

The effect of the direct self curling polymerization on the thermal and structural properties of the Polyaniline doped by unsaturated carboxylic acid

N. Naar^{1*}, M. Satouh¹, A. M. Zerrouk¹, A. Benaboura¹

¹ Macromolecular Laboratory Of Synthesis And Macromolucular Thio-Organics, University of Science and Technology Houari Boumediene ; Faculty of Chemistry BP 32 El Alia Bab- Ezzouar 16111 Algiers, Algeria

Abstract. The polyaniline is a polymer used as electric charge in the thermoplastic composite polymers intended to the electrostatic charges absorption. In this work, we propose two synthesis in order to improve the electrical and structural properties of this charge using a self curling process polymerization in one step. In this considered work, two doping agents containing the combined and unsaturated functioned carboxylic acids (cinnamic acid and crotonic acid) were used. These doping agents were not cited in the other work in the litterature. Several methods of analysis were used to characterize the obtained samples (FTIR, DSC, DRX, and electric conductivity). The presence of ethanol as surfactant agent ensured a micellar dispersion. As result, a good intra and intermolecular rearrangement in the obtained structures with an important electrical conductivity values.

Keywords: Polyaniline, Doping, Emulsion, Polyaniline, Self-Curling, Cinnamic acid, Crotonic acid.

1. Introduction

In 1977, Heeger, MacDiarmid, Shirakawa and their collaborators discovered that the conductivity of films self-supported of *trans-poly* (acetylene) [1] can be increased several orders of magnitude after exposure to vapors of halogens and elucidate the mechanisms of doping by oxydo-reduction. Since, many π -combined polymers, conducting and semiconductor electronic, were discovered and studied. They constitute a big family of macromolecular compounds which combine certain properties of load conducting transport and semiconductor materials conventionally giving place to many applications such as the flexible screens, the light batteries, protection against corrosion, the shielding electromagnetic, etc [2, 3]. Among conducting polymers, we chose the polyaniline (PANI) which is used more and more, because of its low costs of synthesis compared with other conducting polymers, of its doping, its easy implementation and its good thermal stability [4]. Moreover, the polyaniline presents a special case with share constitutes among conducting polymers since it has the characteristic to be able to pass from a semiconductor state to a conducting state not only by redox doping, but also by acid-bases doping, for example by protonation since it's semi-oxidized state. This type of doping allows a great flexibility of improvement the implementation and electronic properties of transport if one takes account of the large doping agents variety thus which can be introduced into the polymeric matrix.

* Corresponding author.

E-mail: naar.nacira@gmail.com (Naar N.).

Address: Faculty of Chemistry BP 32 El Alia Bab- Ezzouar 16111 Algiers, Algeria

Thus, since the discovery of the use of the acid (+)/(-) camphor-10-sulfonic (SCA) which it first made it possible to implement the PANI by way solvent and to obtain films having an electronic conductivity higher than 10^2 S.cm^{-1} , the concept of dysfunctional doping agents developed: they are molecules able to dope the PANI by means of an acid function, and bringing additional properties [4]. During various studies on the doped PANI but also on another π -conjugated polymers, it appeared that it is the choice of doping agent influence on the physico-chemical performances of material on a macroscopic and microscopic scale due to ionic interactions of the order nanometric. In this class of polymers, it's confirmed that was necessary to improve and explain the properties of electronic transport on macroscopic samples [5]. As it is known that hetero-phasic polymerization is a method used to produce polymers of great quality with particularly worked properties with large scale volume [6]. The technique of hetero-phasic polymerization includes various methods of polymerization like precipitation, the emulsion, (mini-emulsion and the microemulsion). Methods of polymerization of the microemulsion: the monomer should be moderately soluble in water (as it must form a separate phase) and form spherical droplets whose size is controlled by a suitable choice of the dispersion techniques (like the exciting, ultrasonic treatment or the homogenization). These droplets are stabilized in aqueous media by the complement of a surface active agent (the stabilizer). The size of the droplets varies according to the method of polymerization. Polymerization by emulsion require a free and separate monomeric phase. The emulsions are divided in this case into two types: "direct" for oil in water; and "opposite", for water in oil. The selection depends on emulsifier chosen, water with the oily proportion and the temperature of polymerization. The microemulsion and the mini-emulsion are subdivided according to the size of the droplet formed in full reaction [7] (microemulsion, the size of the droplet is about 50-500 nm and the mini-emulsion approximately of 5 nm-10 μm). In this work, we choose as dopant, two unsaturated carboxylic acids (cinnamic acid and crotonic acid) or the difference between the proposed acids is the structure of these carboxylic protonic dopants. The presence of the methyl to the extrimity of the crotonic acid structure and the substitution of the grouping methyl proton by the benzene in the cinnamic acid structure. This study is proposed in order to study the effect of unsaturated dopants on the electrical, thermal and the structural properties. The Polymerization is realized by emulsion in the presence of an alcohol which plays the surfactant role by the "self curling" phenomena [8, 9]. A lot of investigation method was used in order to characterize the obtained PANI (FTIR, DSC, DRX and the conductivity measurements).

2- Methodology

2.1. Materials

Ethanol 96%, Aniline 99%, cinnamic and crotonic acid 99% from FLUKA and ammonium peroxydisulfate 99% from PROLABO were used without purification.

2.2. Methods

2.2.1. Synthesis of the polyaniline doped by the cinnamic acid (PANI/AC)

In a balloon tricol, 1.5 ml of aniline, 23 ml of distilled water and 3.68 g quantity of cinnamic acid dissolved in 20 ml of ethanol was mixed under agitation during 2 hours at room temperature until obtaining a homogeneous creamy solution. Thereafter, we decreased the temperature of the reaction until 0°C (by using an ice bath) and we added drop by drop a quantity of the initiator ammonium persulfate $\{(\text{NH}_4)_2\text{S}_2\text{O}_8\}$. We dissolved mass $m=8.22 \text{ g}$ of the initiator in 27 ml of distilled water. After one hour of agitation, a colloidal solution of green color is formed. The purification of the product obtained is ensured by a selective washing with the acetone and chloroform in order to eliminate the cinnamic acid, which did not react and thereafter with distilled water up to a pH value

approximately 7. At the end, we dried product in a drying oven with 50°C during 2 days. The following figure (1) illustrated the mechanism of polymerization. In this case, the doping agent (cinnamic acid) used in the synthesis was not soluble in water, it was soluble in ethanol, the monomer too was not very soluble in water. The type synthesis polymerization was carried out by emulsion such as the aniline monomer are dispersed in an aqueous phase, with the initiator. Other side, there was the organic phase which contains the cinnamic acid like doping agent and the organic phase (ethanol) which plays the part of surface-active to stabilize the formed micellar dispersion [10]. The ethanol contained a polar part (OH) and a non-polar part (C₂H₅).

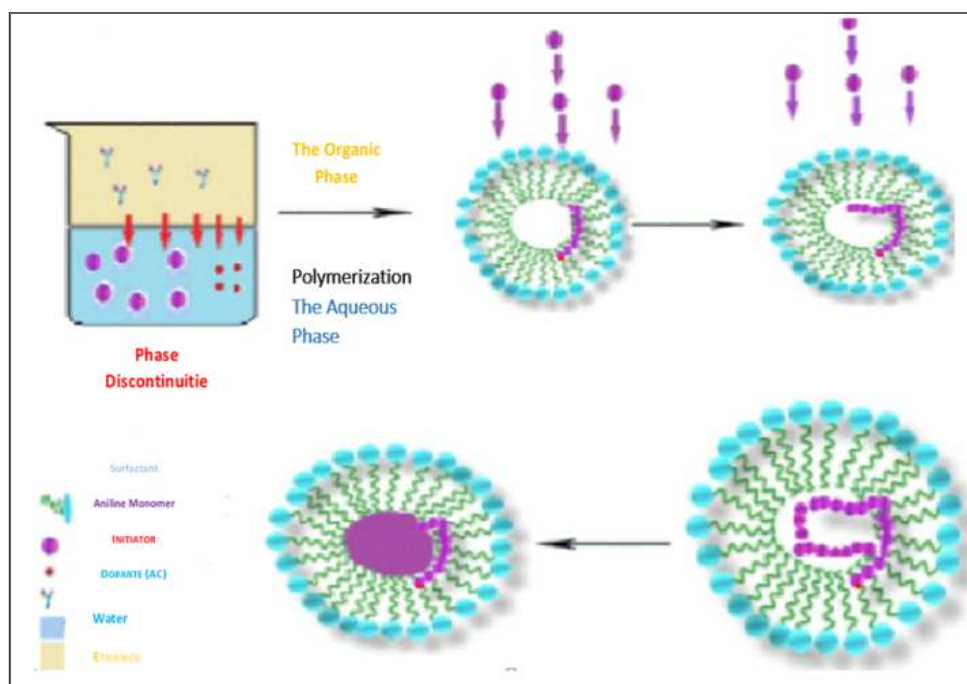


Fig.1 : Illustration of the PANI/AC mechanism

2.2.3. Synthesis of the polyaniline doped by the crotonic acid (PANI/ACro)

In a balloon tricolor, 1.5 ml of aniline, 23 ml of distilled water and 2.066 g quantity of crotonic acid dissolved in 15 ml of ethanol was mixed under agitation during 2 hours at room temperature until obtaining a homogeneous creamy solution. Thereafter, we decreased the temperature of the reaction until 0°C (by using an ice bath) and we added drop by drop a quantity of the initiator ammonium persulfate $\{(NH_4)_2S_2O_8\}$. We dissolved mass $m=8.22$ g of the initiator in 27 ml of distilled water. After one hour of agitation, a colloidal solution of green color was formed. At the end of the reaction, the product was recovered by filtration under filter paper and was purified by a selective washing by water distilled until a pH of 7. We dried product in a drying oven with 50°C during 2 days.

For this synthesis, the doping agent used (crotonic acid) was soluble in both water and ethanol. In this case, we supposed that the aniline monomer is dispersed in only one phase, thus continues polymerization is done by dispersion with the presence of the ethanol, which plays the surface-active part can create a certain regularity in the formation of the polymer motives. In this process of polymerization: the monomer and the doping agent were soluble in the medium of the reaction; the polymer is insoluble under the same conditions. From there, such formed colloids were called dispersions. The particles of colloidal PANI had a typical intermediate size of a few tens to the

hundreds of nanometers and are thus often regarded as nano-colloids. The following figure (2) illustrated the mechanism of polymerization.

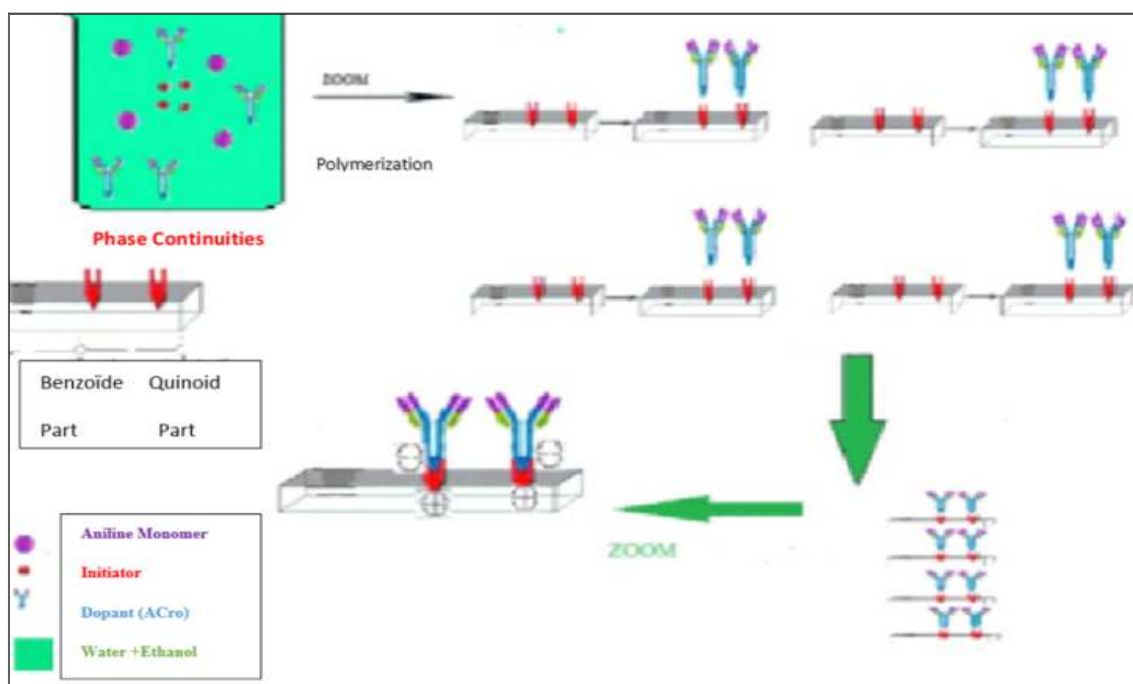


Fig.2: Illustration of the PANI/ACro Mecanism

2.2.4. Characterization techniques

-FT-IR of Polyaniline-KBr pellets were obtained by using Perkin Elmer Spectrometer in the range from 400 to 4000 cm^{-1} and at 2 cm^{-1} resolution.

- In addition, the thermal behavior of PANI was investigated using a differential scanning calorimetry type PERKIN Elmer, operating in the dynamic scanning mode with a constant nitrogen flow with heating rate of 10 $^{\circ}\text{C min}^{-1}$ from 20 to 400 $^{\circ}\text{C}$.

-The experimental device used for DRX consists of a diffractometer with great angles (WAXD for Wide Angle X-Ray Diffraction) system=XPERT-PRO in reflexion at ambient temperature which probes reciprocal space by means goniometry angles 2θ from 2 at 70 $^{\circ}$. Measurements were carried out in the configuration of Bragg-Brentano, i.e. during sweeping in 2θ , the angle ω is determined by $\omega = \theta$. The source in this device is a tube with x-rays provided with a cathode to Copper ($K\alpha_1$, $\lambda=1.5406\text{\AA}$). The measurements were carried out in rotation in its plan in the 1D diffractograms and in an interval of an angle 2θ [2-70 $^{\circ}$]. The distances were calculated by Bragg relation. The width with middle height of the diffraction peaks (FWHM for Full Width at Half Maximum), was calculated by Scherrer formula in order to estimate the coherence length (L) which corresponds to the average size of crystallites:

$$FWHM = 0.89 \lambda / L \cos(\theta), \theta \text{ on radian, } \lambda \text{ and } L \text{ on } \text{\AA}$$

The samples were characterized in the form of powder pastilles in a hurry.

- The electrical conductivity at room temperature of thin films of PANI/ACRO and PANI/AC were measured by the standard four probe method by JANDEL RM3000 Resistivimeter instrument at 25 $^{\circ}\text{C}$.

This model type is characterized by resistance unit ranging sheet of 1 milliohm by square (10^{-3}) to $5 \cdot 10^8$ ohms by square and with 0.3% of precision.

3. Results and discussion

3.1. Treatment of the results obtained by FTIR

3.1.1. PANI doped by the Cinnamic acid

According to the FTIR analysis spectrum of the PANI/AC (see Fig.3), we noted the presence of a bond around 1495 cm^{-1} of the grouping benzene diamine (N-benzene-N), another bond around 1580 cm^{-1} of the grouping quinone diamine (N=Q=N) [11]. Moreover, of the bonds to 1300 cm^{-1} and 1250 cm^{-1} due to C-N stretching, particularly benzoïd and quinoid groups of the systems [12], other bonds around 881 cm^{-1} which ascribed respectively to the C-H deformation of benzene 1,4 disubstituted. These peaks confirmed the structure of the PANI without doping agent. In addition, two peaks are localized around 1640 cm^{-1} correspond to C=C valence bond of trans CHR=CHR' function [13], another around 1385 cm^{-1} corresponding to C=O valence band vibration against ion RCOO⁻ and another vibration around 770 cm^{-1} corresponds to C-H out of the plan deformation band of monosubstituted phenyl. The presence of the last two peaks in the sample of PANI confirms the presence of the cinnamic acid like doping agent.

3.1.2. PANI doped by the crotonic acid

Analysis by FTIR of the pastille PANI/ACro (see fig.4) showed the peaks of absorption around 1494 cm^{-1} , 1577 cm^{-1} , 3340 cm^{-1} and 1246 cm^{-1} which confirm the principal functions of the PANI [11, 12]. In addition, a peak of absorption around 1673 cm^{-1} correspond to the C=C bond valence of trans function CHR=CHR' [13]. Another peak of absorption around 1300 cm^{-1} ascribed to the C=O band valence vibration against ion RCOO⁻. A peak between $2918\text{-}2930 \text{ cm}^{-1}$ agreed with C-H balance of CH₃ group. These last three peaks confirm the presence of crotonic acid in the structure of the PANI. Moreover, In the two spectra of PANI doped by the two acids, a peak of absorption around 1040 cm^{-1} is observed which correspond to HSO₄⁻¹ function [11]. This latter, confirm the existence of HSO₄⁻¹ as a co-doping agent in the structure of the PANI.

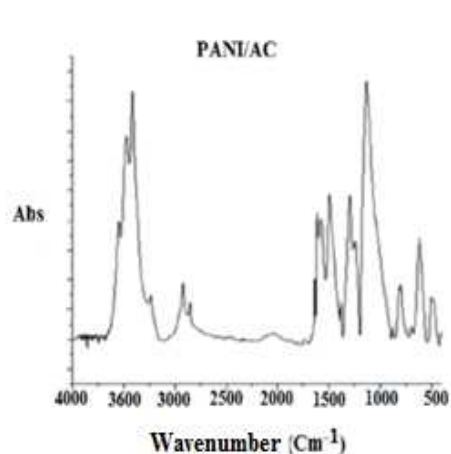


Fig. 3: Spectrum FTIR of the PANI/AC

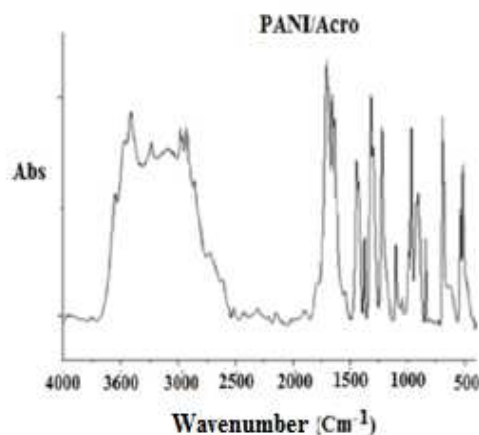


Fig. 4: Spectrum FTIR of PANI/ACro

3.2. Treatment of the results obtained by DSC

The thermogram presented below (see fig.5) illustrated two shoulders in the endothermic direction. A weak shoulder towards 62°C and another shoulder of 64 °C until the 156 °C. The first endothermic transition is allotted at the beginning from slightly bound water and the second transition is allotted at the beginning of the water strongly related [14] and to the reasons from the doping agent followed by a broad exothermic transition is allotted to the molecular rearrangements after the departure from the water reasons and the doping agent. The PANI is stable until 400°C.

According to the figure (6), the thermogram presents two endothermic transitions. A transition appears towards 95°C until the 189°C. These correspond to the last to the departures of the water molecules slightly at the beginning of the molecules of doping agent (melting point of the crotonic acid 75°C).

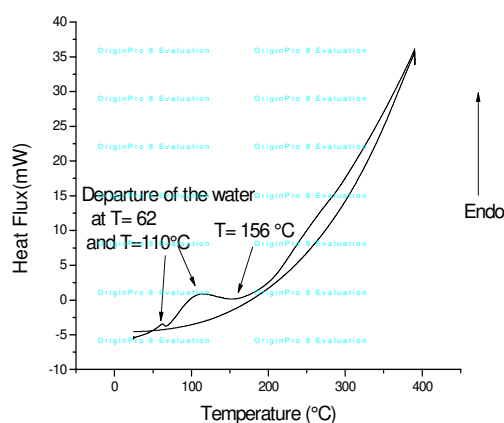


Fig.5 : Thermogram of the PANI/AC

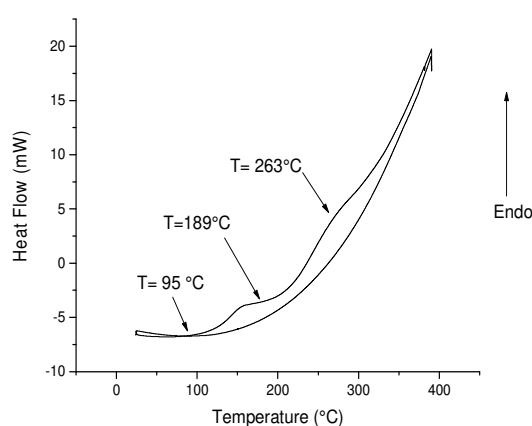


Fig. 6 : Thermogram of the PANI/ACro

3.3. Treatment of the results obtained by Diffraction of x-rays

The two diffractograms obtained (fig.7 and 8) confirm that the PANI/AC and PANI/ACr According to the diffractograms, the peak between $2\Theta=20^{\circ}-25^{\circ}$ [4] indicates the presence of the polyaniline in the two samples what is also confirmed by the comparison with the peaks of the pure PANI (Fig.9). Moreover, the appearance of the three principal lines for each sample confirms that semi crystalline character is present. The values $d=13,4 \text{ \AA}$ (PANI/AC) and $d=13,63 \text{ \AA}$ (PANI/ACro) correspond to the distances inter-chains in a crystalline plate i.e. the distance between two reasons for tetramer of PANI separated by molecules from doping agent. These results are confirmed by the software GAUSS VIEW which makes it possible to calculate this distance. The values found are: $d=13.82 \text{ \AA}$ (PANI/AC) and $d=14.05 \text{ \AA}$ (PANI/ACro).

The comparison between the two values give a light difference (negligible) between the theoretical values and the experimental values what can have only one argument that the intermolecular interactions in only one crystalline layer can slightly minimize the distances to have a good crystalline structural rearrangement. The sizes of crystallites are calculated by the relation of Scherrer. The sizes of the particles of the synthesized PANI are arranged on a nanometric scale (PANI/AC = 20 nm and PANI/ACro = 23,62 nm).

3.4. Treatment of the results obtained by method of Four-terminal sensing

Conductivity is measured by the following relation:

$$\Phi = 1/\delta \quad \text{and} \quad \delta = 0,44 * s * \pi * R_{sq}^*$$

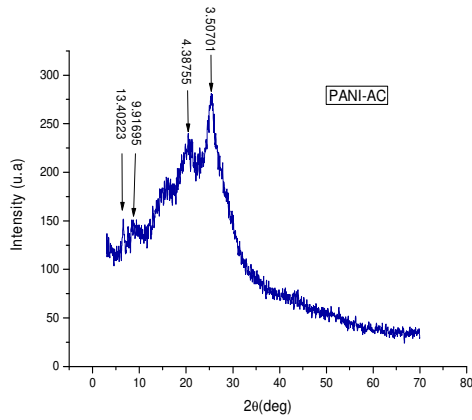


Fig. 7 : Diffractogram X-ray of PANI/AC

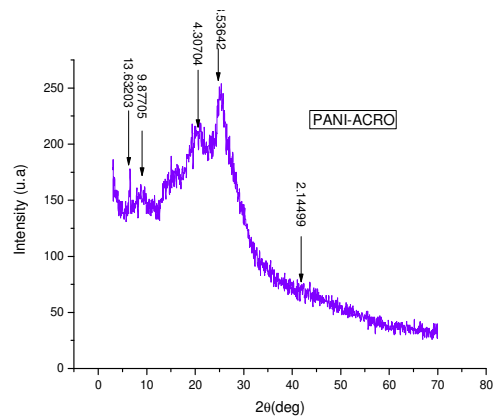


Fig. 8 : Diffractogram X-ray of PANI/ACro

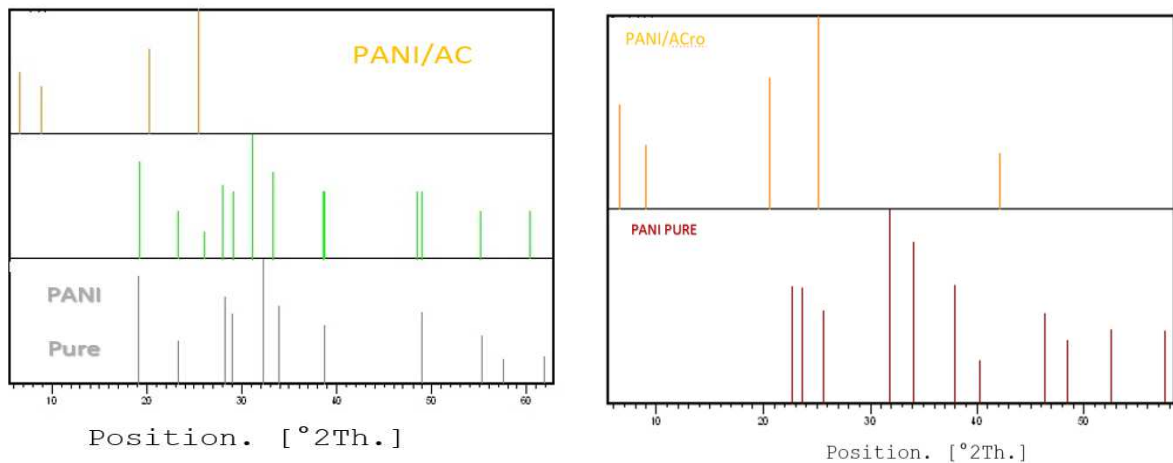


Fig.9 : Comparison between X-ray of pure PANI and (PANI/AC), (PANI/ACro).

Where Φ being electric conductivity (S/cm), δ the resistivity (Ω/cm), S is spacing between the probes (cm) and R_{sq} is square Resistance (Ω).

Table I. the values of the Electric conductivity.

	R_{sq} ($\Omega/Square$)	δ (Ω/cm)	Φ (S/cm)
PANI/AC	$63 * 10^{-3}$	$87,04 * 10^{-3}$	11,48
PANI/ACro	$55 * 10^{-3}$	$75,98 * 10^{-3}$	13,16

The calculated values of conductivity are closer and are in the same size 10^1 S/cm. Therefore, the rate of doping is almost maximum. Indeed, we can say that the structures and the intermolecular rearrangement of the doping agents influence the structural organization of the PANI. In the case of a well organized system, the intramolecular mobility of the species charged along the chain and to a certain extent, by jumps in intermolecular space is increased and from there conductivity also increases [15].

The tetramer which is the reason for repetition in the structure of the PANI, contains two parts different, the benzoide and the quinoide part. According to the conductivity results, we concluded a good distribution between the used doping agent and Co-doping agent (HSO_4^-). Macroscopic conductivity in the conducting polymer samples is the resultant of two elementary mechanisms: conduction intrachaine and interchaîne. Electronic conduction intrachaine is related to the mobility of the system of electrons π and to the process of jumps of carriers between states located on the polymer chain. Conduction interchaîne is ensured by transfers of charge carriers of a conducting polymer molecule towards another close molecule. The doping agents used in both cases are combined organic acids.

3. Conclusion

The study undertaken by the FTIR made it possible to highlight the presence of the polyaniline groups characteristic and also the presence of the groups the doping agents and Co-doping agent (HSO_4^-) characteristic. The analysis carried out by the DSC shows chemical stability (decomposition) and thermic (change of the physical status) of the PANI during heating also indicates the presence of the water traces in the two samples. The results given by DRX analysis made it possible to identify the presence of the PANI stacking (peak between $2\theta=20^\circ-25^\circ$), the size of crystallites starting from the law of Scherrer, the distance inter reticular between the crystallographic networks starting from the law of Bragg, thus the distance interchain between two reasons for the PANI, which confirms the semicrystalline structure of the PANI. these two analyzes justifies the good conductivity which one found by the method of Four-terminal sensing. Lastly, it is judged that the choice of the doping agents and the direct process by self curling polymerization applied to influence on the physicochemical properties of the synthesized PANI.

4. References

- [1] C.K. Chiang, C. R.Jr. Fincher, Y.W. Park, A.J. Heeger, H. Shirakawa, E.J. Louis, S.C. Gau, Alan G. MacDiarmid, Electrical Conductivity in Doped Polyacetylene. *Phys. rev. Lett.* 1977, 39 (17): 1098-1101.
- [2] A.K. Bakhshi, G. Bhalla, "Electrically conducting polymers: materials of twentyfirst century. *J. Sci. Industrial Research* . 2004, 63 (09) :715-728.
- [3] Dubois J. C., Michel P., 1993, *Technique de l'ingénieur*. E1860.
- [4] Munshi M.Z.A., 1996, *Handbook of Solides States Batteries and Capacitors*. Intermedics Inc., USA, 740.
- [5] Atkins P.W., Paula J., 2004, *Physical Chemistry*. 2nd edition Paris.
- [6] J. Santhanalakshmi, K. Anandhi. Graft polymerization of initiators and cosurfactants on microemulsion polymerization of vinyltoluene. *J. Appl. Polym. Sci.* 1996,60 (3): 293-304.
- [7] M. Antonietti, K. Landfester. Polyreactions in Minie-mulsions. *Prog. Polym. Sci.* 2002, 27 (4):689-757.
- [8] N. Naar, S. Lamouri, B. Belaabed, T. Kouroughli, N. Gabouze. Influence of Dibenzoyl Tartaric Acid on the Electrical Performances of the Polyaniline. *Polymer*. 2009, **41** (5) : 432-436.
- [9] Y.F. Huang, C.W. Lin. Introduction of methanol in the formation of polyaniline nanotubes in an acid-free aqueous solution through a self-curling process. *Polymer*. 2009, **50** (3) : 775-782.
- [10] F. Zhang, Y. Ma, L. Liu, W. Yang. Direct observations of three nucleation/growth processes of charge-stabilized dispersion polymerizations with varying water/methanol ratios. *J. Phys. Chem. B*. 2010, **114** (34): 10970-10978.
- [11] N.V. Blinova, J. Stejskal, M. Trchova, J. Prokes, M. Omastova. Polyaniline and polypyrrole : A comparative study of the preparation. *Eur. Polym. J.* 2007, **43** (6): 2331-2341.

- [12] B. Belaabed, S. Lamouri, N. Naar, P. Bourson, S.O.S Hamady. Polyaniline-doped benzene sulfonic acid/epoxy resin composites : structural, morphological, thermal and dielectric behaviors. *Polymer*. 2010, **42** (7): 546-554.
- [13] J. Prokes, J. Stejskal. Polyaniline prepared in the presence of various acids: 2.Thermal stability of conductivity. *Polymer Degradation and Stability*. 2004, **86** (1): 187-195.
- [14] K. Pielichowski, "Kinetic analysis of the thermal decomposition of polyaniline. *Solid State Ionics*. 1997,**104** (1-2):123-132.
- [15] S. Bhadra, S. Chattopadhyay, N.R Singha, D. Khastgir. Improvement of conducting of electrochemically synthesized polyaniline. *J. Appl. Polym. Sci*. 2008, 108 (1): 57-64.