Modification of poly(vinyl chloride) by aromatic amines: application to the extraction of some metal cations

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Abstract: The reaction of poly(vinyl chloride) (PVC) with various aliphatic amines in 1,4-dioxane has been studied. These reactions led to the formation of new polymers (PVC-L), which were characterized by different spectroscopic methods: differential thermal analysis (DTA) and infrared. The extraction percentages were determined by comparing the initial conductivity of the aqueous solution containing the studied metal with the final conductivity of the aqueous solution at extraction equilibrium. One of the obtained polymers gave an extraction rate of 82.05% for Li +, which underlines the importance of the substitution of chlorine atoms by diethylenetriamine groups. A kinetic study of the extraction shows that the optimal duration of extraction was obtained with the polymer most substituted by diethylenetriamine groups.

Keywords: poly(vinyl chloride) (PVC), functionalization, metal cation, extraction, diethylenetriamine, substitution reaction.

Modyfikacja poli(chlorku winylu) aminami aromatycznymi: zastosowanie wybranych kationów metali do ekstrakcji

Streszczenie: Badano reakcję poli(chlorku winylu) (PVC) z różnymi aminami alifatycznymi w 1,4-dioksanie. Reakcje te doprowadziły do powstania nowych polimerów (PVC-L), które charakteryzowano metodami różnicowej analizy termicznej (DTA) i podczerwieni. Procent ekstrakcji określano przez porównanie początkowej przewodności roztworu wodnego zawierającego badany metal z końcową przewodnością roztworu wodnego w stanie równowagi ekstrakcji. Dla jednego z otrzymanych polimerów uzyskano stopień ekstrakcji 82, 05% dla Li +, co podkreśla znaczenie podstawienia atomów chloru przez grupy dietylenotriaminowe. Badania kinetyczne wykazały, że optymalny czas ekstrakcji uzyskano dla polimeru z najbardziej podstawionym grupami dietylenotriaminowymi.

Słowa kluczowe: poli(chorek winylu) (PVC), funkcjonalizacja, kation metali, ekstrakcja, dietylenotriamina, reakcja substytucji.

Poly(vinyl chloride) has been used in various fields such as construction, household appliances, packaging, electrical and electronic products, automobile, furniture, *etc*. A huge amount of PVC waste has been discarded both in the post-manufacturing and post-consumer phases. Worldwide, PVC waste can be managed primarily through landfill (82%) and incineration (15%) [1, 2]. On the other hand PVC finds many applications in the medical field, blood storage bags and their components [3]. PVC is not a polymer compatible with blood, one of the techniques which exists consists in improving this biocompatibility, what includes the polymer surface modification existing the end point of heparin [4, 5]. The animation of PVC was followed by complexation with heparin [6, 7], grafting of hydrophilic polymers on the surface of PVC [8] and modification of the plasma [9]. In another work, PVC was modified for the treatment of wastewater contaminated with cadmium [10]. PVC is also used for recycling of a used lithium-ion batteries (LIB) by a mechanical-chemical process [11, 12].

In this work, given that the pollution of the aquatic environment by heavy metals from industrial and consumer waste is considered as a threat to aquatic organisms and to human health, we focused our work in laboratory on the synthesis of new materials from PVC in order to extract metal cations. Several polymer-based products have been synthesized [13-18]. Several chemical reactions have been applied such as substitution, elimination, reduction and degradation. Nucleophilic substitution is the most studied reaction [13], Abdelaal and Sobahi made substitutions of PVC chlorine by I then by OH in a solution of DMF. Navarro et al. carried out the modification of PVC with several aromatic thiols. This

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work is devoted to the modification of polyvinyl chloride (P_0) by aromatic amines and to the study of the complexing and catalytic properties of various modified polymers [14].

In the present work, we have synthesized new products by grafting amino-alkyl and amino-aryl groups onto P_0 for use in the extraction of the two metal cations cadmium and lithium which are widespread in the environment and known to be harmful to human health.

EXPERIMENTAL PART

Materials

Commercial PVC (P_0) (Mr=48 000) was purchased from Fluka. 1,4-dioxan, triethylamine, N,N Dimethylformamide (DMF), diethylenetriamine (99%), 4-aminovératrole, 4-aminophenol, diethyl ether and LiBr was produced by Sigma-Aldrich. $CdCl_2 \cdot H_2O$ (98 %) was provided by Fluka. Diethyl ether was bought from Panreac. Potassium iodide (KI) and sodium hydroxide (NaOH) were purchased from Prolabo.

Chemical functionalization of PVC

In order to make the polymer (P_0) more reactive, we performed the Conant-Finkelstein reaction to replace the chlorine atoms of pure PVC with iodine atoms using a nucleophilic substitution mechanism [20].

Extraction of some metal ions

The work included the use of polymers modified with amine groups to remove metal ions (Li^+, Cd^{2+}) by solid phase extraction (SPE).

Extraction study

In a 30 mL vial, 20 mL of an aqueous metal salt solution ($5 \cdot 10^{-4}$ M) was mixed with 100 mg of each powdered polymer. Carefully, the mixture was stirred and the initial conductivity (σ_0) was measured.

Percentage of extraction

The results of the metal ion extraction for each synthesized polymer were expressed as percentages of their initial concentration.

The metal ion percentage was calculated using the following equation.

$$E = [(Ci - Cf) / Ci] \cdot 100\ \%$$

where: Ci (mol/cm^3) is the initial concentration of metals in aqueous solution and Cf (mol/cm^3) is the final concentration of the metal in the aqueous solution at equilibrium extraction.

Testing methods

The infrared analysis using the (ATR FT-IR) technique was carried out on a Thermo Scientific Nicolet FTIR 200 spectrophotometer with a scanning range between 4000 and 400 cm^{-1}.

Differential thermal analysis (DTA) was performed on a SETARAM TGA 92 device. The pH was measured with a pH/conductivity meter, VWR / CO 3000L.

Synthesis of veratrole PVC-amine P_1

5 g of PVC (Mw = 48,000 gmol^{-1}), 1 g of potassium iodide and 100 ml of 1,4-dioxane were introduced into a bomb to hydrogenate and stirred at room temperature. Then 60 mg of 4-aminoveratrole and 2ml of triethylamine were introduced. This mixture was stirred until the medium was homogenized. Then it was allowed to react at 100°C for 24 hours. At the end of the reaction, it was washed several times with distilled water. It was observed that two rubbery phases appeared:

A white phase which would be noted as sample 1 subsequently.

A brown phase which would be noted sample 2 later. Each phase is washed several times with distilled water and then with diethyl ether. The synthesized polymer P_1 had a mass of 4.43 g and white in color.

Synthesis of polymer P_2

5 g of commercial PVC (P_0), 1.16 g of KI and 100 ml of 1,4-dioxane were introduced into a bomb to be hydrogenated. The mixture was stirred at room temperature then 120 mg of 4-aminoveratrole and 2 ml of triethylamine were introduced. After homogenization of the medium, it was left to react for 24 hours at 120°C. A black plastic paste was obtained. It was washed several times with distilled water and then with diethyl ether to give a new black color material P_2 with a mass of 5.33 g.

Synthesis of polymer P_3

5 g of commercial PVC (P_0), 1.16 g of KI and 100 ml of 1,4-dioxane were introduced into a bomb to be hydrogenated. The mixture was stirred at room temperature then 130 mg of 4-aminophenol and 2 ml of triethylamine were introduced. After homogenization of the medium, it was left to react for 24 hours at 120°C. A black plastic paste was obtained. It was washed several times with distilled water and then with diethyl ether to give a new material P_3 with a mass of 4.85 g and a black color.

Synthesis of polymer P_4

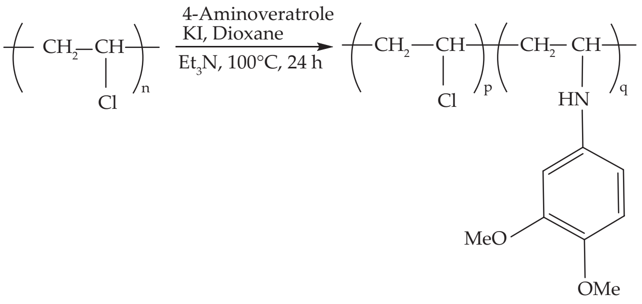
1 g of PVC modified by 4-amino phenol (P_2), 70 ml of 1,2-dioxin and 0.5 g of KI were introduced into a bomb to be hydrogenated. The mixture was stirred at room tem-

perature and then 9 ml of diethylene triamine (DETA) and 3 drops of trietylamine were introduced.

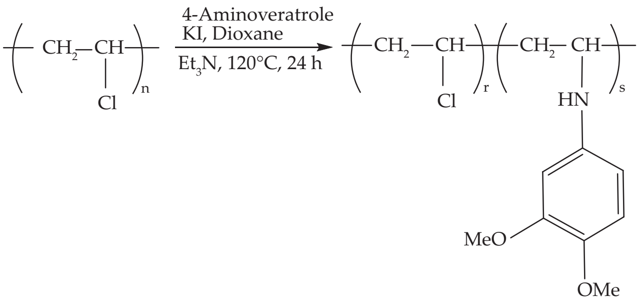
After homogenization of the medium, it was left to react for 24 hours at 100°C. A light brown plastic paste was obtained. It was washed with an aqueous solution of NaOH of 10^{-2} mol/L concentration, then washed several times with distilled water until the filtrate reached the electrical conductivity of distilled water and finally washed with diethyl ether. A new material P_4 with a mass of 0.56 g and a light brown color was obtained.

Proposed structure for polymer P_1

Based on the analysis methods, the following structure is proposed for polymer P_1 (Scheme A).



Scheme A



Scheme B

Proposed structure for polymer P_2

Based on the analysis methods, the following structure is proposed for polymer P_2 (scheme B).

Proposed structure for polymer P_3

Based on the analysis methods, the following structure is proposed for polymer P_3 (scheme C).

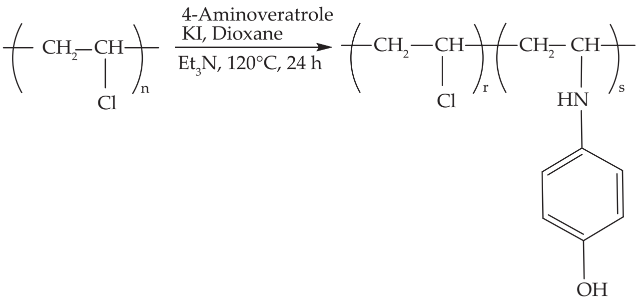
Proposed structure for polymer P_4

Based on the analysis methods, the following structure is proposed for polymer P_4 (scheme D).

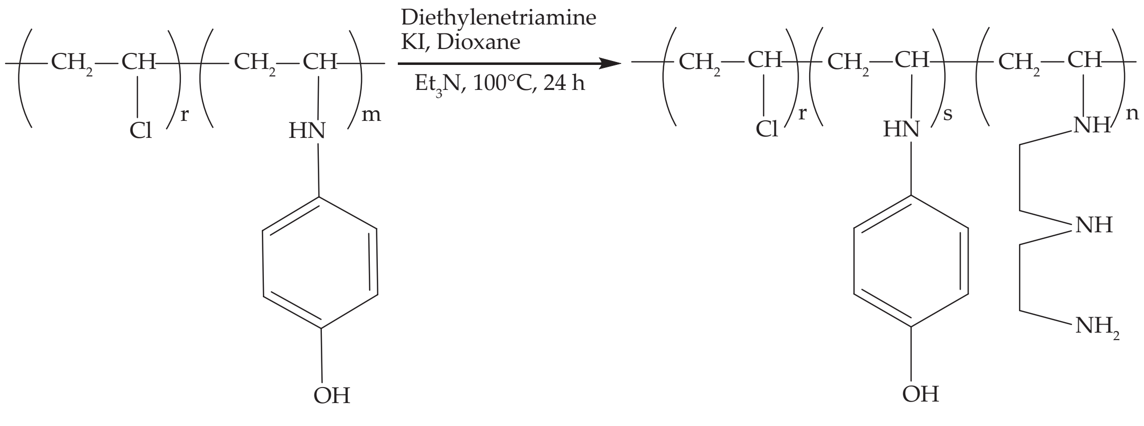
RESULTS AND DISCUSSION

IR spectroscopy

IR spectroscopic analysis of the modified polymer (P_4) clearly shows that a substitution reaction takes place, as indicated by the appearance of characteristic bands of the amino groups at 3390 and 3400 cm^{-1} corresponding to NH_2, as well as an absorption at 1650 cm^{-1} corresponding to the bending of NH in the plane. An absorption at 1431 cm^{-1} is also observed, corresponding to an aromatic C=C, which confirms he presence of the benzene ring in the polymer



Scheme D



Scheme C

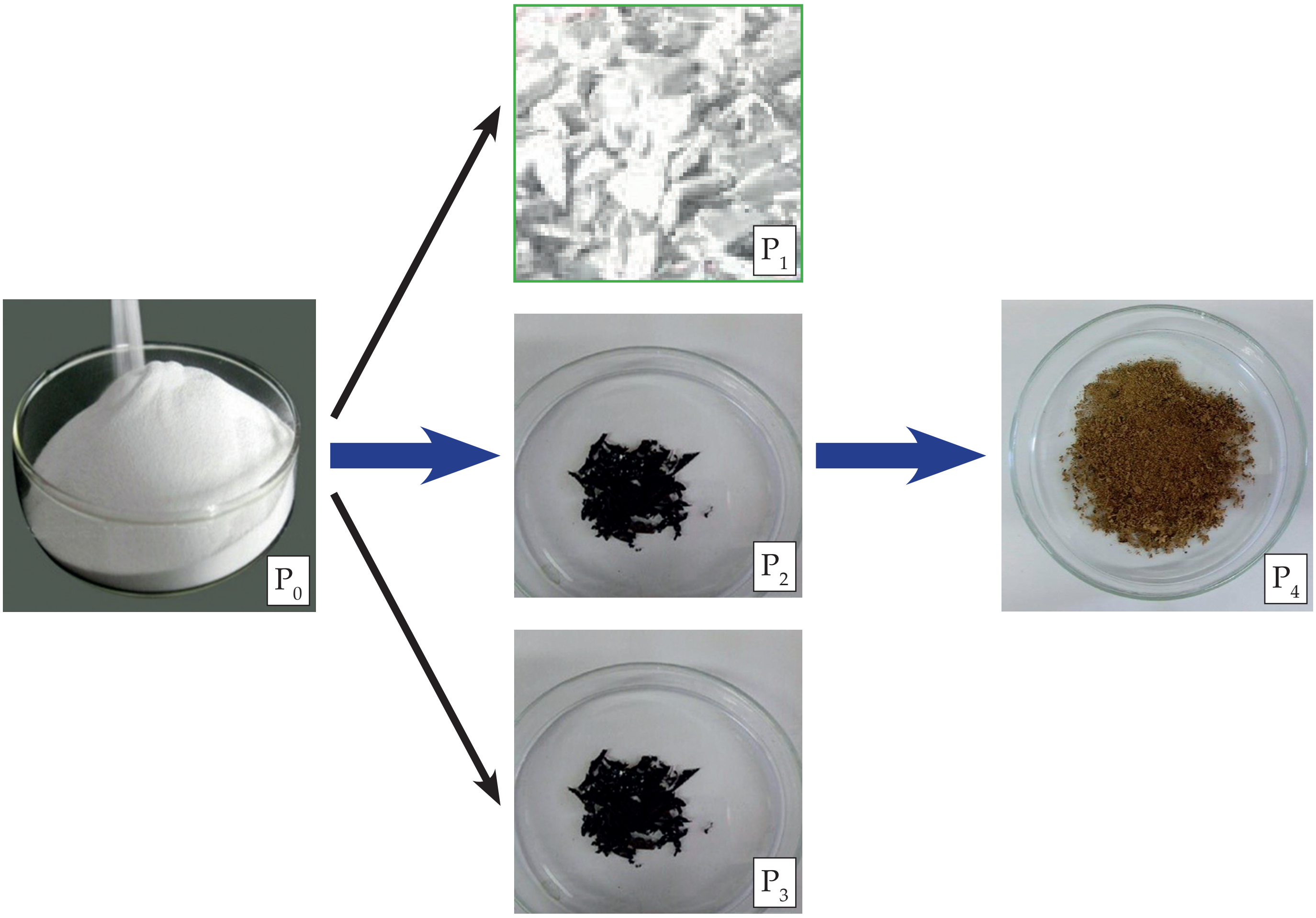


Fig. 1. Polymers obtained after chemical modification of commercial PVC

chains of PVC. All the characteristic bands observed for P1 were also seen in the FT-IR spectrum of P_2 and P_3 (Fig. 2). However; the spectrum also shows the presence of the weak stretching vibration of chlorine (ν_{C-Cl}) at 690 cm^{-1}, indicating that the chlorine atoms have not entirely disappeared. Results are consistent with those of Ammari *et al.* [13].

The IR spectra of the polymers P_1, P_2, P_3 and P_4 are given in the following figure.

Comparison of FT-IR spectra for P_1, P_2, P_3 and P_4 together with that of P_0 clearly shows the modification of P_0 since the P_0 spectrum has absorption bands at 690 cm^{-1}, corresponding to the C-Cl band, and the two absorption bands at 2927 cm^{-1} for symmetric and asymmetric CH_2, middle band respectively, which are only present in P_0 (Table 1). Finally, the absence of the chlorine stretching vibration band (ν_{C-Cl}) between 600 and 800 cm^{-1} in the P_4 spectra

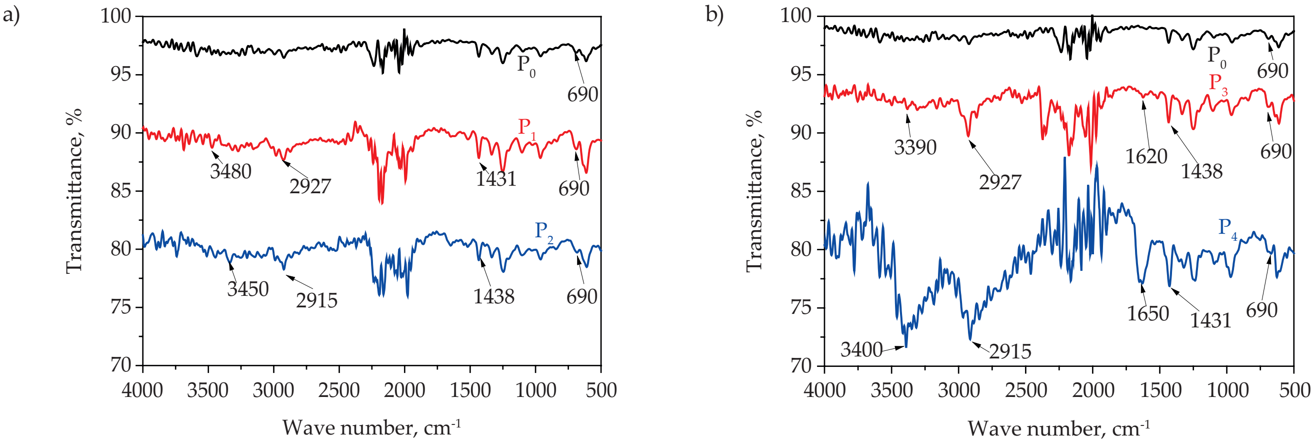


Fig. 2. FT-IR spectra of polymers: a) P_0, P_1, P_2; b) P_0, P_3, P_4

T a b l e 1. FT-IR spectroscopic data for P_0 and modified polymers P_1, P_2, P_3 and P_4

Characteristic vibration	Wave number, cm^{-1}				
	P_0	P_1	P_2	P_3	P_4
-C-Cl vibration	690	690	690	–	–
-CH2 asymmetric and symmetric vibrations	2930–2860	2930–2860	2930–2860	2930–2860	2930–2860
-NH2 asymmetric and symmetric vibrations	–	3300-3400	3300-3450	3300-3390	3330-3400
C=C aromatic	–	1431	1438	1438	1431
N-H bending	–	–	1630	1620	1650

confirms that the chlorine atoms have been substituted by diethylenetriamine [14].

DTA analysis

The DTA diagram of commercial PVC (P_0) shows a melting point at 270°C with the absence of an exothermic peak up to 400°C; it also exhibits a glass transition around 80°C. That of polymer P_1 exhibits 2 endothermic transformations at 88.94.360°C with no exothermic peak up to 400°C. In the case of polymer P_2, we note the presence of an endothermic transformation at 77°C and an exothermic peak at 240°C. Finally, the diagram for polymer P_3 shows two peaks, one exothermic at 180.40°C and the other endothermic at 341°C. The P_4 diagram shows 2 endothermic transformations at 160 and 260°C. The peaks around 80°C are attributed to the departure of the surface solvent molecules, those at around 160°C are due to the departure of amino groups grafted onto the PVC backbone and the peaks around 250°C show the continuation of decomposition of polymers (Fig. 3). Note that these thermal behaviors are similar to those found by Ammari *et al.* [13-15].

The DTA diagrams of the P_1-Li^+ and P_3-Li^+ complexes respectively show the presence of an exothermic peak at around 190° C and an endothermic peak at around 236°C, the latter corresponding to the decomposition of the polymer. On the other hand, we note that for the P_4-Li^+ complex, the appearance of two endothermic peaks around 180°C, 267°C. By comparison with the diagrams of free polymers, there is a slight shift in the temperatures of the various transformations following this complexation (Figs 4, 5). Likewise an endothermic peak around 275°C for (P_4-Cd^{2+}) which has a slight transformation compared to P_4-Li^+ has been attributed to the decomposition of the polymer [14, 15].

Proposed structures of P_4

Various analyzes of denatured polymers (P_4) have shown the transformation of commercial PVC (P_0) into 4-aminophenole substitution reactions. A possible structure of P_4 is shown in Scheme E (a) and (b). Several chlorine atoms are always present in the proposed structures. The IR spectra of P_4 showed that the elongation and oscillation bands of chlorine ($\nu_{C\text{-}Cl}$) did not disappear completely. This indicates the presence of several chlorine atoms in the P_4 structure returned to the structure proposed by Mbarki *et al.* [14].

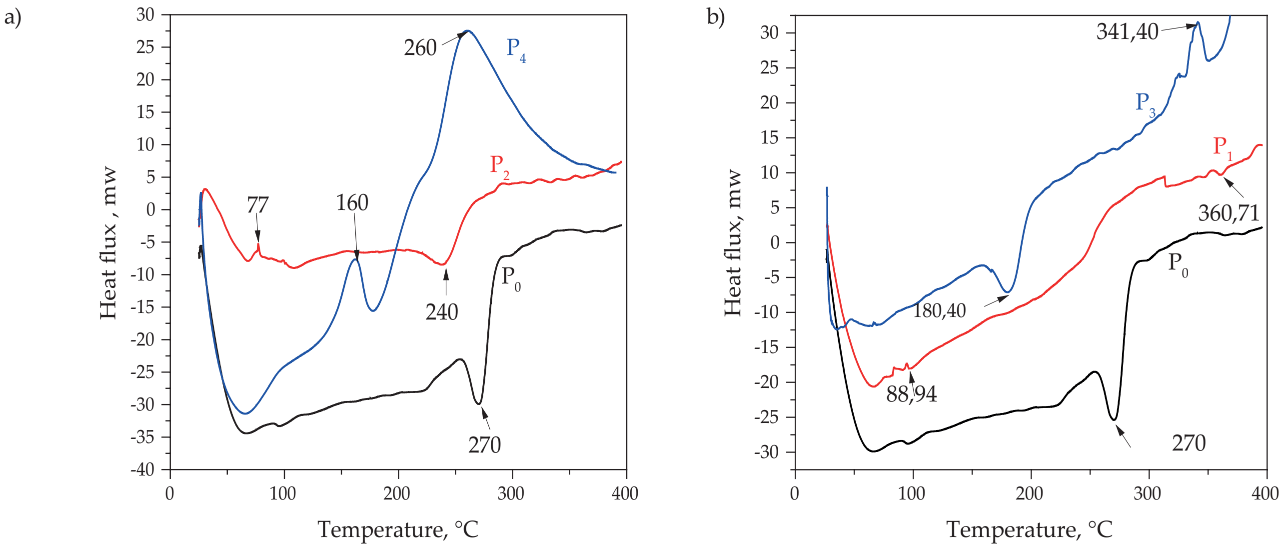


Fig. 3. DTA of polymers: a) P_0, P_2, P_4; b) P_0, P_1, P_3

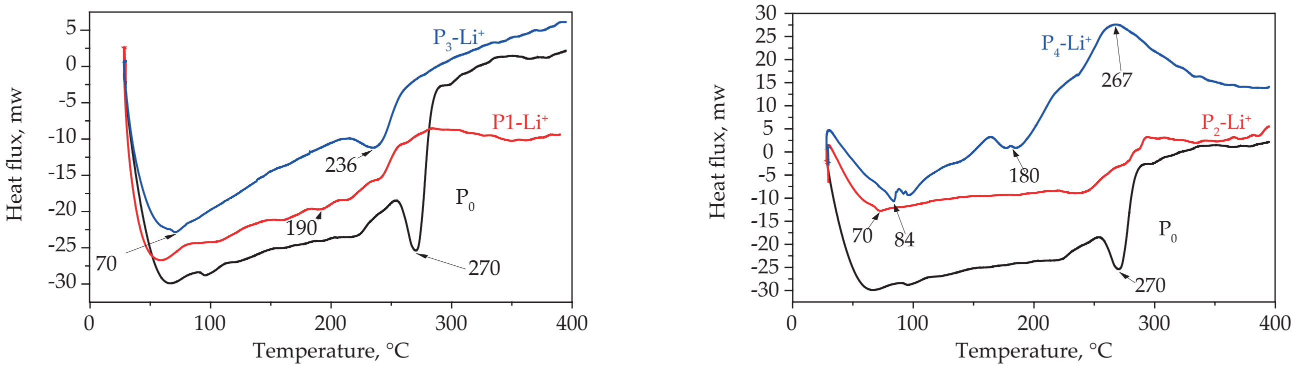


Fig. 4. DTA of polymers: a) P_0, P_1-Li$^+$, P_3-Li$^+$; b) P_0, P_2-Li$^+$, P_4-Li$^+$

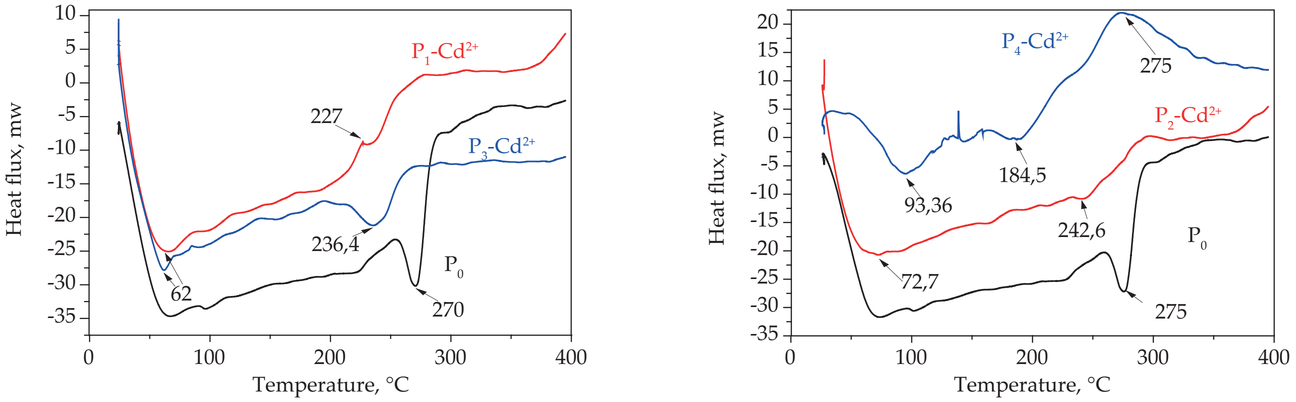
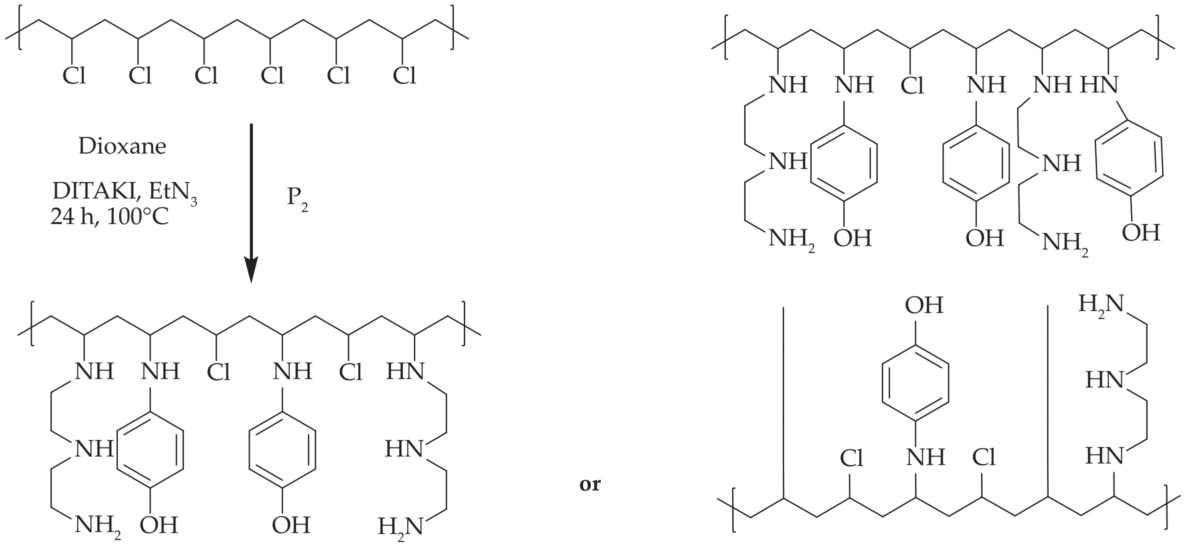


Fig. 5. DTA of polymers: a) P_0, P_1-Cd^{2+}, P_3-Cd^{2+}; b) P_0, P_2-Cd^{2+}, P_4-Cd^{2+}



Scheme E

Metal cation extraction using modified polymers

Kinetic study

Figure 6 below shows the variation of the electrical conductivity as a function of time respectively with P_1, P_2, P_3 and P_4.

The curves representing the change in conductivity in various aqueous solutions over time show that the conductivity decreases and then after a period Δt remains constant. Δt represents the optimal duration of extraction (table 2). The results show that the optimal duration of Li+ cation extraction is the shortest with the four polymers. This is probably due to its small size, thus facilitating its extraction.

Table 2. Optimal extraction time with polymers P_1, P_2, P_3 and P_4

Polymers	P_1	P_2	P_3	P_4
Optimal duration for Li^+, h	26	30	34	36
Optimal duration for Cd^{2+}, h	40	100	135	155

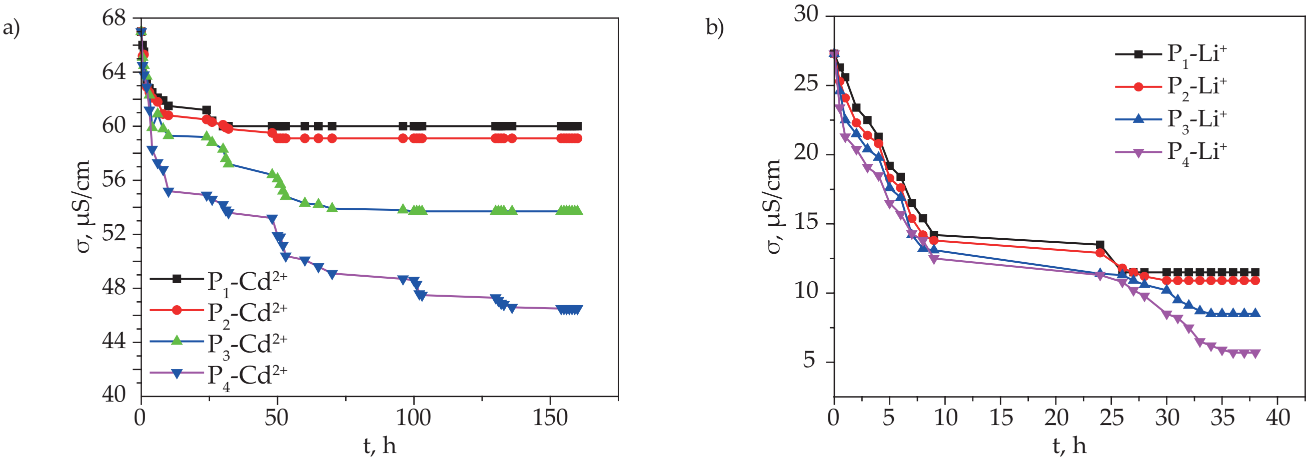


Fig. 6. Conductivity variation curves over time for some cations: a) P_1-Cd^{2+}, P_2-Cd^{2+}, P_3-Cd^{2+}, P_4-Cd^{2+}; b) P_1-Li^+, P_2-Li^+, P_3-Li^+, P_4-Li^+

Interpretation

Figure 7 summarizes the percentage of metal cations removal with the studied materials P_1, P_2, P_3 and P_4. These results are the average of three experiments for each studied metal. These results show that the material P_4 is the best extractant of Li^+ and Cd^{2+} ions with respective extraction efficiency 87.17% and 28.65%. This confirms the structures proposed in scheme E since the material P_4 corresponds to a greater number of substituted chlorine atoms compared to P_2. The presence of oxygen atoms, due to the introduction of amino phenol groups into the structure of P_4 confirmed by IR analysis, promotes the extraction of these metal cations which is in agreement with the theory of hard and soft acid bases (HSAB) since oxygen atoms are hard bases and therefore has affinities for these hard acids.

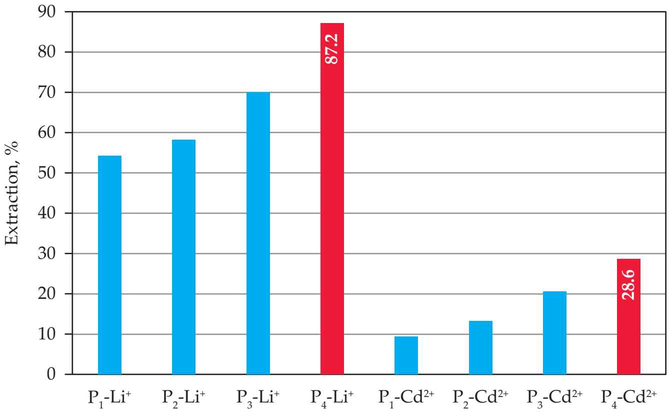


Fig. 7. Histogram of extraction degrees

Atomic absorption spectrometry (AAS)

Method of analysis

In this work, an atomic absorption spectrometry was used for determination of metals using the PerkinElmer... Pin AAcle 900 T spectrometer.

The calibration of the spectrometer was performed using standard solutions for each metal. The calibration range was between 0.2 and 2 ppm.

Interpretation

Table 3 shows the extraction percentages obtained by conductivity measurements and by AAS for the studied metals.

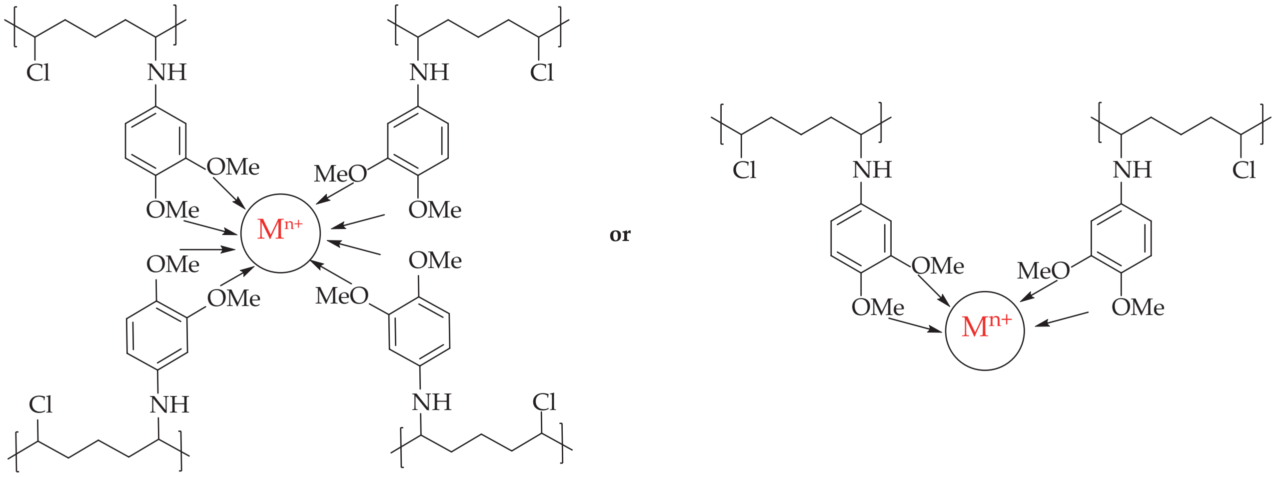
The absorption method gives higher extraction degrees than those found with conductivity. The differences between the extraction degrees obtained by the 2 methods varied between 8% and 12%.

Proposed structures of P_4-Li^+

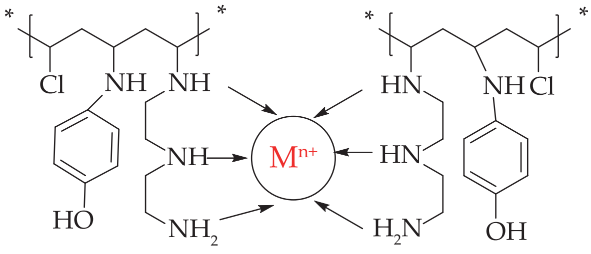
Complexation with Li^+ and Cd^{2+} was the best for P_4 since the extraction degrees were 87.17% and 28.65% respectively, compared to P_1, P_2 and P_3 for which extraction percentages vary from 54.21 % to 69.96% for Li^+ and from 9.4% to 20.59% for Cd^{2+} (Table 3). This type of complex structures is well known in supramolecular chemistry [18]. These results can be explained by the compatibility between the size of the metal ion and the size of the complexing cavity and the type of heteroatom ligands (oxygen and nitrogen atoms). This type of atom (N, O) is capable

Table 3. Extraction efficiency obtained with conductivity and atomic absorption spectrometry (AAS)

Metal cation	Degree of extraction with P_1		Degree of extraction with P_2		Degree of extraction with P_3		Degree of extraction with P_4	
	Conductivity	AAS	Conductivity	AAS	Conductivity	AAS	Conductivity	AAS
Li^+	54.21	62.3	58.24	67.2	69.96	78.1	87.17	95.5
Cd^{2+}	9.4	21.40	13.24	25.28	20.59	30	28.65	38.7



Scheme F



Scheme G

of fixing the metal by non-covalent bonds (van der Waals bonds). Depending on the structures there are different types of macrocyclic complexing cavities (scheme F, G). The retention of metal cations can al`so be explained by the presence of an electron-rich π system (benzene ring), this type of interaction has been explained by the theory of non-covalent cation-π interactions [14–19].

Influence of complexation in IR spectroscopy

In order to study the influence of complexation on the structure of polymers, the IR spectra of the P_i-Li^+ and Pi-Cd^{2+} complexes are given in Figs 8, 9.

The IR absorption spectra of the studied complexes (Figure 8) indicate a slight shift in the characteristic bands of the amines which are linked by coordination bonds to the to the metal ion, but the influence of the complexes on the IR spectra is not very significant. This could be due to the counter-anions of the metal cations, because of the use of these salts: $CdCl_2$, H_2O; Li Br, which strongly bind water molecules making it difficult to interpret these spectra. But we note the extension of the band at 3359 cm^{-1} due to the complexation of the polymers and the increase in the band at 1631 cm^{-1}.

CONCLUSIONS

This work allowed us to obtain four new materials by functionalization of a PVC (Mw=48 000) noted respectively P_1, P_2, P_3 and P_4. The procedure for preparing the reactions depends on the used solvent, the temperature, and the reaction time. These new materials containing electron donor atoms such as nitrogen and oxygen have been used as chelating agents for the extraction of heavy metals. This study shows that increasing the number of substituents through the use of diethylenetriamine improves the properties of functionalized PVC as an extraction agent. This work allowed us to evaluate the extraction of heavy metals by new adsorbents based on modified PVC polymers from aqueous solutions of metal cations. Our next studies will focus on the use of these new materials in the depollution of real wastewater from the Bizerte wastewater treatment plant located in northern Tunisia.

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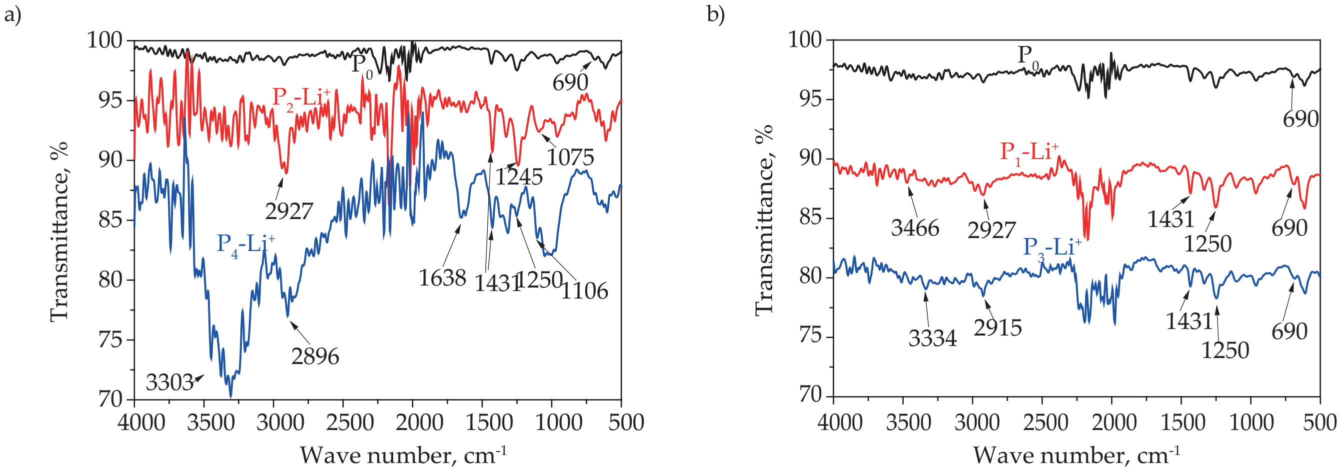

Fig. 8. FT-IR spectra of polymers: a) P_0, P_2-Li^+, P_4-Li^+; b) P_0, P_1-Li^+, P_3-Li^+

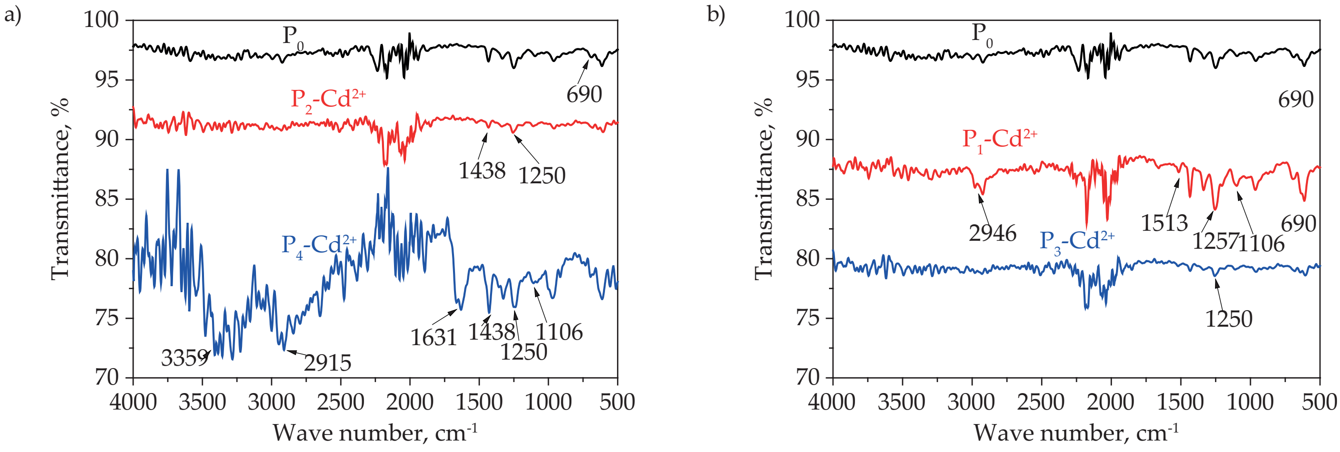

Fig. 9. FT-IR spectra of polymers: a) P_0, P_2-Cd^{2+}, P_4-Cd^{2+}; b) P_0, P_1-Cd^{2+}, P_3- Cd^{2+}

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