

## Synthesis and characterization of poly (ionic liquid) derivatives of N-alkyl quaternized poly(4-vinylpyridine)

Ximena Briones O.<sup>a,\*</sup>, Ricardo A. Tapia<sup>b</sup>, Paola R. Campodónico<sup>a</sup>, Marcela Urzúa<sup>c</sup>, Ángel Leiva<sup>d</sup>, Renato Contreras<sup>c</sup>, Javier González-Navarrete<sup>e</sup>

<sup>a</sup> Centro de Química Médica, Facultad de Medicina, Clínica Alemana Universidad del Desarrollo, C. P. 771-0162 Santiago, Chile

<sup>b</sup> Departamento de Orgánica, Facultad de Química, Pontificia Universidad Católica de Chile, C. P. 7820436, Chile

<sup>c</sup> Departamento de Química, Facultad de Ciencias, Universidad de Chile, C. P. 7800003, Chile

<sup>d</sup> Departamento de Química Física, Facultad de Química, Pontificia Universidad Católica de Chile, C. P. 7820436, Chile

<sup>e</sup> Departamento de Química, Facultad de Ciencias Básicas, Universidad Metropolitana de Ciencias de la Educación, C.P. 7760197, Chile

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### ABSTRACT

The main motivation of this work is to obtain poly (ionic liquids) (PILs) derived from poly (4-vinyl pyridine) of different hydrophobic character containing  $\text{BF}_4^-$ ,  $\text{PF}_6^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  and  $\text{CF}_3\text{SO}_3^-$  as counterions. PILs were synthesized from N-alkyl quaternized poly(4-vinylpyridine) P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup> with different alkyl chain length,  $n = 2, 4, 5$  and different molecular weights (60.000 and 160.000 g/mol). The systems obtained were compared with the polyelectrolyte of origin, i.e., the N-alkyl quaternized poly(4-vinylpyridine). The molecular characterization of PILs was obtained by FT-IR, <sup>1</sup>H NMR and <sup>19</sup>F NMR. Moreover, the thermal analysis of these systems was carried out by differential scanning calorimetry (DSC) and thermogravimetry (TGA) techniques. Thermal degradation profiles obtained from TGA measurements, varied according to the alkyl chain length, which in turn influenced the obtained values of glass transition temperature ( $T_g$ ), due to greater or lesser segmental movement of the alkyl chain. The results obtained for the PILs studied were analysed according to alkyl chain length, molecular weight and counter-anion effects. Additionally, P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> was used in a preliminary study of chromium (VI) removal from aqueous solution, showing a 72.2% removal of Cr (VI).

### 1. Introduction

Obtaining polymers from ionic liquids (ILs) is currently of interest in the development of a new subclass of polyelectrolyte (PE) called polymerizable ionic liquids or poly (ionic liquids) (PILs) and nowadays considered as solid polymer electrolytes (SPEs) or solid electrolytes [1,2]. PILs are characterized by forming macromolecular systems with an architecture and unique properties, such as: i) chemical and thermal stability; ii) glass transition temperature ( $T_g$ ); and iii) ionic conductivity, which incorporate the ILs in their structure, together with the intrinsic properties of polymers [3]. Thus, these systems can expand and diversify their applications with respect to PE. For instance, they can be used in different areas of science and technology, such as lithium batteries, solar cells, supercapacitors and electrochemical devices, among others [2,4–12]. Further, compared to their monomers the PILs possess good processability and membrane forming ability with potential in polymeric electrolytes, carbon dioxide absorbing materials, catalytic membranes, ionic conductive materials and absorbing materials [13]. On the other hand, the hydrophobicity/hydrophilicity

balance of the IL monomers that show thermoresponsive phase properties in solvents has been found to maintain their thermoresponsiveness in the resulting polyelectrolytes [14]. Currently, the relevance of PILs lies in their hydrophobic character which provides the possibility to absorb heavy metal ions or organic pollutants from water [15]. Thus, due to their unique combination of properties derived from an ionic and thermoresponsive nature, the PILs will attract considerable interest, and their wide applications are expected in the fields of separation, sensing and desalination [14].

Welton et al., determined the partition coefficients octanol-water,  $K_{OW}$ , to quantify the hydrophobicity a number of imidazolium ionic liquids. They found that  $K_{OW}$  increases in the order  $[(\text{CF}_3\text{SO}_3)]^- < [\text{BF}_4]^- < \text{Br}^- < [\text{NO}_3]^- < \text{Cl}^- < [\text{PF}_6]^- < [(\text{CF}_3\text{SO}_2)_2\text{N}]^-$ , thereby suggesting that hydrogen bonding to the anion is a significant contribution to the hydrophilicity of the ionic liquid [16]. Based on this analysis, it would be interesting to perform a systematic study between a PE and a PILs containing a counterion of similar hydrophobicity, for instance  $\text{Br}^-$  and  $\text{BF}_4^-$  and a side chain with different hydrophobicity.

\* Corresponding author.

E-mail address: [ximenabriones@udd.cl](mailto:ximenabriones@udd.cl) (X. Briones O.).

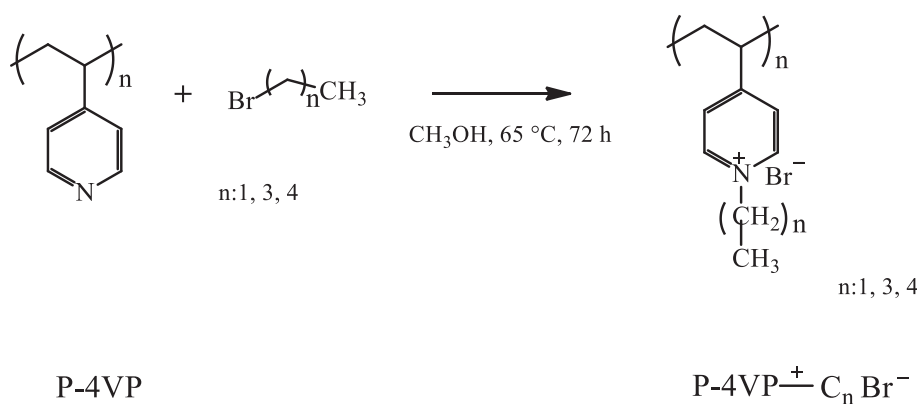


Fig. 1. Structural unit of P-4VP and P-4VP quaternized. (a) P-4VP, (b) P-4VP<sup>+</sup> C<sub>n</sub>Br<sup>-</sup> with n = 2, 4 and 5.

The differences of PILs as compared to conventional PEs are mainly expressed in their solubility. A PE is water soluble and dissociates in aqueous solution, while a PILs is insoluble in water but soluble in several organic solvents of varying polarity. This response is attributed to the hydrophobic nature of the counterion present in the structure of a PIL, which reduces coulombic interactions and makes its ionization state independent of the solvent that contains it [17]. Marcilla et al., studied the solubility of derivatives of 1-vinyl-3-ethylimidazolium and 1-vinyl-3-butylimidazolium in different organic solvents, finding that when the PIL contained [BF<sub>4</sub><sup>-</sup>] or [PF<sub>6</sub><sup>-</sup>] as counterion it was not soluble in water but soluble in methanol and polar aprotic solvents such as acetone, dimethylformamide and dimethylsulfoxide, while the PE of the same nature, but containing Cl<sup>-</sup> or Br<sup>-</sup> in its structure was completely soluble in water [18]. These studies have been pioneers in the characterization and understanding of the properties of PILs. However, few studies have related the effect of alkyl side chain length, molecular weight and the chemical nature of the counterion present in the PILs on their physicochemical properties compared to its corresponding PE.

N-alkyl quaternized poly(4-vinylpyridine), P4VP-C<sub>n</sub> is a cationic PE, which contains in its side chain alkyl halides of different chain lengths, giving the ability to control the amphiphilic character of the PE [19,20]. These properties make these systems to extend their applications as materials with interesting antimicrobial properties [20] and versatility in retaining heavy metals, such as Cr (VI), among other applications [21,22]. Mi et al., synthesized the PIL, poly (3-ethyl-1-vinylimidazolium bis (trifluoromethanesulfonyl)-imide), and used it as an adsorbent in the separation and removal of heavy metal ions of Cr(VI) and methyl blue from their water solutions [13].

It is worth noting that the N-alkyl pyridinium group and N,N'-imidazolium cationic salts are mainly used in the synthesis of ILs [23]. However, most PILs reported to date are based on the group N,N'-imidazolium [24–28], while few studies have been reported on PILs based on the N-alkyl pyridinium group.

In this context, the objective of this work was to synthesize and

characterize PILs of different hydrophobic character derived from N-alkyl quaternized poly(4-vinylpyridine) with different alkyl chain length and molecular weight. The PILs obtained were characterized by Fourier transformed infrared spectroscopy (FT-IR) and nuclear magnetic resonance (<sup>1</sup>H NMR and <sup>19</sup>F NMR). The alkyl chain length, molecular weight and counterion effects were studied by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). Furthermore, these results were compared with those obtained from the PE of origin including the effect of the chemical nature of the counterion present in their structures. Finally, one of the synthesized and characterized PILs, P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup>, was used as matrix for the removal of heavy metal ions of Cr(VI). Detection of Cr (VI) was corroborated with UV-Vis spectroscopy, scanning electron microscopy (SEM) and by energy-dispersive X-ray spectroscopy (EDX).

## 2. Experimental

### 2.1. Materials

Poly (4-vinylpyridine) (P-4VP) with average molecular weight 60.000 and 160.000 g/mol was obtained from Sigma-Aldrich Inc. (Fig. 1). Ethyl, butyl and pentyl bromides and sodium tetrafluoroborate, sodium hexafluorophosphate, bis(trifluoromethane)sulfonamide lithium salt and lithium trifluoromethanesulphonate were obtained from Sigma-Aldrich Inc. Methanol and ethyl acetate were purchased from Merck AG, Germany. All the chemicals used were of analytical grade and used without further purification. Bidistilled and ultrafiltered water with a specific conductivity of 0.055 μS/cm was used.

### 2.2. Synthesis of N-alkylquaternized poly(4-vinylpyridine), P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup>

The synthesis of P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup> (n = 2, 4 and 5) is shown in Fig. 1. The quaternization was performed by refluxing P-4VP (4 g) in 20 mL methanol, adding 0.35 mol of alkylbromide with alkyl chain lengths 2,

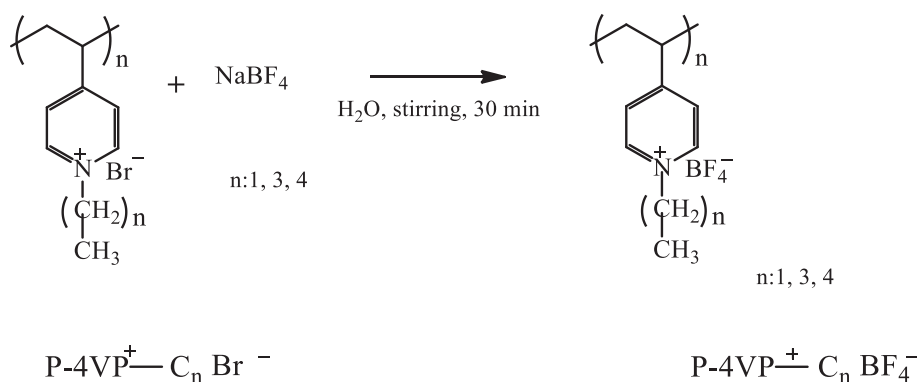


Fig. 2. Structural units of P-4VP<sup>+</sup> C<sub>n</sub>Br<sup>-</sup> and P-4VP<sup>+</sup> C<sub>n</sub>BF<sub>4</sub><sup>-</sup> with n = 2, 4 and 5.

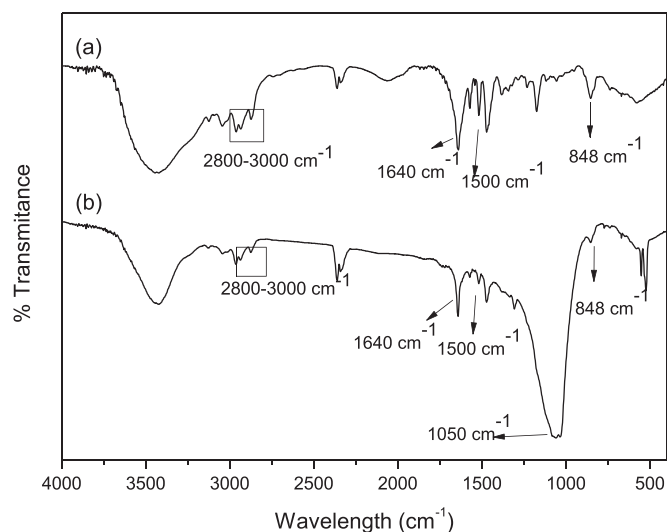


Fig. 3. IR-Spectra of (a) P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> and (b) P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup>.

4 and 5. The added alkylbromide was in 10-fold excess with respect to P-4VP. The reaction mixture was stirred magnetically (600 rpm) and heated at 65 °C for 72 h to achieve complete quaternization, after which quaternized P-4VP was obtained [29]. The reaction was considered finished when the band at 1600 cm<sup>-1</sup> disappeared almost completely and appears IR band of the pyridine ring to 1640 cm<sup>-1</sup> characteristic of the quaternized group, the extent of quaternization was ~98% (See Supplementary material). Quaternized P-4VP was purified by dissolution in methanol and precipitation in ethyl ether three times successively [29] and finally dried to a constant weight in a vacuum oven at room temperature. In this study, the quaternized P-4VP products are abbreviated as P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup>, where C<sub>n</sub> represents the number of carbon atoms in the side chains attached to the pyridinium ring via the quaternization reaction.

### 2.3. Synthesis of poly(ionic liquid) derived P-4VP-C<sub>n</sub>

To prepare poly-(4-vinylpyridine) tetrafluoroborate (P-4VP<sup>+</sup>-C<sub>n</sub>BF<sub>4</sub><sup>-</sup>) as shown in Fig. 2, a solution of 6 g of NaBF<sub>4</sub> in 12 mL of deionized water and a solution of 1 g of P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup> in 20 mL of deionized water was mixed in a 50 mL round-bottom flask. After stirring for 30 min at room temperature, the resulting white solid insoluble in water was filtered and washed several times with deionized water. Finally, the solid obtained was dried in a vacuum oven until constant weight at room temperature. This procedure was used with other salts, obtaining a viscous material for the PIL containing (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>; a solid yellow for CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and unstable white solid sublimated for PF<sub>6</sub><sup>-</sup>. The PILs were abbreviated as P-4VP<sup>+</sup>-C<sub>n</sub>BF<sub>4</sub><sup>-</sup>, P-4VP<sup>+</sup>-C<sub>n</sub>(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup>, P-4VP<sup>+</sup>-C<sub>n</sub>CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> and P-4VP<sup>+</sup>-C<sub>n</sub>PF<sub>6</sub><sup>-</sup> with n = 2, 4 and 5, respectively.

### 2.4. FTIR analysis

FTIR analysis of systems was performed using a VECTOR 22 FTIR (Bruker, Germany).

### 2.5. <sup>1</sup>H NMR analysis

<sup>1</sup>H NMR and <sup>19</sup>F NMR measurements were carried out using an Advance-400 spectrometer. 50 mg P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup> were dissolved in D<sub>2</sub>O and P-4VP<sup>+</sup>-C<sub>n</sub>BF<sub>4</sub><sup>-</sup> in acetone-d<sub>6</sub> (0.5 mL), respectively, at 25 °C.

### 2.6. Thermogravimetric analysis

TGA measurements were performed using a Mettler TGA/SDTA 851<sub>e</sub> calorimetric system. These measurements were processed using the STAR program. All samples were heated in Al<sub>2</sub>O<sub>3</sub> pans. The measurements were carried out between 298.1 and 973.1 K at 20 K/min under a nitrogen atmosphere at 60 mL/min flow.

### 2.7. Differential scanning calorimetry

DSC measurements were performed using a Mettler Toledo DSC 821 (Switzerland) calorimetric system. All samples were heated until 538 K at 20 K/min, an isothermal step at 538 K was included for equalization of the thermal history of all samples. So all samples were cooled from 538 to 173 K at 20 K/min; T<sub>g</sub> was determined in a second heating process until 538 K. The experiments were carried out under a nitrogen atmosphere at 60 mL/min flow.

### 2.8. Cr(VI) adsorption experiments

For Cr (VI) adsorption experiments P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> was used because this PIL is hydrophobic, thermally stable and due to its homogeneity after being subjected to a milling and sieving process. This characteristic is important for the adsorption process on the solid phase to be homogeneous. For these experiments, milling and subsequent sieving at 270 mesh of P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> of molecular weight 60.000 g/mol were carried out. The adsorption experiments were performed according to the following method: 50 mg of P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> (adsorbent) was added to 100 mL of a solution of Cr (VI) (10 mg/L). The solution was stirred for 1 h at room temperature. P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> was separated by filtration and the residual concentration of Cr (VI) in solution was determined by UV-Vis spectrophotometry using a Shimadzu UV-160, in a 1 cm quartz cell.

The percentage of Cr (VI) adsorbed on the adsorbent (R (%)) was calculated using the following equation:

$$R\% = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

where C<sub>0</sub> and C<sub>e</sub> are the initial and equilibrium solution concentrations of Cr (VI) (mg/L), respectively.

### 2.9. Scanning electron microscopy

To corroborate the adsorption of Cr(VI), SEM-EDX analysis of the PIL with Cr(VI) adsorbed was performed. The samples were studied by SEM using a Zeiss EVO MA-10 microscope with a tungsten filament gun and by EDX spectra which were collected using an Oxford Instruments X-act system attached to a microscope equipped with a Penta FET Precision detector. Prior to imaging, the samples were mounted on conductive adhesive and sputter coated with silver film to protect the surface from damage and calcination and to minimize charge related artifacts.

## 3. Results and discussion

### 3.1. Synthesis of PILs

In order to investigate the extent of the anion exchange reaction, the obtained PILs were characterized by FTIR and <sup>1</sup>H NMR spectroscopy. Fig. 3 shows the IR spectra of P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> and P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup>. Note that the characteristic absorption band of the quaternized pyridinium group at 1640 cm<sup>-1</sup> is observed in both spectra [19]. In addition, the bands attributed to the polycation at 2800–3000 cm<sup>-1</sup>, 1500 cm<sup>-1</sup> and 848 cm<sup>-1</sup> is observed after the anion exchange, similar to that reported by Marcilla et al., in the synthesis of polycations using ionic

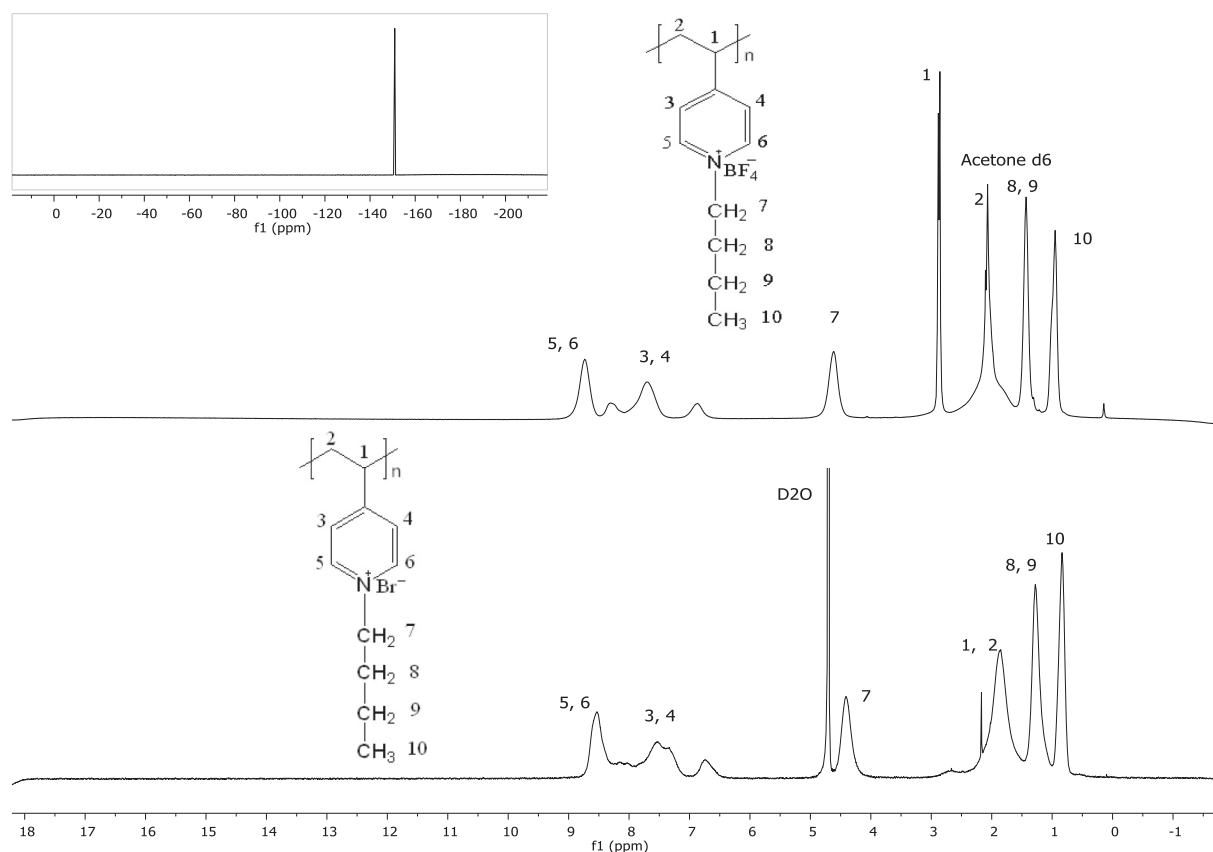


Fig. 4.  $^1\text{H}$  NMR spectra of P-4VP $^+$ -C $_4$ Br $^-$  (D $_2$ O) and P-4VP $^+$ -C $_4$ BF $_4^-$  (Acetone- $d_6$ ). Inset  $^{19}\text{F}$  NMR spectrum of P-4VP $^+$ -C $_4$ BF $_4^-$ .

Liquids [30]. In the second IR spectrum (Fig. 3b) a new band is observed at  $1050\text{ cm}^{-1}$  which can be attributed to the exchanged  $\text{BF}_4^-$ , this band was also observed in the IR spectrum of the salt  $\text{NaBF}_4$  (see Supplementary material). In the case of poly (ionic liquids) containing as counterion  $(\text{CF}_3\text{SO}_2)_2^-$  new bands were found at  $1342\text{ cm}^{-1}$ ,  $1190\text{ cm}^{-1}$ ,  $1130\text{ cm}^{-1}$  and  $1050\text{ cm}^{-1}$  and for the poly (ionic liquid) containing  $\text{CF}_3\text{SO}_3^-$   $1258\text{ cm}^{-1}$ ,  $1165\text{ cm}^{-1}$  and  $1030\text{ cm}^{-1}$  (See Supplementary material). Similar response has been found for poly (ionic liquids) derived from imidazole containing as counter ion  $(\text{CF}_3\text{SO}_2)_2^-$  and  $\text{CF}_3\text{SO}_3^-$  [18].

The characterization of these systems was confirmed by  $^1\text{H}$  NMR.

Fig. 4 shows  $^1\text{H}$  NMR spectra of P-4VP $^+$ -C $_4$ Br $^-$  and P-4VP $^+$ -C $_4$ BF $_4^-$ . In both spectra a signal corresponding to pyridinium ring protons (7.8–8.9 ppm) is observed. However, the anion exchange of  $\text{Br}^-$  to  $\text{BF}_4^-$  modifies the shape and chemical shifts of these signals. In order to verify the presence of the counterion  $\text{BF}_4^-$  in the PIL a  $^{19}\text{F}$  NMR analysis was performed (Inset Fig. 4). Similar response was found for the molecular characterization of the remaining systems.

### 3.2. Solubility studies

The anion-exchange reaction affected the solubility of the polymers

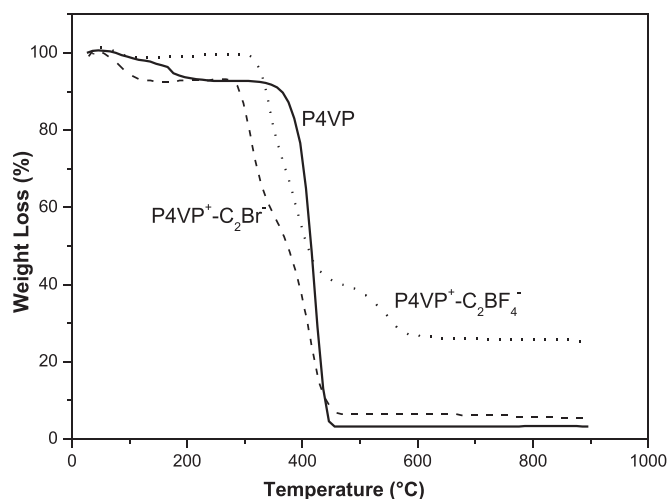


Fig. 5. Thermogravimetric analysis of P4VP (—), P-4VP $^+$ -C $_2$ Br $^-$  (---) and P-4VP $^+$ -C $_2$ BF $_4^-$  (...) of  $M_w$  160.000 g/mol.

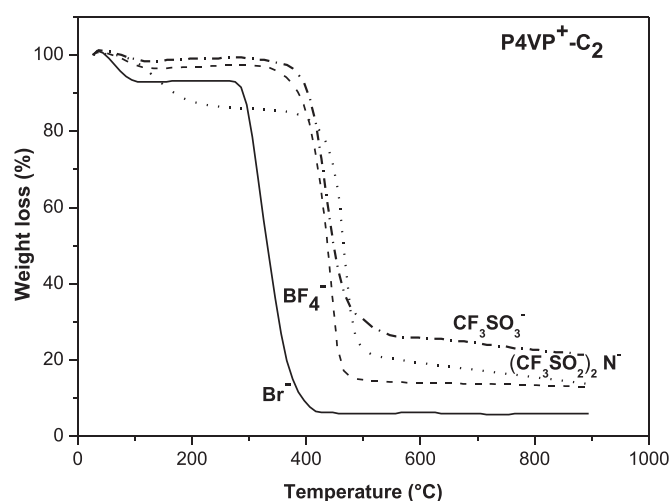


Fig. 6. Thermogravimetric analysis of P-4VP $^+$ -C $_2$ Br $^-$  (—), P-4VP $^+$ -C $_2$ BF $_4^-$  (---), P-4VP $^+$ -C $_2$ (CF $_3$ SO $_2$ ) $_2$  N $^-$  (...) and (---) P-4VP $^+$ -C $_2$ CF $_3$ SO $_3^-$  of  $M_w$  60.000 g/mol.

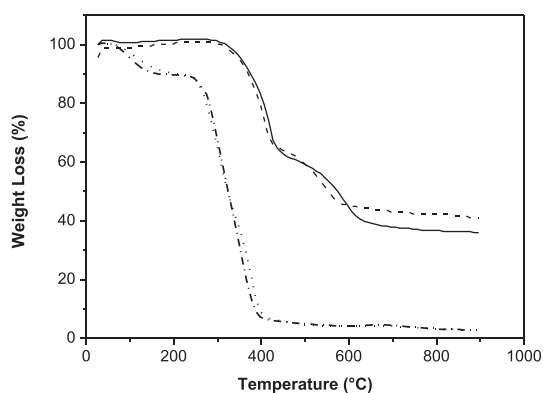


Fig. 7. Thermogravimetric analysis of (...) P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> and (—) P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> of M<sub>w</sub> 160.000 g/mol; (-.-.) P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> and (---) P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> and of M<sub>w</sub> 60.000 g/mol.

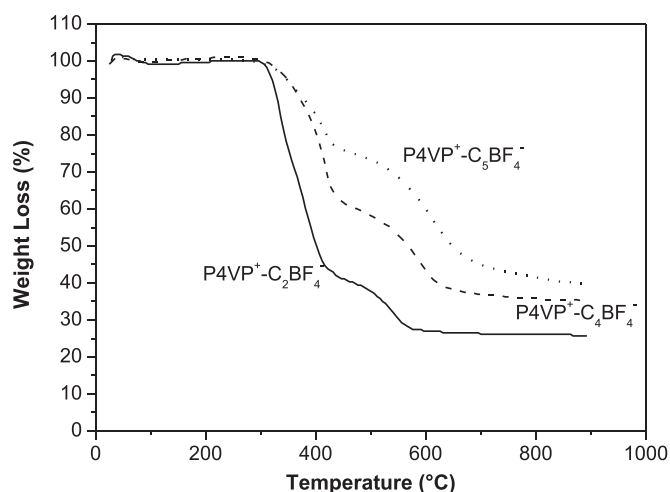


Fig. 8. Thermogravimetric analysis of (a) P-4VP<sup>+</sup>-C<sub>n</sub>BF<sub>4</sub><sup>-</sup> n = 2 (—), n = 4(---), n = 5 (...), of M<sub>w</sub>160.000 g/mol.

studied in this work. Whereas the P-4VP<sup>+</sup>-C<sub>n</sub>Br<sup>-</sup> with n = 2, 4 and 5 is soluble in water and methanol, the PILs obtained are insoluble in water, but soluble in acetonitrile, dimethylformamide and dimethylsulfoxide. For example, P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup> is soluble in chloroform and P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> and P-4VP<sup>+</sup>-C<sub>5</sub>BF<sub>4</sub><sup>-</sup> are soluble in acetone. It was found that the solubility of the PILs is favored in polar aprotic solvents, with higher dielectric constant.

### 3.3. Thermal stability of PILs

The TGA curves of polymers including P4VP, P-4VP<sup>+</sup>-C<sub>2</sub>Br<sup>-</sup> and P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup> are shown in Fig. 5. Note that P4VP showed a significant weight loss between 275 and 465 °C and the final mass loss was 95%. On the other hand, P-4VP<sup>+</sup>-C<sub>2</sub>Br<sup>-</sup> exhibited a slightly earlier weight

Table 1

Glass transition temperature, T<sub>g</sub> of polyelectrolyte, P4VP-C<sub>n</sub><sup>+</sup> Br<sup>-</sup> and poly (ionic liquid), P4VP-C<sub>n</sub><sup>+</sup> BF<sub>4</sub><sup>-</sup>.

M <sub>w</sub> (g/mol)	Polymer	T <sub>g</sub> °C	PE	T <sub>g</sub> °C	PILs	T <sub>g</sub> °C
60.000	P4VP	149.4	P4VP <sup>+</sup> -C <sub>2</sub> Br <sup>-</sup>	183.1	P4VP <sup>+</sup> -C <sub>2</sub> BF <sub>4</sub> <sup>-</sup>	50.3
			P4VP <sup>+</sup> -C <sub>4</sub> Br <sup>-</sup>	210.8	P4VP <sup>+</sup> -C <sub>4</sub> BF <sub>4</sub> <sup>-</sup>	77.3
			P4VP <sup>+</sup> -C <sub>5</sub> Br <sup>-</sup>	215.6	P4VP <sup>+</sup> -C <sub>5</sub> BF <sub>4</sub> <sup>-</sup>	34.9
160.000	P4VP	147.3	P4VP <sup>+</sup> -C <sub>2</sub> Br <sup>-</sup>	102.8	P4VP <sup>+</sup> -C <sub>2</sub> BF <sub>4</sub> <sup>-</sup>	63.8
			P4VP <sup>+</sup> -C <sub>4</sub> Br <sup>-</sup>	198.5	P4VP <sup>+</sup> -C <sub>4</sub> BF <sub>4</sub> <sup>-</sup>	70.5
			P4VP <sup>+</sup> -C <sub>5</sub> Br <sup>-</sup>	203.9	P4VP <sup>+</sup> -C <sub>5</sub> BF <sub>4</sub> <sup>-</sup>	57.5

loss than P4VP at 230 °C and the final mass loss was 90% at 470 °C close to that of P4VP. This fact could be attributed to the degradation of the alkyl chain connecting on the pyridinium ring. Finally, P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup> presented an initial weight loss of about 60% between 270 and 440 °C and the final weight loss was about 70% around 600 °C. Note that the final mass loss was 20% less than P-4VP<sup>+</sup>-C<sub>2</sub>Br<sup>-</sup>. This fact could be attributed to the strong electrostatic interactions between BF<sub>4</sub><sup>-</sup> and the pyridinium cation, this contraction gives a greater thermal stability to poly (ionic liquid) and its decomposition occurred around 470 °C.

However, for P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup> decomposition occurred around 600 °C. Similar outcomes were found by Mi et al. for the hydrophobic PIL, poly (3-ethyl-1-vinylimidazoliumbis(trifluoromethanesulfonyl) imide) (PVI-TFSI) [13]. From these results, it can be concluded that the thermal degradation profiles show that P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup> has a higher thermal stability than P4VP and P-4VP<sup>+</sup>-C<sub>2</sub>Br<sup>-</sup>.

On the other hand, Fig. 6 shows TGA curves of P-4VP<sup>+</sup>-C<sub>2</sub> of molecular weight 60.000 g/mol with different counter-anions including Br<sup>-</sup>, BF<sub>4</sub><sup>-</sup>, (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> and CF<sub>3</sub>SO<sub>3</sub><sup>-</sup>. In particular a slight mass loss at the beginning of the TGA curve of P-4VP<sup>+</sup>-C<sub>2</sub>(CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> is observed, this behavior may be due to this PIL is very viscous and could occlude small amounts of water. These curves showed that the thermal stability of the PILs also depends on the nature of the counter-anion, showing that the thermal stability improves in the order CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> > (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> > BF<sub>4</sub><sup>-</sup> > Br<sup>-</sup>. It was not possible to work with the poly (ionic liquid) bearing hexafluorophosphate [PF<sub>6</sub>]<sup>-</sup> counterion, because this PIL generated white vapors, therefore it could not be characterized. Similar trends have been reported for other systems containing PF<sub>6</sub><sup>-</sup>, surely due to its poor thermal stability [30].

On the other hand, Fig. 7 shows the thermal degradation profiles of: P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> and P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup>, at different molecular weights. Note that P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> showed an initial mass loss of about 40% between 270 and 450 °C, but the final mass loss was 60% for the of higher molecular weight and 55% for the PIL of lowest molecular weight. Furthermore, it was observed that P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> of 160.000 g/mol resulted slightly more stable than P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> of 60.000 g/mol. This fact is attributed to decomposition occurring around 580 °C for the lowest molecular weight PIL, while it occurred at about 640 °C for the PIL of highest molecular weight. On the other hand, P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> exhibited earlier weight loss at 200 °C and a total mass loss of about 95%. The molecular weight does not have a significant effect on the thermal stability of this PE. Therefore, these results show that P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> is more stable than P-4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> at both molecular weight values. This effect could be attributed to the presence of a hydrophobic counterion (BF<sub>4</sub><sup>-</sup>) which gives a greater thermal stability, in agreement with the experimental results. Similar results, not discussed in the text, were obtained for P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup> and P-4VP<sup>+</sup>-C<sub>5</sub>BF<sub>4</sub><sup>-</sup>.

Fig. 8 shows P-4VP<sup>+</sup>-C<sub>n</sub>BF<sub>4</sub><sup>-</sup> of different alkyl chain lengths (n = 2, 4 and 5). P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup>, P-4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> and P-4VP<sup>+</sup>-C<sub>5</sub>BF<sub>4</sub><sup>-</sup> showed an initial mass loss at about 270 °C. However, this mass loss was different for each PIL (60%, 40% and 25% respectively), decreasing with the increasing number of carbon atoms in the alkyl chain. The final mass loss of about 55% for P-4VP<sup>+</sup>-C<sub>5</sub>BF<sub>4</sub><sup>-</sup>, i.e. ~ 20% less than P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup>, corresponded to 75% for P-4VP<sup>+</sup>-C<sub>2</sub>BF<sub>4</sub><sup>-</sup>. The difference observed can be attributed to the increased alkyl chain length, which confers a greater hydrophobicity, thereby contributing to the thermal stability of the systems.

### 3.4. Effect of side chain of PIL in the glass transition temperature

Table 1 shows the values of T<sub>g</sub> for the PILs under study. Note that T<sub>g</sub> values considerably differ for each series of polymer, PE and PILs. For instance, the T<sub>g</sub> for P4VP, P4VP<sup>+</sup>-C<sub>4</sub>Br<sup>-</sup> and P4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> were 149.4, 210.8 and 77.3, respectively. T<sub>g</sub> depends not only on the chemical composition of the polymer backbone but also on the counterion present in its structure. This response could be attributed to the

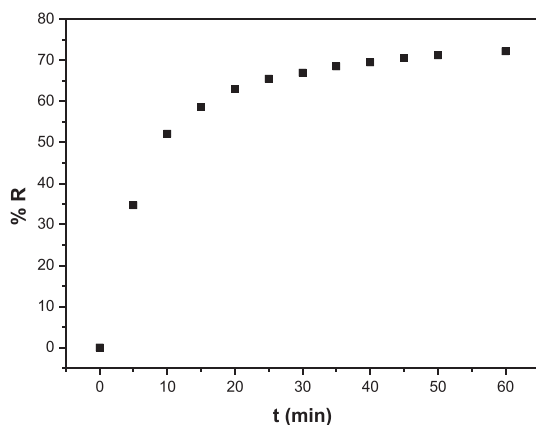


Fig. 9. Dependence of removal of Cr (VI) with the stirring time.

electrostatic interaction involved in all cases. This fact allowed us to confirm that the presence of anions tends to avoid the movement of positively charged chains by electrostatic interactions of the ion-pairs [19]. Therefore, these interactions should be lower in the case of  $\text{BF}_4^-$  due to its bigger size compared to  $\text{Br}^-$ . Similar response has been reported by Vygodskii et al. for poly (trimethylammonium-2-ethyl) $\text{X}^-$  methacrylate at 164 °C for  $\text{Cl}^-$  and 130 °C for  $\text{BF}_4^-$ . Another example reported in the literature is poly (1-vinyl-3-ethylimidazolium) $\text{X}^-$  for which the  $T_g$  value was 173 °C when the counter-anion was  $\text{CF}_3\text{SO}_3^-$  and 235 °C for  $\text{Br}^-$  [31]. On the other hand,  $T_g$  values varied with the

alkyl chain length, both for the PE and the corresponding PIL. The PE  $\text{P4VP}^+-\text{C}_2\text{Br}^-$ , presented a lower  $T_g$  value than  $\text{P4VP}^+-\text{C}_4\text{Br}^-$  and  $\text{P4VP}^+-\text{C}_6\text{Br}^-$ , which had marginal differences in their  $T_g$  values. This response could be attributed to the PE of short chain  $\text{C}_2$  causing less hindrance to the movement of the positively charged backbone, which is reflected in its lower  $T_g$  value. Furthermore, in the PILs there was not a clear correlation between alkyl chain length and  $T_g$  value. In this case the size effect of  $\text{BF}_4^-$  counterion was independent of alkyl chain length.

It should be noted that we have synthesized PILs with other anions, such as  $\text{PF}_6^-$ ,  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  and  $\text{CF}_3\text{SO}_3^-$ . However in the first case an unstable white sublimated solid was obtained. The values of  $T_g$  for the PIL containing  $(\text{CF}_3\text{SO}_2)_2\text{N}^-$  as counter-anion was 6.3 °C, resulting in a material very viscous and not suitable to be tested as matrices for the heavy metal removal and in the last case it was not possible to determine the  $T_g$  by DSC. In several reports, authors concluded that it was difficult to determine a  $T_g$  by DSC [30].

### 3.5. Adsorption of Cr (VI)

Hexavalent chromium (Cr(VI)) has attracted special attention due to its high toxicity, its potential to bioaccumulate, and its persistence in the environment. This chromium pollution of the water environment mainly comes from industrial processes, including leather tanning, metal polishing, electroplating and paint manufacturing [32–34].

Considering the hydrophilic-hydrophobic balance of  $\text{P4VP}^+-\text{C}_4\text{BF}_4^-$  and the background reported in the literature, this PIL was used as a matrix for the removal of Cr (VI) from aqueous solution. Fig. 9

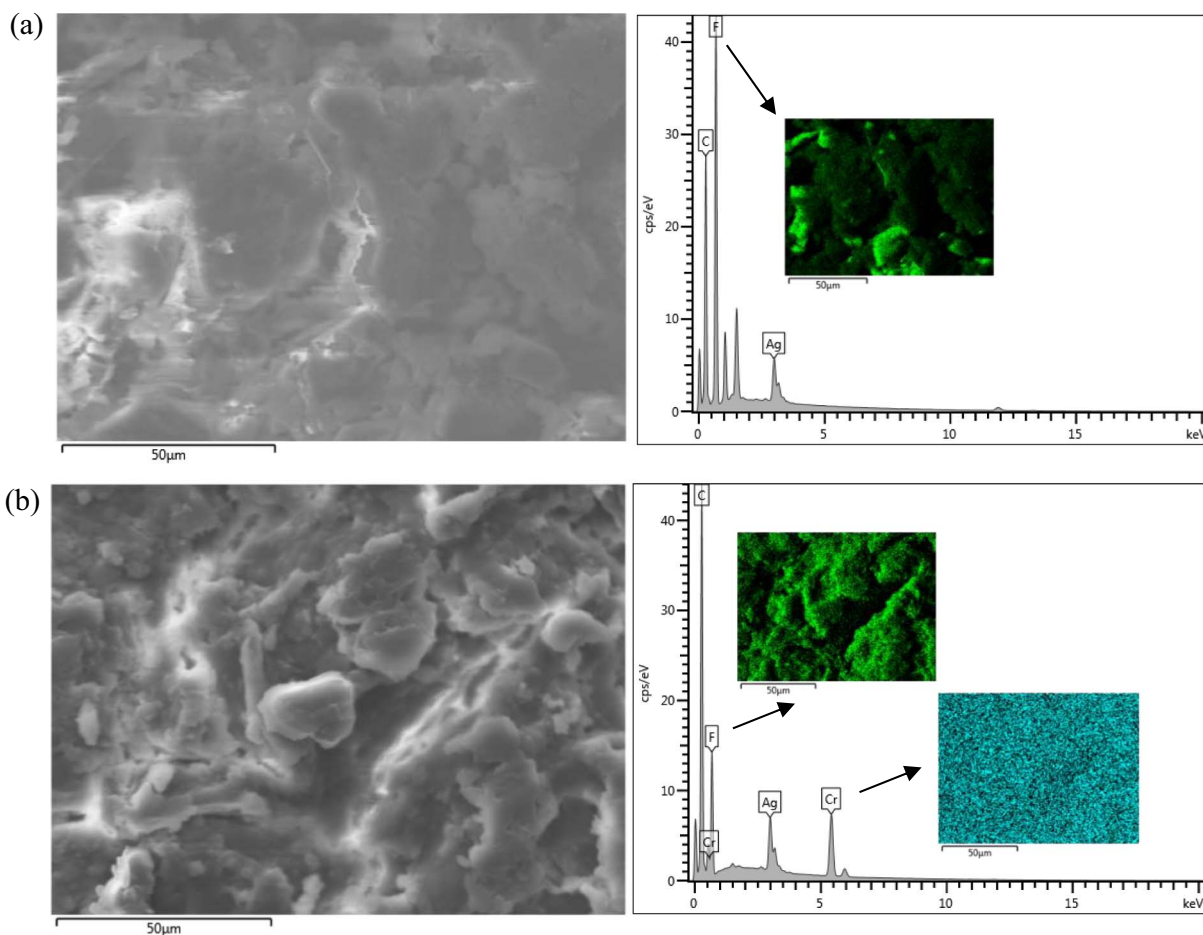


Fig. 10. SEM-EDS Image of  $\text{P4VP}^+-\text{C}_4\text{BF}_4^-$  without Cr (a) and with Cr(VI) (b). EDS layered image F (green) and Cr (light blue). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

shows the dependence of adsorption of Cr (VI) with stirring time. It may be noted that the amount of Cr (VI) adsorbed increased with agitation time. At the same time, the decreased concentration of Cr (VI) remaining in solution indicated that Cr(VI) was adsorbed on P4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup>. Moreover, rapid adsorption was observed in the first 20 min of stirring, due to the greater availability of charged sites of the polymer matrix that could interact with the Cr(VI) ions in solution, reaching 63.0% removal. Then, for 25 min of stirring, partial saturation of available sites was observed, whereby the removal percentage became constant, reaching a maximum value of 72.2%. Thus, a stirring time of 60 min must be considered as the time where the balance of the adsorption of Cr(VI) is reached.

Hao et al. used poly(3-ethyl-1-vinylimidazolium bis(trifluoromethanesulfonyl) imide) (PVI-TFSI) as the adsorbent in separation and removal of heavy metal ions of Cr (VI) from water solutions [13]. They found that PVI-TFSI showed a fast adsorption in the initial stage, where 72% of Cr (VI) were effectively adsorbed within the first 6 h, and that adsorption reached equilibrium within 24 h, obtaining a maximum value of 98% Cr (VI) adsorbed. Although the maximum percentage of Cr(VI) obtained by these authors was higher than that obtained in the present work, the time taken to reach equilibrium adsorption was much lower for the PIL studied here.

Moreover, one should consider that Cr(VI) in aqueous solution can exist as dichromate (Cr<sub>2</sub>O<sub>7</sub><sup>2-</sup>), hydrochromate (HCrO<sub>4</sub><sup>-</sup>) or chromate (CrO<sub>4</sub><sup>2-</sup>) depending on the pH [19], so it is necessary to study the effect of pH on the removal of Cr (VI) to verify which sort of Cr (VI) is being adsorbed as a majority. Note that this result suggests that PILs can be considered for further optimization studies of experimental conditions for the removal of Cr(VI), currently in development.

In order to evaluate surface morphology and to elucidate the chemical composition of the samples further SEM-EDS studies were performed. In some studies on the use of adsorbents for the removal of heavy metal ions, SEM-EDS has been used to characterize the morphology and chemical composition before and after removal. For instance, Luo et al. studied graphene oxide/chitosan composite with disodium ethylene-diaminetetraacetata) as an adsorbent for removal of hexavalent chromium (Cr(VI)) from aqueous solutions. Morphology of prepared materials under different magnifications was observed by SEM [32].

Panoramic (low magnification) micrographs and elemental mapping are shown in Fig. 10. All samples were homogeneous and exhibited relatively smooth surfaces. In addition, the elemental mapping of PE showed that it was mainly composed of carbon and bromine (SEM-EDS image not shown). The presence of a fluorine ion (Fig. 10, green EDS layered image) in the PIL comes from the counterion change. Finally, homogeneous distribution of chromium (light blue EDS layered image) in PIL confirms the potential application of this material in industrial devices as a filter for removal of chromium ions from aqueous solutions.

#### 4. Conclusions

PIL derivatives of N-alkyl quaternized P4VP of different alkyl chain length and different molecular weight were synthesized by anion exchange of the halide anion by a more hydrophobic counter-anion.

The thermal degradation profiles obtained by TGA measurements varied according to the alkyl chain length, which also influenced the values of T<sub>g</sub>, due to the segmental motion associated with the alkyl chain length of the PIL. On the other hand, the anion structure influenced the thermal stability in the order CF<sub>3</sub>SO<sub>3</sub><sup>-</sup> > (CF<sub>3</sub>SO<sub>2</sub>)<sub>2</sub>N<sup>-</sup> > BF<sub>4</sub><sup>-</sup> > Br<sup>-</sup>.

P4VP<sup>+</sup>-C<sub>4</sub>BF<sub>4</sub><sup>-</sup> was used as matrix for the adsorption of Cr(VI) to obtain 72.2% removal. This result can be traced to the interaction of the positive charge present in the main chain of the PIL with the negatively charged anionic species of Cr(VI).

Therefore, this system has potential use in the separation and removal of heavy metal ions for water treatment.

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.reactfunctpolym.2018.01.003>.

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