Functional groups grafted on poly(vinyl chloride) – evaluation of new modified polymers in metal ions adsorption

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Abstract: Poly(vinyl chloride) (PVC) has been subjected to numerous chemical modifications which were undertaken in order to improve its properties, the use of PVC in new applications and understanding of PVC-related phenomena. This work describes the chemical modification of PVC by amino groups (benzylamine and diethylenetriamine) through nucleophilic substitution reactions of its chlorine atoms to obtain $\mathbf{P_1}$ polymer. The modified polymer was subsequently reticulated with dichlorodiethyl ether to obtain $\mathbf{P_2}$ polymer. The obtained polymers were characterized using infrared spectroscopy (FT-IR), elemental analysis (CHN), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), differential thermal analysis (DTA), and X-ray diffraction (XRD). The modified polymers ($\mathbf{P_1}$ and $\mathbf{P_2}$) were tested for metal ion extraction (cadmium, cobalt, lead, or chromium) using the solid-phase extraction (SPE) method and the inductively coupled plasma atomic emission spectrometry (ICP-AES) technique. Quantitative adsorption measurements were performed using solutions containing $2 \cdot 10^{-4}$ M of heavy metal ions with pH = 3.5–4.5 at a flow rate of 0.6 dm^3/min. The new extractants based on modified PVC ($\mathbf{P_1}$ and $\mathbf{P_2}$) were able to remove the negative effects of heavy metals contained in aqueous solutions. For Pb^{2+}, the extraction percentage was 98 % using $\mathbf{P_1}$ and 90.3 % using $\mathbf{P_2}$.

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

Szczepienie funkcyjnych grup aminowych na poli(chlorku winylu) – ocena przydatności otrzymanych polimerów w adsorpcji jonów metali

Streszczenie: Przeprowadzono chemiczną modyfikację poli(chlorku winylu) (PVC) w reakcji nukleofilowego podstawienia atomów chloru grupami aminowymi (benzyloamina i dietylenotriamina). Otrzymany polimer $\mathbf{P_1}$ szczepiono następnie eterem dichlorodietylowym – uzyskano polimer $\mathbf{P_2}$. Wytworzone polimery scharakteryzowano za pomocą spektroskopii w podczerwieni (FT-IR), analizy elementarnej (CHN), różnicowej kalorymetrii skaningowej (DSC), analizy termograwimetrycznej (TGA), różnicowej analizy termicznej (DTA) i dyfrakcji rentgenowskiej (XRD). Polimery $\mathbf{P_1}$ i $\mathbf{P_2}$ testowano w procesie ekstrakcji jonów metali (kadmu, kobaltu, ołowiu lub chromu), stosując ekstrakcję w fazie stałej (SPE) i metodę atomowej spektrometrii emisyjnej z plazmą wzbudzaną indukcyjnie (ICP-AES). Pomiary ilościowe adsorpcji prowadzono w roztworach wodnych zawierających $2 \cdot 10^{-4}$ M jonów metali ciężkich, o pH = 3,5–4,5 i przy szybkości przepływu 0,6 dm^3/min. Nowe ekstrahenty na bazie zmodyfikowanego PVC ($\mathbf{P_1}$, $\mathbf{P_2}$) adsorbowały metale ciężkie zawarte w roztworach wodnych – w wypadku jonów Pb^{2+} ekstrakcja za pomocą $\mathbf{P_1}$ wyniosła 98 %, a za pomocą $\mathbf{P_2}$ – 90,3 %.

Słowa kluczowe: poli(chlorek winylu), benzyloamina, dietylenotriamina, eter dichlorodietylowy, reakcja podstawienia, ekstrakcja jonów metali.

Poly(vinyl chloride) (PVC) is one of the most important polymers due to its versatility and excellent physicochemical properties. PVC is employed in a wide range of fields [1, 2]. PVC has been subjected to numerous reactions, mainly dehydrochlorination [3] and nucleophilic substitutions [4, 5], degradation [6, 7], grafting and cross-linking [8–10]. The chemical modification of the PVC has been important in the development of macromolecular chemistry.

It is well known that PVC can be chemically modified in solution by the nucleophilic substitution of its chlorine atoms [11–13]. The modification of PVC through the formation of C_{PVC}–X with X = N, O or S, is easier than that

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with C_{PVC}–C [14]. The present work is aimed to perform a functionalization of PVC by nucleophilic substitution reactions with amine groups (benzylamine and diethylenetriamine) and by chemical grafting of dichlorodiethyl ether group. The new products based on modified PVC (**P$_1$** and **P$_2$**) were able to remove toxic pollutants from wastewater. Several techniques are available for the study of the elimination of these toxic products from wastewater. Adsorption process is one of the most important methods for the removal of toxic organics, using several types of adsorbents, such as polymeric adsorbents [15].

This work has evaluated the efficiency of a modified polymer in the removal of toxic metals from the environment and especially from wastewater since water pollution is a major worldwide issue caused by contamination from several toxic pollutants [16, 17].

EXPERIMENTAL PART

Materials

Commercial PVC (**P$_0$**) (M_r = 48 000) and benzylamine were purchased from Fluka. *N,N*-Dimethylformamide (DMF), diethylenetriamine (99 %), dichlorodiethyl ether and $Cr(NO_3)_3 \cdot 9\ H_2O$ (99 %) were produced by Sigma-Aldrich. $CdCl_2 \cdot H_2O$ (98 %), $Pb(NO_3)_2$ (98 %) and $CoCl_2 \cdot 6\ H_2O$ (99 %) were 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 (PVC) more reactive, we performed the Conant–Finkelstein reaction with the aim to replace the chlorine atoms of the pure PVC with iodine ones through a nucleophilic substitution mechanism [18].

Preparation of amino-PVC

2 g of PVC polymer (32 mmol Cl/g) were dissolved in 30 cm^3 of DMF and 2 cm^3 of benzylamine (1.96 g, 18.3 mmol), 0.5 g of KI and 2 cm^3 of diethylenetriamine (1.91 g, 18.5 mmol) were then added. The reaction mixture was stirred at 125 °C for 24 h and then cooled to the room temperature. The compound was collected by filtration, treated with a 0.1 M aqueous solution of NaOH, filtered and washed several times with distilled water. The modified polymer was dried for 24 h at the room temperature, crushed and washed with diethyl ether and distilled water. Finally, the obtained polymer (**P$_1$**) was dried in an oven for 12 h at 60 °C to evaporate water and the residual solvent was evaporated under vacuum at 70 °C for 48 h.

Grafting of dichlorodiethyl ether on amino-PVC

2 g of previously modified PVC (**P$_1$**) was dissolved in 30 cm^3 of DMF and 6 cm^3 of dichlorodiethyl ether were added to the solution. The reaction mixture was stirred and heated at 125 °C for 24 h. The resulting product was filtered and washed with water. Then, the modified polymer was dried for 24 h at the room temperature and washed with diethyl ether and distilled water. The obtained polymer (**P$_2$**) was dried in an oven for 12 h at 60 °C and finally dried under vacuum at 70 °C for 48 h.

Extraction of some metal ions

The work consisted in using the polymers modified by amino and dichlorodiethyl ether groups for the removal of metal ions (Cr^{3+}, Cd^{2+}, Pb^{2+}, or Co^{2+}) using solid phase extraction method (SPE).

Metal ion extraction method

Aqueous metal salt solutions of $Cr(NO_3)_3 \cdot 9\ H_2O$, $CdCl_2 \cdot H_2O$, $Pb(NO_3)_2$, and $CoCl_2 \cdot 6\ H_2O$ were prepared at a known concentration of $2 \cdot 10^{-4}$ mol/dm^3 with the pH of each aqueous solution varying between 3.5 and 4.5. Then 0.1 g of the modified polymer (powder was crushed in a mortar and was sieved through $a \leq 100$ μm sieve) was washed several times with distilled water to remove any possible salts present. The washed polymer was directly added to a flask (V = 30 cm^3) containing 20 cm^3 of the metal ion solution at the room temperature and subjected to stirring in order to determine the optimal extraction time according to the change in conductivity (σ) of the aqueous solution with time. Finally, the suspension was filtrated and the metal content in the filtrate evaluated by the inductively coupled plasma atomic emission spectrometry (ICP-AES) analysis.

Methods of testing

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 scanning calorimetry (DSC) was performed on a SETARAM DSC 131. Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a SETARAM TGA 92 device.

The X-ray diffraction analysis (XRD) was done on a Bruker D8 Advance apparatus.

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.

The extraction percentage of each metal ion by synthesized polymers was obtained with inductively coupled plasma atomic emission spectrometry (ICP-AES) which was done on a Horiba Jobin Yvon spectrometer (Activa model). The wavelengths of the metal ions (Cr, Cd, Pb, or Co) were recorded in the following order: 267.719, 226.502, 220.353, and 238.892 nm.

The results of the metal ion extraction for each synthesized polymer were expressed as percentages, of their initial concentration. The percentage was calculated using the following expression: $E = [(Ci - Cf) / Ci] \cdot 100\ \%$

where: *Ci* – the initial concentration of the metal in aqueous solution, *Cf* – the concentration of the remaining quantity of the metal ion in aqueous solution after 24 hours.

RESULTS AND DISCUSSION

Analysis of the modified polymers

IR spectroscopy

The IR spectroscopy analysis of the modified polymer (**P$_1$**) clearly shows that a substitution reaction takes place, as indicated by the appearance of characteristic bands of the amino groups at 3434 and 3310 cm^{-1} corresponding to NH$_2$ and NH, respectively, and also an absorption at 1665 cm^{-1} corresponding to N-H bending in plane. An absorption at 1467 cm^{-1} corresponding to aromatic C=C is also observed, confirming the presence of the benzene ring in polymeric chains of PVC. However, the spectrum also shows the presence of the chlorine stretching vibration bands ($\nu_{C\text{-}Cl}$) with low intensity at 701 cm^{-1}. This indicates that some chlorine atoms have not entirely disappeared. All the characteristic bands observed for **P$_1$** were also seen in the FT-IR spectrum of **P$_2$** (Fig. 1), with an increase in the intensity of the valence band corresponding to C–O–C which appears at around 1050–1170 cm^{-1}. This finding confirmed the grafting of ether group (dichlorodiethyl ether) on the amino-PVC.

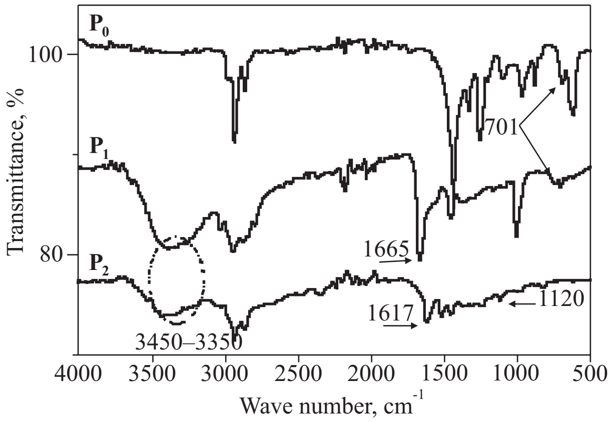


Fig. 1. FT-IR spectra of: P$_0$, P$_1$, and P$_2$

Comparison of the FT-IR spectra for **P$_1$** and **P$_2$** with that of **P$_0$** clearly shows the modification of **P$_0$** given that the **P$_0$** spectrum has absorption bands at 701 cm^{-1}, corresponding to the C-Cl band, and two absorption bands at 2860 cm^{-1} and at 2930 cm^{-1} for symmetric and asymmetric CH$_2$, respectively, which are only present in **P$_0$** (Table 1). Finally, the absence of the chlorine stretching vibration band ($\nu_{C\text{-}Cl}$) between 600 and 800 cm^{-1} in the **P$_2$** spectra confirms that chlorine atoms have been substituted by benzylamine and diethylenetriamine.

Table 1. FT-IR spectroscopic data for P$_0$ and modified polymers P$_1$ and P$_2$

Characteristic vibration	Wave number, cm^{-1}		
	P$_0$	**P$_1$**	**P$_2$**
-CH$_2$ asymmetric and symmetric vibrations	2930–2860	2930–2860	2930–2860
-C-Cl vibration	701	701	–
-NH$_2$ asymmetric and symmetric vibrations	–	3434–3310	3437–3310
N-H bending	–	1665	1617
C=C aromatic	–	1467	1465
C-O-C ether	–	–	1170–1050

Elemental analysis

Comparing the element percentages (% C, % H, and % N) for **P$_1$** and **P$_2$** with those of **P$_0$** clearly proves that a chemical change has happened. This is especially clear from the nitrogen percentage which increased from 0 % (**P$_0$**) to 6.31 % and 5.08 % for **P$_1$** and **P$_2$**, respectively. The percentage of other elements (C and H) also increased (Table 2).

Table 2. Elemental analysis for P$_0$ and modified polymers P$_1$ and P$_2$

Sample name	% C	% H	% N	% $\sum_{C, H, N}$
P$_0$	38.85	4.73	0.00	43.58
P$_1$	65.25	8.29	6.31	79.85
P$_2$	69.08	5.43	5.08	79.59

DSC and DTA-TGA characterization of P$_0$, P$_1$ and P$_2$

The DSC curve of the commercial PVC (**P$_0$**) recorded from a sample of mass m = 7.6 mg with a heating rate of 20 °C/min in the temperature range from 25 to 500 °C showed that the T_g is 83 °C (Fig. 2) and the melting point is 279 °C .

On the other hand, the DTA-TGA curves of **P$_0$** (m = 14.5 mg) also showed the presence of endothermic peak (melting point) around 276 °C which was accompanied by a significant weight loss of 62.62 % (Fig. 3).

The DSC curve of **P$_1$** recorded from a sample of mass m = 8.68 mg with the heating rate of 20 °C/min in the temperature range from 25 to 500 °C, showed three peaks: two endothermic and one exothermic. The first endothermic peak was observed at 95 °C and probably corresponds to the evaporation of residual water; the exothermic peak was observed at 184 °C showing the reorganization of

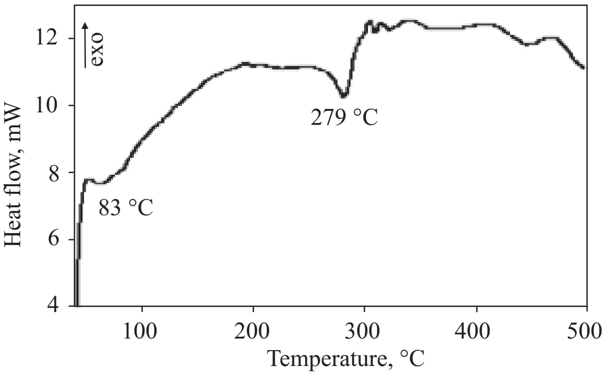


Fig. 2. DSC thermogram of P_0

polymeric chains without weight loss. The other endothermic peak at 328 °C shows the decomposition of the polymer (Fig. 4). On the other hand, the DTA-TGA curves of $\mathbf{P_1}$ recorded from a sample of $m = 8.4$ mg with the heating rate of 20 °C/min in the temperature range of 25 to 500 °C (Fig. 5) showed an endothermic peak at 63 °C corresponding to the weight loss of 5.95 % that can be explained with the departure of water molecules. The range between 271 °C and 450 °C corresponds to a significant weight loss of 39 %; this has been attributed to the start of the polymer decomposition. The decomposition continues for temperatures above 450 °C until the total decomposition of the polymer chains.

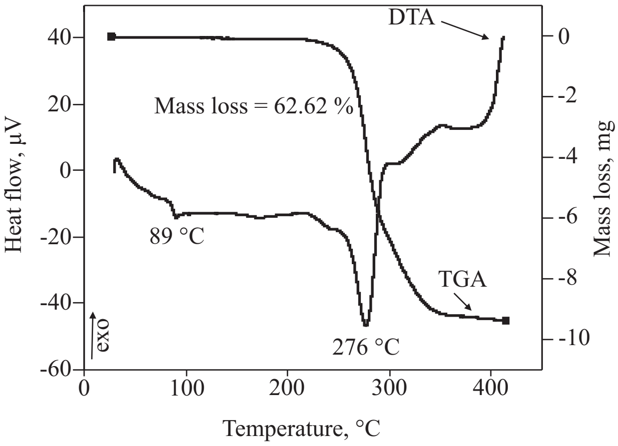


Fig. 3. DTA-TGA curves of P_0

The DSC curve of $\mathbf{P_2}$ (Fig. 6) was obtained from a sample of $m = 5.53$ mg and showed three peaks: one endothermic and two exothermic observed at 93 °C, 185 °C, and 338 °C, respectively. The first peak (93 °C) could be attributed to the evaporation of residual water. The exothermic peak in the temperature range between 150 °C and 250 °C marks the start of the polymer decomposition. The peak

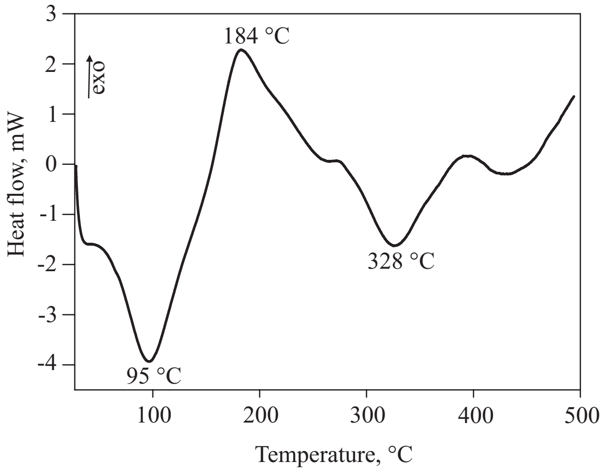


Fig. 4. DSC thermogram of P_1

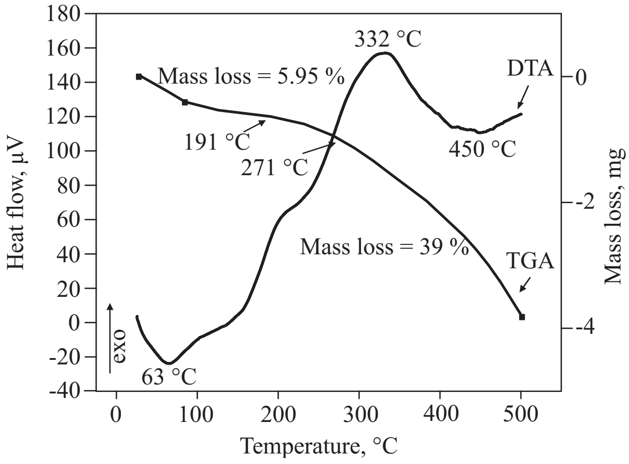


Fig. 5. DTA-TGA curves of P_1

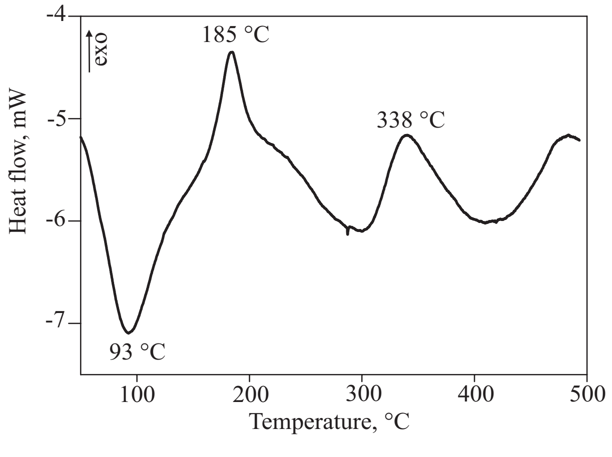


Fig. 6. DSC thermogram of P_2

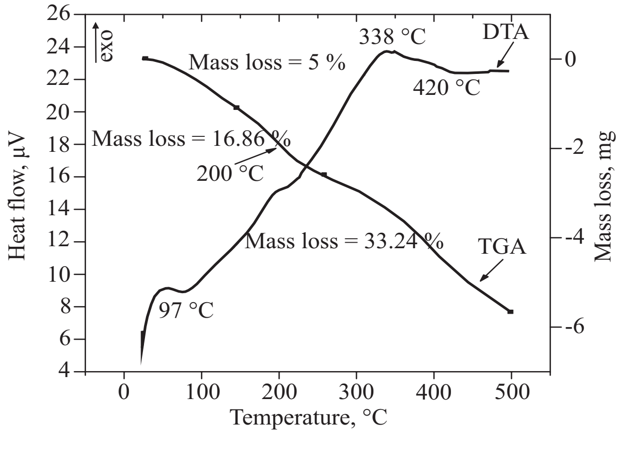


Fig. 7. DTA-TGA curves of P_2

at 338 °C has been attributed to the decomposition of the polymer. The DTA-TGA curves for **P$_2$** were performed on 12.3 mg samples with the heating rate of 20 °C/min. The results were recorded between 50 and 450 °C (Fig. 7).

The analysis showed three peaks: one endothermic and two exothermic. The first peak at 97 °C was accompanied by the weight loss of 5 % corresponding to the departure of water molecules. The other peaks, observed at 200 and 338 °C, respectively, were accompanied by a significant weight loss of 33.24 % which may suggest that the polymer decomposition took place stepwise. In fact, the decomposition continues for temperatures above 400 °C until the total decomposition of the polymer chains (Table 3).

Table 3. DSC analysis of P$_0$, P$_1$ and P$_2$ and their structures by XRD

Sample name	T_g °C	T_{endo} °C	T_{exo} °C	X-ray
P$_0$	83	279	–	Amorphous
P$_1$	–	95; 328	184	Amorphous
P$_2$	–	93	185; 338	Amorphous

T_g – glass transition temperature, it only appears in the case of **P$_0$** (Fig. 2), T_{endo} – endothermic transformation, T_{exo} – exothermic transformation.

XRD characterization of the samples

The suspension of the final modified polymer with the metallic aqueous solution was filtered, and the compound collected in the filter paper was dried at the room temperature and then analyzed with X-ray.

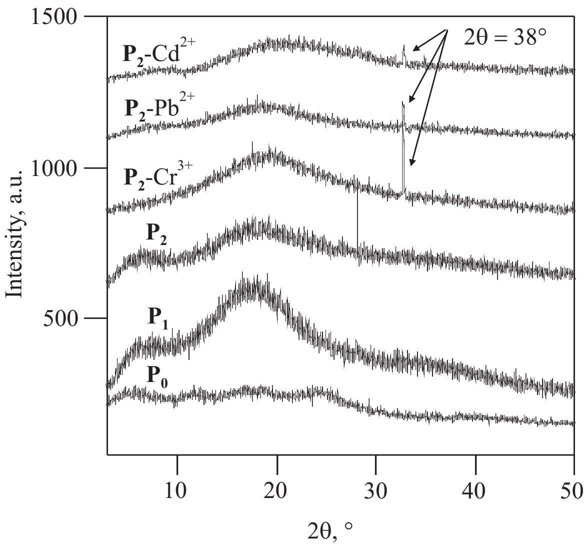
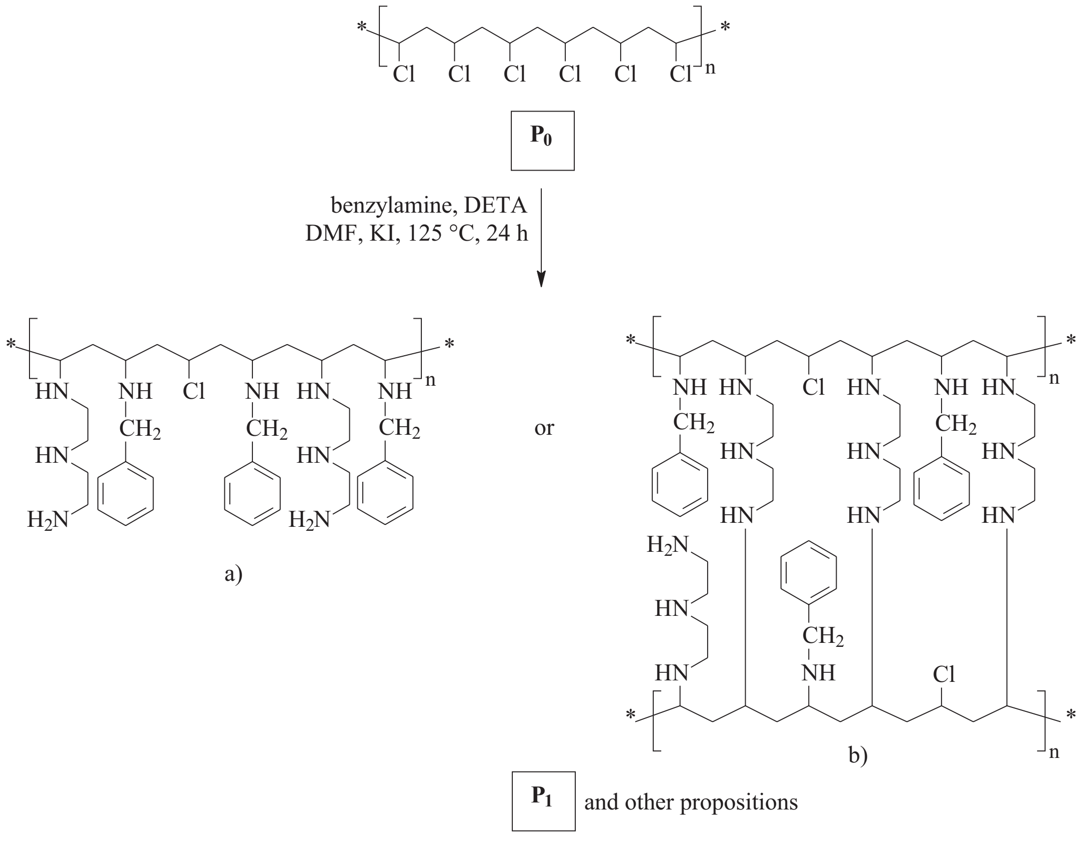


Fig. 8. X-ray diffractograms of: P$_0$, P$_1$, P$_2$, P$_2$-Cr^{3+}, P$_2$-Pb^{2+}, and P$_2$-Cd^{2+}

The X-ray diffractograms for **P$_0$**, **P$_1$** and **P$_2$** in the 2θ = 5–60° range do not show any diffraction peaks. This result indicates that these polymers have an amorphous structure. Their XRD for **P$_2$**-Cr^{3+}, **P$_2$**-Pb^{2+} and **P$_2$**-Cd^{2+} have a characteristic peak at 2θ = 38° which is absent for **P$_1$** and **P$_2$** in the 2θ = 5–60° range. The diffractograms also show the absence of a bump at 2θ = 10° for **P$_2$**-Cr^{3+}, **P$_2$**-Pb^{2+} and **P$_2$**-Cd^{2+} complexes. The significance of this situation in-



Scheme A

dicates the insertion of the M^{n+} cation [Cr(III), Pb(II), or Cd(II)] in $\mathbf{P}_2$ cavity (Fig. 8).

Proposed structures of $\mathbf{P}_1$ and $\mathbf{P}_2$

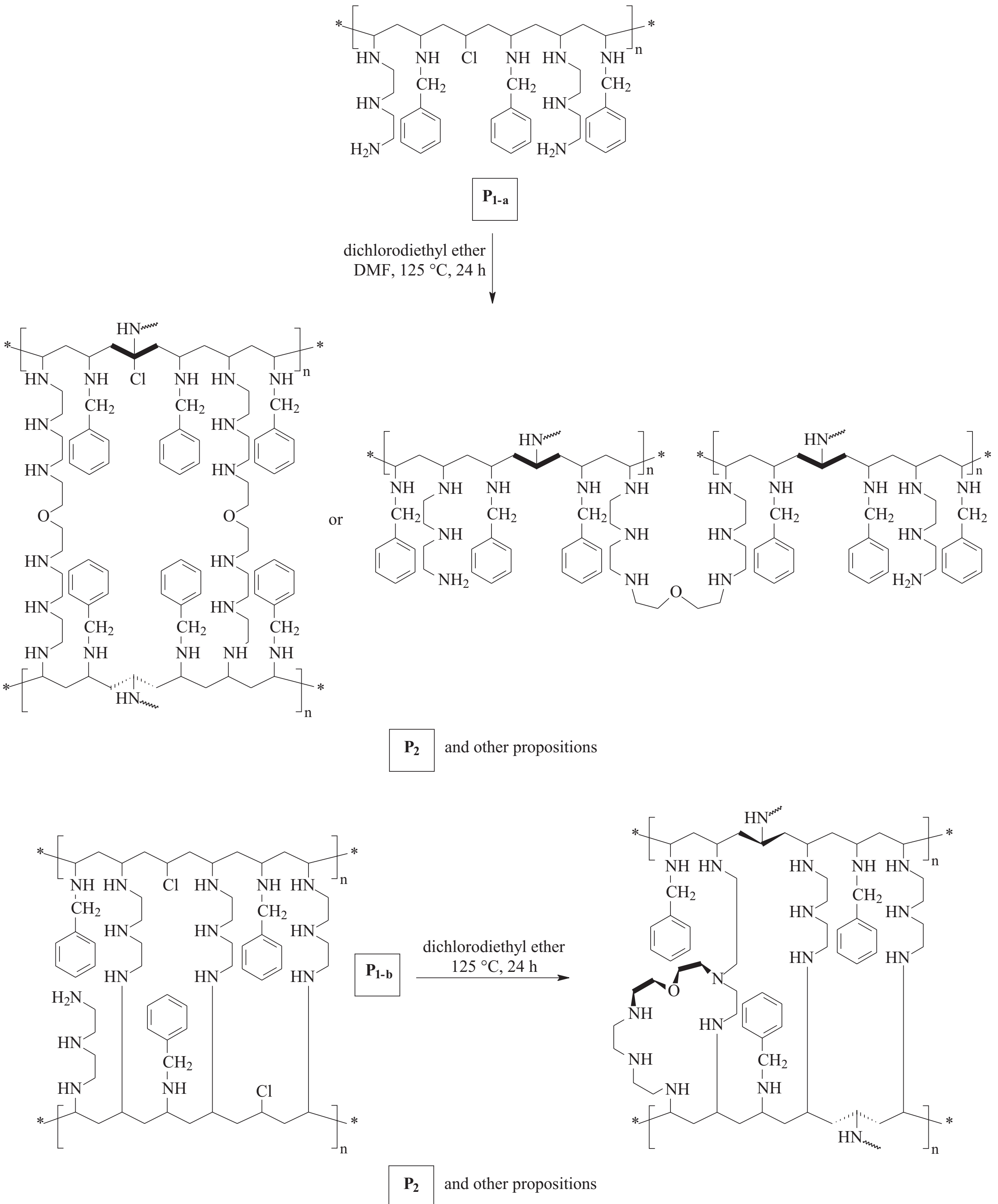
$\mathbf{P}_1$ structure

The different analyses of the modified polymer ($\mathbf{P}_1$) prove the modification of commercial PVC ($\mathbf{P}_0$) during the substitution reactions by benzylamine and diethylenetriamine. A possible structure of $\mathbf{P}_1$ is shown in Scheme A. Some chlorine atoms are still present in the proposed structures.

The IR spectrum of $\mathbf{P}_1$ shows that the chlorine stretching vibration bands (ν_{C-Cl}) have not entirely disappeared; this suggests the presence of some chlorine atoms in $\mathbf{P}_1$ structures.

$\mathbf{P}_2$ structure

$\mathbf{P}_1$ has been grafted with dichlorodiethyl ether. A possible structure of $\mathbf{P}_2$ is shown in Scheme B. The proposed



Scheme B

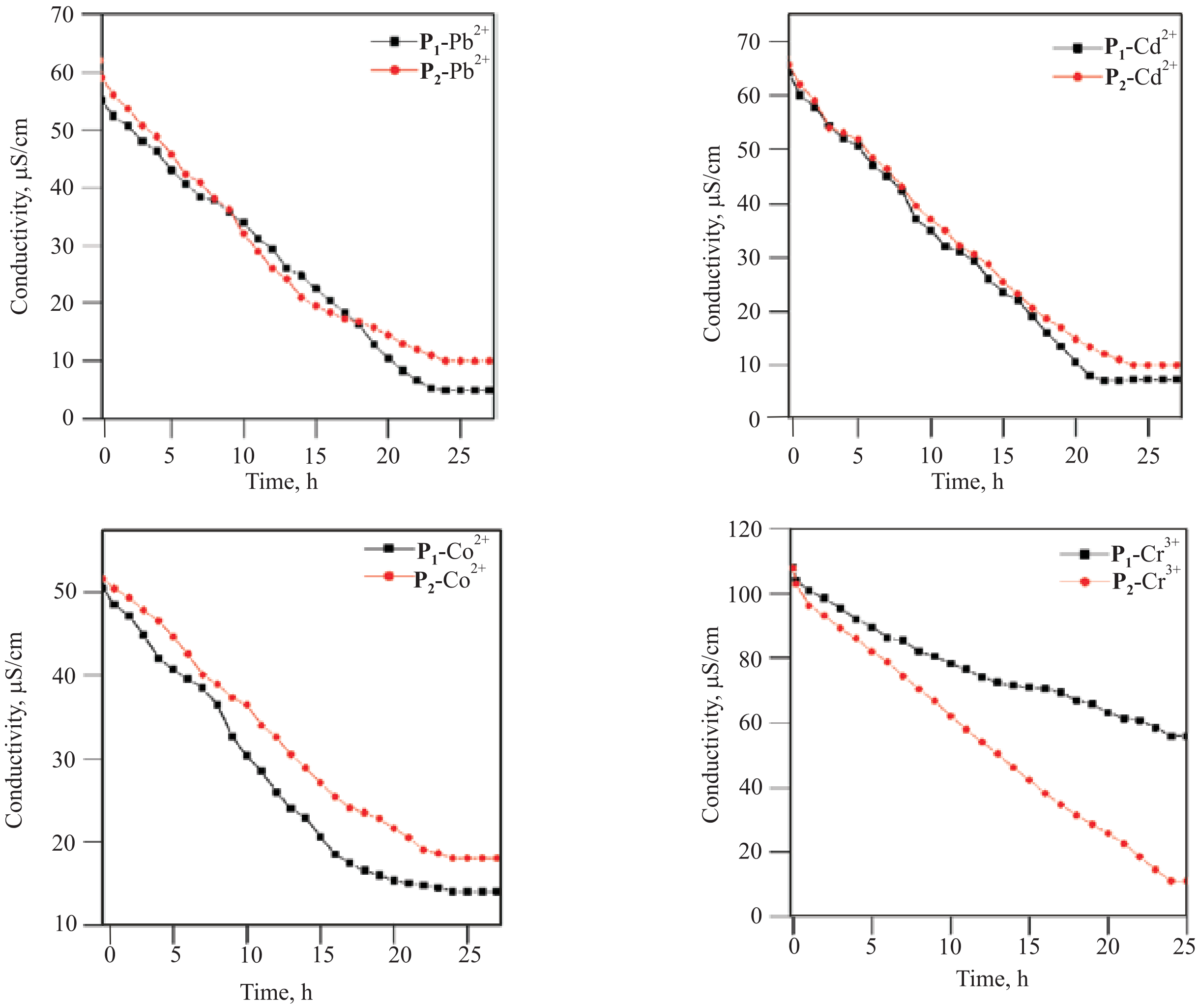


Fig. 9. Variation curves of electrical conductivity with time for aqueous solutions of metal cations (Pb^{2+}, Cd^{2+}, Co^{2+}, or Cr^{3+}) in contact with P$_1$ and P$_2$

structures are suggested by the complete disappearance of the ν_{C-Cl} band from the IR spectrum.

Metal cation extraction using modified polymers

Kinetic study

The kinetic study showed that the optimum extraction time obtained with polymers **P$_1$** and **P$_2$** is of approximately 24 h. The extraction results are the average of three experiments.

Figure 9 shows variation curves of average electrical conductivity with time for metal cations (Pb^{2+}, Cd^{2+}, Co^{2+}, or Cr^{3+}) in contact with the modified polymers (**P$_1$** and **P$_2$**).

Percentages of metal cations extraction

The extraction percentages of metal ions (Cr^{3+}, Co^{2+}, Cd^{2+}, or Pb^{2+}) with the synthesized polymer (**P$_1$**) varied between 45 and 98 % and between 65.1 and 96.65 % for the other polymer (**P$_2$**) (Table 4, Fig. 10).

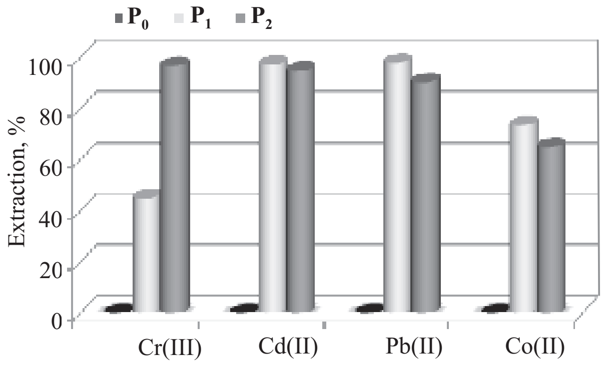


Fig. 10. Percentages of metal cations extraction with the polymers P$_0$, P$_1$ and P$_2$

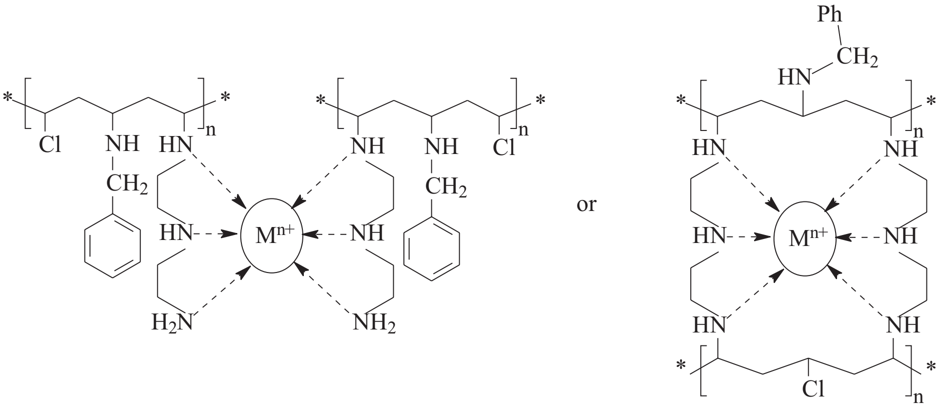
The extraction power of **P$_1$** in the cases of the studied metals followed the following increasing selectivity order: $Cr^{3+} \ll Co^{2+} < Cd^{2+} < Pb^{2+}$, while the second polymer followed another order: $Co^{2+} \ll Pb^{2+} < Cd^{2+} < Cr^{3+}$. The extraction percentages using **P$_1$** indicated more selectivity for Pb(II) with the percentage of 98 %, while **P$_2$** showed more selectivity for Cr(III) with the percentage of 96.65 %.

T a b l e 4. Extraction percentages of metal cations (Cr^{3+}, Pb^{2+}, Cd^{2+}, or Co^{2+}) with modified polymers

Metal ions	Utilized salts	pH ($C = 2 \cdot 10^{-4}$ M)	*E* with $\mathbf{P_0}$ %	*E* with $\mathbf{P_1}$ %	*E* with $\mathbf{P_2}$ %
Cr^{3+}	$Cr(NO_3)_3 \cdot 9\ H_2O$	3.5	0	45.00 ± 0.23	96.65 ± 0.79
Cd^{2+}	$CdCl_2 \cdot H_2O$	4.0	0	97.20 ± 0.41	94.85 ± 0.67
Pb^{2+}	$Pb(NO_3)_2$	3.7	0	98.00 ± 0.62	90.30 ± 0.80
Co^{2+}	$CoCl_2 \cdot 6\ H_2O$	4.5	0	73.50 ± 1.13	65.10 ± 1.23

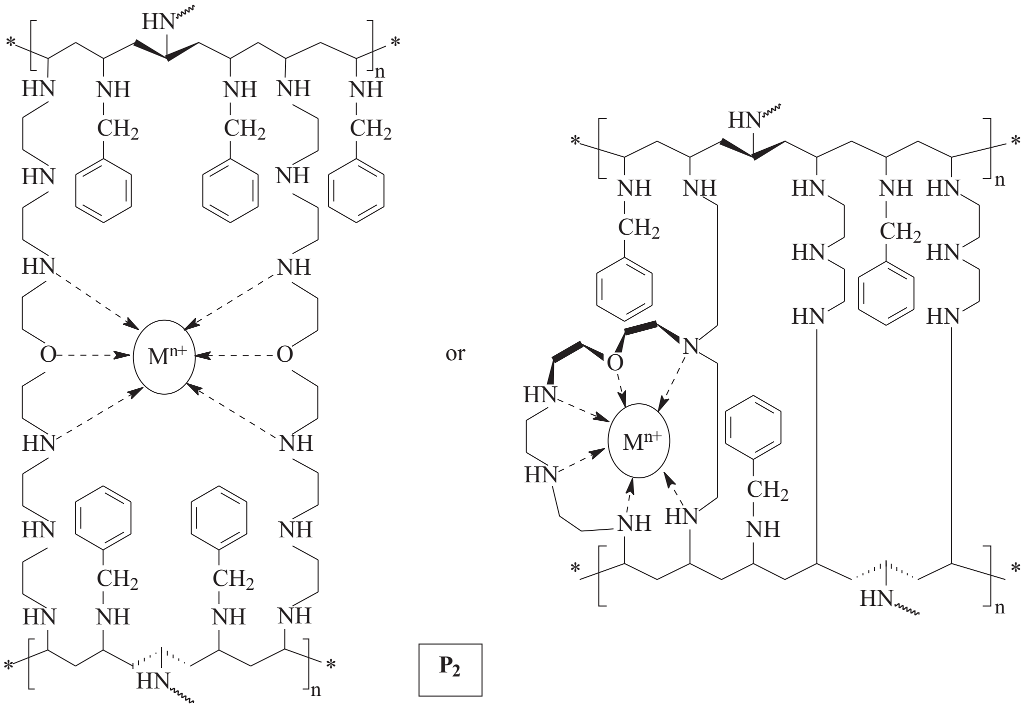
Complexation with M^{2+} (Pb^{2+}, Cd^{2+}, and Co^{2+}) proved to be the best for $\mathbf{P_1}$ given that the extraction percentages were 98, 97.2 and 73.5 % respectively for Pb^{2+}, Cd^{2+}, and Co^{2+}. These results can be explained by the compatibility between the size of the metal ion and the size of the complexing cavity and the type of hetero-atom ligands (oxygen and nitrogen atoms). This type of atoms (N, O) is able to fix the metal through noncovalent bonds (van der Waals bonds). According to the $\mathbf{P_1}$ and $\mathbf{P_2}$ structures (Schemes A and B), there are several types of macrocyclic complexing cavities (Schemes C and D).

The retention of metal cations can also be explained by the presence of an electron-rich π system (benzene ring), this type of interaction was explained by the noncovalent cation-π interactions theory [19]. In the case of Cr(III), the polymer $\mathbf{P_2}$ (96.65 %) is a better extractant than $\mathbf{P_1}$ (45 %); $\mathbf{P_2}$ accepts Cr^{3+} better, which is the least voluminous ion of those studied. Based on the hard-soft acid-base the-



P1

Scheme C



P2

Scheme D

ory, Cr(III) was classified as a hard ion, and has affinities to hard ligands which contain oxygen atoms like in $\mathbf{P_2}$ cavity (Scheme D), but Cd(II) was classified as a soft ion and Pb(II) and Co(II) were classified as intermediate ions. Therefore, the chemical modification of commercial PVC is important for the extraction of heavy metals, and the chemical grafting with a bifunctional group has an important effect on extraction. In our case it improved the extraction power of $\mathbf{P_1}$ to the point that the percentage of the trivalent Cr ion increased from 45 to 96.65 %. Polymeric adsorbents based on modified PVC are able to remove metal ions with great efficiency. The obtained results with these modified polymers can be compared with some published in the literature, however the reactants used are not the same. For Cd^{2+}, the extraction percentage by the modified polymer ($\mathbf{P_1}$) (substituted by an aliphatic and aromatic amine) is higher (97.2 %) than the extraction percentage obtained and published in another work (22.6 %) [20].

CONCLUSIONS

The substitution reactions of commercial PVC (M_r = 48 000) by amino groups and the grafting by ether groups on the amino-PVC show the importance of chemical modification for the synthesis of long polymer chain functionalized materials. In this work these new materials containing electron-donating atoms such as nitrogen and oxygen were used as chelating agents for heavy metal extraction. The simple preparation procedure of the reactions depends on the used solvent, the temperature, and the reaction time. The simple (SPE) technique based on polymeric adsorbents proved to be an effective method for the metal ion extraction from aqueous phases [Pb(II), Cd(II), Co(II), or Cr(III)]. The extraction power of $\mathbf{P_1}$ for the studied metals followed this increasing selectivity order: $Cr^{3+} \ll Co^{2+} < Cd^{2+} < Pb^{2+}$, while the modified polymer $\mathbf{P_2}$ followed a different order: $Co^{2+} \ll Pb^{2+} < Cd^{2+} < Cr^{3+}$. $\mathbf{P_1}$ was selective for Pb(II) and Cd(II) and the final polymer $\mathbf{P_2}$ was selective for Cr(III). This work has enabled us to evaluate the extraction of heavy metals by new adsorbents based on modified PVC polymers.

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