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A poly (vinyl chloride) functionalization by some amines. Electrical study and inductively coupled plasma study of the extraction of La(III) and Bi(III) by modified PVC polymers.

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Abstract: The aim of this work was to study the structural and electrical properties of a new polymer obtained by functionalization of a commercial poly (vinyl chloride) (PVC) (Mw = 48000) by 1-chloro-2-phenylaminomethyl-6-phenylaminomethylene-cyclohex-1-ene groups and to evaluate the efficiency of two new polymers obtained by functionalization of the same PVC by grafting L-alanine and 1-(2-aminoethyl) piperazine groups to extract some metal cations from aqueous solutions. The structural properties of the polymers were investigated by different analytical methods; namely elemental analysis (EA), infrared spectroscopy (FT-IR) and differential scanning calorimetry (DSC) and the electrical properties of the polymer were studied by electrochemical impedance spectroscopy (EIS).

The percentage of extraction was determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES). One of the obtained polymers gave an extraction ratio of Bi^{3+} = 98.77% which highlight the importance of the substitution of chlorine atoms by amino groups.

keywords: Poly (vinyl chloride), functionalization, electrical properties, metal cations, extraction, inductively coupled plasma- atomic emission spectrometry.

INTRODUCTION

Taking into account its low energy consumption and its low cost, poly (vinyl chloride) (PVC) has been used in a great variety of electrochemical devices such as high energy density batteries, fuel cells, sensors and electrochromic devices [1-3]. The development of PVC polymer with high ionic conductivity is one of the main objectives in polymer research. In fact, various approaches have been made to modify the structure of PVC polymer in order to improve their electrical, electrochemical and mechanical properties [4]. Jesse and al. [5] realized the sulfonation of the poly (vinyl chloride); this modification is done by incorporating a sulfuric acid group in the PVC which has been confirmed by IR spectroscopy and elemental analysis. PVC materials have shown a significant improvement of the conductivity and the absorption of solvent relative to that of the unmodified material after reaction for 120 minutes. Sulfuric acid groups not only involved in the movement of protons through the membrane, but also act as a hydrophilic surface to enhance the retention of solvent in dry conditions. Fuel cell trials are currently underway for the new materials in a sensor application. Nawel Zoubeidi and al. [6] modified PVC by triethylamine (TEA), this modified PVC contains alkylammonium sites having the object of increasing the ionic conductivity of medium especially when the platinum micro particles are incorporated.

On the other hand, pollution of aquatic environment by heavy metals from industrial and consumer waste is considered as a major threat to the aquatic organism including fishes and thus to the human health. In addition to that heavy metals are of serious concern due to their persistence in the environment and carcinogenicity to human

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beings. They cannot be destroyed biologically but are only transformed from one oxidation state or organic complex to another. Thus, it would be interesting to develop new materials in order to remove heavy metals from natural waters. To extract metal cations several products based on polymers have been synthesized. Arsalani and al. studied the removal of Ni (II) ions from synthetic solutions using new amino resins based on polyacrylonitrile with diethylenetriamine and triethylenetetramine [7]. In another work Arsalani and al. [8] prepared resins based on polyacrylonitrile and diethylenetriamine which have been used for removing heavy metal ions such as Cu (II), Zn (II) and Cd (II) from aqueous solutions. Rhazi and al. [9] studied the influence of the nature of metal ions on the complexation with chitosan. Abdelaal and Sobahi [10] modified PVC in a charged polymer triazole and imidazole. The modification of PVC plays a key role in the manufacture of new organic materials for specific applications (purification, depollution) [11,12], generally in the removal of toxic organic compounds.

In this work, we synthesized new products by grafting 1-chloro-2-phenylaminomethyl-6-phenylaminomethylene-cyclohex-1-ene, L-alanine and 1-(2-aminoethyl) piperazine groups on PVC firstly to an electrical study and secondly for use in the extraction of a series of metal cations such as bismuth and lanthanum which are widespread in the environment and known to be dangerous to human health.

EXPERIMENTAL SECTION

1. Chemicals

The commercial Poly (vinyl chloride) Mw = 48000 (packed in Switzerland) was purchased from Fluka, L-alanine and 1-(2-aminoethyl) piperazine were purchased from Aldrich-Chemistry D-7924 Steinheim West-Germany. 1-chloro-2-phenylamino-methyl-6-phenylaminomethylene-cyclohex-1-ene was a gift from C. Girard laboratory ENSCP France. Diethyl ether, triethylamin (TEA) and Tetrahydrofuran (THF) were purchased from Prolabo (Groups Rône Poulenc). Chemicals including $Bi(NO_3)_3,5H_2O$ and $La(NO_3)_3,H_2O$ were obtained from Germany (Aqueous monometallic solutions of $Bi(NO_3)_3,5H_2O$ and $La(NO_3)_3,H_2O$ were prepared at a concentration of 2.10^{-4} mol L^{-1} in relation with each metal ion in distilled water (pH=6)).

2. Instrumentation

Electrochemical Impedance Spectra (EIS) were obtained using a Hewlett-Packard HP 4192 analyzer (99 Washington Street Melrose, MA 02176-6024). IR analyses were accomplished with a Thermo Scientific Nicolet FTIR 200 spectrophotometer, using the ATR/FTIR technique (Verona road Madison WI 53711-4495 USA). Setaram DSC 131 (7 L'oratory street 69300 Caluire-France) was used for differential scanning calorimetry analyses. Elemental analysis (EA) of N was performed by using a Perkin-Elmer Analyzer CHN Series II 2400. ICP-AES: HORIBA JOBIN (HORIBA Jobin Yvon S.A.S., 16-18 Canal Street 91165 Longjumeau Cedex).

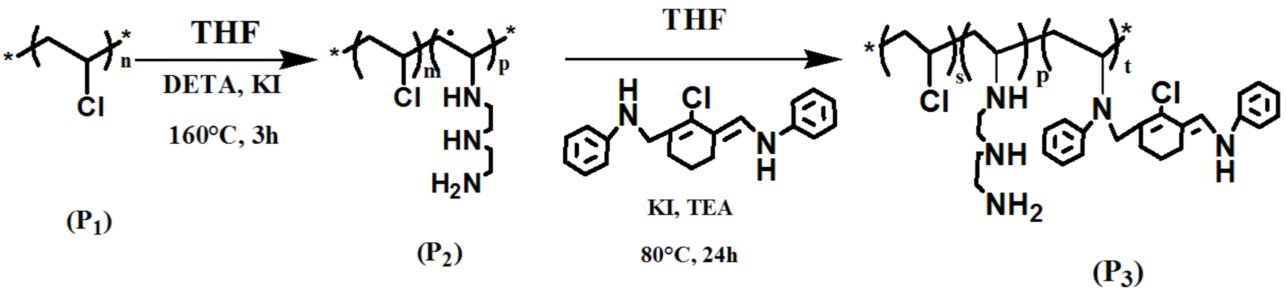
3. Synthesis

3.1. Structures of amino-PVC (P_2) and of the polymer (P_3)

Synthesis is described in our precedent work [12] (Scheme 1).

3.2. Preparation of amino-PVC (P_4)

In a hydrogenating bomb, 2 g of commercial PVC, 1 g of L-alanine, 1 g of potassium iodide and 4 ml of triethylamin were mixed in 70 ml of THF. After stirring for 24 h at 100 °C, we obtained a paste which was washed several times with distilled



Scheme 1. Synthetic scheme of amino-PVC (P_2) and the polymer (P_3) from poly (vinyl chloride) (P_1).

water to obtain a black powder that was crushed and then washed several times with distilled water, with a dilute sodium hydroxide solution, with diethyl ether and with acetone and finally dried in an oven at 65 °C to obtain a mass m = 2.6 g of (P_4).

3.3. Preparation of aminoethyl piperazine-PVC (P_5)

In a hydrogenating bomb, 1 g of amino-PVC (P_1), 3 ml of 1-(2-aminoethyl) piperazine, 3 ml of triethylamin and 0.5 g of potassium iodide were mixed in 70 ml of THF. After stirring for 24 h at 80 °C, a paste was obtained. Washed several times with distilled water it turns into powder which was crushed and washed several times with distilled water, with a dilute sodium hydroxide solution, with diethyl ether and finally dried in an oven at 65 °C to get a yellow-brown powder (P_5) of mass m = 2.41 g.

3.4. Technique of extraction by I.C.P.

In a 30 ml vial, 20 ml of aqueous solution of metal salt (2×10^{-4} M) have been mixed with 100 mg of each polymer (P_1, P_4 or P_5). At the extraction equilibrium and after filtration, each sample was diluted with distilled water and assayed to determine the final concentration of metal remaining at the extraction equilibrium.

3.5. Electrical measurements

The polymer denoted (P_3) was ground in an agate mortar and then pressed at 5MPa into cylindrical pellets with 13 mm in diameter and 1.8 mm in thickness. Impedance spectra (IS) were obtained using a Hewlett-Packard HP 4192 analyzer. The impedance measurements were taken in an open circuit using two electrode configurations with signal amplitude of 50 mV and a frequency band ranging from 10 Hz to 13MHz. Both pellet surfaces were coated with silver pastes electrodes while the platinum wires attached to the electrodes were used as current collectors. Measurements were performed at equilibrium potential at a temperature ranging between 25°C and 150°C. In order to obtain the conductivity, the resulting data was analyzed using the equivalent circuit of the Z-View software.

RESULTS AND DISCUSSION

1. Characterizations of synthesized polymers P_4 and P_5

1.1. IR spectroscopy

Figure 1 shows the IR spectra of the powder form of the studies polymers. On the commercial PVC (P_1) spectrum, we notice a high intensity band assigned to the stretching vibration $\nu_{C\text{-}Cl}$ at 687 and 614 cm^{-1}. The spectrum of (P_4) shows peaks around 3320 cm^{-1} attributed to the stretching vibration of NH secondary amines, a bending vibration of NH at 1654 cm^{-1} and a stretching vibration of CN at 1030 cm^{-1}, we note also that the band $\nu_{C\text{-}Cl}$ at 687 cm^{-1} becomes very low compared to that corresponding to the polymer (P_1) as a result to the high-temperature reaction which induces the increase of the number of chlorine atom substituted by groups amine. The IR spectrum of the polymer (P_5) shows some bands of stretching vibration $\nu_{C=O}$ at 1720 cm^{-1}.

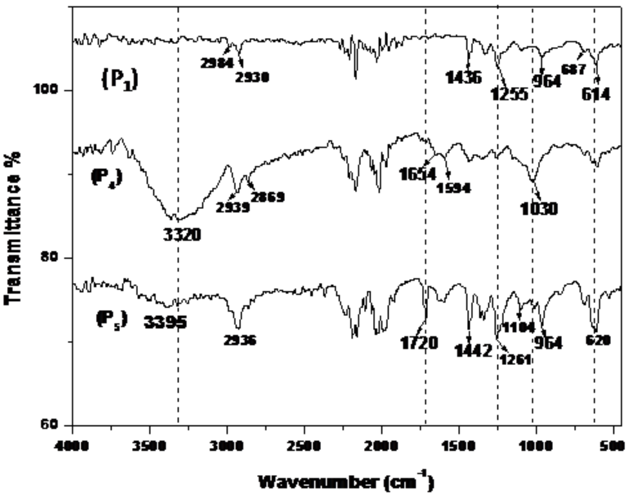


Figure 1. IR spectra of PVC (P_1); amino-PVC (P_4) and aminoethyl piperazine -PVC (P_5).

1.2. Elemental analysis

Table I presented the N percentage in polymers determined by elemental analyses. An elemental analysis was also used to prove the success of the reaction as well as to estimate the reaction yield based on the mole fraction concept [10]. Obtained results show that the content of N in these polymers (P_4) and (P_5) were respectively, 0.558 and 2.279 which is in agreement with the structures proposed in (Scheme 1). These findings suggest that the polymer structure, particularly

Table I. Elemental analysis of the synthesized polymers

Sample name	C (%)	H (%)	N (%)
(P_4)	51.11	5.276	0.558
(P_5)	58.36	6.042	2.279

Table II. DSC analysis of materials P_4 and P_5.

Sample name	Endothermic transformation $T_{endo.}$ (°C)	Exothermic transformation $T_{exo.}$ (°C)
(P_4)	257	197
(P_5)	185 and 257	-

polyamine chain length and nitrogen atoms composition, influence the N content.

1.3. DSC characterization of P_4 and P_5

Differential scanning calorimetry (DSC) was performed on 5 mg samples and the results were recorded between 50 and 340ºC at a speed of 5ºC min^{-1}.

The DSC diagram (Figure 2) of the polymer (P_4) presents an exothermic peak at 197 °C attributed to the elimination of L-alanine and an endothermic transformation at 257 °C attributed to the final degradation of the polymeric structure. In the case of polymer (P_5) we note the presence of two endothermic transformations at 185 and 257 °C that can be attributed to the elimination of L-alanine or aminoethyl piperazine groups and the final degradation of the polymeric structure, respectively we also note the absence of an exothermic peak up to 340 °C (Table II).

1.4. Proposed structures of amino-PVC (P_4) and of aminoethyl piperazine -PVC (P_5)

Based on the analytical results obtained by different physicochemical analyses, (elemental analysis EA, infrared spectroscopy FT-IR and differential scanning calorimetry DSC), we propose the following structures for the materials (P_4) and (P_5) in (Scheme 2).

2. Metal ions extraction by the modified polymers

2.1. Technique of extraction

In this work, ICP-AES was performed in order to assay the metals using a HORIBA JOBIN spectrometer. The wavelengths used were 223.061 and 331.749 nm for Bi and La respectively (Power 1050 Watts, flow nebulization 0.75 l/min, nebulization pressure 2.74 bar). The extraction percentage of the metal is given by the following relationship:

$$\%E = (C_0 - Cf) / C_0 \times 100 \qquad (1)$$

C_0: initial concentration of the metal in the aqueous solution.

C_f: final concentration of the metal in the aqueous solution at the extraction equilibrium.

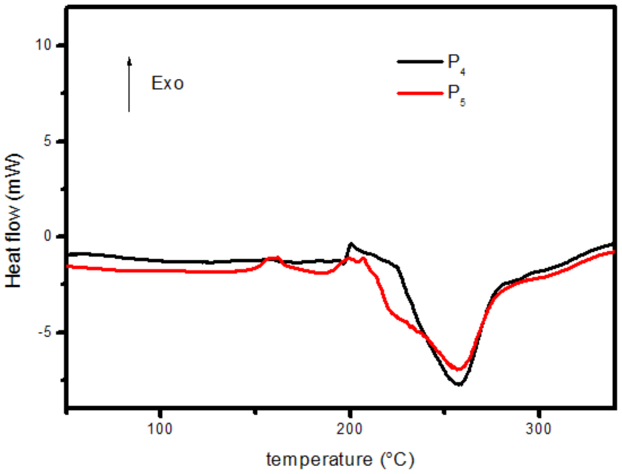
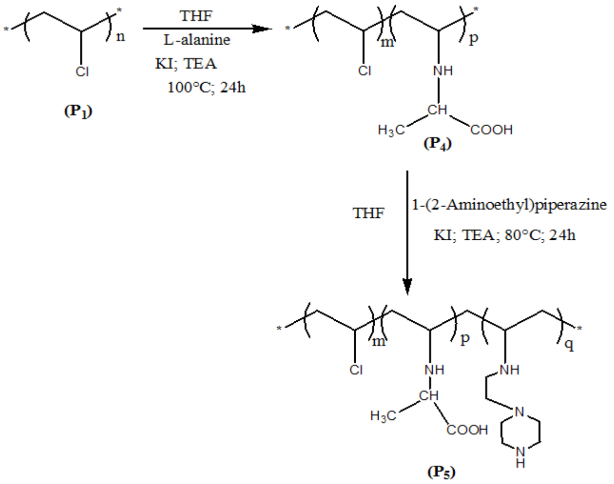


Figure 2. DSC diagrams of amino-PVC (P_4) and aminoethyl piperazine -PVC (P_5).



Scheme 2. Synthetic scheme of amino-PVC (P_4) and aminoethyl piperazine -PVC (P_5).

Table III. Extraction percentages with the synthesized polymers obtained by ICP-AES.

Metal cation	La^{3+}	Bi^{3+}
Percentage of extraction with (P_1)	0	0
Percentage of extraction with (P_4)	77.01	98.77
Percentage of extraction with (P_5)	57.03	98.61

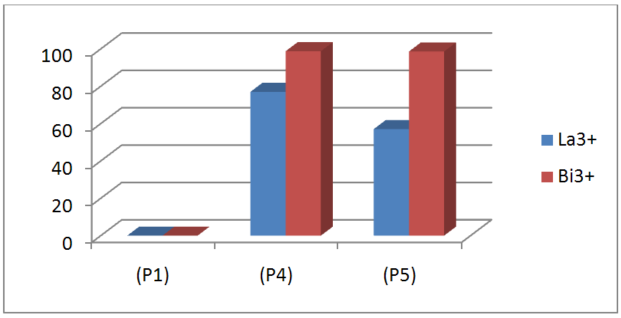


Figure 3. Extraction percentages with PVC (P_1); amino-PVC (P_4) and aminoethyl piperazine -PVC (P_5).

2.2. Results and discussion

Table III shows the extraction percentages obtained by ICP-AES for the studied metals (Figure 3).

On the basis of hard–soft acid–base (HSAB) theory, La(III) was classified as hard ion and Bi (III) was classified as intermediate ions, they have affinities respectively to hard and intermediate ligands which contain oxygen or nitrogen atoms of carboxyl or polyamine groups this result which can be explain by the structures proposed for complex (Figure 4) confirm the percentage extraction of the La which was 77 and 57% respectively with the polymers P_4 and P_5. Moreover, the difference of adsorption capacity of La^{3+} and Bi^{3+} by the synthesized polymers P_4 and P_5 can be mainly explained by the compatibility factor between the cations' size and the ligands' cavity size in polymer matrix, which was probably influenced by the cross-linking degree.

This type of complex structures (Figure 4) is well known in supramolecular chemistry [13].

2.3. Influence of extracted metals on some physical characteristics (IR spectra) of new materials

The IR absorption spectra of the studied complexes (Figure 5) indicate that the influence of free polymers and their complexes on IR spectra is not very significant. This could be due to the counter-anions of metal cations because of the use of these salts: $Bi(NO_3)_3,5H_2O$ and $La(NO_3)_3,H_2O$. Apparently, the anion NO_3^- fix easily water molecule via hydrogen bonds which makes difficult the drying of new materials. We note the decrease of the band at 3320 cm^{-1} and of the band at 1654 cm^{-1} due to the complexation of the polymer (P_4) (Figure 5-a). We also note the decrease of the band at 1720 cm^{-1} in the case of the polymer (P_5) (Figure 5-b).

3. Electrical study

3.1. Impedance Spectroscopy

The ionic conductivity measurement was performed in air in the temperature range of 25 °C-

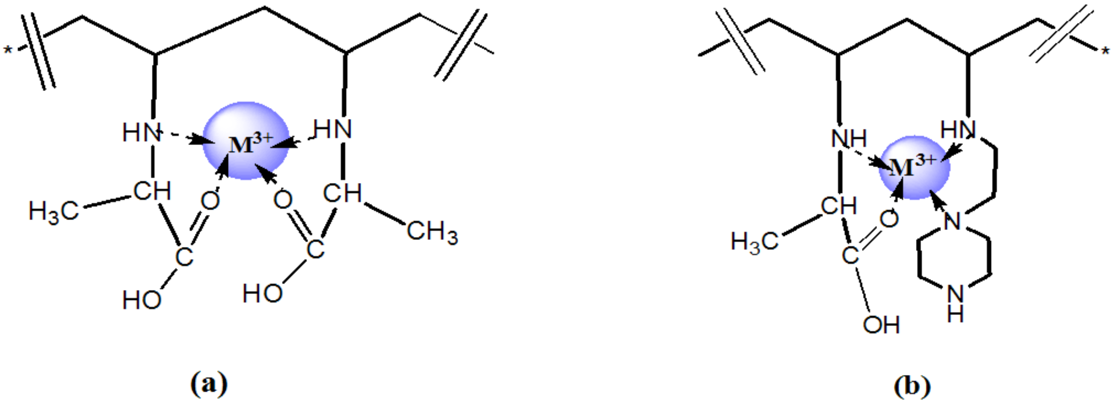


Figure 4. Structures of (a) complex (P_4-M^{3+}) and (b) complex (P_5-M^{3+}). M = Bi or La.

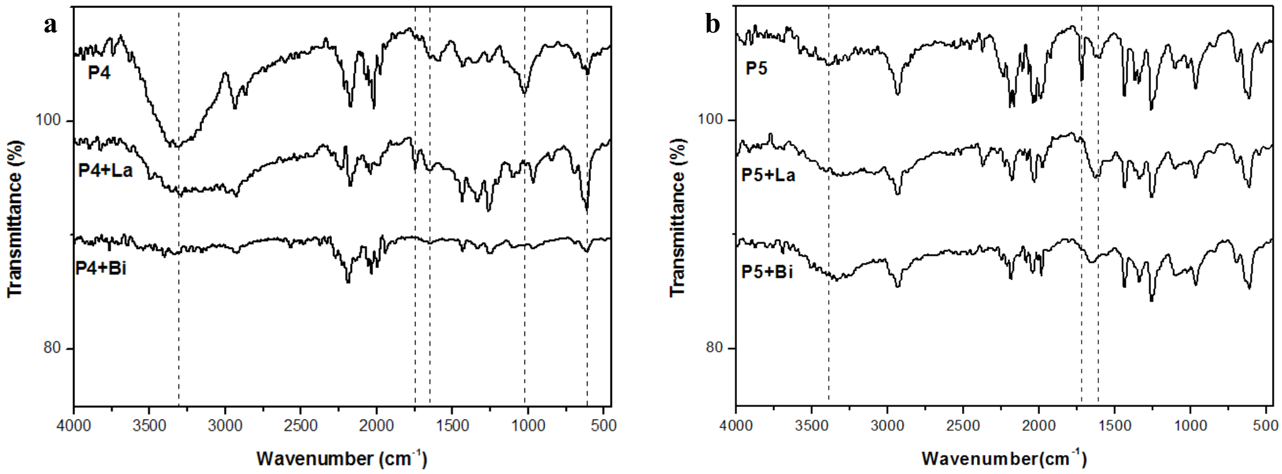


Figure 5. IR spectra of (a) (P_4) and complex (P_4-La^{3+}), (P_4-Bi^{3+}); (b) (P_5) and complex (P_5-La^{3+}), (P_5-Bi^{3+}).

150 °C. A complex plane plot of real impedance, Z', versus imaginary impedance, Z'', was prepared for the set of data.

Impedance spectra measured between 25 °C-150 °C under air with equivalent circuit is illustrated in (Figure 6). The data of the impedance spectra (IS) was fitted to the equivalent circuit of the R_s(R// CPE) type shown in (Figure 6), where R_s is the ohmic resistance of the pellets compound and the connected elements (R// CPE). R is resistance and CPE is a constant phase element representing time-dependent capacitive elements.

3.2. DC conductivity study

For the impedance spectra mentioned above, the conductivity can be obtained using the following equation:

$$\sigma = e/s \times 1/R \qquad (2)$$

Where e is the thickness of the sample and s is the electrode surface area. The ratio e / s is the sample's geometric factor.

Activation energies (Ea) were calculated by fitting the conductivity data to the Arrhenius relation for thermally activated conduction, given by the following relation:

$$\sigma = \frac{\sigma_0}{T} \exp\left(-\frac{Ea}{kT}\right) \qquad (3)$$

where σ, T, k, Ea and σ_0 are the conductivity, absolute temperature, Boltzmann constant, activation energy and a pre-exponential factor, respectively.

Figure 7 shows the Arrhenius plot of the total electrical conductivity for the polymer (P_3) sample in the temperature range 25 °C to 150 °C.

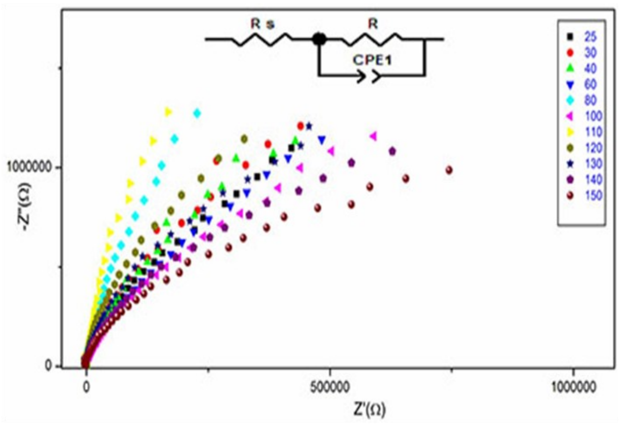


Figure 6. Complex plane impedance plots of polymer (P_3) at different temperatures.

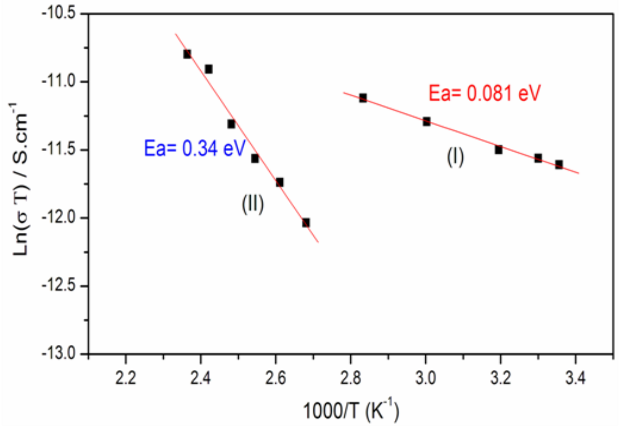


Figure 7. Arrhenius plots of the conductivity of polymer (P_3) solid solutions.

It can be seen that the conductivity increases with increasing temperature. The results showed that a sample has the highest conductivity at 150°C, equal to 4.84×10^{-8}S.cm^{-1}, which is comparable or better than the results of other studies found in reports [14, 15].

Note that the Arrhenius curve of (P_3) sample cannot be fitted by a single straight line. This implies that the mechanism for conduction changes at a transition temperature. According to the Arrhenius plots of all samples (shown in Figure 7), there are two parts named (I) (25°C - 80°C) and (II) (100 - 150°C) in which the linearity of the plots change; and thus, the activation energy of the conductivity change with increasing temperature. This change of the linearity plots between 80 and 100 °C is attributed to phase transition as revealed by DSC analysis which shows that the polymer (P_3) exhibits an endothermic transformation at 91 ° C [12]. The calculated activation energies obtained by the linear fit of both regions are Ea(I) = 0.081 eV and Ea(II) =0.34 eV.

CONCLUSIONS

In this paper, we have suggested, firstly the electrical study of the polymer (P_3). These obtained results show that the new material (P_3) may be useful in a great variety of electrochemical devices such as rechargeable batteries, super-capacitors and gas sensors and a new technique to purify wastewater by solid-liquid extraction process using modified PVC. After chemical modification, the PVC leads to polymers amino-PVC (P_4) and aminoethyl piperazine-PVC (P_5) which was used as adsorbents of metals. The polymers (P_4) and (P_5) were tested for extraction of two metals (La (III) and Bi (III)). The study of this extraction with the obtained polymers was followed by ICP-AES. The percentage of extraction of cation Bi^{3+} was found to increase from 98.61 % for (P_5) to 98.77% for (P_4) and those of La^{3+} from 57.03% for (P_5) to 77.01% for (P_4). Thus, (P_4) and (P_5) could be used as extractants of toxic metals La^{3+} and Bi^{3+}.

In conclusion, synthesized polymers were shown to be able to minimize the negative effects of toxic metals on the environment.

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