Application of poly(vinyl chloride) modified with β-amino alcohols derived from limonene oxide for removal of hazardous metal ions

Faten Brahmi[1], Abir Bel Hadj Amor[1, *], Faouzi Meganem[1]

DOI: dx.doi.org/10.14314/polimery.2018.4.5

Abstract: In the present work, we have investigated the modification of poly(vinyl chloride) using three β-amino alcohols synthesized from limonene oxide (LO). Three polyamines: ethylenediamine (EDA), diethylenetriamine (DETA) and triethylenetetramine (TETA) were reacted with limonene oxide using water as a catalyst. Afterwards, the reaction of β-amino alcohols with poly(vinyl chloride) was conducted successively, which gave three novel polymers P1, P2, P3 and polymer P4 derived from the cross-linking of P1 by DETA. The products have been characterized using Fourier transform infrared spectroscopy (FT-IR), differential scanning calorimetry (DSC), element analysis (EA) and X-ray diffraction (XRD). The novel chelating polymers were used in the extraction of hazardous metal ions: bismuth, iron, chromium, aluminum and lead from aqueous solutions. The polymers functionalized with various β-amino alcohols showed a high selectivity in extraction of Bi(III) and Fe(III), especially in the case of P3. The efficiency of metal extraction process depends on the amine group content in the polymer as well as the sizes of cations and ligand cavities.

Keywords: limonene oxide, β-amino alcohols, poly(vinyl chloride), extraction, hazardous metal ions.

Zastosowanie poli(chlorku winylu) modyfikowanego β-aminoalkoholami syntetyzowanymi z tlenku limonenu do usuwania jonów metali szkodliwych

Streszczenie: Poli(chlorek winylu) (PVC) modyfikowano za pomocą trzech β-aminoalkoholi syntetyzowanych z tlenku limonenu (LO) i etylenodiaminy (EDA), dietylenotriaminy (DETA) lub trietylenotetraminy (TETA) w obecności wody jako katalizatora. W reakcji β-aminoalkoholi z PVC otrzymano trzy nowe polimery P1, P2, P3. Polimer P4 uzyskano w wyniku sieciowania P1 za pomocą DETA. Produkty scharakteryzowano metodami: spektroskopii w podczerwieni z transformacją Fouriera (FT-IR), różnicowej kalorymetrii skaningowej (DSC), analizy elementarnej (EA) i rentgenowskiej analizy dyfrakcyjnej (XRD). Próbki zmodyfikowanego PVC wykorzystano w ekstrakcji z roztworów wodnych jonów metali: bizmutu, żelaza, chromu, aluminium i ołowiu. Stwierdzono, że otrzymane chelatujące pochodne PVC, zwłaszcza P3, wykazują wysoką selektywność w wychwytywaniu z roztworów wodnych jonów Bi(III) i Fe(III), a wydajność procesu zależy od zawartości grup aminowych w polimerze oraz rozmiarów kationów i centrów koordynacyjnych.

Słowa kluczowe: tlenek limonenu, β-aminoalkohole, poli(chlorek winylu), ekstrakcja, jony metali szkodliwych.

Water pollution by metallic ions in anionic or cationic forms and other pollutants is becoming an expanding concern. In view of potential alteration of the natural ecosystems and human health, many efforts have been going in the direction to develop a sophisticated methods and technology of depollution, prevent health risks and save biotopes and biosystems. Among them, the active matrices for extraction of metallic ions from the solutions have been developed.

Moreover, hazardous metals are toxic substances originating from various natural or human activities such as industrial activities, agriculture and combustion of fossil fuels also waste disposal, battery manufacture, and petroleum refining [1]. These are characterized to be non-biodegradable and they can be accumulated in internal organs, and cannot be utilized by living organisms, thus causing various problems and disorders [2–5]. Therefore, these toxic metals must be removed from wastewater

---

[1] University de Carthage, Laboratory of Organic Synthesis, Faculty of Sciences of Bizerte, 7021 Jarzouna, Bizerte, Tunisia.

[*] Author for correspondence; e-mail: abir_belhadj@yahoo.fr

to prevent their release to the environment [4–6, 7] first, otherwise many precautions have to be developed in order to limit or minimize their harmful effects. Among many techniques, solid phase extraction (SPE) is an adequate technique for trace metals separation/preconcentration, and it consists on a simple and flexible principle, it is also easy of automation, and having a high enrichment factor [8]. Accordingly, several selective solid phase extractors have been prepared either by physical loading or chemical binding of selected chelating reagents [9] to different solid supports such activated carbon [10], alumina [11], polyurethane foam [12], chelating ion exchange resins [13] and polystyrene [14, 15].

Moreover, poly(vinyl chloride) (PVC) due to many advantages including high surface area, physical and chemical stability in concentrated acidic and basic media as well as organic solvents is a suitable support for SPE. The surface of PVC could be modified by a sorbent to obtain reversible and efficient enrichment of metal ions capture [16]. Therefore, by chemical modification of PVC with appropriate compounds, new polymers with improved physical properties can be obtained [17, 18]. These modifications are presented according to the bond formed (C_{PVC}–X) between the PVC carbon C_{PVC} and the atom X (X = N, O, S, Hal) of the modified used molecule [19]. The advantages of the insoluble functionalized polymers are generally associated with a simplification of the workup, separation processes, and the possibility to be recycled and reused for different applications [20].

In this context, specialty chemicals such as β-amino alcohols are an important class of organic compounds due to their bi-functional nature having alcohol and amine functional groups holt in the same compound, which allow them to react in a wide variety of ways [21]. Chemical modifications of PVC with β-amino alcohols and the reticulated polymer by EDTA are useful to remove hazardous metals ions from aqueous solutions with solid phase extraction.

In this work, new chelating polymers were synthesized by grafting three β-amino alcohols derived from limonene oxide on poly(vinyl chloride). The products P1, P2 and P3 as well as P4, prepared *via* crosslinking of P1 by DETA were used for the extraction of hazardous metal cations (Bi^{3+}, Fe^{3+}, Cr^{3+}, Al^{3+} and Pb^{2+}), which are widespread in the environment and are known to be dangerous to human health.

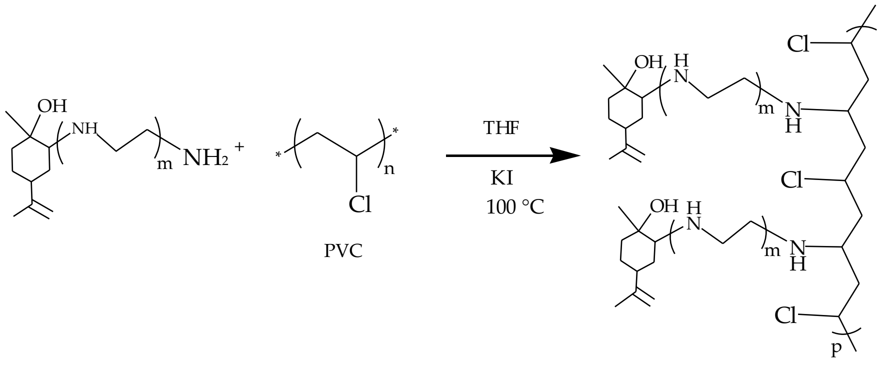
EXPERIMENTAL PART

Materials

Reactions were carried out in oven-dried glassware under an inert atmosphere. All reagents were purchased from commercial suppliers and used without further purification. Tetrahydrofuran (THF) was used as the solvent. *R*-(+)-limonene oxide (LO), ethylenediamine (99 %), diethylenetriamine (99 %) and triethylenetetramine (97 %), reagents used were supplied by Sigma-Aldrich. Absolute ethanol, triethylamine (TEA) and diethyl ether were purchased from Prolabo. Poly(vinyl chloride), high molar mass (*M* = 48 000 g/mol, 16 mmol Cl/g, 99 %) was purchased from Fluka. Potassium iodide (KI) (99 %), $Fe(NO_3)_3 \cdot 9\,H_2O$ (99 %) and $Pb(NO_3)_2$ (99 %), $AlCl_3$ (99 %), $Cr(NO_3)_3 \cdot 9\,H_2O$ (99 %) and $Bi(NO_3)_3 \cdot 9\,H_2O$ (98 %) were produced by Sigma-Aldrich. Aqueous monometallic solutions were prepared at a concentration of $2 \cdot 10^{-4}$ mol/dm^3 in relation with each metal ion in distilled water (pH = 6–7).

Synthesis of β-amino alcohols AA1, AA2 and AA3

Three β-amino alcohols were prepared according to the literature [22–24]. Three polyamines: EDA, DETA and TETA (30 mmoles), each amine was combined with *cis*/*trans*-(+)-limonene oxide mixture (50 mmoles) and deionized water (1 cm^3). The reaction was maintained for 24 h at 100 °C. The reaction mixture was cooled at room temperature. The excess of polyamines and limonene oxide were distilled off giving crude β-amino alcohols: orange oil (AA2) and yellow oil (AA1 and AA3). Each product was purified by acid-base extraction: the oil was dissolved in methanol. To the stirred solution, a solution of oxalic acid in methanol was slowly added. White solid formed. The solid was cooled to 0 °C and stirred for 0.5 h. The solid was isolated by filtration, washed with cold methanol, and vacuum dried at 50 °C to give the oxalate salt of β-amino alcohols as a white solid. A sample of the oxalate salt was mixed with a solution potassium hydroxide and diethyl ether. The mixture was shaken and the



Scheme A. Synthesis of polymers P1, P2 and P3

layers separated. The aqueous layer was extracted with diethyl ether (3 times). The combined ether fractions were washed with deionized water. The ether solution was dried over anhydrous magnesium sulfate. The diethyl ether was removed in vacuo (rotary evaporator) giving orange oil for AA2 and yellow oil for AA1 and AA3.

Synthesis of PVC modified with β-amino alcohols

PVC (1 g, 16 mmol Cl) was suspended in 40 cm^3 THF, KI (1 g) and β-amino alcohols (64 mmol, 4 eq.) were added. The reaction mixture was charged in a hydrogenation bomb at 100 °C for 10 h. The product was precipitated, then filtered and washed with distilled water and diethyl ether. Finally, the obtained polymer was dried at room temperature, and then at 65 °C for 24 h. The same reaction was repeated except changing the β-amino alcohols. These obtained products have a weak solubility in THF and are not soluble in organic solvents such as: ethanol, methanol, acetone, chloroform and dichloromethane. The obtained polymers are designated as: P1, P2 and P3. A yellow powder was obtained for P1 and P2, dark brown powder was obtained for P3 (Scheme A).

Modification of P1 by diethylenetriamine: P4

Polymer P1 (1 g) was suspended in 50 cm^3 THF followed by the addition of DETA (3 cm^3) and 50 mg of KI used as catalysts. The reaction mixture was charged in hydrogenation bomb at 100 °C for 10 h. The obtained product is filtered and washed with distilled water, then with diethyl ether to remove adsorbed amines. After that, the product was dried for 24 h in an oven at 65 °C, a light yellow powder was obtained in case of P4 (Scheme B).

Extraction procedure of metal cations

Five aqueous metallic solutions of $AlCl_3$, $Fe(NO_3)_3 \cdot 9\,H_2O$, $Bi(NO_3)_3 \cdot 9\,H_2O$, $Pb(NO_3)_2$, and $Cr(NO_3)_3 \cdot 9\,H_2O$ were prepared at a concentration of $2 \cdot 10^{-4}$ mol/dm^3 each in distilled water. Then, 0.1 g of modified PVC (P1, P2, P3 and P4) was introduced with 20 cm^3 of the metal ion solution at 25 °C for 24 h. These polymers were separated by filtration and washed in deionized water. The filtrate was analyzed by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The results were demonstrated as percentages of metal extraction, based on its initial concentration.

The extraction percentage (%) was calculated using the following equation:

$$\%\ \text{Extraction} = \frac{C_0 - C_f}{C_0} \cdot 100\,\% \qquad (1)$$

where: C_0 – concentration of the metal ion in initial solutions, C_f – concentration of the metal ion in final solutions.

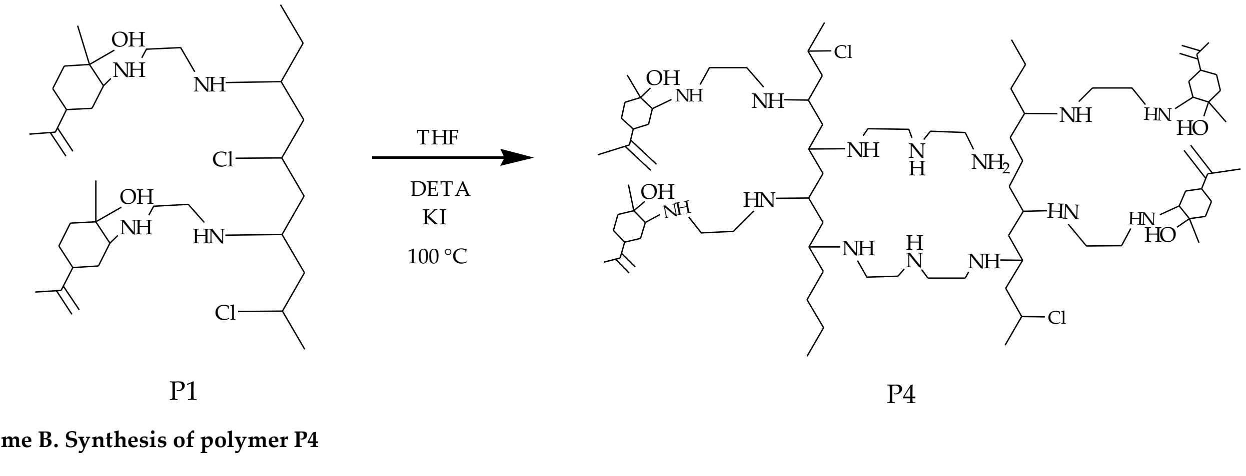
Methods of testing

Infrared analysis was carried out by using the attenuated total reflectance technique (ATR/FT-IR), with a Nicolet FTIR 200 spectrophotometer (Thermo Scientific, France). ^1H NMR and ^{13}C NMR spectra were recorded with $CDCl_3$ solvent containing TMS (tetramethylsilane) as the internal standard on a Bruker 300 spectrometer (^1H: 300 MHz, ^{13}C: 75.47 MHz). Elemental analysis of C, H and N was performed by using Perkin Elmer Analyzer CHN Series II 2400. Differential scanning calorimetry (DSC) was performed on a SETARAM DSC 131 apparatus (Caluire, France). X-ray diffraction (XRD) was recorded on a Bruker D8 Advance device (Germany). The amount of remaining metal ions in solution was evaluated by ICP-AES: HORIBA JOBIN (HORIBA Jobin Yvon S.A.S., 16-18 Canal Street, 91165 Longjumeau Cedex).

RESULTS AND DISCUSSION

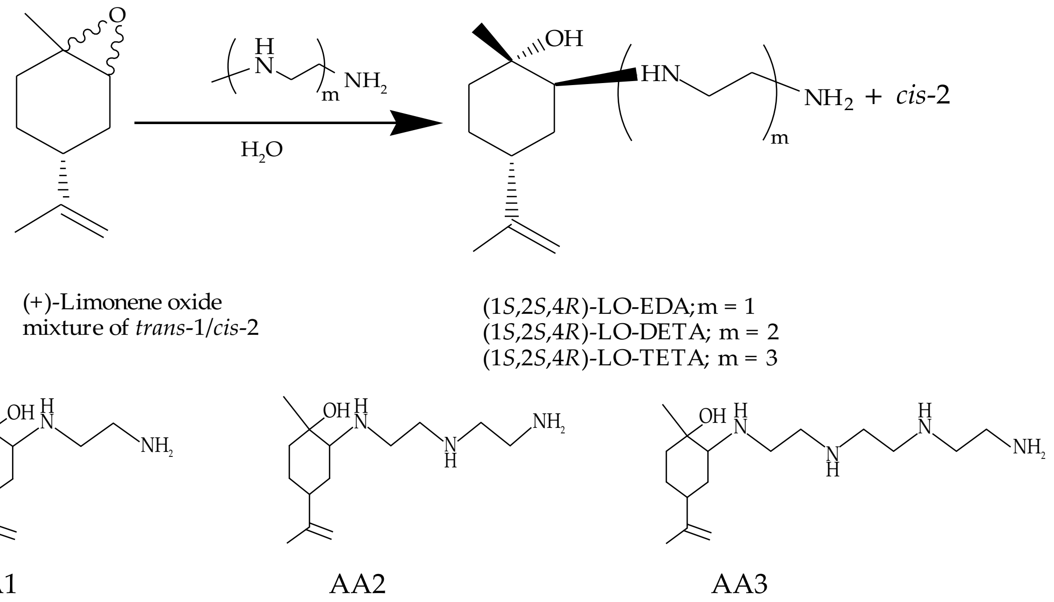
Preparation of ligands: AA1, AA2 and AA3

Synthesis of the ligands AA1, AA2 and AA3 in one simple step is shown in Scheme C. The nucleophilic ring opening of epoxides with amine group is a well known route for the synthesis of β-amino alcohols [25–29]. Ethylenediamine, diethylenetriamine and triethylenetetramine – nucleophilic polyamines open the epoxide ring of the *trans*-isomer, leaving the *cis*-limonene oxide largely unreacted. The unreacted *cis*-(*R*)-limonene oxide



P1 P4

Scheme B. Synthesis of polymer P4



Scheme C. Synthesis of β-amino alcohols AA1, AA2 and AA3 from limonene oxide

was recovered from the reaction mixture. Fractional distillation was used for the separation of the diastereomers [30]. Recently we reported that the *cis*-diastereomer of (*R*)-(+)-limonene oxide can be separated in its diastereomerically pure form from the commercially available diastereomeric mixture of limonene oxides [30]. The observed regioselectivity of the opening has been explained by conformational differences between the two epoxides [30].

Characterization data of the synthesized ligands AA1, AA2 and AA3 are presented respectively in Table 1. The preparation of three β-amino alcohols *via* the opening of epoxides with polyamines is confirmed by the IR and NMR spectra.

AA1: $C_{12}H_{24}N_2O$. *M* = 212 g/mol, yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.1 (s, 3H), 1.3 (m, 2H), 1.5 (m, 4H), 1.8 (m, 3H), 2.2 (m, 1H), 2.4 (m, 1H), 2.7 (m, 2H), 2.8 (m, 2H), 4.7 (s, 1H), 4.8 (s, 1H) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 21.75, 26.4, 26.5, 30.35, 34.84, 39.85, 44.42, 49.75, 66.09, 71.58, 108.98, 149.22 ppm.

AA2: $C_{14}H_{29}N_3O$. *M* = 255 g/mol, orange oil; ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.1 (s, 3H), 1.3 (m, 2H), 1.47 (m, 4H), 1.7 (m, 3H), 2.1 (m, 1H), 2.2 (m, 1H), 2.67 (m, 4H), 2.86 (m, 4H), 4.7 (s, 1H), 4.8 (s, 1H) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 21.89, 27.34, 27.68, 30.75, 34.74, 37.95, 44.92, 46.22, 48.12, 52.33, 61.59, 71.47, 108.70, 148.92 ppm.

Table 1. Characterization data of prepared ligands AA1, AA2 and AA3

Ligand	Formula	*M* g/mol	Yield %
AA1	$C_{12}H_{24}N_2O$	212	92
AA2	$C_{14}H_{29}N_3O$	255	88
AA3	$C_{16}H_{34}N_4O$	298	90

AA3: $C_{16}H_{34}N_4O$. *M* = 298 g/mol, yellow oil; ^{1}H-NMR (300 MHz, $CDCl_3$, δ): 1.1 (s, 3H), 1.3 (m, 2H), 1.5 (m, 4H), 1.7 (m, 3H), 2.1 (m, 1H), 2.4 (m, 1H), 2.7 (m, 8H), 2.87 (m, 4H), 4.7 (s, 1H), 4.87 (s, 1H) ppm.

^{13}C NMR (75.5 MHz, $CDCl_3$, δ): 22.5, 26.4, 26.98, 30.50, 35.11, 39.98, 44.26, 48.15, 50.9, 52.65, 55.12, 56.50, 61.30, 76.58, 108.80, 149.73 ppm.

Using this reaction, a series of (1*S*,2*S*,4*R*)-stereoisomers of β-amino alcohols: AA1, AA2 and AA3 derived from (+)-limonene oxide was synthesized.

Characterization of chelating polymers

ATR/FT-IR analysis

The structures of the synthesized chelating resins P1, P2 and P3 were confirmed by comparing the ATR/FT-IR spectra of PVC before and after reaction with β-amino alcohols AA1, AA2 and AA3 as shown in Fig. 1. FT-IR spectra of the commercial PVC presents a high intensity band that can be assigned to the stretching vibration C–Cl at 690 cm^{-1}, this result is confirmed by Ammari *et al.* [31]. P1, P2 and P3 show two broad peaks around 3388 cm^{-1} and 3325 cm^{-1} due to the stretching vibration of NH primary, secondary amines and OH. A bending vibration of NH appears at 1647 cm^{-1}. A stretching vibration of CN was recorded at 1303 cm^{-1}. The most significant change observed in the spectra of the modified PVC is very low intensity of the characteristic C–Cl band at 690 cm^{-1} compared to that corresponding to commercial PVC. This indicates the substitution of chlorine atoms by β-amino alcohols groups in the modification products.

The variation of the chemical structure through the grafting of diethylenetriamine onto the modified PVC P1 was confirmed by ATR/FT-IR. The spectra of P and P1 were compared to that of P4. As a result of grafting and

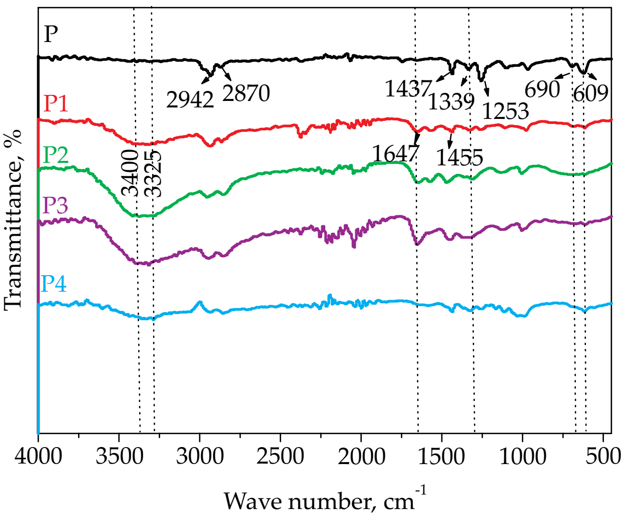


Fig. 1. ATR/FT-IR spectra of polymers P (PVC), P1, P2, P3 and P4

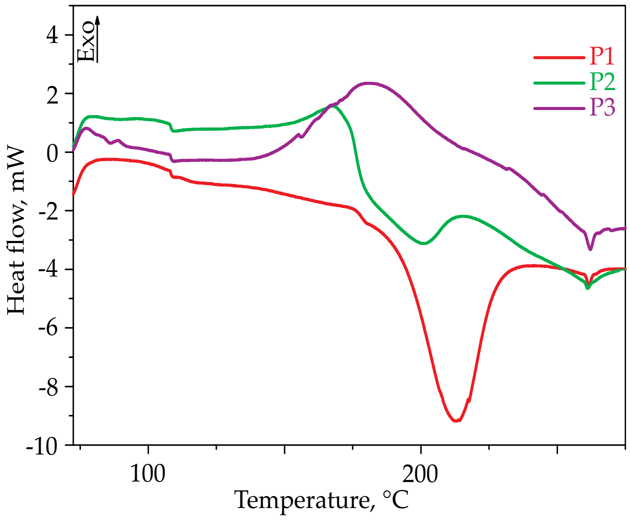


Fig. 2. DSC thermograms of P1, P2 and P3

crosslinking reactions, the band C–Cl at 690 cm^{-1} becomes smaller and a broadening of two peaks around 3382 cm^{-1} and 3305 cm^{-1} due to the asymmetrical and symmetrical NH stretching vibrations is observed.

Elemental analysis

The elemental analysis results are illustrated in Table 2. 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 [32]. The presence of 0.39 wt %, 2.80 wt % and 10.43 wt % of nitrogen in polymers P1, P2 and P3, respectively, confirms the success of grafting of three amino alcohols AA1, AA2 and AA3 on commercial PVC. These findings suggest that the resin structure and polyamine chain length influence the nitrogen content [33]. In the cases of P1 and P4, the aminated PVC were found to contain 0.39 wt % and 2.36 wt % of nitrogen, respectively. The higher amine content in P4 compared to P1 indicates the higher percentage of conversion of the modified PVC.

DSC analysis

DSC diagrams of novel polymers P1, P2 and P3 are presented in Fig. 2. The thermogram of polymer P1 presents two endothermic transformations at 221 °C and 292 °C, whereas, in the case of polymer P2 four transformations are observed: two endothermic at 205 °C and 293 °C and two exothermic at 158 °C and 221 °C. Finally, the diagram of polymer P3 shows an endothermic peak at 294 °C and an exothermic transformation at 175 °C. These transformations have been attributed to the decomposition of these polymers.

T a b l e 2. Elemental analysis results of polymers

Sample	C, wt %	H, wt %	N, wt %
P1	68.33	4.70	0.39
P2	72.96	6.46	2.80
P3	80.13	8.28	10.43
P4	62.70	5.61	2.36

XRD analysis

The XRD patterns of PVC before and after their modifications with three β-amino alcohols P1, P2, P3 and P4 derived from the grafting and crosslinking of P1 by DETA are shown in Fig. 3. The three broads peaks at 2θ = 6°, 2θ = 18° and 2θ = 25° revealed an amorphous structure of the commercial PVC [34, 35], which remained the same after β-amino alcohols loading. The absence of any crystalline regions in the samples is related to the presence of polymeric chains [36]. It can be concluded that these polymers P1, P2, P3 and P4 have amorphous structures.

Use of the modified polymers for the metal extraction

Alkylamines like diethylenetriamine has been successfully used to impart metal ion-extracting properties to polymers [37]. The successful extraction of metal ions can be attributed to the interaction of metal cations with amine nitrogen atom.

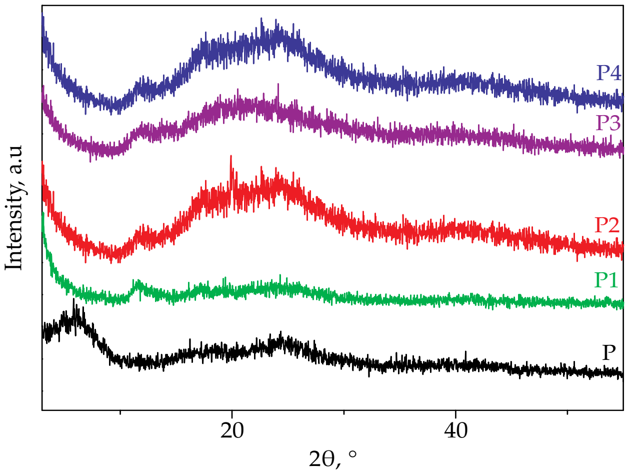
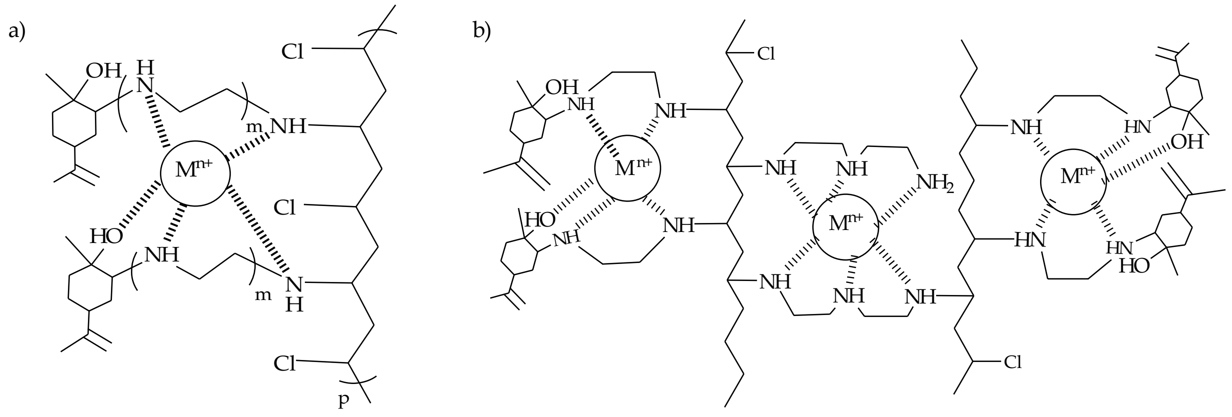


Fig. 3. XRD of polymers P (PVC), P1, P2, P3 and P4



Scheme D. a) Structure of complex P1-M^{n+}, P2-M^{n+} and P3-M^{n+}, b) structure of complex P4-M^{n+}

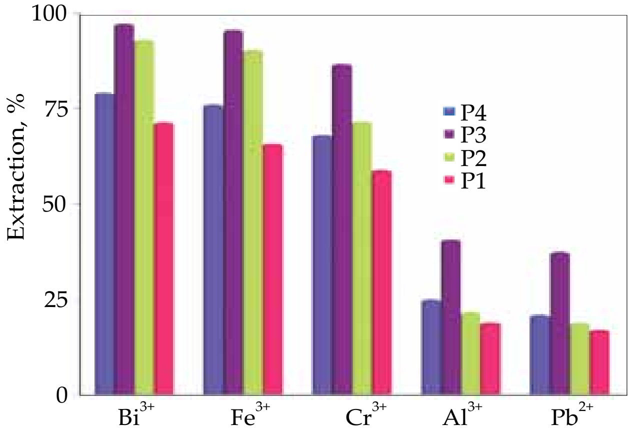


Fig. 4. Percentages of metal cations extraction for the polymers

The extraction of metal cations using the PVC modified with β-amino alcohols and DETA, were carried out in the aqueous solutions of $AlCl_3$, $Fe(NO_3)_3 \cdot 9\ H_2O$, $Bi(NO_3)_3 \cdot 9\ H_2O$, $Pb(NO_3)_2$, and $Cr(NO_3)_3 \cdot 9\ H_2O$ prepared at $2 \cdot 10^{-4}$ mol/dm^3. The functionalized polymers were tested for its extractant properties of hazardous metals. Based on the experiments, the time required to extract the hazardous metal ions was assumed to be 24 h. The extraction percentages varied depending on the metal ion. The extraction experiments showed that the modified polymers are highly selective for Bi(III), Fe(III), and Cr(III) cations and provide good extraction efficiencies. Obviously, polymers P3 and P2 have better extraction percentages for Bi(III), Fe(III), Cr(III), Al(III) and Pb(II) ions than P1, especially polymer P3, which can be explained by a higher content of nitrogen atoms in the functional groups and better coordination with metallic ions (Scheme D).

Also, as it can be seen from Fig. 4, the yield of extraction ranged in ascending order: Pb(II) < Al(III) < Cr(III) < Fe(III) < Bi(III).

In order to further improve the extraction properties of polymer P1, it was additionally modified by reaction with diethylenetriamine. The resulting polymer P4 showed good extraction capacities for Bi(III), Fe(III), Cr(III), Al(III) and Pb(II) (Fig. 4). Obviously, the polymer P4 had higher extraction yields – 79 % for Bi(III), 76 % for Fe(III), 68 % for Cr(III), 25 % for Al(III), and 21 % for Pb(II) – compared to P1.

The high extraction selectivity for Bi(III), Fe(III) and Cr(III) ions can be explained on the basis of the hard-soft acid-base (HSAB) theory. Fe(III) and Cr(III) were classified as a hard ions, Bi(III) was classified as intermediate ion, they have affinities to two types of soft ligands which contain nitrogen atoms and hard ones which contain oxygen atoms of β-amino alcohols.

The differences in extraction percentages of individual metal ions can be ascribed to the compatibility factor between the cation size and the ligand cavity size in the polymer as well as the number and type of heteroatom ligands (oxygen and nitrogen atoms of β-amino alcohols and nitrogen atom of DETA).

CONCLUSIONS

We have shown a simple and an eco-friendly way to synthesize novel chelating resins *via* chemical grafting of β-amino alcohols derived from limonene oxide on PVC. The synthesized polymers were characterized with FT-IR spectroscopy, elemental analysis, DSC and XRD. These PVC-based β-amino alcohols were tested for their ability to extract metallic ions from aqueous solutions, particularly for Bi(III), Fe(III), Cr(III), Al(III) and Pb(II). The polymers were found to extract these ions with a clear selectivity and affinity following the order: Pb < Al < Cr < Fe < Bi. The removal extent of these hazardous and toxic metals was substantial, more than 97 %. These chelating polymers can be used as complexing agents that can be simply filtered, regenerated and reused repeatedly. The supported ligands prepared in this work can be applied to minimize the negative effects of hazardous metals on the environment.

ACKNOWLEDGMENT

The authors are very grateful to Tunisian 05/UR/12-05 that financed this project.

REFERENCES

[1] Srivastava N.K., Majumder C.B.: *Journal of Hazardous Materials* **2008**, *151*, 1. http://dx.doi.org/10.1016/j.jhazmat.2007.09.101

[2] Harrison P., Waites G.: "Cassell dictionary of chemistry", Cassell, London 1999.

[3] Gomez-Sagasti M.T., Alkorta I., Becerril J.M. *et al.*: *Water, Air and Soil Pollution* **2012**, *223*, 3249. http://dx.doi.org/10.1007/s11270-012-1106-8

[4] Chung S.G., Ryu J.C., Song M.K. *et al.*: *Journal of Hazardous Materials* **2014**, *267*, 161. http://dx.doi.org/10.1016/j.jhazmat.2013.12.056

[5] Wan Ngah W.S., Hanafiah M.A.: *Bioresource Technology* **2008**, *99*, 3935. http://dx.doi.org/10.1016/j.biortech.2007.06.011

[6] Farooq U., Kozinski J.A., Khan M.A., Athar M.: *Bioresource Technology* **2010**, *101*, 5043. http://dx.doi.org/10.1016/j.biortech.2010.02.030

[7] Yu B., Zhang Y., Shukla A. *et al.*: *Journal of Hazardous Materials* **2000**, *80*, 33. http://dx.doi.org/10.1016/S0304-3894(00)00278-8

[8] Zhang N., Peng H., Hu B.: *Talanta* **2012**, *94*, 278. http://dx.doi.org/10.1016/j.talanta.2012.03.040

[9] Pyell U., Stork G.: *Fresenius' Journal of Analytical Chemistry* **1992**, *342*, 376. http://dx.doi.org/10.1007/BF00322189

[10] Ghaedi M., Ahmadi F., Soylak M.: *Journal of Hazardous Materials* **2007**, *147*, 226. http://dx.doi.org/10.1016/j.jhazmat.2006.12.070

[11] Ghaedi M., Fathi M.R., Shokrollahi A., Shajarat F.: *Analytical Letters* **2006**, *39*, 1171. http://dx.doi.org/10.1080/00032710600622167

[12] Gurnani V., Singh A.K., Venkataramani B.: *Talanta* **2003**, *61*, 889. http://dx.doi.org/10.1016/S0039-9140(03)00373-4

[13] Tewari P.K., Singh A.K.: *Analyst* **1999**, *124*, 1847. http://dx.doi.org/10.1039/A906479F

[14] Ouerghui A., Elamari H., Dardouri M. *et al.*: *Reactive and Functional Polymers* **2016**, *100*, 191. http://dx.doi.org/10.1016/j.reactfunctpolym.2016.01.016

[15] Zhang Y., Chen Y., Wang C., Wei Y.: *Journal of Hazardous Materials* **2014**, *276*, 129. http://dx.doi.org/10.1016/j.jhazmat.2014.05.027

[16] Marahel F., Ghaedi M., Shokrollahi A. *et al.*: *Chemosphere* **2009**, *74*, 583. http://dx.doi.org/10.1016/j.chemosphere.2008.09.034

[17] Anzai J.I., Liu C.C.: *Sensors and Actuators B: Chemical* **1991**, *5*, 171. http://dx.doi.org/10.1016/0925-4005(91)80240-K

[18] Bromberg L., Levin G., Kedem O.: *Journal of Membrane Science* **1992**, *71*, 41. http://dx.doi.org/10.1016/0376-7388(92)85004-3

[19] Moulay S.: *Progress in Polymer Science* **2010**, *35*, 303. http://dx.doi.org/10.1016/j.progpolymsci.2009.12.001

[20] Senkal B.F., Bildik F., Yavuz E., Sarac A.: *Reactive and Functional Polymers* **2007**, *67*, 1471. http://dx.doi.org/10.1016/j.reactfunctpolym.2007.07.042

[21] "Kirk-Othmer Encyclopedia of Chemical Technology Fourth Edition" (Eds. Kroschwitz J., Howe-Grant M.), Wiley-Interscience Publishers, New York 1992, Vol. 2, p. 1.

[22] Steiner D., Sethofer S.G., Goralski C.T., Singaram B.: *Tetrahedron: Asymmetry* **2002**, *13*, 1477. http://dx.doi.org/10.1016/S0957-4166(02)00342-7

[23] Ferrarini S.R., Graebin C.S., Limberger J. *et al.*: *Memórias do Instituto Oswaldo Cruz* **2008**, *103*, 773. http://dx.doi.org/10.1590/S0074-02762008000800005

[24] Chrisman W., Camara N.J., Marcellini K. *et al.*: *Tetrahedron Letters* **2001**, *42*, 5805. http://dx.doi.org/10.1016/S0040-4039(01)01135-2

[25] Huerta G., Ordonez G.C., Alvarez-Toledano C. *et al.*: *Synthetic Communications* **2004**, *34*, 2393. http://dx.doi.org/10.1081/SCC-120039493

[26] Wei S.W., Stingl K.A., Weiss K.M., Tsogoeva S.B.: *Synlett* **2010**, *5*, 707.

[27] Hodgson D.M., Gibbs A.R., Lee G.P.: *Tetrahedron* **1996**, *52*, 14 361. http://dx.doi.org/10.1016/0040-4020(96)00888-5

[28] Hanson R.M.: *Chemical Review* **1991**, *91*, 437. http://dx.doi.org/10.1021/cr00004a001

[29] Rao A.S., Paknikar S.K., Kirtane J.G.: *Tetrahedron* **1983**, *39*, 2323. http://dx.doi.org/10.1016/S0040-4020(01)91961-1

[30] Steiner D., Ivison L., Goralski C.T. *et al.*: *Tetrahedron: Asymmetry* **2002**, *13*, 2359. http://dx.doi.org/10.1016/S0957-4166(02)00646-8

[31] Ammari F., Meganem F.: *Turkish Journal of Chemistry* **2014**, *38*, 638. http://dx.doi.org/10.3906/kim-1306-24

[32] Abdelaal M.Y., Sobahi T.R.: *Journal of Applied Polymer Science* **2007**, *104*, 2304. http://dx.doi.org/10.1002/app.25694

[33] Fayemi O.E., Ogunlaja A.S., Kempgens P.F.M. *et al.*: *Minerals Engineering* **2013**, *53*, 256. http://dx.doi.org/10.1016/j.mineng.2013.06.006

[34] Vasanthkumar M.S., Bhatia R., Arya V.P. *et al.*: *Physica E* **2014**, *56*, 10. http://dx.doi.org/10.1016/j.physe.2013.08.010

[35] Mallakpour S., Abdolmaleki A., Tabebordbar H.: *European Polymer Journal* **2016**, *78*, 141. http://dx.doi.org/10.1016/j.eurpolymj.2016.03.022

[36] Yan B., Guo M.: *Journal of Photochemistry and Photobiology A: Chemistry* **2013**, *257*, 34. http://dx.doi.org/10.1016/j.jphotochem.2013.02.013

[37] Chen Y., Pan B., Zhang S. *et al.*: *Journal of Hazardous Materials* **2011**, *190*, 1037. http://dx.doi.org/10.1016/j.jhazmat.2011.04.049

Received 19 VI 2017.