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Chemical modifications of poly(vinyl chloride) to poly(vinyl azide) and "clicked" triazole bearing groups for application in metal cation extraction



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ABSTRACT

Chemical modification of poly(vinyl chloride) (PVC) by the replacement of chlorine atom presents a considerable interest in this work. In the first phase, PVC was partially azided with a sodium azide. Click-chemistry based on Copper (I)-catalyzed Huisgen's reaction (CuAAC) was then used to form polymer-grafted 1,4-triazoles using some synthesized substituted alkynes. In the second phase, the new synthesized polymers were used in extraction studies of heavy metals (Cd, Cu, Ni and Pb). The obtained polymer-supported triazoles were characterized by infrared spectroscopy and thermal analysis (DSC). Evaluation of metallic cation extraction was done by atomic absorption of the remaining solutions. Three polymers efficiently removed Ni Cu and Pb with extraction yields between 50 and 90%. Two of the polymers studied had a high selectivity of extraction for Cadmium with a good efficiency (around 80%).

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1. Introduction

The domain of applications of polyvinyl chloride (PVC) and its uses is widespread and includes the following: windows, frames, flooring, pipes, window blinds, wallpaper, hoses, cables and wires, coatings, plastisols, packing, medical tubing and blood bags [1,2]. It's for this reason that the chemical modifications of PVC for its recycling had been of great interest in the recent years [3–6]. The extraction of heavy metals presents the primary objective of the chemical modification of PVC in this work, because pollution by these metals has become one of the main problems for environmental protection [7,8]. The polymeric membrane is one of the procedures used for removing heavy metals nowadays [9–17]. Studies of metal extraction using polymers substituted with chelating entities, ionic or not, have been developed [18–20]. The preparation of some polymers was based on the use of "click-chemistry",

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and moreover by the "Copper (I)-catalyzed azide/alkyne cycloaddition" (CuAAC or Copper (I)-catalyzed Huisgen's reaction) in this field [21–25]. Following our work on poly(styrene) scaffold, we were interested in the evaluation of PVC in order to make comparisons and to propose another recycling possibility for this widely used polymer [20].The use of the well known CuAAC, the Copper (I)-catalyzed Huisgen's reaction, can give us the opportunity to introduced all appendage we want to test for their chelating properties. Using PVC after azidation, it is in fact possible to graft the chelating moieties by using a properly substituted terminal alkyne to for the triazole link between the polymer network and the chelating entity [26]. The goal is to test the ability of the introduced molecular units to chelate metals for removal from aqueous solutions. This chelation can be made by a single unit (pendant chelation), or by several ones due to the distribution and proximity onto the network. However, we can't rule out possible chelation from the triazole link through its donating nitrogen (triazole chelation), neither than chelation by both the chelating moiety and the triazole (participative chelation) (Fig. 1) [27-29].We thus present in this article the preparation of polymer-supported triazoles starting from PVC, followed by its transformation in azido-PVC, and CuAAC with selected alkynes. These polymers were then tested for extraction metals salts $(Cd^{2+}, Pb^{2+}, Cu^{2+} and Ni^{2+})$ from aqueous solutions.

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Fig. 1. General scheme for the preparation of triazolic polymers and possible mono- and poly-chelation ways (pendant, triazole and participative).

2. Experimental

2.1. Materials and apparatus

2.1.1. Materials

Poly(vinyl chloride), with high molecular weight (MW = $48,000 \text{ g} \cdot \text{mol}^{-1}$, 16 mmol of $\text{Cl} \cdot \text{g}^{-1}$, 99%), was purchased from Fluka. Acyl chlorides (99%), propargyl amine (98%), substituted anilines, *N*,*N*-dimethylaminopyridine (DMAP) (99%), triethyl and diisopropylethyl (DIPEA) amines (99%), phenylacetylene (99%), sodium azide (99%) and Copper (I) iodide (98%) were provided by Sigma-Aldrich and used without further purification. Methylene chloride and dimethyl-formamide (DMF) were bought from Acros Organics and used as received. Tetrahydrofurane (THF) was from the same source, but distilled from benzophenone ketyl under nitrogen prior to use. CdCl₂·H₂O (98%), NiCl₂·6H₂O (98%), Pb(NO₃)₂ (98%) and CuSO₄·5H₂O (98%) were produced by Fluka, and used as such. Organic syntheses (Schemes 1 to 3) were conducted under nitrogen, otherwise stated, using standard methods and procedures.

2.1.2. Apparatus

Characterizations were made as described below. Melting points (mp) were measured on a Kofler apparatus after calibration around the observed fusion of the product. Elemental analysis of (C, H and N) was performed by using Perkin Elmer Analyzer CHN Series II 2400 (France). Infrared analysis using the attenuated total reflectance technique (ATR/FTIR) was made on a Nicolet IR 200 FTIR (France) spectrometer between 4000 and 400 cm⁻¹. Only the main and relevant absorption bands are indicated as vibrations (ν) and angular deformations (δ). Nuclear magnetic resonance spectroscopy (NMR) was recorded on a Bruker Avance 300 (France) at 300 MHz for the proton spectra

 (^{1}H) and 75.5 MHz for the carbon spectra (^{13}C) . Chemical shifts (δ) are indicated after calibration on the residual undeuterated solvent peak in part per million (ppm) and as follow: s (singlet), d (doublet), t (triplet), m (multiplet). Coupling constants (*J*) are given in Hz. Differential scanning calorimetry (DSC) was performed on a DSC 1 STARe System (METTLER TOLEDO) apparatus between 25 and 400 °C. Analtik Jena Nova 400 (Japan) model atomic absorption spectrometer (AAS) operating with an air-acetylene flame was used to measure residual metal ion concentrations.

2.2. Organic synthesis

2.2.1. Chemical modification of PVC(A): synthesis of PVC-N₃ (**B**)

Poly(vinyl chloride) (1 g, 16 mmol of Cl) was suspended in 50 mL DMF and 1.60 g NaN₃ (24.6 mmol, 1.54 eq.) was added. The reaction mixture was slowly magnetically stirred at 100 °C for 2 h (Scheme 1). The cooled mixture was filtered on sintered glass, washed with DMF (2 × 40 mL), water (3 × 50 mL), and finally dried under vacuum at 70 °C for two days, the obtained polymer was not explosive under the conditions studied. The isolated polymer weighted 1.07 g after purification. The obtained polymer was not soluble in organic solvents (CHCl₃, CH₂Cl₂, MeOH, EtOH, Acetone and DMF), but have a low solubility in THF. The effect of DMF washes on % N in the polymer **B** was tested by control washes onto PVC (**A**). The percentage obtained was 0.033% N, and was taken into account for the azide substitution. From the results of elemental analysis the number of moles of substituted chlorine by the azide group (N₃) on the polymer mass was calculated as 23.77 mmol N \cdot g⁻¹, or 7.92 mmol N₃ \cdot g⁻¹).

ATR/FTIR: $\nu = 2940 \ (\nu_{CH2})$, 2101 (ν_{N3}), 1636 ($\nu_{C=C}$), 616 (ν_{C-CI}) cm⁻¹.

Elemental analysis: % C = 33.197; % H = 4.795; % N = 33.334.





Scheme 2. Reaction for synthesis of alkynes 1a-dfrom acyl chlorides and propargylamine.

Corrected % N = 33.301.

2.2.2. Synthesis of alkyne derivatives **1a-d** (general method)

A stirred solution of 0.65 mL of propargyl amine (0.56 g, 10 mmol), 1.4 mL of triethylamine (1.0 g, 10 mmol, 1.0 eq.) and 24 mg of DMAP (0.20 mmol, 2.0% mol) in 20 mL of CH₂Cl₂ was cooled to 0 °C (Scheme 2). A solution of the acyl chloride (10 mmol, 1.0 eq.) in 20 mL of CH₂Cl₂ was then added drop wise. The reaction mixture was then stirred at 0 °C for 0.5 h and over-night at room temperature. The mixture was then extracted with 0.1 M aqueous solutions of HCI (2 × 10 mL) and NaOH (2 × 10 mL), washed with water (3 × 20 mL), dried over MgSO₄, filtrated and the solvent evaporated under vacuum. The resulting amides **1a–d** were sufficiently pure to be used without further purification.

2.2.2.1. *N*-prop-2-ynylacetamide (**1a**). $C_5H_7NO.$ MW = 97.12 g·mol⁻¹. Yield = 76%. mp = 82 °C. ATR/FTIR: ν = 3231, 2928, 2852, 2115, 1641 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, δ): 2.05 (s, 3H), 2.27 (t, *J* = 2.57, 1H), 4.09 (dd, *J* = 5.25, 2.57 Hz, 2H), 5.72 (s, 1H) ppm. ¹³C NMR (75.5 MHz, CDCl₃, δ): 22.94, 29.19, 71.38, 79.67, 170.11 ppm.

2.2.2.2. *N*-prop-2-ynylbutyramide (**1b**). $C_7H_{11}NO. MW = 125.17 \text{ g} \cdot \text{mol}^{-1}$. Yield = 67%. mp = 27 °C. ATR/FTIR: ν = 3294, 3049, 2928, 2117, 1641 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, δ): 0.98 (t, *J* = 7.37 Hz, 3H), 1.72 (sex, 2H), 2.22 (m, 3H), 4.08 (dd, *J* = 5.23, 2.56 Hz, 2H), 5.72 (s, 1H) ppm. ¹³C NMR (75.5 MHz, CDCl₃, δ): 13.74, 19.03, 29.11, 38.33, 71.44, 79.75, 172.75 ppm.

2.2.2.3. *N*-prop-2-ynylcaprylamide (**1c**). $C_{11}H_{19}NO$. MW = 181.28 g·mol⁻¹. Yield = 66%; mp = 64 °C. ATR/FTIR: ν = 3294, 2958, 2920, 2118, 1642 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, δ): 0.91 (t, *J* =

6.85 Hz, 3H), 1,33 (m, 8H), 1.66 (m, 2H), 2.23 (m, 3H), 5.95 (s, 1H), 4.07 (dd, J = 5.20, 2.52 Hz, 2H) ppm. ¹³C NMR (75.5 MHz, CDCl₃, δ): 13.91, 22.37, 25.25, 29.12, 31.41, 36.42, 71.44, 79.72, 172.86 ppm.

2.2.2.4. N-prop-2-ynylbenzamide (**1d**). $C_{10}H_9NO.MW = 159.19 \text{ g} \cdot \text{mol}^{-1}$. Yield = 79%. mp = 106 °C.ATR/FTIR: ν = 3286, 3049,2930, 2123, 1641, 1599, 1537 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, δ): 2.33 (t, *J* = 2.56 Hz, 1H), 4.31 (dd, *J* = 2.54, 5.17 Hz, 2H), 6.31 (s, 1H), 7.56 (m, 1H), 7.48 (m, 2H), 7.82 (m, 2H) ppm. ¹³C NMR (75.5 MHz, CDCl₃, δ): 29.80, 71.80, 79.61, 127.13, 128.62, 131.80, 133.79, 167.29 ppm.

2.2.3. Synthesis of polymer-supported triazoles (2a-e)

Coupling reactions onto the polymer using CuAAC were conducted accordingly to the general procedure indicated below in round bottom flasks equipped with a reflux condenser. Polymer **2e** was synthesized using commercially available phenylacetylene [26], the others with the synthesized amides respectively (Scheme 3). To a suspension of 0.15 g of PVC-N₃ (1.2 mmol of N₃) in THF (10 mL) was added 4.5 mmol (3.7 eq.) of the alkyne, 1.0 mL of DIPEA (0.76 g, 6.0 mmol, 5.0 eq.) and 1.4 mg of Copper (I) iodide $(7.3 \times 10^{-3} \text{ mmol}, 0.6 \text{ mmol} \%)$. The suspension was slowly stirred at room temperature until the complete disappearance of the IR band of the azide (2101 cm⁻¹). The resulting polymers **2a–e** were filtrated and washed with MeOH, CH₂Cl₂ (5 × 5 mL) and water (5 × 50 mL), and finally dried under vacuum at 70 °C for two days. Since no residual azide vibration was observed in infrared, reactions were considered as quantitative.

[4-(Acetamidomethyl)triazol-1-yl]polyvinylchloride (**2a**) ATR/FTIR: $\nu = 3283, 2946, 2865, 1650, 1551, 591 cm⁻¹.$ [4-(Butyramidomethyl)triazol-1-yl] polyvinylchloride (**2b**) $ATR/FTIR: <math>\nu = 3316, 2938, 2873, 1642, 1535, 608 cm⁻¹.$



Scheme 3. Cu(I)-catalyzed Huisgen's reaction of azido-PVC (B) with various alkynes (1a-e).

[4-(*Caprylamidomethyl*)*triazol*-1-*yl*] polyvinylchloride (**2c**) ATR/FTIR: $\nu = 3308, 3059, 2938, 1650, 1535, 698 cm⁻¹.$ [4-(*Benzamidomethyl*)*triazol*-1-*yl*] polyvinylchloride (**2d**) $ATR/FTIR: <math>\nu = 3291, 2962, 2889, 1642, 1551, 764 cm⁻¹.$ (4-Phenyltriazol-1-*yl*) polyvinylchloride (**2e**) $ATR/FTIR: <math>\nu = 3141, 2954, 1617, 1429, 764, 690 cm⁻¹.$

2.3. Characterizations by ATR/FTIR and thermal analysis (DSC) of PVC-N₃ (**B**) and polymer-supported triazoles 2a-e

Infrared analyses using the attenuated total reflectance technique (ATR/FTIR) was previously described in Figs. 2 and 3. Differential scanning calorimetry (DSC) was presented in Fig. 4 and Table 1. The samples (2.8 mg) were placed in 40 μ L aluminum pans, and the DSC recorded under argon between 25 and 400 °C at a speed of 10 °C min⁻¹.

2.4. Metal ion extraction method

Aqueous solutions of CdCl₂·H₂O, NiCl₂·6H₂O, CuSO₄·5H₂O and $Pb(NO_3)_2$ were prepared at a concentration of 50 mg $\cdot L^{-1}$ in relation with the metal cation, and were filtrated on filter paper prewashed with distilled water before their use in the extraction of metals. The polymer (45 mg) was incubated with 5 mL of the metal ion solution at 25 °C for 48 h, (pH = 5–6). The suspension was filtrated on filter paper prewashed with distilled water. The amount of remaining metal ions in solution was evaluated by atomic absorption spectroscopy (AAS) analysis of the filtrate after a 10 fold dilution in distilled water. The atomic absorption spectrometer was calibrated with solutions of the metals studied: (0.5 to 5 mg·L⁻¹) for Cd and Ni, (1 to 7 mg·L⁻¹) for Cu and (5 to 15 mg \cdot L⁻¹) for Pb. Values of extraction percentages were corrected for the amount of metallic ions absorbed onto cellulose by the filter paper itself. These values were calculated after passing solutions on the paper alone and were found to be of 0.34% (Ni²⁺), 1.10% (Cu^{2+}), 2.06% (Pb^{2+}) and 0.40% (Cd^{2+}). The results, average of three experiments, were expressed as percentages of extraction of the metal, based on its initial concentration (Fig. 5).

3. Results and discussion

3.1. Characterization of PVC-N₃ (**B**) and substituted alkynes (a-d)



 $PVC-N_3$ (**B**), now commercially available, was prepared following the method of Yoshioka et al. [3]. The poly(vinyl chloride) was treated

Fig. 2. ATR/FT-IR spectra of PVC (**A**) and PVC-azide (**B**).



Fig. 3. ATR/FT-IR spectra: polyvinyl chloride (**A**), PVC azide (**B**), [4-(acetamidomethyl)triazol-1-yl]polyvinyl chloride (**2a**), [4-(butyramidomethyl)triazol-1-yl] polyvinyl chloride (**2b**), [4-(caprylamidomethyl)triazol-1-yl] polyvinyl chloride (**2c**), [4-(benzamidomethyl)triazol-1-yl] polyvinyl chloride (**2c**), [4-(benzamidomethyl)triazol-1-yl] polyvinyl chloride (**2d**) and (4-phenyltriazol-1-yl)polyvinylchloride (**2e**).

with sodium azide (Scheme 1). Elementary analysis of PVC-N₃ (**B**) was performed to determine the percentage of the elements: % C = 33.197; % H = 4.765 and % N = 33.334. Using a control experiment on PVC to evaluate the effect of DMF washed on the nitrogen content gave us a value of % N = 0.033 The azide bearing polymer **B** isolated from this reaction had a final loading of 7.92 mmol N₃ g⁻¹. The presence of the azido group was confirmed by infrared spectroscopy on which its strong characteristic absorption was seen at 2101 cm⁻¹ (ν_{N3}). The substitution of Cl in PVC (**A**) by the nucleophile group was accompanied by the elimination of HCl since a $\nu_{C=C}$ band is visible at 1636 cm⁻¹. Both reactions were not complete, because the IR spectrum of **B** (Fig. 2) displayed a small residual vibration of C–Cl at 605 cm⁻¹. The band observed at 3351 cm⁻¹ was attributed to the presence of residual water molecules in the polymeric structure.

The substituted alkynes, needed for the grafting onto the polymer, were prepared using usual procedures. The amides (**1a**-**d**) were



Fig. 4. DSC diagrams of PVC azide (**B**), [4-(acetamidomethyl)triazol-1-yl]polyvinyl chloride (**2a**), [4-(butyramidomethyl)triazol-1-yl] polyvinyl chloride (**2b**), [4-(caprylamidomethyl)triazol-1-yl] polyvinyl chloride (**2c**), [4-(benzamidomethyl)triazol-1-yl] polyvinyl chloride (**2e**).

Table 1	
Loadings and DSC studies of syn	thesized polymers B and 2a–e .

Polymer ^a	Loading $(mmol \cdot g^{-1})^b$	T _{exo} (°C)	Tg (°C)
2a	4.48	-	132
2b	3.97	-	131
2c	3.25	-	126
2d	3.50	-	123
2e	4.38	-	119
В	7.92	210	90

^a For structures, see Scheme 3.

^b mmol triazole for **2a–e** and N₃ for **B**.

synthesized using the corresponding acyl chlorides and coupling them on propargylamine in the presence of a base and a catalyst (Scheme 2). The obtained yields were modest (66–79%) but the products were pure enough to be used without further purification. The structure of **1a–d** was confirmed by characteristic signals in NMR (*ca.* $\delta = 2.25$ (triplet, =C–H) ppm in ¹H and 70, 80 (C=C), 170 (C=O) ppm in ¹³C) and IR spectroscopy (*ca.* 3300 ($\nu_{=C-H}$), 2100 ($\nu_{C=C}$), 1640 ($\nu_{C=O}$) cm⁻¹).

3.2. Characterization of polymer-supported triazoles (2f-j)

The reaction between alkynes 1a-d and azido-PVC (**B**) was performed using a CuAAC procedure to obtain polymer-supported 1,2,3-triazoles 2a-d with various substituents onto the triazole in the fourth position (Scheme 3). PVC-N₃ (**B**) was treated with an excess of the alkyne in the presence of a base (DIPEA) and cuprous iodide as a catalyst, to increase both the reaction speed and yield. Another polymer 2e was synthesized using phenylacetylene which does not have an amide bond in order to evaluate this influence of this link [26]. The cycloadditions were followed by ATR/FTIR and considered as finished when the azide vibration was not visible anymore. The yields of the cycloadditions were difficult to evaluate using a mass increase on the scale used. The reactions were considered as quantitative based on the ATR/FTIR analysis and previous work.

Residual vibrations form the azido group of **B** or from the starting alkynes **1a–e** were not observed onto the IR spectra of polymers **2a–e** (Fig. 3). On these spectra, vibrations form amide bonds (NH, C=O), with the exception of **2e**, can be observed together with vibrations coming from the triazole ring and its substituent, when compared to the spectrum of the starting polymer **B**.

The DSC curves of azido-PVC (**B**) and the polymers **2a–e** are shown in Fig. 4. The glass-transition temperatures (Tg) of the polymers were determined from inflection points of DSC curves and are listed in Table 1 [30,31]. The T_c and T_m temperatures are not easy to find. In the case of PVC-N₃ (**B**), an exothermic peak was also observed at



Fig. 5. Percentages of metal cation extraction for the polymers 2a-e, in comparison to the values found for PVC (A) and PVC-N₃ (B) as blanks.

210 °C. This transition can be attributed to the decomposition of the azido group of the polymer [20].

3.3. Metal ion extraction

The results of extraction as determined by AAS, mean values of three readings of each of three extraction experiments, were calculated as percentages of extraction based on the initial concentration, and are presented in Fig. 5.

As a first observation, the extraction of the metals by blanks A (PVC) and **B** (PVC- N_3) is low, the extraction yields do not go over a maximum value of 10%; 10 \pm 4.06% and 8 \pm 1.54% respectively. Only the percentage of Cadmium extraction reached $15 \pm 0.18\%$ with the polymer **A**. In a second observation, the extraction of Nickel is very low with polymers **2c–e**, the yield of extraction never exceeded 10 \pm 1.52%. The best performance of extraction for this metal is obtained with polymers 2b and 2a with yields of extraction of 22 \pm 5.95% and 19 \pm 1.84% respectively. The extraction of Copper is better than the one of Nickel, the extraction yields being of 63 \pm 8.72% (**2a**), 58 \pm 4.48% (**2b**), 54 \pm 8.83% (2c), and not exceeding $9 \pm 2.07\%$ for the others polymers. The average yield for this metal by polymers 2a-c is in the order 58 \pm 4.51%, this value being comparable with that found by Pellera et al. using aqueous solutions using agricultural by-product for removal of Copper [32]. The result of Lead extraction with polymers **2a–c** reached up to 74 \pm 7.87%, but only a maximum of 21 \pm 8.64% with the others. Extraction yields of Pb by polymers **2a–c** are a little better than those obtained by Chaari et al., which have achieved an adsorption performance around 65% using a Tunisian smectic clay [33].

The extraction of Cadmium is better than with the other metals, one of the polymer-supported triazole **2a** was found to extract Cadmium selectively with a high efficiency of 92 \pm 7.49%. These results are comparable with those obtained by us using the same appendages onto poly(styrene) [20]. The extraction yields for this metal by polymers **2d** and **2e** are good and similar around 83 \pm 0.75%, while polymer **2b** (72 \pm 7.03%) and polymer **2c** (52 \pm 7.86%) were a bit less efficient. The results for Cadmium extraction found for those polymers (**2a**, **2b**, **2d** and **2e**) are similar to those found by M'leyh et al. using natural clays of Borj Chekir [34]. For the polymeric triazoles **2a–e**, the average extraction yields are in the following order: Cd²⁺ > Pb²⁺ > Cu²⁺ > Ni²⁺. These results are comparable to those obtained by Sprynskyy et al. with the adsorption–diffusion column filled by the zeolite [35].

At the beginning of our work onto this set of alkynes, we became interested on the possible chelations when the triazole formed was bearing an amide function. Polymers described in the literature are incorporating amine or pyridine sidearm's ("pendant" or "integrated design") or only "simple" triazoles ("triazole design") in order to chelate a metal ion before their reduction inside dendrimeric structures, as an example. Catalysis was the ultimate goal for most of them [36–40].

For the study of our supported pendant amide triazole, we evaluated the polymers 2a-e. The amino methyl substituent of the triazole ring was linked under an amide form to alkyl chain, as well as a phenyl ring, in order to evaluate the effect of steric hindrance and/or hydrophobicity. In this series, the polymer **2e** was prepared to act as a blank, since no amide function nor the amino methyl was included. From the results of Cadmium extraction by the polymers 2a (92 \pm 7.49%), 2b (72 \pm 7.03%) and 2c (52 \pm 7.86%), we can observe that the extraction yield is dropping with the chain length increase. For the polymers 2d and **2e**, they have the same extraction yield for Cadmium (around 83%), suggesting that the amide function has no effect onto the chelation of Cadmium, but a phenyl ring increases the extraction yield to almost the level of the methyl substituant of the amide like in 2a. The extraction yields of Cadmium by polymers **A** ($15 \pm 0.18\%$) and **B** ($7 \pm 2.69\%$) with no amide neither triazole are low, which seems to confirm that the triazole is responsible for the chelation of Cadmium by the polymers studied.

For Lead, the tendance is reversed: if the alkyl chain increases in size, the extraction of this metal increases from **2a** ($66 \pm 3.85\%$) to **2b** ($77 \pm 5.07\%$) and to **2c** ($81 \pm 1.48\%$). The results of Pb extraction by the other polymers **2d** ($27 \pm 4.08\%$) and **2e** ($15 \pm 0.76\%$) are much lower. We can observe that the polymer **2d** gives a slightly better performance than the one of polymer **2e**. For this metal, the behavior is different than the one for Cadmium: the absence of an amide in **2e** when compared to the polymer **2d**, while the two polymers contain a phenyl group which suggests that the amide function participates to a certain extent into the chelation of this metal. The length of the side chain of the amide seems to have an importance, but the relation between a higher hydrophobicity and chelation properties is difficult to draw. It's possible that the chelate will be more stable for ligand exchange if it forms a structure protected by long alkane chains as substituant.

For the extraction of Copper, the extraction efficiency is similar to the one for Cadmium. If the alkyl chain increases in size, the percentage of extraction decreases from **2a** ($63 \pm 8.72\%$), **2b** ($58 \pm 4.48\%$) to **2c** ($54 \pm 8.83\%$). The other polymers have a very low complexing hability (**A** ($11 \pm 2.82\%$), **B** ($9 \pm 2.19\%$), **2d** ($6 \pm 1.70\%$) and **2e** ($8 \pm 3.19\%$)) so it is difficult to draw a clear conclusion about the complexation mechanism which can be, however, like the one encountered for Cadmium.

Last but not the least, none of the polymers studied have a selectivity for Nickel. The extraction efficiency is staying below 20%, suggesting that these polymers can be used as selective non-chelating polymers for Ni.

4. Conclusions

In this work, we made the first chemical grafting of chelating units onto poly(vinyl chloride) using CuAAC procedure between the azided polymer and selected alkynes. The synthesized polymers were characterized by the way of FTIR, DSC and elemental analysis. They were then evaluated for their ability to extract metallic ions from solutions; namely Cd^{2+} , Ni^{2+} , Pb^{2+} , and Cu^{2+} . The polymers were found to extract these ions with some selectivity, and seemed to have an affinity following the order $Cd^{2+} > Pb^{2+} > Cu^{2+} > Ni^{2+}$. The polymers **2a**-**c** were not very selective, but were able to chelate with some efficiency of Cu^{2+} , Pb^{2+} , and Cd^{2+} . Polymers **2d** and **2e** were very selective and efficient for Cd^{2+} removal over the three other metals.

These results, and the very good selectivity of **2d** and **2e** for Cadmium (II), encourage us to pursue polymer modifications using click chemistry in order to design new extractants. Further studies will be reported in due course as well.

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