Aminated PVC cross-linked with 2,2'-dichlorodiethyl ether as heavy metal absorber

Adnen Mabrouki[1), *)], Faycel Bouzayene[1)], Soltani Awatef[1)], Fayçel Ammari[1), *)] (ORCID ID: 0000-0003-3541-0854)

Abstract: The paper describes the chemical modification of PVC consisting in the introduction of amino groups (1,4-dioxane, diethylenetriamine), and then cross-linking with dichlorodiethyl ether. The optimal extraction time was obtained for the polymer that had more chlorine atoms substituted with diethylenetriamine groups and ether. The obtained polymers were characterized by infrared spectroscopy (FTIR), elemental analysis (CHN) and differential thermal analysis (DTA).

Keywords: poly(vinyl chloride), metal extraction, diethylenetriamine, dichlorodiethyl ether.

Aminowany PVC sieciowany za pomocą eteru 2,2'-dichlorodietylowego jako absorber metali ciężkich

Streszczenie: W pracy opisano chemiczną modyfikację PVC polegającą na wprowadzeniu grup aminowych (1,4-dioksan, dietylenotriamina), a następnie sieciowaniu eterem dichlorodietylowym. Optymalny czas ekstrakcji uzyskano w przypadku polimeru, który miał więcej atomów chloru podstawionych grupami dietylenotriaminowymi i eterem. Otrzymane polimery scharakteryzowano za pomocą spektroskopii w podczerwieni (FTIR), analizy elementarnej (CHN) oraz różnicowej analizy termicznej (DTA).

Słowa kluczowe: poli(chlorek winylu), ekstrakcja metali, dietylenotriamina, eter dichlorodietylowy.

In polymer chemistry, great progress has been made in discovering and improving polymerization methods that can lead to new polymeric materials [1]. Nowadays, polymeric materials are used in many fields, from commodities to high-tech and sophisticated applications such as polymer-based batteries [2]. The desired polymer surface sometimes cannot be obtained from the material itself, but by modifying it. Modification of the polymer surface can be carried out by various chemical or physical processes [3–5]. PVC has been subjected to many reactions, dehydrochlorination [6] and nucleophilic substitutions [7, 8], degradation [9, 10], grafting and crosslinking [11–13]. It is well known that PVC can be chemically modified in solution by nucleophilic substitution of its chlorine atoms. It is easier to modify PVC by forming CPVC-X with X = N, O than by using CPVC-C. That is, formation of the polyvinyl chloride carbon bond and the oxygen or nitrogen atom from C-PVC.

The current work aims to achieve the functionalization of PVC by the nucleophilic substitution reaction with amine groups and chemical grafting of dichlorodiethyl ether groups [14–17]. The new modified PVC-based products (P_{1R}, P_{2R}, and P_{3R}) can be applied to pollutants in wastewater. Several techniques can be used to investigate the removal of these toxics from wastewater. The adsorption process is one of the most important methods to remove toxic organics, using several types of adsorbents, such as polymeric adsorbents [18]. This work evaluated the effectiveness of modified polymers to remove toxic metals from the environment, especially wastewater, as water pollution is a major global problem caused by a variety of toxic pollutants [19, 20].

EXPERIMENTAL PART

Materials

Commercial polyvinyl chloride (PVC) (Mw = 48 000) was purchased from Fluka. 1, 4-dioxan, triethylamine, N, N dimethylformamide (DMF), diethylenetriamine (99%), 4-aminovératrole, 4-aminophenol, dichlorodiethyl ether and LiBr lithium bromide (98%) was produced by Sigma-Aldrich. $CdCl_2 \cdot H_2O$ (98%) aqueous solution of cadmium nitrate was provided by Fluka. Panreac supplied diethyl ether and Prolabo supplied potassium iodide (KI) and sodium hydroxide (NaOH).

Chemical functionalization of PVC

To make the polymer (PVC) more reactive, we performed the Conant–Finkelstein reaction to replace the

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[1)] University of Carthage, Faculty of Sciences Bizerte, Laboratory of Organic Synthesis, 7021 Jarzouna, Bizerte, Tunisia.
[*)] Author for correspondence: mabroukiadnen1990@gmail.com, ammari1971@gmail.com

chlorine atoms of the pure PVC with iodine ones through a nucleophilic substitution mechanism [21].

Amino-PVC preparation

The polymer P_1 was obtained as following. 5 g of PVC (Mw = 48,000 g/moll), 1 g of potassium iodide, and 100 ml of 1,4-dioxane were stirred in an autoclave at room temperature. Then 60 mg of 4-aminoveratrol and 2 ml of triethylamine were added and stirring was continued until the reaction mixture was homogeneous. The temperature was then increased to 100°C and the process was continued for 24 h. The product was washed several times with distilled water. The same procedure was used for the polymer P_2, but temperature was 120°C. For polymer P_3, 5 g of commercial PVC, 1.16 g of KI and 100 ml of 1,4-dioxane were stirred at room temperature and then 130 mg of 4-aminophenole and 2 ml of triethylamine were introduced. After reaction mixture homogenization, the process was conducted at 120°C for 24 hours.

Grafting of dichlorodiethyl ether on amino-PVC

2 g of previously modified PVC was dissolved in 30 cm³ of DMF and 2 cm³ of diethylenetriamine was added to the

solution and heated at 125°C for 3 h. Then 6 cm³ of dichlorodiethyl ether was added to the solution; the reaction mixture was stirred and heated at 125°C for 24 h. The resulting products were filtered and washed with water. Then, the modified polymers were dried for 24 h at room temperature and washed with diethyl ether and distilled water. The cross-linked polymers named P_{1R}; P_{2R}; and P_{3R} were dried in an oven for 12 h at 60°C and finally dried under vacuum at 70°C for 48 h. The obtained material for the removal of mineral ions presents in wastewater. The idea of this work is summarized in Scheme A.

Methods

The infrared analysis using the ATR FTIR technique was conducted 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 and conductivity meter, VWR/CO 3000L. An elemental analysis of N was performed using a Perkin-Elmer Analyzer CHN Series II 2400.

Metals were determined by atomic absorption spectrometry using a Pin AAcle 900 T spectrometer. Calibration of the spectrometer was performed using
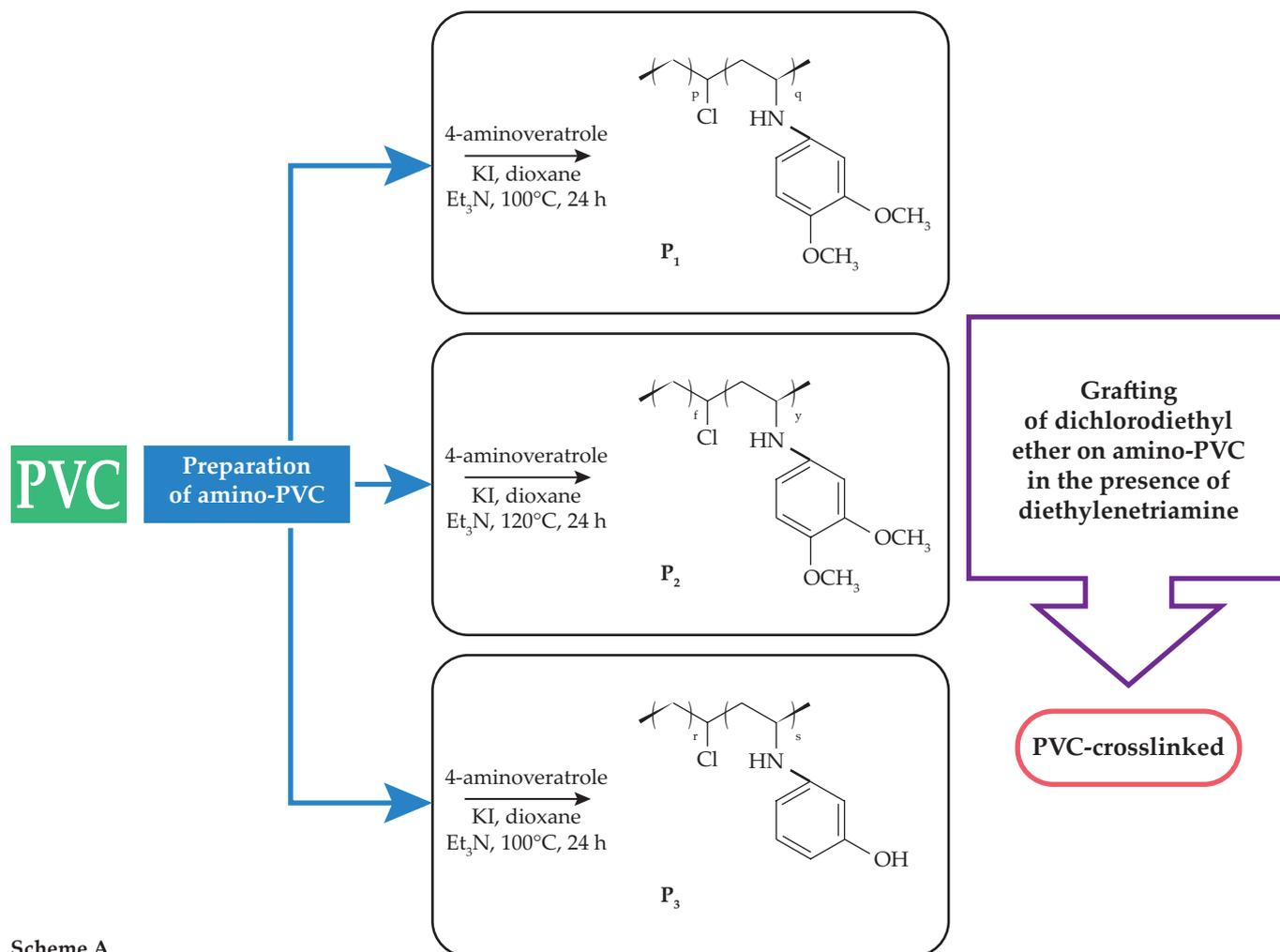
Scheme A

standard solutions for each metal. The calibration range was 0.2 to 2 ppm.

Extraction of certain metal ions

The work consisted in using the polymers modified by amino and dichlorodiethyl ether groups for the removal of metal ions (Li^+, Cd^{2+}) using solid phase extraction method (SPE). Aqueous solutions of metal salts were prepared at a known concentration of $2 \cdot 10^{-4}$ mol/dm³. Then 0.1 g of the modified polymer (powder ground in a mortar and sieved on a sieve ≤ 100 μm) was washed several times with distilled water to remove the salts present. The washed polymer was directly added to a flask (V = 30 cm³) containing 20 cm³ of the metal solution at room temperature and subjected to agitation to determine the optimal extraction time based on the evolution of the conductivity (σ) of the aqueous solution as a function of time. The percentage of extracted heavy metals was determined using the following relationship:

$$E = [(C_i - C_f) / C_i] \cdot 100\%$$

Where: C_i (mol/cm³) is an initial concentration of metals in aqueous solution and C_f (mol/cm³) is a final concentration of the metal in the aqueous solution at equilibrium extraction.

RESULTS AND DISCUSSION

DTA characterization of P_{1R}, P_{2R} and P_{3R}

The DTA curve of commercial PVC shows a melting point at 270°C with no exothermic peak up to 400°C; it also shows a glass transition around 80°C. The P_{2R} polymer shows an endothermic transformation at 238°C which corresponds to the degradation of the polymer with no exothermic peak up to 400°C. In the case of the
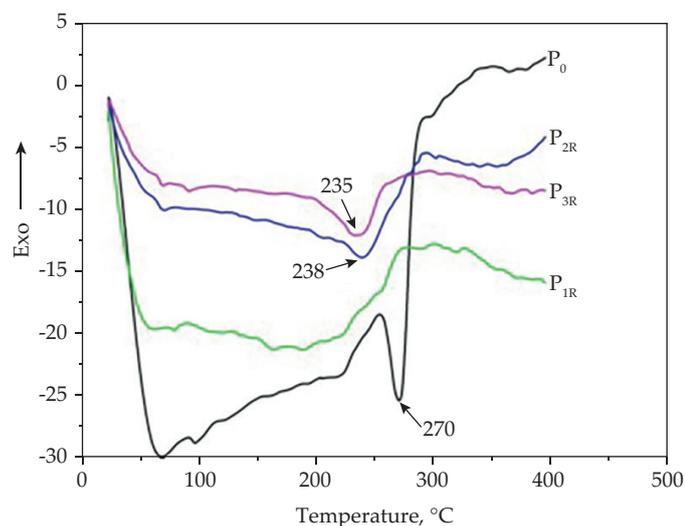
P_{3R} polymer, we note the presence of an endothermic transformation at 235°C due to the decomposition of the polymer [22].

IR spectroscopy

IR spectroscopic analysis of the modified polymer (P_{1R}) clearly shows that a substitution reaction is taking place, as indicated by the appearance of characteristic bands for amino groups at 3434 and 3310 cm⁻¹ corresponding to NH_2 and NH, respectively, and absorption at 1680 cm⁻¹ corresponding to in-plane N-H bending. Absorption at 1467 cm⁻¹ corresponding to aromatic C=C confirmed the presence of a benzene ring in the PVC chains. However, the spectrum also shows the presence of weak chlorine band-stretching vibrations (VC-Cl) at 690 cm⁻¹. This means that not all chlorine atoms have reacted. All characteristic bands observed for P_{2R} also occurred in the FTIR spectrum of P_{3R} (Fig. 2), with an increase in the intensity of the valence band corresponding to C-O-C appearing in the P_{1R} spectrum around 1050-1170 cm⁻¹. This finding confirmed the grafting of the ether group (dichlorodiethyl ether) onto the amino-PVC. [23].

Comparison of the FTIR spectra for P_{1R}, P_{2R} and P_{3R} with the P_0 spectrum clearly shows the P_0 modification, as we observed a decrease in the νC-Cl band at 690 cm⁻¹ and the appearance of the ν C-O-C band at 1167 cm⁻¹ for P_{1R}.

T a b l e 1. FTIR data for P_0 and P_{1R}, P_{2R}, P_{3R}.

Characteristic band	Wavenumber, cm⁻¹			
	P_0	P_{1R}	P_{2R}	P_{3R}
C-Cl	690	690	–	690
CH₂	2930–2860	2930–2860	2930–2860	2930–2860
NH	–	3300–3400	3330–3450	3330–3390
aromatic C=C	–	1437	1437	1426
ether C-O-C	–	1050–1070	1050–1185	1106

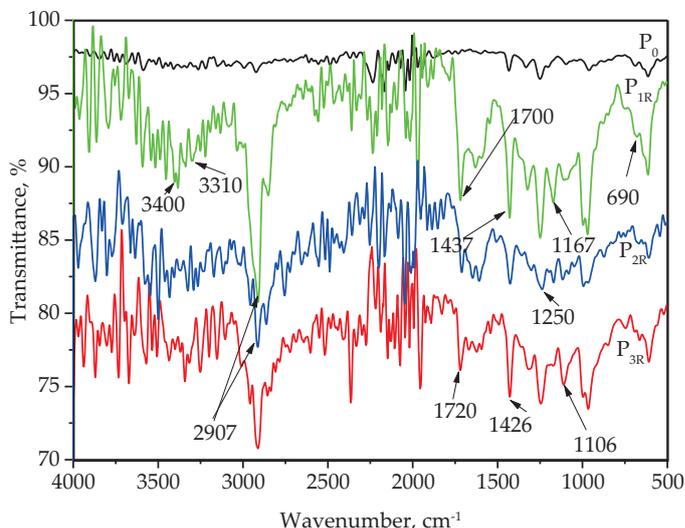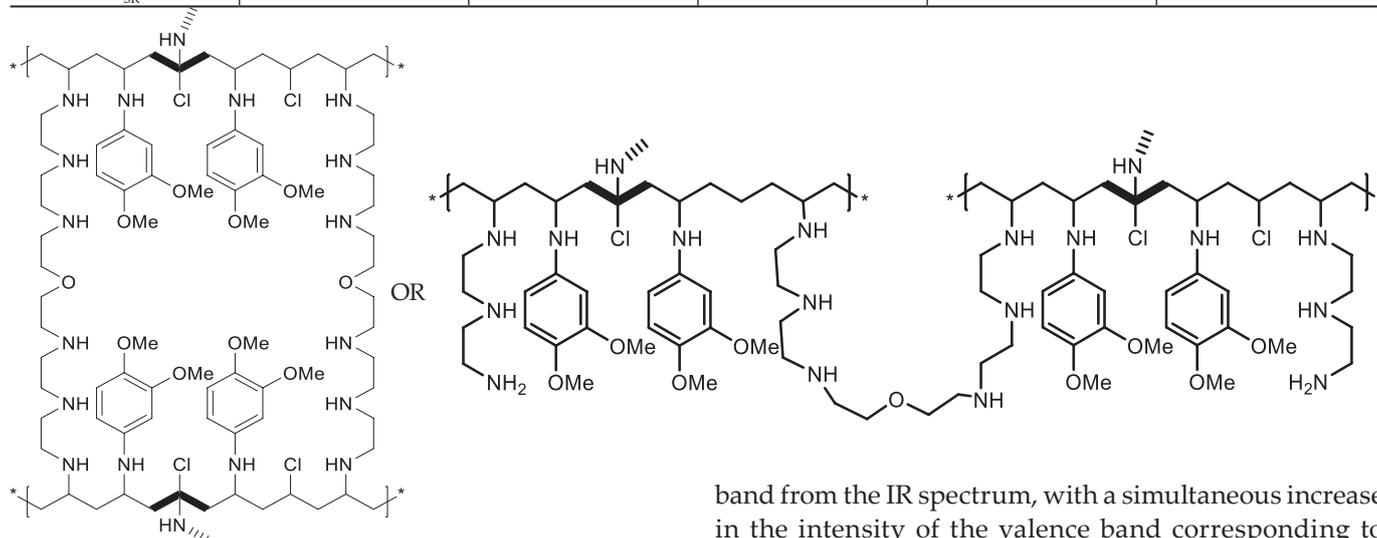Fig. 1. DTA curves of P_{1R}, P_{2R} and P_{3R} polymers

Fig. 2. FTIR spectra of the P_0, P_{1R}, P_{2R} and P_{3R} polymers

T a b l e. 2. Elemental analysis for P_0 and crosslinked polymers

Polymer	N, %	O, %	H, %	C, %	∑N, H, C; %
P_0	0.00	0.00	4.56	36.50	41.06
P_{1R}	14.22	8.55	6.73	62.88	92.38
P_{2R}	12.80	6.80	5.30	60.30	85.20
P_{3R}	11.30	5.70	4.70	58.40	80.10

Scheme B

Elemental analysis

Element percentage comparison for P_{1R}, P_{2R} and P_{3R} with P_0 clearly show that there has been a change in the chemical structure of the polymer. This is due to the difference in the percentage of nitrogen, which increased from 0 to 7.3% and 5.8% for P_{1R} and P_{2R}, respectively, and about 4.5% for P_{3R}. The percentage share of other elements (C and H) also increased.

Proposed structures of P_{1R}

Scheme 1 shows the P_{1R} possible structure which may be evidenced by the complete disappearance of the V_{C-Cl} band from the IR spectrum, with a simultaneous increase in the intensity of the valence band corresponding to C-O-C, which appeared at the wavenumber of about 1050-1170 cm^{-1}.This finding confirmed the grafting of ether group (dichlorodiethyl ether) on the amino-PVC according to scheme B.

Extraction of metal cations with modified polymers

Kinetic study

The curves representing the evolution of conductivity with time in different aqueous solutions show that the conductivity decreases, then Δt remains constant after a certain time, and t represents the shortest time (Table 3). The results show that the three cross-linked polymers have the shortest optimal extraction time for Li^+ cations; this may be due to their small size and thus easy extraction (Fig. 3.)
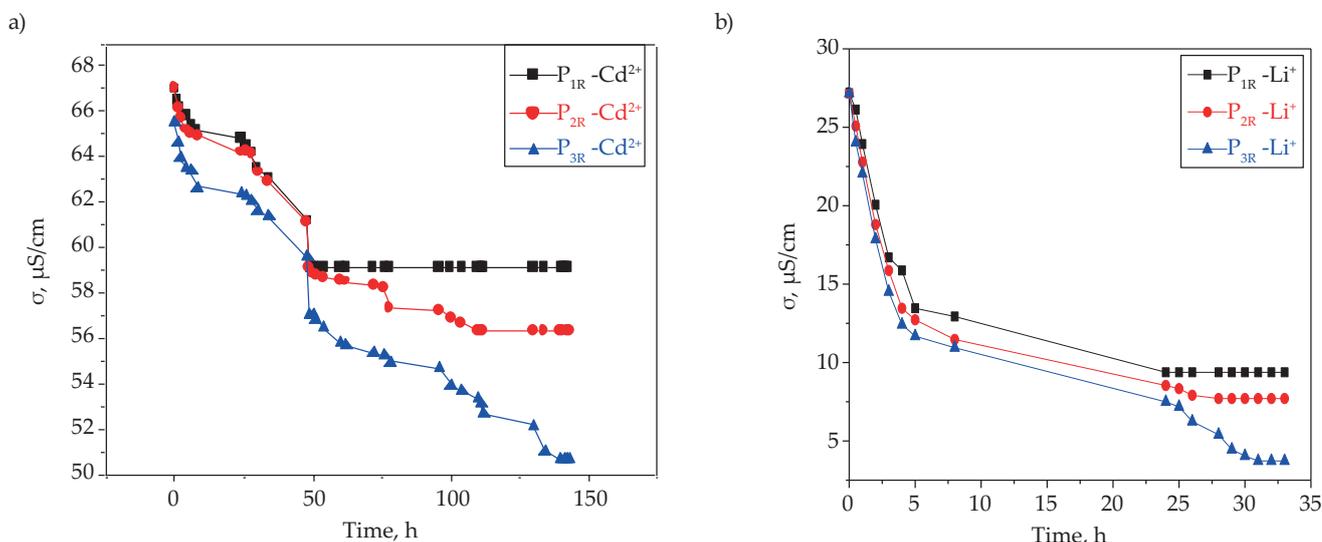

Fig. 3. Variation of electrical conductivity as a function of time for certain cations: a) P_{1R}-Cd^{2+}, P_{2R}-Cd^{2+}, P_{3R}-Cd^{2+}; b) P_{1R}-Li^+, P_{2R}-Li^+, P_{3R}-Li^+

T a b l e 3. Optimal extraction time with P_{1R}, P_{2R}, P_{3R} polymers

Polymers	P_{1R}	P_{2R}	P_{3R}
Optimal time for Li$^+$ per hour	25	30	34
Optimal time for Cd^{2+} per hour	55	110	140

The studied materials P_{1R}, P_{2R} and P_{3R} remove metal cations in percentages ranging from 70% to 94%. These results are the average of three experiments for each metal studied. These results indicate that the P_{1R} material is the best extractant for Li$^+$ and Cd^{2+} cations. This confirms the structure proposed in Scheme 1, 2, as the P_{1R} material corresponds to a greater number of substituted chlorine atoms than P_{3R}. The presence of oxygen atoms, due to the introduction of aminoveratrol groups in the structure of P_{1R}, was confirmed by infrared analysis to promote the extraction of these metal cations, which is consistent with the theory of hard and soft acids (HSAB), for the oxygen atom and Li$^+$ cation that confirmed by this theory. They therefore have an affinity for these hard acids. 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 heteroatomic ligands (oxygen and nitrogen atoms). This type of atoms (N, O) can bind the metal by non-covalent bonds (van der Waals bonds). According to the structures there are several types of macrocyclic complexing cavities. The retention of metal cations can also 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.

The extraction was performed using the atomic absorption spectrometry technique. Table 4 shows the heavy metal extraction determined by conductivity measurements and by AAS.
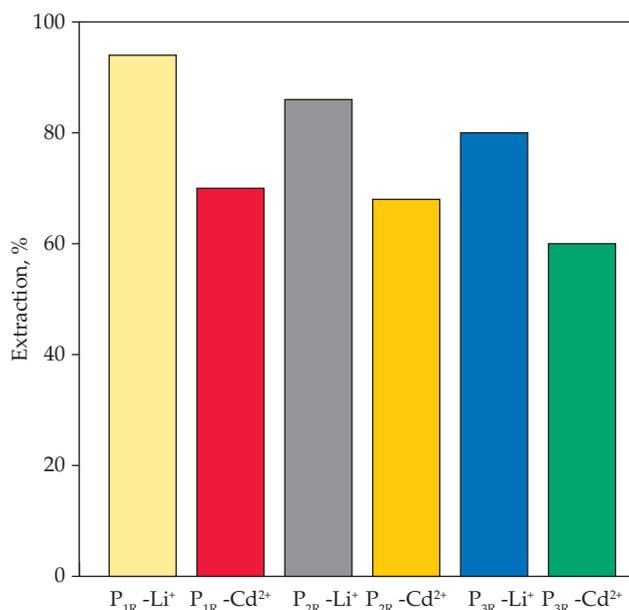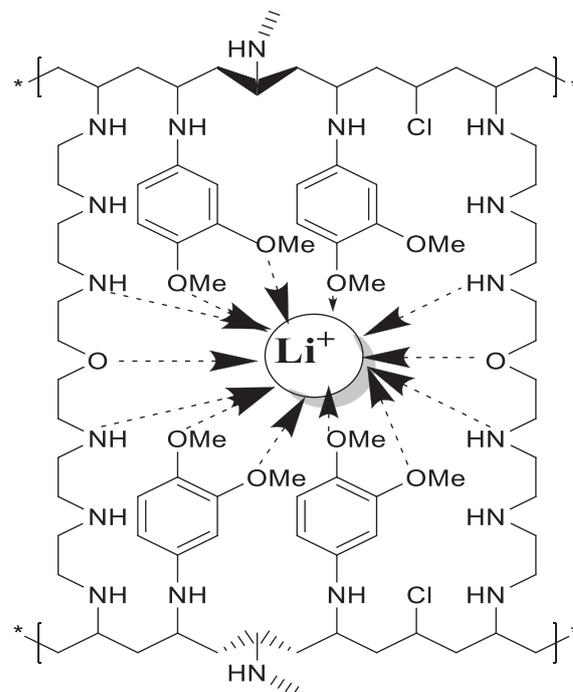
The absorption method is better than conduction extraction. The difference between the extraction determined by these two methods is between 8% and 10%.

Proposed structures of P_{1R} –Li$^+$

P_1 was grafted with dichlorodiethyl ether. The possible structure of P1R is shown in Scheme 1. The structural proposal is suggested by the complete disappearance of the VC-Cl band from the IR spectrum, with an increase in the intensity of the valence band corresponding to C-O-C that appears around 1050-1170 cm^{-1}. This finding confirmed the grafting of ether group (dichlorodiethyl ether) on the amino-PVC [23].

Fig. 4. Extraction of Li$^+$ and Cd^{2+} with modified polymers

Scheme C

Influence of complexation in IR spectroscopy

Fig. 5 presents the IR spectra of P_i-Li$^+$ and P_i-Cd^{2+} complexes. The IR spectra of the P_{1R}-Mn$^+$, P_{2R}-Mn$^+$ and P_{3R}-Mn$^+$ complexes show that there is a decrease in the intensity of the characteristic band of the amine (υ NH$_2$-alkyl) around
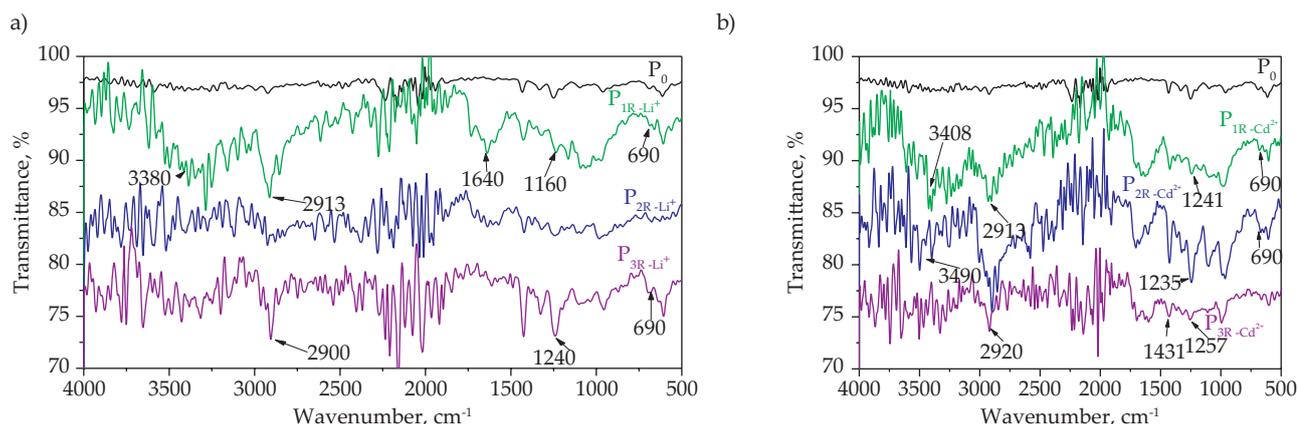
T a b l e 4. Extraction percentages obtained by conductivity and AAS

Metal cation	Extraction with P_{1R}, %		Extraction with P_{2R}, %		Extraction with P_{3R}, %	
	Conductivity	ASS	Conductivity	ASS	Conductivity	ASS
Li$^+$	94%	84.5%	86%	67.2%	80%	70.1%
Cd^{2+}	70%	60.5%	68%	57.5%	60%	50.7%

Fig. 5. FTIR spectra of polymers: a) P$_0$, P$_{1R}$-Li$^+$, P$_{2R}$-Li$^+$ et P$_{3R}$-Li$^+$, b) P$_0$, P$_{1R}$-Cd^{2+}, P$_{2R}$-Cd^{2+}, P$_{3R}$-Cd^{2+}

3378 cm^{-1}. Two major peaks were previously reported and assigned as follows: the band characteristic of the substituted benzene ring; 1236 cm^{-1} and 1094 cm^{-1}, aromatic para-substitution, and C–H vibrations of aromatic structures, respectively. Also, the band at about 690 cm^{-1} attributed to C-Cl stretching vibrations decreases and shifts to lower wavenumbers clearly indicating that some of the chlorine has been removed. According to the literature [22, 23] in the FTIR spectrum of PVC, the asymmetric stretching vibration mode (-CH-) can be observed at 2951 cm^{-1}. After PVC crosslinking, the peak corresponding to C-O-C stretching vibrations decreases, while the spectral position of this peak shifts to lower wavenumbers appeared. Therefore, we believe that the extraction of Li$^+$ and Cd^{2+} with cross-linked polymers and an attractive green alternative, and the transfer operation of Li$^+$ through these polymers are used in certain pre-treatment occasions, such as wastewater treatment.

DTA analysis

The DTA curves of the studied polymers are presented in Fig. 6. The DTA thermograms of the P$_i$-Li$^+$ and P$_i$-Cd^{2+} polymers show the existence of an exothermic peak

observed at 160°C for P$_{1R}$-Li$^+$ and around 170°C for P$_{2R}$-Li$^+$, probably corresponding to the start of the decomposition of the polymer, this peak was absent on the DTA curve of the P$_{3R}$-Li$^+$ polymer, these results show that the polymers are not identical. On the other hand, for the polymer P$_{3R}$-Cd^{2+} we notice the absence of the endothermic peak around 295°C corresponds to the fusion of this polymer (Fig. 6)

CONCLUSIONS

The reaction of commercial PVC substituted with ether groups containing donor atoms shows the importance of the chemistry used for the modification of long chain functionalized synthetic polymeric materials. These new cross-linked materials containing electron donor atoms, such as nitrogen and oxygen, are used as chelating agents to remove heavy metals. The studied materials can remove metal cations with percentages from 58.4 % to 91.7 %.
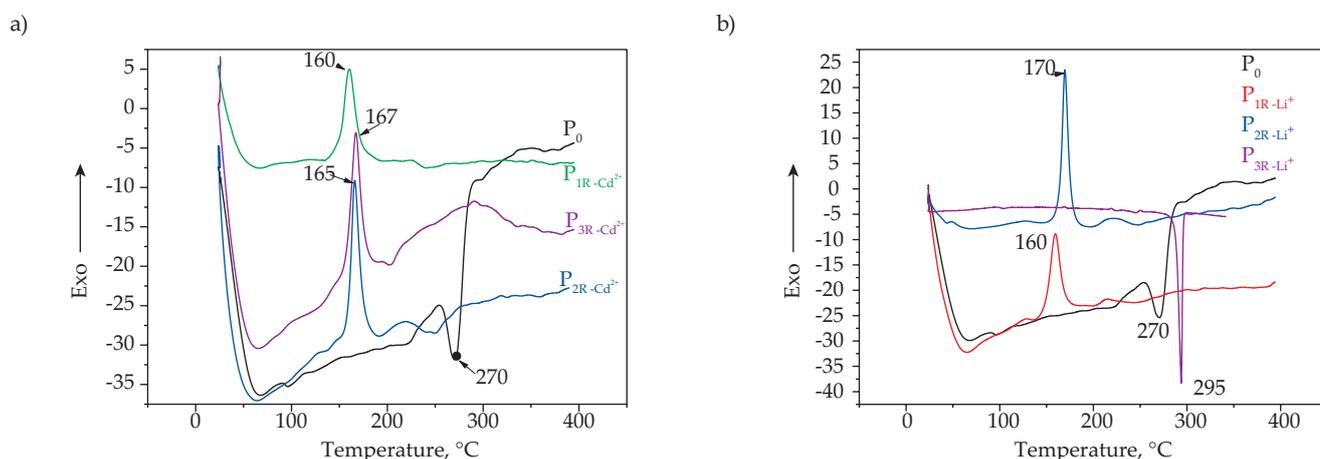
Fig. 6. DTA of polymers: a) P$_i$-Li$^+$, b) P$_i$-Cd^{2+}

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