigorous stirring. The reaction mixture was then submitted to microwave irradiation at 160 °C and for 4 min. The mixture was cooled (5–10 min at room temperature), filtered and washed extensively with distilled water and methanol to remove maghnite and any unreacted aniline until the washing solution became neutral and air-dried.

Synthesis of copolymer PANI–PEO

We aim to prepare PANI–PEO, with different PEO weights (400, 2000 and 30.000 g/mol) starting from aniline in an acid medium. To this end, adequate amount of aniline (ranging from 0.05 mol) is added to a solution of PEO (0.05 g in 25 mL of distilled water) under vigorous stirring. Then, 5 wt% of Maghnite-H⁺ as an initiator was added to the above solution. The mixture was stirred for 15 min. Then it is treated in a microwave oven at the power of 950 W. Temperature and viscosity of the

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

Fig. 1 FT-IR spectra of polyaniline (PANI) obtained by the intercalated method between aniline and Maghnite-H⁺ (black powder) at 160 °C

reactive mixture increase fast. The gelation point is reached after 4 min at 160 °C and a recognizable odor (Scheme 1).

Results and discussion

Spectroscopy characterization

Figure 1 shows the FT-IR 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 quinonering, 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 at 694–593 cm^{-1} corresponds to aromatic ring and 507 cm^{-1} is stretching at out of the plane. In pure PEO₂₀₀₀ spectrum, a large broad band appears centered at 3442 cm^{-1} which is due to the hydration of PEO₂₀₀₀ which confirms that PEO₂₀₀₀ is highly hydrophilic and gets hydrated. Thus, pure PEO₂₀₀₀ shows a large broad band of CH₂

stretching between 2950 and 2840 cm^{-1} . It is also been observed that CH_2 vibration of all modes appear in PEO_{2000} at 1467 cm^{-1} which corresponds to asymmetric CH_2 bending and 1344 cm^{-1} which corresponds to symmetric CH_2 wagging [36].

The infrared spectra for PANI– PEO_{2000} copolymer is also shown in Fig. 2. There are significant changes in both the intensities and the frequencies in the product (PANI– PEO_{2000}). They 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 [37].

The ^1H NMR spectral of the PANI homopolymer polymer exhibits strongest sharp peaks centered at 7 ppm and 7.8 ppm due to protons from phenylene and disubstituted phenylene units, the weak peak at 4.81 ppm and medium broad peak at 6.22 ppm due to (–NH– and – NH_2) end group, respectively, another broad peaks centered at 1.78 and 8 ppm may be due to the water protons bonded by (–NH– and – NH_2) groups and (H–N^+), respectively, as show in Fig. 3 [33].

An investigation was devoted to the analysis of the polyethylene oxide (PEO_{2000}) by ^1H NMR spectroscopy at 300 MHz (Fig. 4). According to the work published by Yahiaoui et al. [38], ^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 copolymer (PANI– PEO_{2000}), a wide signal in the region of 6.8–8 ppm was assigned to benzenoid hydrogen of polyaniline [39]. Three peaks in these region were assigned to para position of polyaniline linked for the polymerization. Signals at 3.25–3.75 ppm indicate peak of CH_2O – and $\text{CH}_2\text{CH}_2\text{O}$ – hydrogen of polyethylene oxide reported [40]. Peak at 1.5–2 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_{2000} appeared at 4.25 ppm, to note that the chemical displacement of this peek was changed from polyaniline (4.81 ppm) to PANI– PEO_{2000} copolymer (4.25 ppm) which shows the copolymerization of PANI and PEO_{2000} (Fig. 5) [41].

Fig. 2 FT-IR spectra of block copolymer (PANI– PEO_{2000}) obtained by the intercalated method between aniline, polyethylene oxide and Maghnite-H+ (black powder) at 160 °C

Fig. 3 ^1H NMR spectra of (PANI) obtained by the intercalated method between aniline and Maghnite-H+ (black powder) at 160 °C

Fig. 4 ^1H NMR spectra of pure polyethylene oxide (PEO₂₀₀₀)

Optical properties

Conductive polymers (PANI and PANI-PEO₂₀₀₀) 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 [42]. The UV–visible spectral peak in the 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 350–400 nm regions (Fig. 6).

Fig. 5 ^1H NMR spectra of the copolymer (PANI-PEO₂₀₀₀) obtained by the intercalated method between aniline, PEO₂₀₀₀ and Maghnite-H+ (black powder) at 160 °C

Fig. 6 UV spectral of the different form of (PANI-PEOs)

Thermophysical properties

Thermal stability of polyaniline/maghnite and polyaniline/PEO/maghnite composites of different composition has been analyzed and compared with that of pure PANI.

(A) *Thermal analysis of Maghnite-H+* The thermal characterization of the composites includes thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

Fig. 7 DSC measurements of Maghnite-H+ (heating rate 10 °C/mn)

Fig. 8 TGA curves of a Maghnite-H⁺ obtained in nitrogen atmosphere at heating rate of 10 °C/min

Weight losses (%) versus temperature (°C) curves for pure Maghnite-H⁺ are shown in Fig. 7. TGA of pure Maghnite-H⁺ shows two stages of weight loss. The first weight loss in maghnite below 100 °C is a result of the release of free water. The second weight loss around 600 °C is associated with the dehydroxylation of silicate structure [43]. The total weight loss is only 13.94% up to 800 °C. As can be expected, Maghnite-H⁺ shows a high thermal stability (Fig. 8).

(B) *Thermal analysis of PANI* The TGA thermogram of the polyaniline (PANI) at a heating rate of 10 °C/min in nitrogen is shown in Fig. 9. It can be found that at the temperature range of 187–600 °C the weight loss amounted to 61, 17%, which can be reasonably attributed to the weight loss of the polymerized polyaniline (PANI) and to thermal decomposition of the polyaniline chains [44]. Polyaniline is known to be a hygroscopic polymer [45]. Some authors assigned the endothermic effect registered by DSC in the range from ambient temperature up to approximately 120 °C to the evaporation of water.

Figure 10 is the DSC thermogram of the PANI powder in the first run and second run. In the first run, there were two endothermic peaks at 55.99 and 103.46 °C and the PANI had discernible moisture content [46]. Therefore, these endothermic peaks were most likely due to the evaporation of water. This was in agreement with the TGA results [47]. In the second run, there were almost no significant endothermic or exothermic peaks, as shown in Fig. 10, because no apparent moisture existed in the sample but T_g appears at 74.06 °C [48].

(C) *Thermophysical properties of PANI-PEO₂₀₀₀* were studied by TGA, TDA and DSC The weight loss (%) was recorded as function of temperature for both PANI and PEO₂₀₀₀ 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 °C/min. The curves of weight loss versus temperature showing the behavior of PANI-PEO₂₀₀₀ sample are presented in Fig. 11. The first significant weight loss occurs already at temperature between 50 and 100 °C. It is known that PANI-PEO₂₀₀₀ is hygroscopic and during the heating to 100 °C the residual water evaporates [49]. Then the main mass loss, which corresponds to polymer degradation, starts at about 200 °C and 500 °C [50].

Thermal behavior of pure PANI and PANI-PEO₂₀₀₀ was also verified by differential scanning calorimetry in which the first and second scans are shown in

Fig. 9 TGA curves of PANI prepared in the presence of Maghnite-H+ (0.25 M)

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

Fig. 11 TGA curves of PANI-PEO₂₀₀₀ prepared in the presence of Maghnite-H+ (0.25 M)

Fig. 12 DSC measurements of PANI-PEO₂₀₀₀ (heating rate 10 °C/mn)

(Fig. 12). The first scan gives very little information on the thermal behavior of the homopolymer and copolymer. First we notice the presence of an endothermic effect (68.39 °C and 190.09 °C), the first is associated to the evaporation of water absorbed by the copolymer and the second for melting POE₂₀₀₀ block [51]. These second scanning will foresee it no effect on this temperature range, because the copolymer was heated to 280 °C, which facilitates the onset of glass

Table 1 Thermodynamics properties of PANI and its homologue PANI-PEO₂₀₀₀

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

T (°C), ΔH (J/g) and ΔC_p (J/g °C)

Fig. 13 GPC chromatogram of PANI with 5% Maghnite-H+ at 160 °C for 4 in; number-average molecular weight=644 g/mol, weight-average molecular weight=746 g/mol and polydispersity=1.15

Fig. 14 GPC chromatogram of PANI-PEO₂₀₀₀ with 5% Maghnite-H+ at 160 °C for 4 min, number-average molecular weight=2641 g/mol, weight-average molecular weight=2701 g/mol and polydispersity=1.01

transition temperature ($T_g = 16.79$ °C) which is in agreement with the literature [52] (Table 1).

Results of GPC

Gel permeation chromatography was performed with a Spectra-Physics chromatograph, equipped with four columns connected in series and packed with Ultrastyrigel

Table 2 GPC of homopolymer PANI composite in THF

Sample name	RT	Area	% Area	M_n	M_w	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 3 GPC of copolymer PANI–PEO₂₀₀₀ composite in THF

Sample name	RT	Area	% Area	M_n	M_w	Polydispersity
PANI–PEO ₂₀₀₀	17.917	130,748	1.30	2664	2701	1.013,896
	23.032	9,960,549	98.70	50	264	5.342,141

103, 104, 105, 106A°, tetrahydrofuran (THF) was used as solvent and the instrument was calibrated to a first approximation with polystyrene of known molecular weights. The GPC curves for PANI and PANI–PEO indicate a bimodal distribution. The molecular weight distribution averages for the polymer and its homologue copolymer are presented in Tables 2, 3 and Figs. 13, 14. This bimodal distribution has been reported previously for PANI in (NMP) [53] and of PANI–PEO₂₀₀₀ in (DMSO) [54]. The molecular weight of the polymer shows the growth of PANI on PAN–maghnite. The gel permeation chromatograph (GPC) measurements of the product are in a good agreement with the PANI and poly(PANI–PEO) structure. The macromolecular weight distribution of the obtained polymer and copolymer is narrow, and this suggests that chain transfer does not occur confirming the formation of the polymer PANI and the block copolymer PANI–PEO (Table 4).

Conductivity measurement

The electrical conductivity was measured by the four-point method. Four points aligned and spaced in the same distance are applied by simple pressure on the sample. A current I is injected through the outer tips with a current source, thus creating a potential variation. Voltage U can be measured between two points connected to internal voltmeter [18, 19]. The measured value of the transverse strength of the PANI and its homologue PANI–PEO₂₀₀₀ are converted to volume resistivity, using Eq. (1) [55] and then the electrical conductivity is calculated from Eq. (2) [56]. In applying these equations, the value of (σ) is presented in the following Table 5:

$$\rho = R (\pi \cdot r^2 / e) (\Omega \text{ cm}) \quad (1)$$

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

Table 4 Results of electrical conductivity of PANI and its homologue PANI–PEO₂₀₀₀

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 5 Solubility of PANI and PANI-PEO₂₀₀₀ composites in different solvents (g/100 mL)

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

Fig. 15 UV spectral of the copolymer (PANI-PEO₂₀₀₀) in different solvents

Solubility study

Solubility of PANI and PANI-PEO₂₀₀₀ composites was determined in a number of organic solvents (see Table 5 and Fig. 15). The composites in powder form were added to 100 mL of each solvent including: DMF, acetonitrile, toluene, dichloromethane, THF and chloroform and stirred for 1 h before filtering. The dry weight of the filter paper was used to calculate the solubility of the composites. It was found that PANI and its homologue PANI-PEO₂₀₀₀ composites are relatively soluble in all above-mentioned solvents [57, 58]. The best solvents for PANI and its homologue are determined to be DMF and toluene. By UV-vis spectra, on taking the soluble PANI and PANI-PEO₂₀₀₀ in various solvents, we can calculate the band of energy by this equation.

$$\Delta E = h\nu = hc/\lambda$$

The solubility parameter (δ) is usually expressed in (cal/cm³)^{1/2} or preferably (J/cm³)^{1/2} units for many compound and is defined from Hildebrand-Scotchard solution theory as:

Table 6 Viscosimetric properties of pure PANI

Concentration	C(0)	2C/3	C/2	C/3	C/4
Average	3.60	3.60	3.60	3.60	3.59
Cinema (cst)	0.61	0.60	0.60	0.60	0.6
Dynamic (cp)	0.90	0.90	0.90	0.89	0.89
Relative	1.01	1.01	1.01	1.00	1
Specific	0.01	0.00	0.01	0.00	0
Reduced	12.20	13.98	19.46	20.95	22.43
Inhérent	12.13	13.91	19.46	20.95	22.43
Solomon	12.15	13.93	19.49	20.97	22.45
Visct. Intr (ml/g ⁻¹)	25.83		25.76		25.78

Table 7 Viscosimetric properties of PANI–PEO₂₀₀₀

Concentration	C(0)	2C/3	C/2	C/3	C/4
Average	3.60	3.60	3.60	3.60	3.59
Cinema (cst)	0.61	0.61	0.61	0.60	0.60
Dynamic (cp)	0.90	0.90	0.90	0.89	0.89
Relative	1.01	1.01	1.01	1.00	1.00
Specific	0.01	0.01	0.01	0.00	0.00
Reduced	7.48	12.12	14.38	13.54	18.04
Inhérent	7.44	12.04	14.29	13.49	17.98
Solomon	7.45	12.06	14.32	13.50	18.00
Visct. Intr (ml/g ⁻¹)	19.74		19.67		19.69

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

Viscosity measurements

Viscosity measurements were carried out with an Ubbelohde capillary viscosimeter (viscologic TII, 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: $[\eta] \text{ (mg l}^{-1}\text{)} = K [M]^a$. Intrinsic viscosity and physical properties of PANI and PANI–PEO₂₀₀₀ are shown in Tables 6 and 7.

Kinetics studies

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

Fig. 16 Effect of the amount of Mag-H+ (catalyst) on the yield of copolymerization. Maghnite-H+ = 5 wt%, $t = 4$ min, aniline = $0.55 \cdot 10^{-1}$ mol and PEO = 0.25×10^{-4} mol

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

Effect of the amount of Mag-H+ on the yield

Copolymerization of polyaniline by poly(ethylene oxide) induced by the Mag-H+ was carried without solvent under the effect of the microwave irradiation. Figure 9 shows the effect of the amount of catalyst on the yield of this copolymerization. As can be seen in this Fig. 16, 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. These results clearly indicate that the optimum conditions of these reactions are 160 °C and 5% by molecular weight of the catalyst. 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 Ferrahi et al. [56, 59].

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 molecular weight of copolymer PANI–PEO. We have used (2%, 5% and 10%) by weight as the amount of maghnite and varying time after keeping the other parameters (the amount of monomers and the temperature). The percentage by weight of Maghnite-H+/monomer is 5%. It is observed that the average molecular weight increases with time and reaches a maximum at 4 min of reaction (Fig. 10).

Fig. 17 Effect of the amount of Mag-H+ on the viscosimetric molecular weight of copolymerization

There is also increase in molecular weight, between 2.5 and 3.5 min and decrease from 4 min. 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 [60].

Effect of molar ratio aniline/PEO on the yield

As all the reactions were carried out in solution, it was interested to study the effect of molar ratio on the copolymerization of aniline/PEO. Under the experimental conditions (160 °C, 4 min), we used a series of aniline/PEO and maintaining the amount of the Mag-H+ (2 wt%, 5 wt% and 10 wt%), the time (4 min). All reactions were held in a temperature (160 °C) under microwave irradiation. Figure 11 summarizes the influence of the molar ratio on aniline/PEO upon the reaction yield. 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. Figure 11 shows that the yield decreases as amount of poly(ethylene oxide) increases. This result shows that increasing the amount of poly(ethylene oxide) water equivalent gave fewer yields. This phenomenon can explain by the high reactivity and solubility of the POE in water compared to the aniline in particular at high temperature [61].

Fig. 18 Effect of molar ratio (ANI/PEO) upon the yield of chemical transformation (Maghnite-H+=2, 5 and 10 wt%, temperature 160 °C and time (4 min)

Fig. 19 Effect of temperature on the yield of copolymerization. Maghnite-H+=5%, $t=4$ min, aniline= 0.55×10^{-1} mol, PEO= 0.25×10^{-4} mol

Fig. 20 Proposed mechanism of homopolymer (PANI) catalyzed by Maghnite-H⁺ at 160 °C. **1** Initiation—the mechanism of the reaction occurs within the layers of the maghnite exchanged by H⁺ protons, which are capable of initiating cationic polymerization. **2** Propagation—propagation is by the successive addition of monomers on the chain macromere growing. **3** Termination—the termination takes place during the recombination of two radical ions giving rise to the final polymer

Proposed mechanism of polymerization and copolymerization

In the present study, the process of synthesis of PANI–Maghnite-H⁺ and its homologue PANI–PEO₂₀₀₀–Maghnite-H⁺ composites can be divided into the following three steps as shown in Figs. 16, 17, 18, 19, 20 and 21.

Conclusion

Formation of PANI–PEO inside the maghnite (Algerian MMT) has been confirmed by HNMR spectroscopy. Infrared spectroscopy studies reveal the presence of physicochemical interaction, probably hydrogen bonding, between MMT, PANI and PEO. From the TGA result, it is observed that weight loss of PANI–MMT and PANI–PEO/MMT composite is less compared to pure PANI.

1

2

3

Fig. 21 Proposed mechanism of copolymer (PANI-PEO₂₀₀₀) catalyzed by Maghnite-H⁺. **1** Initiation. **2** Propagation. **3** Termination

In conclusion, PANI-maghnite and PANI-PEO₂₀₀₀-maghnite copolymers were successfully polymerized by chemical method under effect of ecological catalyst called Maghnite-H⁺ (Algerian MMT). In this present work, authors have carried out the green copolymer of polyaniline by poly(ethylene oxide) based on Maghnite-H⁺ (Algerian ecologic catalyst MMT) under microwave irradiation. This copolymer was prepared in order to combine the mechanical and physical properties of PEO₂₀₀₀ with conducting properties of PANI. The kinetics studies indicated that the polymerization and copolymerization rates are first order with respect to monomer concentration. A possible mechanism of this cationic polymerization is discussed based on the results of the ¹H NMR. Spectroscopic analysis is of these model reactions. Thus, all the two types of composites provide opportunities and rewards creating new worldwide interest in these new materials.

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