



## New poly(ether-phosphoramidate)s sulfides based on green resources as sensitive films for the specific impedimetric detection of nickel ions

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### ABSTRACT

For the development of selective and sensitive chemical sensors, we have developed a new family of poly(ether-phosphoramidate) polymers. These polymers were obtained with satisfactory yields by nucleophilic aromatic polycondensation using isosorbide as green resources, and bisphenol A with two novel difluoro phosphinothioic amide monomers. Unprecedented, the thiophosphorylated aminoheterocycles monomers, functionalized with two heterocyclic amine, N-methylpiperazine and morpholine were successfully obtained by nucleophilic substitution reaction of P(S)-Cl compound. The resulting polymers were characterized by different analytical techniques (NMR, MALDI-ToF MS, GPC, DSC, and ATG). The resulting partially green polymers, having tertiary phosphine sulfide with P-N side chain functionalities along the main chain of polymers are the sensitive film at the surface of a gold electrode for the impedimetric detection of Cd, Ni, Pb and Hg. The bio-based poly(ether-phosphoramidate) functionalized with N-methylpiperazine modified sensor showed better analytical performance than petrochemical based polymers for the detection of Ni<sup>2+</sup>. A detection limit of 50 pM was obtained which is very low compared to the previously published electrochemical sensors for nickel detection.

### 1. Introduction

The heavy metal ions, such as nickel (Ni), lead (Pb), mercury (Hg), copper (Cu) and cadmium (Cd) can cause ruthless health nuisance for animals and human, especially due to their ability to bind to nucleic acids, proteins and metabolites, by stopping or altering some biological tasks [1–3]. In the last decade, the European Union took actions and made progress in various environmental fields, such as the implantation of the Water Framework Directive 2000/60/EC (WFD). WFD proposes, as minimum requirement Environmental Quality Standards (EQS) value for the four toxic heavy metals Ni, Cd, Pb, and Hg, respectively, 341, 0.7–2.2, 35, and 0.25 nM [4]. Therefore, it is very necessary to monitor and detect such trace heavy metals ions for water quality control [5]. Conventional analytical detection methods used for the above mentioned heavy metals involve sophisticated instrumentation including the atomic absorption spectroscopy (AAS) [6], inductively

coupled plasma/atomic emission spectrometry (ICP-AES) [7] and inductively coupled plasma/mass spectrometry (ICP-MS) [8]. The disadvantage of these traditional analytical techniques are the necessity of highly trained personnel for measurement and evaluation, tedious sample preparation and preconcentration, and the high cost of the instruments. Due to the capability of short analytical time, simplicity, low power cost, high sensitivity and easy adaptability for *in-situ* measurement, electrochemical sensors are becoming more popular and worthy for the detection of heavy metal ions [9,10]. The development of more sensitive and selective chemical sensors for heavy metal detection requires the design of more selective ion-complexing units assembled as recognition layers at the surface of the electrochemical devices [11]. Dimethylglyoxime is the most widely used synthetic ligand for the complexation of nickel ion and its gravimetric detection. It has been inserted in polymeric matrices for its electrochemical detection (see for example [12]). Many potentiometric sensors for the detection of nickel

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ion are based on newer molecules such as Schiff bases. A tetradentate chelate is formed with the nickel ion and imine nitrogen and other nitrogen and heteroatoms such as oxygen [13] or sulfur [14]. These Schiff bases are inserted in a polyvinylchloride matrix, which limits the shelf lifetime of the sensor, due to the leakage of the ionophore molecule. To generate sensors with enhanced performance, many have turned to polymer-based technologies. Advantages of polymer-based materials are that their chemistry can be easily modified to tune their reactivity, flexibility/stretchability, biocompatibility and resistance to degradation [15].

In recent years, polymers derived from biomass have been extensively studied, and numerous investigations were conducted including the development of polymers containing heterocyclic moieties derived from biomass [16–18]. Recently, it has been shown that the development of heterocyclic bio-based polymers derived from Gluc [19] and isosorbide [20,21] offers a good capacity to adsorb a wide variety of chemical compounds with diverse chemical structures. ISB has a relatively high thermostability and low segmental mobility, and can be used to improve the glass transition temperatures of the resulting polymers [18,22]. The petro-based monomer is the bisphenol-A (BPA), the key diol monomer for improving the thermal and mechanical properties of engineering plastics due to its aromatic, heavy, rigid and distorted molecular structure [23,24]. As a part of our interest in development of impedimetric sensors for the detection of heavy metal ions, bio-based poly(ether-phosphine) oxide modified gold electrode has been attempted previously and the heterocyclic structure of this polymer has resulted in enhancing the metal-binding ability [25]. This was due to the increased number of metal-binding centers leading to enhanced adsorption efficiency.

Prompted by these results, we propose in this work, the synthesis of novel heterocyclic phosphine sulfide polymer structure by incorporation of nitrogen-containing heterocyclic functionality for development of an impedimetric sensor with better complexation characteristics towards nickel ions. The proposed designed structure, is a new class of poly(ether-phosphoramidate) sulfide polymer. It is prepared by polycondensation of a bio-based heterocyclic monomer (ISB) or a petro-based aromatic monomer (BPA) and two synthesized difluoro phosphinothioic amide monomers (morpholinophosphine sulfide and methylpiperazine phosphide sulfide). The repeating units then present many neighbouring tertiary amine and ether groups allowing nickel ion coordination.

The synthesized polymers were fully characterized using MALDI ToF Mass spectrometry, NMR spectroscopy, GPC, DSC and ATG and then the analytical performance of the modified electrodes for the detection nickel ions was determined using electrochemical impedance spectroscopy.

## 2. Materials and methods

### 2.1. Reagents and standards

The reagents used in the synthesis of monomers, thiophosphoryl chloride ( $\text{PSCl}_3$ , 98%), fluorobenzene (99%), aluminum chloride anhydrous ( $\text{AlCl}_3$ , 99%), morpholine ( $\geq 99.0\%$ ), N-methylpiperazine ( $\geq 99\%$ ) and triethylamine ( $\text{Et}_3\text{N}$ ,  $\geq 99.5\%$ ) were purchased from Sigma-Aldrich. The reagents used for the polymerization, 2,2-bis(4-hydroxyphenyl)propane (bisphenol A, 99%, recrystallized from toluene), isosorbide (98%, recrystallized from acetone), anhydrous potassium carbonate and N,N-dimethylacetamide (DMAC, 99%) were purchased from Sigma-Aldrich. Other solvents were of reagent-grade quality and were used without further purification. Solutions of metallic ions were prepared from standard solutions for AAS in nitric acid (Sigma-Aldrich). Potassium citrate tribasic monohydrate (98%) was purchased from Sigma-Aldrich.

### 2.2. Monomer synthesis

The monomers useful for the polycondensation reactions were obtained in two steps as presented in Fig. 1 and described afterwards.

The novel difluoro phosphinothioic amide monomers, bis(4-fluorophenyl) (morpholino) phosphine sulfide (2a), bis(4-fluorophenyl) (4-methylpiperazin-1-yl)phosphine sulfide (3a) were synthesized according the route described in Fig. 1, with satisfactory yields. The synthesis of this two thiophosphorus P(S)–N monomers involves two steps, starting in the preparation of the bis(4-fluorophenyl)chlorophosphine sulphide (1a) via a Friedel-Crafts chemistry. Then, this intermediate (2a) was reacted with an amino compound (N-methylpiperazine or morpholine) to obtain the desired phosphinothioic amide. Thiophosphorylated aminoheterocycles have been synthesized using the same methodology [32]. The reaction was carried out in an inert organic reaction medium (chloroform), and in the presence of tertiary organic amine (triethylamine) as hydrogen chloride acceptor. The structure and the high purity of the synthesized monomers (Fig. 1) was confirmed by  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{31}\text{P}$  NMR analysis (Figure S1). These monomers were incorporated in the novel poly(ether-phosphoramidate) sulfides structures by aromatic nucleophilic substitution as described later in Fig. 2.

#### 2.2.1. Synthesis of bis(4-fluorophenyl)chlorophosphine sulfide (1a)

The (1a) intermediate was synthesized via Friedel-Crafts chemistry as specified in our previous work [22].

#### 2.2.2. Synthesis of bis(4-fluorophenyl) (morpholino)phosphine sulfide (2a)

9.81 g (0.034 mol) of Bis(4-fluorophenyl)chlorophosphine sulfide and 16 mL of chloroform were mixed in a 250 mL three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel, and a  $\text{N}_2$  inlet. The mixture was agitated in an ice-bath under nitrogen atmosphere. Five minutes later, 6.53 g (0.075 mol) of morpholine dissolved in chloroform (16 mL) was added over 30 min. Then 10.32 g (0.102 mol) of triethylamine was added to the solution. After completing the addition, the solution was heated to  $85^\circ\text{C}$  for 6 h until the reaction completely finished. The solution was cooled to room temperature and then filtered. The filtrate was evaporated under reduced pressure to obtain the crude product. The crude product was washed with water, and then extracted with dichloromethane. The organic phase was dried over  $\text{MgSO}_4$ , concentrated under vacuum, and then purified on a column chromatography column [ $\text{SiO}_2$ :Dichloromethane:Acetonitrile (9:1)] with a yield of 75% as a brown solid.

#### 2.2.3. Synthesis of bis(4-fluorophenyl) (4-methylpiperazin-1-yl)phosphine sulfide (3a)

13.86 g (0.048 mol) of bis(4-fluorophenyl)chlorophosphine sulfide and 23 mL of chloroform were mixed in a 250 mL three-necked round-bottom flask equipped with a reflux condenser, a dropping funnel, and a  $\text{N}_2$  inlet. The mixture was agitated in an ice-bath under nitrogen atmosphere. Five minutes later, 10.51 g (0.105 mol) of N-methylpiperazine dissolved in chloroform (23 mL) was added over 30 min. Then 14.57 g (0.144 mol) of triethylamine was added to the solution. After completing the addition, the solution was heated to  $75^\circ\text{C}$  for 6 h until the reaction completely finished. The solution was cooled to room temperature and then filtered. The filtrate was evaporated under reduced pressure to obtain the crude product. The crude product was washed with water, and then extracted with dichloromethane. The organic phase was dried over  $\text{MgSO}_4$ , concentrated under vacuum, and then purified on a chromatography column [ $\text{SiO}_2$ :Dichloromethane:Ether:Acetonitrile(6:3:1)] with a yield of 64% as a white solid.

### 2.3. Synthesis of polymers

The typical polymerization procedure for the synthesis of poly(ether-phosphoramidate)s P1–P4 based on green monomer, isosorbide and/or from bisphenol A (BPA) was as follows: isosorbide (1.6415 g, 5 mmol)

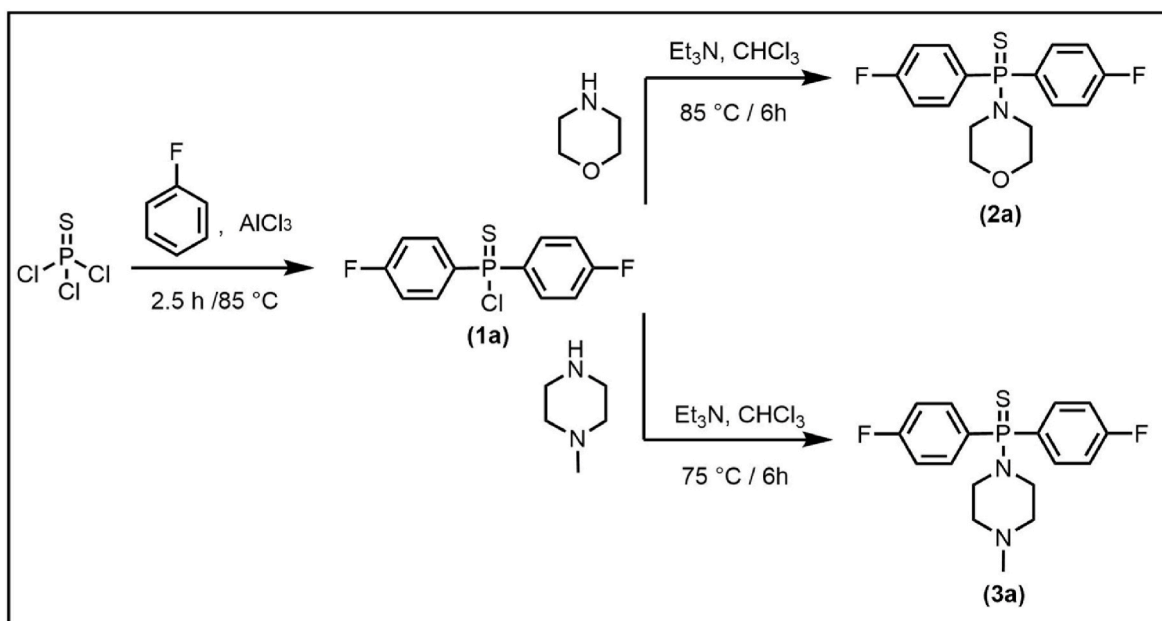


Fig. 1. Different steps for the synthesis of the monomers used for the novel poly(ether-phosphoramidate) sulfides.

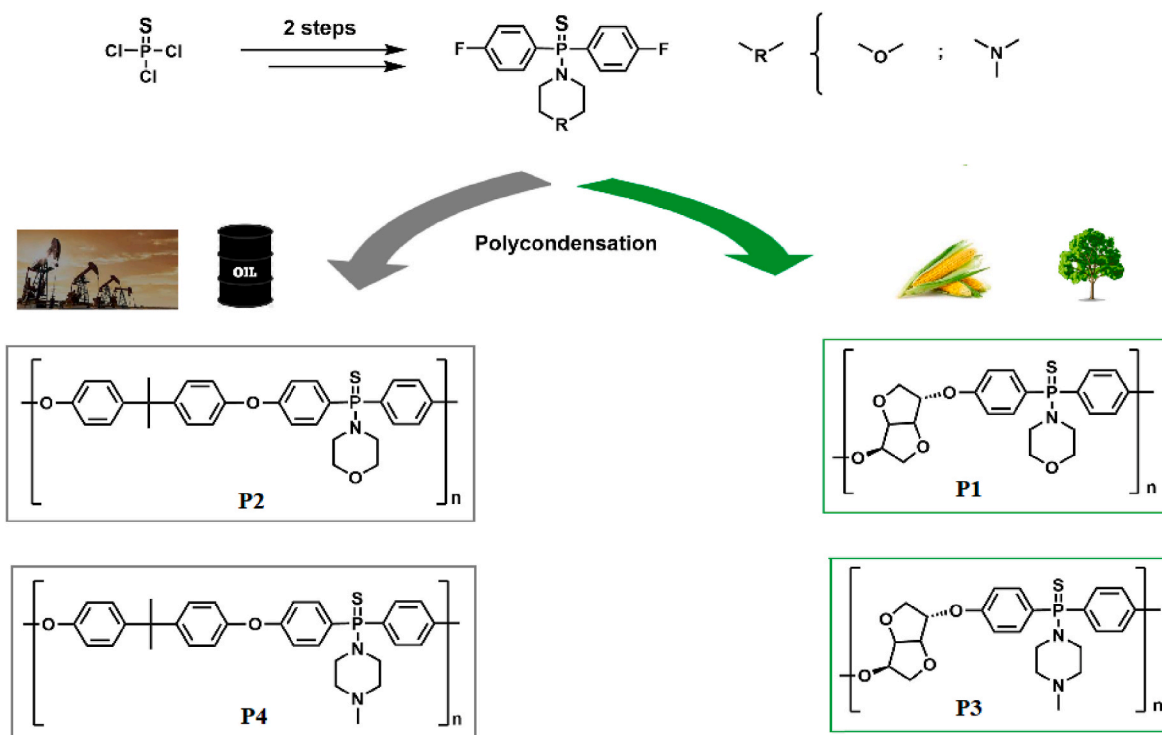


Fig. 2. Synthetic routes of partially green poly(ether-phosphoramidate)sulfides P1–P4, derived from ISB and from BPA. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

[or BPA (1.1414 g, 5 mmol)], bis(4-fluorophenyl) (morpholino)phosphine sulfide (2a) (1.7619 g, 5 mmol) [Bis(4-fluorophenyl)chlorophosphine sulfide (1a) (1.6967 g, 5 mmol)], and K<sub>2</sub>CO<sub>3</sub> (3.040 g, 22 mmol) were added to 13.5 mL of dimethylacetamide (DMAC) (20% solid) and heated at 160 °C for 24 h, in a two-necked reactor equipped with a N<sub>2</sub> inlet and a mechanical stirrer. After cooling, the mixture was poured into water. The precipitated polymer was collected by filtration, washed with methanol using soxhlet for 24 h, and then dried under vacuum at 80 °C for 7 h.

#### 2.4. Characterization methods and apparatus

<sup>1</sup>H, <sup>19</sup>F, and <sup>31</sup>P nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Avance 300 spectrometer operating at the following frequencies of 300 MHz for <sup>1</sup>H, 282 MHz for <sup>19</sup>F, and 121 MHz for <sup>31</sup>P. Tetramethylsilane (TMS), CFC<sub>3</sub>, and 85% H<sub>3</sub>PO<sub>4</sub> were used as internal standards for <sup>1</sup>H, <sup>19</sup>F and <sup>31</sup>P, respectively.

The thermal behavior of the polymers was investigated using a Mettler-Toledo DSC822e equipment under nitrogen atmosphere (50

mL/min) from 25 °C to 300 °C at a scan rate of 10 °C/min. The glass transition temperature values were obtained from the second heat scan by the mid-point method. The thermal degradation of synthesized polymers was followed by thermogravimetric analysis (TGA) using a TA Q50 Instrument under nitrogen atmosphere from 25 °C to 500 °C at a scan rate of 10 °C/min.

Molecular weights of the synthesized polymers were measured using gel permeation chromatography (GPC). The experiments were performed with a PL gel 5 µm Mixed C (300 × 7.5 mm, polystyrene/divinylbenzene) column, equipped with a Wyatt TREOS 3 angle light scattering detector, a Shimadzu RID 10 A refractometer. Chloroform was used as mobile phase with a velocity of 1 mL/min. Reported values (number average molecular weight (Mn), weight average molecular weight (Mw) and polydispersity index (PD) were determined from a polystyrene calibration curve.

An Autoflex Max MALDI mass spectrometer (Bruker Daltonik, Bremen, Germany) was used for mass spectrometric analysis. Spectra were recorded in the reflector instrument mode. The samples were dissolved in Dimethylformamide. DCTB (trans-2-[3-(4-tert-butylphenyl)-2-methyl-2-propenylidene] malononitrile, was used as a matrix and doped with KTFA (potassium trifluoroacetate) to selectively enable the formation of potassium adduct ions.

Electrochemical impedance spectroscopy measurements were carried out using a potentiostat (Biologic-EC-Lab VMP3) analyzer. EIS measurements were obtained using a cell with three electrodes: gold working electrode modified with polymer film (0.07 cm<sup>2</sup> active area), a Ag/AgCl/KCl<sub>sat</sub> electrode as reference electrode, and a Platinum plate as counter electrode.

Contact angles (θw) of water on the polymeric film surface were obtained using the sessile drop method with Contact Angle System OCA Instrument at 23 °C in air. The drop image was stored by a video camera and an image analysis system was used for the calculation of the contact angle (θw) from the shape of the drop. The volume of the drop was about 2 µL. The digital images were analyzed for their profile and the contact angle was extracted at both sides of the drops by the tangent method. The angles reported in Figure S10, are the average of at least three measurements on different parts of each sample.

### 2.5. Preparation of polymer-modified gold electrodes and impedimetric measurements

Firstly, the gold substrates (SiO<sub>2</sub>/Si/SiO<sub>2</sub>/Ti/Au hetero-structure), provided by the French RENATECH network (LAAS, CNRS Toulouse), was rinsed with acetone for 15 min, rinsed with deionized water then dried with nitrogen flow. Then, the gold surface was cleaned for about 5 min in a piranha solution (25% (H<sub>2</sub>O<sub>2</sub> 35%)+ 75% (H<sub>2</sub>SO<sub>4</sub> 96%) mixture) in order to activate the surface, and then rinsed with deionized water under ultrasonication for 10 min and was finally dried under nitrogen flow. For preparation of poly(ether-phosphoramidate)s sulfides-modified electrodes a solution of the polymer in chloroform (5 µL, 1w/w %) was dropped on the surface of the gold electrode. Solvent was evaporated under a nitrogen flow at room temperature. Drop-coating was chosen because spin-coating was not applicable, due to the volatility of chloroform.

Electrochemical Impedance Spectroscopy (EIS) (Initial potential E = -0.150 V, frequency range 100 mHz to 100 kHz) was used to investigate the charge transfer resistance of the polymer film in contact with a 0.1 M potassium citrate solution (pH = 4, total volume 5 cm<sup>3</sup>) with different concentrations of the metallic ions (5 × 10<sup>-7</sup> M to 5 × 10<sup>-11</sup> M). EIS measurements were performed after 20 min of incubation time to reach equilibrium conditions between modified electrode and the solution.

## 3. Results and discussion

### 3.1. Physicochemical characterization of the resulting poly(ether-phosphoramidate)s sulfides P1 – P4

The polymerization reaction was performed by condensation of the synthesized monomers (2a) and (3a) with isosorbide as bio-based monomer or bisphenol A as petroleum based monomer in polar aprotic solvent (DMAc, 20% cc) in the presence of K<sub>2</sub>CO<sub>3</sub> (as catalyst and HF acceptor), at 160 °C. At the end of the polymerization, the polymers were isolated by precipitation in water. After filtration, the beads were placed in a Soxhlet extractor and extracted with methanol and then dried in vacuum during 7 h at 80 °C. As shown in Table 1, the four poly(ether-phosphoramidate)s sulphides were obtained with good yields in the range of 87–99%. The average molecular weight (Mn) of the synthesized polymers, determined by gel permeation chromatography, is between 4541 and 13,180 Da and the dispersity index range from 1.51 to 2.7. The polycondensation with the difluoro monomer with morpholine as substituent (2a) provide polymer with high molecular weight (polymerization degree in the range of 17–25) comparing with the monomer substituted by N-methylpiperazine (polymerization degree in the range of 9–10). These results can be explained by the difference in reactivity of these two monomers.

The chemical structure of the prepared poly(ether-phosphoramidate) was characterized by MALDI ToF and NMR spectroscopies. Firstly, the P1–P4 polymers were characterized by MALDI ToF MS in order to ascertain the chemical composition and to elucidate their end-group combinations. The potential structures that could be obtained by the polycondensation of Isosorbide or Bisphenol A with the two difluoro phosphinothioic amide monomers are depicted in Figure S2 [P1: ISB/(2a)] and Figure S3 [P2: BPA/(2a)].

In the MALDI ToF mass spectrum of P1 (ISB/(2a)), the repeating unit of 445.47 Da reveals the presence of several distribution of ions (Figure S2). It can be observed, the MALDI ToF mass spectrum presents a strong predominance of linear structures (La, Lb and Lc). The cyclic structures are also present but less abundant. These results demonstrate that the conversion was far to complete. In the spectrum enlargement (1500–50,000 Da) of P2 (BPA/(2a)), the repeating unit of 527.16 Da revealed the major presence of the cyclic structures with the linear structures (La, Lb and Lc) in the minority. This result is in agreement with Kricheldorf's theory concerning the kinetically controlled polycondensation [26], which assumes that the cyclization competes with chain growth at any concentration and at any stage of the polycondensation. Thus, when side reactions are absent, the chain growth was limited by the cyclization.

For the other polymers P3 and P4 based on monomer (3a), the same structure types are observed (Figure S4 and Figure S5), the isosorbide based polymer (ISB/(3a)) revealed the major presence of linear structures and bisphenol A based polymer (BPA/(3a)) revealed the major presence of cyclic structures. These results can be explained by the different spatial conformation of isosorbide compared to Bisphenol A. The peculiar V-shaped configuration of isosorbide formed by two cis-connected tetrahydrofuran rings with a 120 opening angle [18] promote the elaboration of linear polymers with helix structure [27,28], while the tetrahydic geometry of Bisphenol A promote the elaboration of cyclic polymers [20,29].

The chemical composition of the resulting poly(ether-phosphoramidate)s sulfide were ascertained by <sup>1</sup>H and <sup>31</sup>P NMR analysis. A detailed description of the NMR data recorded from P1–P4 are given in Figure S6 and the <sup>1</sup>H and <sup>31</sup>P NMR spectra of the bio-based poly(ether-phosphoramidate), P1, are given in Figure S7 for illustration. The <sup>1</sup>H NMR spectrum exhibits the characteristic protons of isosorbide (H1–H6) and of the difluoro phosphinothioic amide monomer 2a (H7–H10). Furthermore, spectral analyses show the presence of peaks with low intensity corresponding to protons at the end groups of isosorbide (H4\*, H2\*, H1\*, H6\*) and of the difluoro monomer (2a) (H7\*

**Table 1**  
Physico-chemical characteristics of the resulting polymers P1–P4.

Ref. Polymer	Monomers	Yield <sup>a)</sup> (%)	T <sub>g</sub> <sup>b)</sup> (°C)	T <sub>d5%</sub> <sup>c)</sup> (°C)	M <sub>n</sub> <sup>d)</sup> (Da)	M <sub>w</sub> <sup>d)</sup> (Da)	PD <sup>d)</sup>
P1	(2a)/ISB	97	218	365	7294	12,850	1.76
P2	(2a)/BPA	99	206	380	13,180	27,310	2.07
P3	(3a)/ISB	87	198	401	4541	6857	1.51
P4	(3a)/BPA	95	187	405	4815	7415	1.54

a) After precipitation into water and washing with methanol using soxhlet extractor, evaporation under vacuum at 80 °C.

b) Determined by DSC with a heating rate of 10 °C/min under a Nitrogen flow of (50 mL/min).

c) Temperature at which 5% of weight loss was observed in the TGA traces recorded at 10 °C/min under Nitrogen atmosphere.

d) Number and weight-averaged molecular weights (M<sub>n</sub>, M<sub>w</sub>) and polydispersity (PD) determined by GPC in CHCl<sub>3</sub> (calibrated with polystyrene).

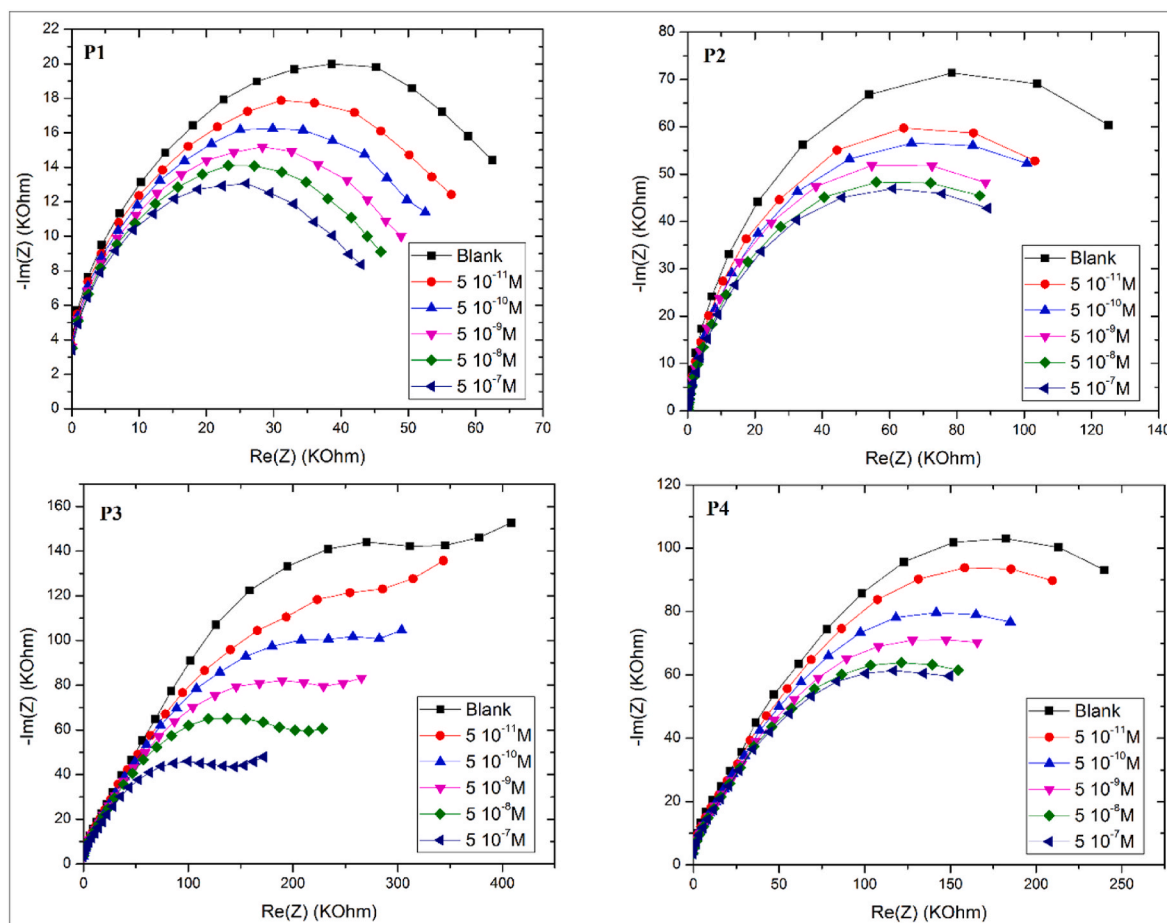
and H8\*), confirming the presence of different linear structures (La, Lb and Lc). For the phosphorus NMR analysis, the spectrum of P1 presents a single peak at 66 ppm, which is assigned to the phosphorus nucleus of phosphine sulfide group (SP(N) (R)<sub>2</sub>).

The thermal behaviors of the polymers is an important property, this study enlarges their potential application field. The thermal properties of the new poly(ether-phosphoramidate)s sulfides P1–P4 was carried out by Differential scanning calorimetric (DSC) and Thermogravimetric analysis TGA. The thermal behavior data concerning the glass transition temperature and the decomposition temperature are presented in Table 1. The presence of a single inflexion point in all DSC thermograms (Figure S8) corresponding to the glass transition temperature (T<sub>g</sub>) reveals the amorphous nature of all the obtained poly(ether-phosphoramidate)s.

The T<sub>g</sub> values (Table 1) range from 206 to 286 °C for P1 and P2, and 187–198 °C for P3 and P4. These distinctly lower former value most

properly depend on both the difluoro monomer structure and on the obtained molar mass. It can be seen from the DSC results of the polymers that the biosourced polymers present the highest glass transition temperature compared to that of the conventional BPA-based polymers. In a previous work, a similar behavior for poly(ether-phosphine) from isosorbide and bisphenol A was obtained [25]. The thermal stability of P1–P4 were recorded by TGA in nitrogen atmosphere. The TGA thermograms displayed in Figure S9, indicated a single decomposition process, attributed to the decomposition of polymer main chain.

The 5% weight-loss temperatures (T<sub>d5%</sub>) of the polymers based on (3a), P3 and P4, was observed to be higher than 400 °C (Table 1). This T<sub>d5%</sub> is higher than that of the poly(ether-phosphoramidate)s sulfides based on (2a), with T<sub>d5%</sub> of 365 and 380 °C for P1 and P2, respectively. Despite this, the T<sub>d5%</sub> of the newly synthesized poly(ether-phosphoramidate)s were higher than 365 °C in nitrogen, still demonstrating excellent thermal stability.



**Fig. 3.** Nyquist plots of the gold electrode/poly(ether-phosphoramidate)s sulfides/electrolyte obtained in presence of Ni<sup>2+</sup> ion. Measuring solution: 0.1 M potassium citrate solution at pH 4.0. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)



In order to study the hydrophilic/hydrophobic character of the polymer-modified gold electrode surface, the contact angles of the water drops were measured. The obtained contact angles ranged ( $\theta_w$ ) from  $75.8^\circ$  to  $85.7^\circ$  (Figure S10).

The lower  $75.8^\circ$  contact angle value, for the P3 polymer-modified gold electrode, indicates that its surface is more hydrophilic due to the presence of nitrogen atom (in N-methylpiperazine group) and oxygen atoms (in isosorbide structure) in the chemical structure of the polymer. The higher contact angle value ( $85.7^\circ$ ), measured for the P2 polymer-modified gold electrode, can be explained by the aromatic rings of bisphenol A and the low hydrophilicity of morpholine substituted compared to N-methylpiperazine ones.

### 3.2. Detection of $\text{Ni}^{2+}$ ion by EIS measurements

The prepared polymer-modified gold electrode P1–P4 were used as a platform for sensing  $\text{Ni}^{2+}$  ion in aqueous solutions. The electrochemical impedance measurements performed in the presence of various concentrations of  $\text{Ni}^{2+}$  are presented in Fig. 3.

As shown in Fig. 3, a gradual decrease of EIS plots was observed with the increase of  $\text{Ni}^{2+}$  concentration, indicating a correlation between  $\text{Ni}^{2+}$  concentration and the polymer-modified electrode/interface impedance.

The experimental data generated by the EIS measurements are analyzed using the Randles equivalent electrical circuit model (Figure S11). This electrical circuit is composed of the solution resistance  $R_s$  in series with a parallel circuit composed of the polarization resistance  $R_p$  and the constant phase element CPE. The expression of CPE admittance is the following one:  $Y_{\text{CPE}} = Q\omega^n$ , where  $Q$  is inverse of the impedance modulus, and  $n$  is between 0 and 1 (for  $n = 0$ , CPE is a pure resistor and for  $n = 1$ , CPE is a pure capacitance). The full data of the different elements of the equivalent circuit are given in Table S1, for each polymer, with various concentrations of  $\text{Ni}^{2+}$ . A low standard deviation ( $X^2$ ) between the experimental curve and the curve of the electrical model is obtained ( $X^2 < 10^{-1}$ ).

Comparing the different values of  $n$ , it comes that for BPA based polymers, P2 and P4,  $n$  values are respectively 0.9 and 0.7. These values are higher than for P1 and P3 (respectively 0.5 and 0.6). This point shows that BPA leads to more capacitive films. ISB based polymer present a more resistive character, in connection to their higher hydrophilicity shown by their lower contact angle values (Figure S10).

The relative variation of the charge transfer resistance of each electrode is presented using the following equation  $|R-R_p|/R_p$  ( $\Delta R/R$ ). It is found that this parameter is proportional to the logarithmic value of the  $\text{Ni}^{2+}$  concentrations (Fig. 4).

The analytical performance of the four polymer-modified gold electrode for  $\text{Ni}^{2+}$  detection is presented in Table 2. The sensitivity of detection is defined as the slope of the calibration curves of  $\Delta R/R$  versus  $\log$  of  $\text{Ni}^{2+}$  concentration (Fig. 4).

The relative variation of ( $\Delta R/R$ ) of the poly(ether-phosphoramidate)sulfides (P1–P4) polymers modified-electrodes is proportional to the logarithmic value of  $\text{Ni}^{2+}$  ion concentration in the range of 50 pM to 0.5  $\mu\text{M}$ , as shown in Table 2. The limit of detection of the polymer-modified sensors determined as  $3\sigma/S$ ,  $\sigma$  being the background of the blank and  $S$  the sensitivity, was estimated to be 50 pM. The sensitivity study revealed that the gold electrode modified with the N-methylpiperazine functionalized bio-based polymer P3 presents the best sensitivity value. This result clearly indicates that the presence of nitrogen donor group in the N-methylpiperazine and the bio-based isosorbide improves the complexation efficiency. The P3 modified gold electrode is the more hydrophilic polymer compared to the other polymer, with a contact angle value of  $75^\circ$ . The higher hydrophilicity of the bio-based polymer-modified electrode P3 compared to P1, P2 and P4 modified gold electrodes favours the interaction of the  $\text{Ni}^{2+}$  ions with the functional groups of the polymer and also its diffusion through the polymer film.

When comparing the detection limit of the P3 polymer based sensor

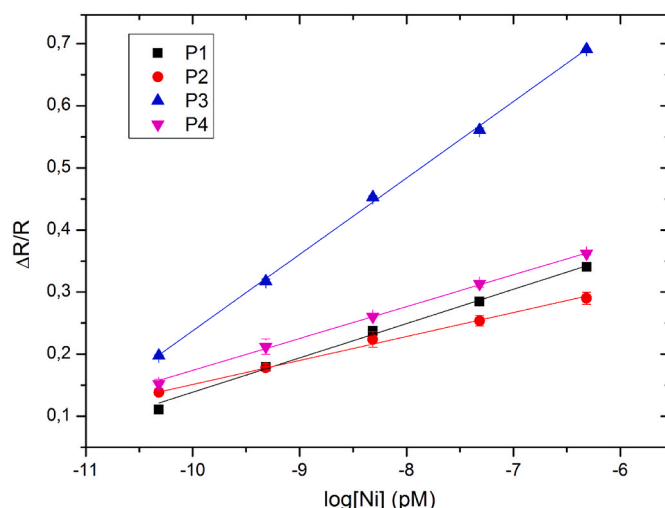


Fig. 4. Relative variation of the polarization resistance of the polymer-modified gold electrode interface as a function of  $\log$  concentration of  $\text{Ni}^{2+}$  ion (pM). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

Table 2

Comparative study: responses of the P1–P4 polymer-based sensors for the  $\text{Ni}^{2+}$  ion.

Sensing polymers	Sensitivity (S)	LOD [M]	Linear range [M]
P1	0.055	$5 \times 10^{-11}$	$5 \times 10^{-11} - 5 \times 10^{-7}$
P2	0.038	$5 \times 10^{-11}$	$5 \times 10^{-11} - 5 \times 10^{-7}$
P3	0.123	$5 \times 10^{-11}$	$5 \times 10^{-11} - 5 \times 10^{-7}$
P4	0.051	$5 \times 10^{-11}$	$5 \times 10^{-11} - 5 \times 10^{-7}$

for the detection of  $\text{Ni}^{2+}$  to that of the previously published electrochemical sensors (Table 3), it comes that it is more than 50 times lower than the lower obtained detection limits and  $10^5$  times lower than the higher obtained ones. Compared to the required EQS value from the WFD ( $3.3 \times 10^{-7}$  M), this value is in the dynamic range of the P3 polymer based sensor.

In order to investigate the selectivity of the chemical sensor based on P3 polymer, The sensitivities for the three other metallic ions of the Water Framework Directive:  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  were determined. The electrochemical impedance measurements were performed in the presence of each metal separately. The full data of the equivalent circuits are given in Table S2 for increasing concentrations of  $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  ions. The results obtained for nickel ion are the same than those presented in Fig. 4 and Table 2.

The calibration for each metallic ion is presented in Fig. 5. The linear range, the limits of detection and the sensitivities obtained for the different metallic ions are reported in Table 4.

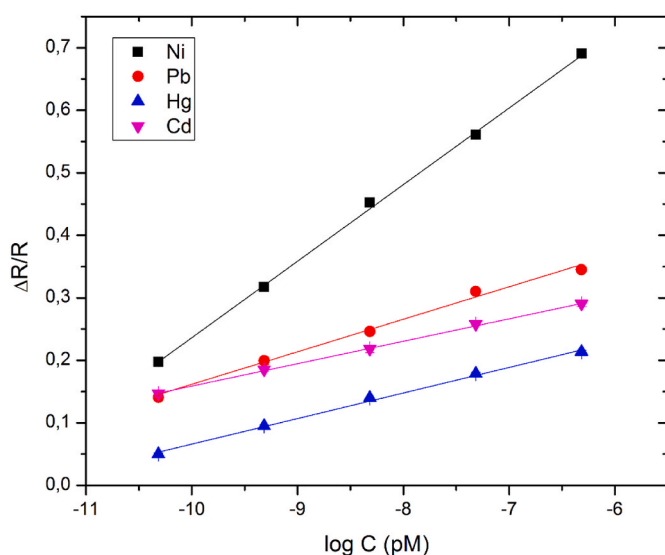
As it can be concluded from the obtained results, a good response for the detection of the four metals is revealed, higher for  $\text{Ni}^{2+}$ . The ratio of the sensitivities for the different metallic ions are the following ones: the sensitivity for  $\text{Ni}^{2+}$  is 3.4 times higher than that of  $\text{Cd}^{2+}$ , 2.4 times higher than that of  $\text{Pb}^{2+}$  and 3.0 times higher than that of  $\text{Hg}^{2+}$ . Detection limit for each metal ion is 50 pM.

The higher sensitivity for nickel ions compared to the other heavy metals can be explained by the ability of  $\text{Ni}^{2+}$  to interact more strongly with the amine and oxygen sites in the polymer chain, due to its smaller ionic radius and higher Mulliken electronegativity compared to the other WFD ions. Specific intrachain interactions between polymer chain and nickel ions is proposed to explain its high affinity (Fig. 6).

**Table 3**

Comparison of the analytical performance of the P3 polymer based sensor to that of the previously published electrochemical sensors for nickel ion detection.

Complexing agent	Electrochemical transduction	Detection Limit	Dynamic range	Ref.
benzylbis(thiosemicarbazone)	Potentiometry	$4 \times 10^{-8}$ M	$10^{-7}$ M – $10^{-2}$ M	[14]
(2-mercapto-4-methylphenyl)-2-benzamido-3-ethoxy-thiopropenoate	Potentiometry	$6 \times 10^{-8}$ M	$10^{-7}$ M – $10^{-2}$ M	[30]
N-(2-hydroxybenzylidene)-N'-(2-picolyl)ethylenediamine	Potentiometry	$\sim 3 \times 10^{-6}$ M	$3.2 \times 10^{-6}$ M – $5 \times 10^{-2}$ M	[13]
3-hydroxy-N-(2-[(3-hydroxy-N-phenylbutyrimidoyl)-amino]-phenyl)-N-phenylbutyramidine	Potentiometry	$\sim 1.6 \times 10^{-7}$ M	$1.6 \times 10^{-7}$ M – $10^{-2}$ M	[31]
sulfamethoxazole diazonium resorcinol	Potentiometry	$\sim 5 \times 10^{-6}$ M	$5 \times 10^{-6}$ M – $10^{-1}$ M	[32]
2,5-thiophenyl bis(5-tert-butyl-1,3-benzoxazole)	Potentiometry	$5 \times 10^{-9}$ M	$10^{-8}$ M – $10^{-3}$ M	[33]
N,N0-(ethane-1,2-diyl)bis(3,4-dimethoxybenzenesulfonamide)	LSV	$0.8 \times 10^{-9}$ M	$10^{-9}$ M – $10^{-3}$ M	[34]
	Impedimetry	$5 \times 10^{-11}$ M	$5 \times 10^{-11}$ M – $5 \times 10^{-7}$ M	This work

**Fig. 5.** Relative variation of the polarization resistance of the P3 polymer-modified gold electrode interface as a function of co-log concentration [Ion] ( $\text{Pb}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Cd}^{2+}$  ions). (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)**Table 4**Comparative study: responses of polymer P3 based sensor for the different ions  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Ni}^{2+}$  and  $\text{Cd}^{2+}$ .

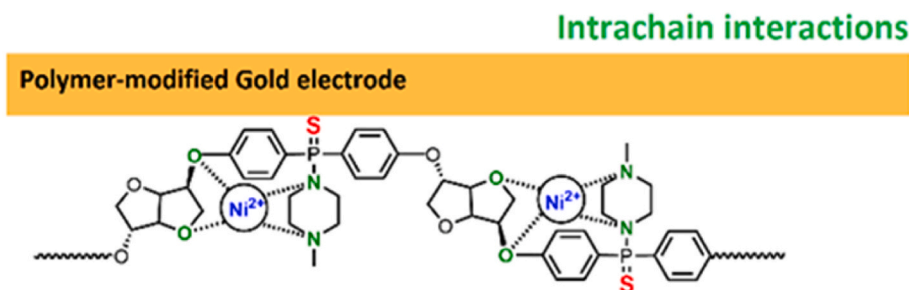
Ions	Sensitivity	LOD [M]	Linear range [M]
$\text{Pb}^{2+}$	0.051	$5 \times 10^{-11}$	$5 \times 10^{-11}$ – $5 \times 10^{-7}$
$\text{Ni}^{2+}$	0.123	$5 \times 10^{-11}$	$5 \times 10^{-11}$ – $5 \times 10^{-7}$
$\text{Cd}^{2+}$	0.036	$5 \times 10^{-11}$	$5 \times 10^{-11}$ – $5 \times 10^{-7}$
$\text{Hg}^{2+}$	0.041	$5 \times 10^{-11}$	$5 \times 10^{-11}$ – $5 \times 10^{-7}$

#### 4. Conclusion

The aim of this work was to synthesize tertiary phosphine sulfide functionalized heterocyclic amine containing monomers and heterocyclic poly(ether-phosphoramidate) sulfide followed by application as recognition layers at the surface of gold electrode for the impedimetric detection of the WFD Metals. Thus, difluoro phosphinothioic amide monomers with high purity was successfully synthesized by nucleophilic substitution of Bis(4 fluorophenyl)chlorophosphine sulfide with N-methylpiperazine and morpholine, as two heterocyclic amine. The thiophosphorylated aminoheterocycles monomers was employed for the preparation of poly(ether-phosphoramidate)sulfides polymers with bisphenol A and Isosorbide with the goal to synthesize effective heterocyclic polymer to improve the kinetics of adsorption of heavy metals. The resulting polymers were obtained with high yields and average molecular weights in the range 4541–13180 g/mol range. MALDI-ToF mass spectrometry in association with NMR spectroscopy allowed us to identify the nature of the structures obtained and of the end-chain moieties. The DSC measurements gave high glass transition temperature in the range of 187–218 °C. All the polymers have a good thermal stability, show 5% weight loss up to 365 °C, under nitrogen atmosphere. After the characterization, impedimetric sensors were developed for the detection of the four WFD heavy metals  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$  and  $\text{Ni}^{2+}$ , by the modification of a gold electrode with four poly(ether-amino-phosphine) sulfide polymers. The bio-based poly(ether-amino-phosphine) sulfide (P3) modified gold electrode showed better analytical performance than petrochemical-based polymers and a higher affinity for  $\text{Ni}^{2+}$  is observed. The hydrophilicity of this polymer and specific interactions with amine and oxygen sites can explain this high affinity.

#### Credit author statement

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**Fig. 6.** Metal-poly(ether-phosphoramidate) interactions.

editing, Nicole Jaffrezic-Renault; funding acquisition, Abdelhamid Errachid, Mohamed Hammami.

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## Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Nicole Jaffrezic-Renault reports financial support was provided by University of Lyon. Nicole Jaffrezic-Renault reports a relationship with University of Lyon that includes: employment. No additional relationship.

## Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.talanta.2022.123550>.

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