

# Preparation, characterization and ion adsorption properties of functionalized polystyrene modified with 1,4-phenylene diisocyanate and diethylenetriamine

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Received 17 February 2015; Revised 28 May 2015; Accepted 29 June 2015

In the present work, linear polystyrene (PS) was functionalized by a sulfonation reaction providing sulfonated polystyrene (PSS). Then, the PSS polymer chains were cross-linked with the 1,4-phenylene diisocyanate (PPDI) group in tetrahydrofuran (THF), which led to a PSS–PPDI polymer. The PSS–PPDI was grafted by diethylenetriamine (DETA) in a solution of THF to obtain polymer PSS–PPDI–DETA. Their structures were characterized by infrared spectroscopy (ATR-FTIR), elemental analysis (EA), differential scanning calorimetry (DSC), thermogravimetric (TGA), thermodynamic (DTA) and differential thermogravimetric (DTG) analysis. Subsequently, the obtained polymers were tested for their ability to remove some metal ions from aqueous media such as  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Co}^{2+}$ .

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**Keywords:** cross-linking, chelating groups, functionalization, adsorption

## Introduction

Sulfonation of polystyrene has been widely studied by researchers (Kučera & Jančář, 1996). Generally, sulfonation of a polymer can be carried out as a heterogeneous or a homogeneous reaction (Kučera & Jančář, 1998) and compounds such as  $\text{H}_2\text{SO}_4$  and  $\text{SO}_3$  are commonly used as sulfonating agents for various polymers, including polystyrene. In addition, sulfonated polystyrene is the source of several chemical modifications leading to resins used in different research fields. In this context, Song-Ping et al. (1996) treated chloro-sulfonated polystyrene-divinylbenzene with ethylenediamine to obtain a polymer attached with an  $-\text{SO}_2\text{NHCH}_2\text{CH}_2\text{NH}_2$  ligand. Besides, many polymers have been reported to contain chelating functional groups with an organosulfur compound finding application in the depollution due to their ability to interact with different metals such as polymers-supported xanthate (Tiravanti et al., 1996), thiourea (Zuo & Muhammed, 1995), pyridine-based thiols (Matlock et al., 2001), dithiozone (Shah & Devi, 1996), iminodi-

acetamides (Sonmez et al., 2003) and sulfonamide (Senkal & Senkal, 2007); as well as their usefulness in cadmium, lead and mercury ions extraction.

In the present paper, an attempt to synthesize new materials with the ability to absorb some metallic ions in the aqueous phase by grafting of 1,4-phenylene diisocyanate and diethylenetriamine groups on sulfonated polystyrene

## Experimental

Commercial polystyrene (PS;  $M = 350000 \text{ g mol}^{-1}$ , Sigma–Aldrich, Tunisia), concentrated sulfuric acid (Sharlau Chemie, 95–97 mass %, Tunisia), dichloromethane (Sigma–Aldrich, 99.5 mass %, Tunisia), tetrahydrofuran (Prolabo, 99 mass %, Tunisia), 1,4-phenylene diisocyanate (PPDI; Sigma–Aldrich, 98 mass %, Tunisia), diethylenetriamine (DETA; Sigma–Aldrich, 99 mass %, Tunisia), diethyl ether (Prolabo, Tunisia), zinc chloride (tetrahydrate; Fluka, Tunisia), cadmium chloride (hexahydrate; Fluka, Tunisia) and

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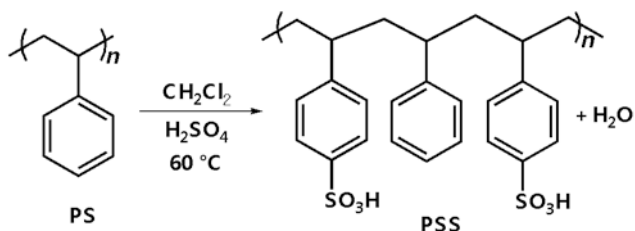


Fig. 1. Possible structure of sulfonated polystyrene PSS.

cobalt chloride (hexahydrate; Riedel–Haen, Tunisia) were used in the experiments.

Infrared analysis was performed using the attenuated total reflectance technique (ATR-FTIR) on a Nicolet FTIR 200 spectrophotometer (Thermo Scientific, Tunisia). Elemental analysis of C, H and N was performed using a Perkin Elmer Analyzer CHN series II, 2400 (Tunisia). Elemental analysis of S was performed by the ICP-OES analysis on a HORIBA Scientific (Tunisia). DSC was carried out on an SETARAM DSC 131 apparatus. The TGA, DTA and DTG analyses were performed on a Mettler Toledo TGA/DSC 1 Star System Puissance 400W under air at the heating rate of  $5^\circ\text{C}\ \text{min}^{-1}$  in the range of  $25^\circ\text{C}$  to  $600^\circ\text{C}$  (Tunisia). The amount of the remaining metal ions in the solution was evaluated by flame atomic absorption spectroscopy (FAAS) analysis on a Perkin–Elmer PinAAcle 900T (Tunisia). Detection limits for  $\text{Cd}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$  are:  $0.8\ \text{mg}\ \text{L}^{-1}$ ,  $9\ \text{mg}\ \text{L}^{-1}$  and  $1.5\ \text{mg}\ \text{L}^{-1}$ , respectively, and the corresponding wavelengths for the studied metals are:  $228.8\ \text{nm}$ ,  $241.16\ \text{nm}$  and  $213.86\ \text{nm}$ , respectively. Aqueous monometallic solutions of  $\text{CdCl}_2$ ,  $\text{ZnCl}_2$  and  $\text{CoCl}_2$  were prepared at the concentration of  $2 \times 10^{-4}\ \text{mol}\ \text{L}^{-1}$  of each metal ion in distilled water (pH 6). The polymer (0.1 g) was incubated with 20 mL of the metal ion solution at  $25^\circ\text{C}$  for 24 h.

### Sulfonation of PS

The amount of 2 g of PS was dissolved in 50 ml of dichloromethane. Then, 40 mL of  $\text{H}_2\text{SO}_4$  were slowly added and the mixture was stirred for 1.5 h at  $60^\circ\text{C}$ . After cooling, the obtained product was washed several times with distilled water to ensure the residual sulfuric acid was removed from the polymer and dried under vacuum at  $40^\circ\text{C}$  for 1 h to obtain a gray powder (Fig. 1). The synthesis procedure was done according to Bekri-Abess et al. (2008) and the best degree of sulfonation was obtained for samples treated at  $60^\circ\text{C}$  for 1.5 h.

### Reticulation of PSS by 1,4-phenylene diisocyanate

The amounts of 2 g of PSS and 0.5 g of PPDI were mixed in 30 mL of THF. Stirring was maintained for 24 h at  $60^\circ\text{C}$ . The obtained product was washed several times with distilled water, dichloromethane and finally dried under vacuum at  $50^\circ\text{C}$  for 24 h to get a gray solid (Fig. 2).

### Diethylenetriamine grafted on PSS–PPDI

The amount of 2 g of PSS–PPDI was suspended in 30 mL of THF. Then, 10 mL of diethylenetriamine were added. After stirring for 5 h at  $80^\circ\text{C}$ , the obtained black solid was washed several times with distilled water and diethyl ether and dried under vacuum at  $50^\circ\text{C}$  for 24 h to obtain a yellow solid (Fig. 3).

## Results and discussion

### ATR-FTIR analysis

ATR-FTIR spectra of PS and PSS are presented in Fig. 4. They show the presence of two characteris-

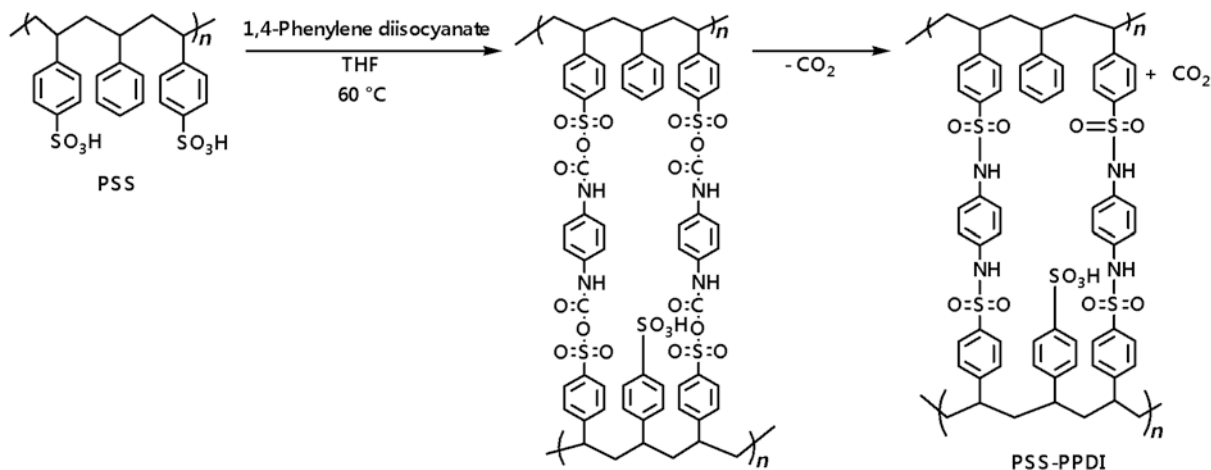


Fig. 2. Possible structure of the PSS–PPDI polymer.

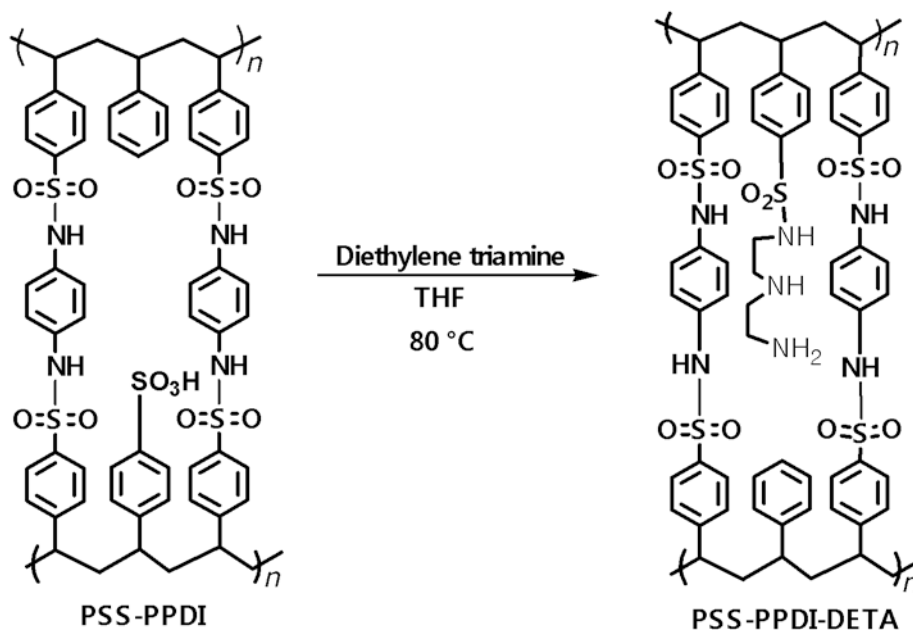


Fig. 3. Possible structure of the PSS-PPDI-DETA polymer.

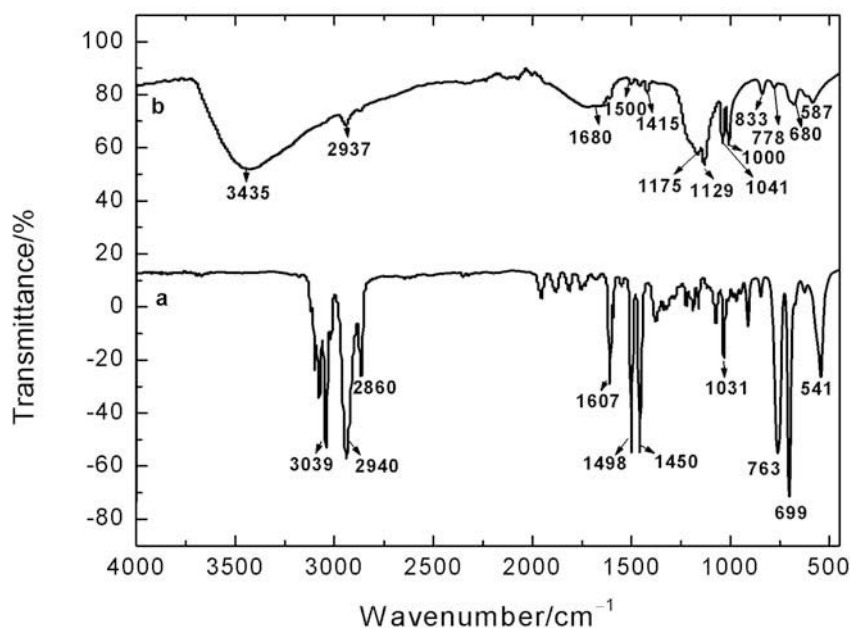


Fig. 4. ATR-FTIR spectra of PS (a) and PSS (b).

tic bands of the OH of the sulfonic group and water sorption (hygroscopic nature of sulfonated material) as a broad band centered at  $3435\text{ cm}^{-1}$  associated with the O—H stretching vibration, and an intense band at around  $1680\text{ cm}^{-1}$  assigned to the deformation vibration of the OH group (Ozer et al., 2013). The spectra exhibited also a decrease of the intensities of the bands at  $1450\text{ cm}^{-1}$ ,  $1498\text{ cm}^{-1}$  and  $1607\text{ cm}^{-1}$  attributed to the C=C groups in the benzene ring. The appearance of a band at  $1175\text{ cm}^{-1}$ , attributed to the symmetric stretching of the ( $\text{SO}_2$ ) group, was

used to confirm the sulfonation of PS (Reis Brandão et al., 2005). In another study (Martins et al., 2003), the bands at  $1175\text{ cm}^{-1}$ ,  $1129\text{ cm}^{-1}$  and  $1041\text{ cm}^{-1}$  indicated the presence of a sulfonic group in the ATR-FTIR spectra of sulfonated polystyrene. The presence of a peak at  $833\text{ cm}^{-1}$  is indicative of a para substitution. The two peaks at  $777\text{ cm}^{-1}$  and  $680\text{ cm}^{-1}$  were assigned to (S—OH) and (C—S) stretching absorption, respectively.

ATR-FTIR spectrum of PSS-PPDI is shown in (Fig. 5). Bands observed at  $1385\text{ cm}^{-1}$  and  $1130\text{ cm}^{-1}$

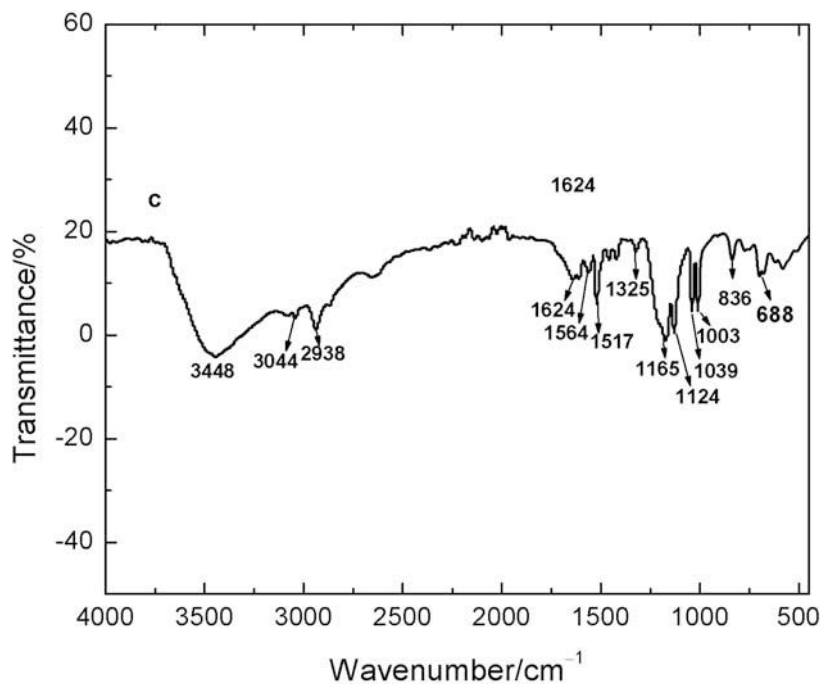


Fig. 5. ATR-FTIR spectrum of PSS-PPDI.

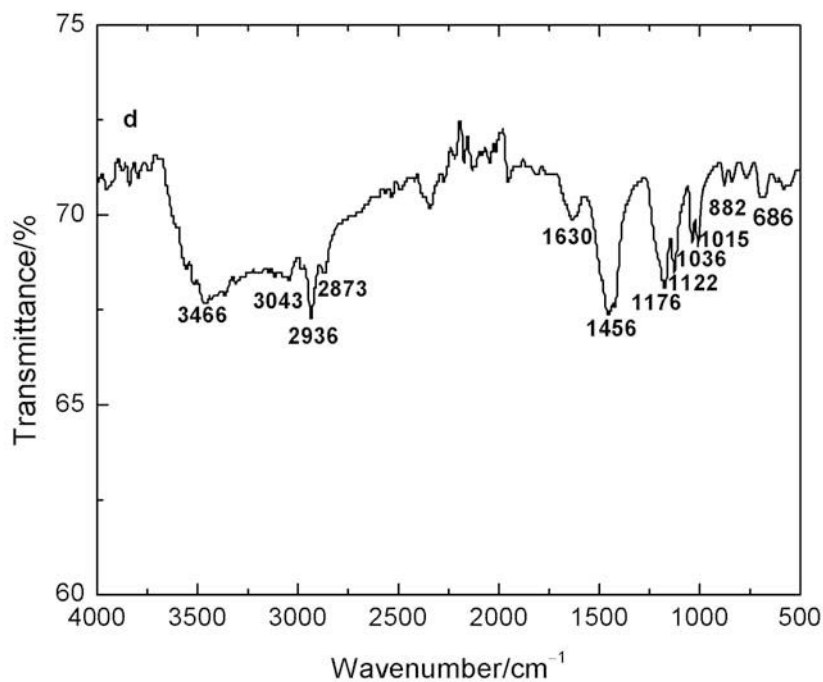


Fig. 6. ATR-FTIR spectrum of PSS-PPDI-DETA.

in the IR spectrum and those at  $1399\text{ cm}^{-1}$  and  $1120\text{ cm}^{-1}$  can be theoretically assigned to the  $\text{SO}_2$  stretching modes (Chandran et al., 2011, 2012). The asymmetric and symmetric stretching modes of the  $\text{SO}_2$  group appear in the region of  $1360\text{--}1310\text{ cm}^{-1}$  and  $1165\text{--}1135\text{ cm}^{-1}$  (Roges, 1994). Bands observed at  $1325\text{ cm}^{-1}$  and  $1165\text{ cm}^{-1}$  in the IR spectrum were also assigned to the  $\text{SO}_2$  stretching modes. These

modes are not pure but include significant contributions from other modes. Although the region of  $\text{SO}_2$  scissors ( $560 \pm 40\text{ cm}^{-1}$ ) and that of  $\text{SO}_2$  wagging ( $500 \pm 55\text{ cm}^{-1}$ ) partly overlap, the two vibrations appear separately (Roges, 1994). Chohan et al. (2010) reported  $\text{SO}_2$  stretching vibrations at  $1345\text{ cm}^{-1}$  and  $1110\text{ cm}^{-1}$  and SN and CS stretching modes at  $833\text{ cm}^{-1}$  for sulfonamide derivatives. Hangan et al.

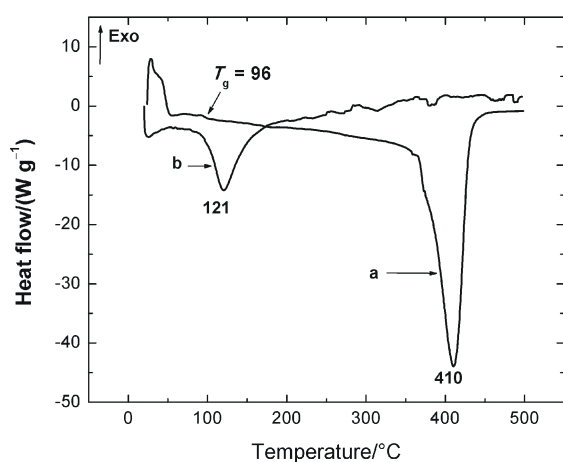


Fig. 7. DSC curves of the PS (a) and PSS (b) polymers.

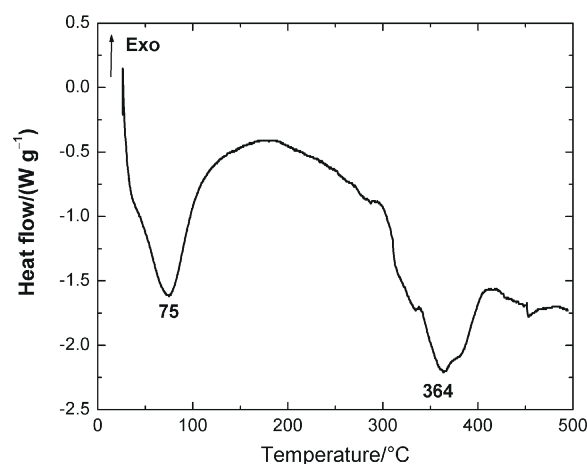


Fig. 8. DSC curve of the PSS-PPDI polymer.

(2010), reported  $\text{SO}_2$  modes at  $1314\text{ cm}^{-1}$ ,  $1308\text{ cm}^{-1}$ ,  $1274\text{ cm}^{-1}$ ,  $1157\text{ cm}^{-1}$ ,  $1147\text{ cm}^{-1}$  and  $1133\text{ cm}^{-1}$  and SN stretching modes at  $917\text{ cm}^{-1}$ ,  $920\text{ cm}^{-1}$ ,  $932\text{ cm}^{-1}$  and  $948\text{ cm}^{-1}$  for sulfonamide derivatives. In addition, the IR spectrum shows the absence of the band corresponding to the carbonyl function of the urethane functional group ( $-\text{NHCOO}-$ ) which appears at around  $1700\text{ cm}^{-1}$  and  $1730\text{ cm}^{-1}$ . Consequently, these results confirm the presence of sulfonamide groups in the structure of PSS-PPDI. The ATR-FTIR spectra of PSS-PPDI show also the disappearance of a band at  $2285\text{ cm}^{-1}$  characteristic of the free isocyanate group, which indicates the cross-linking of polymer chains by the PPDI groups. The results indicate that PSS-PPDI was successfully synthesized. Based on the IR results, the probable structure of PSS-PPDI with a sulfonamide derivative was obtained as a product of the reaction between the isocyanate functions and a sulfonic acid group (Fig. 2), which is matched analogically with the reaction between a carboxylic acid group and an isocyanate function leading to an unstable carbamic anhydride which decomposes to an amide and carbon dioxide (Hawkins et al., 1997; Sugama et al., 1988; Nabuurs et al., 1999; Melchioris et al., 2000; Sasaki & Crich, 2011).

ATR-FTIR spectrum of PSS-PPDI-DETA (Fig. 6) showed a band stretching vibration centered at  $3466\text{ cm}^{-1}$  and a band deformation vibration at  $1630\text{ cm}^{-1}$  ascribed to the  $\text{NH}/\text{NH}_2$  groups, which can be overlapped with the band of the OH stretching vibration. Also, a low intensity band appeared at  $882\text{ cm}^{-1}$  which can be assigned to the S-N stretching vibration. The results indicate that PSS-PPDI-DETA was successfully synthesized.

### DSC analysis

DSC curves for PS and PSS are shown in Fig. 7. The DSC curve of pure PS showed a glass tran-

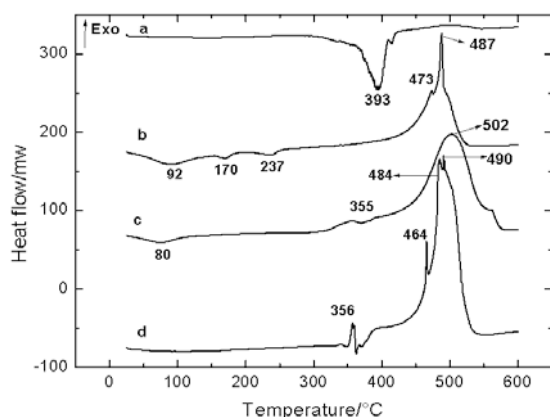
Table 1. Elemental analysis results for the synthesized polymers

| Mass %        | C     | H    | S     | N    |
|---------------|-------|------|-------|------|
| PS            | 89.95 | 7.88 | –     | –    |
| PSS           | 32.81 | 4.87 | 22.81 | –    |
| PSS-PPDI      | 30.09 | 5.48 | 14.61 | 1.72 |
| PSS-PPDI-DETA | 30.86 | 6.21 | 10.40 | 5.76 |

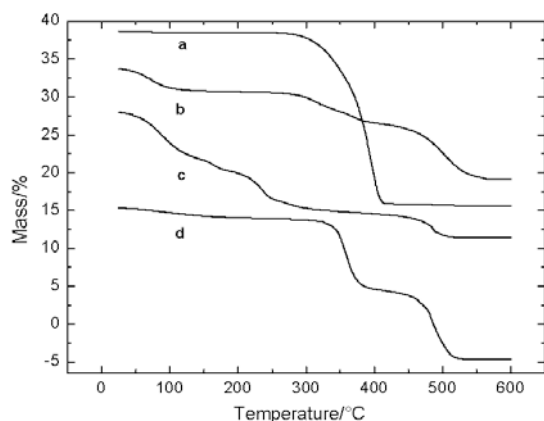
sition,  $T_g$ , at  $96^\circ\text{C}$  and an endothermic peak at around  $410^\circ\text{C}$  which indicates the decomposition of the polymer. Sulfonated polystyrene resulted in an endothermic peak at  $121^\circ\text{C}$ , which can be assigned to the presence of sulfonated groups in the polymer chains (Pan et al., 2014). The DSC curve of PSS-PPDI (Fig. 8) recorded in a sample of  $2.5\text{ mg}$  at the heating rate of  $5^\circ\text{C min}^{-1}$  shows two endothermic bands. The first band is centered at  $75^\circ\text{C}$  and the second at  $364^\circ\text{C}$ , which shows that the decomposition of the polymer is a step wise process.

### Elemental analysis

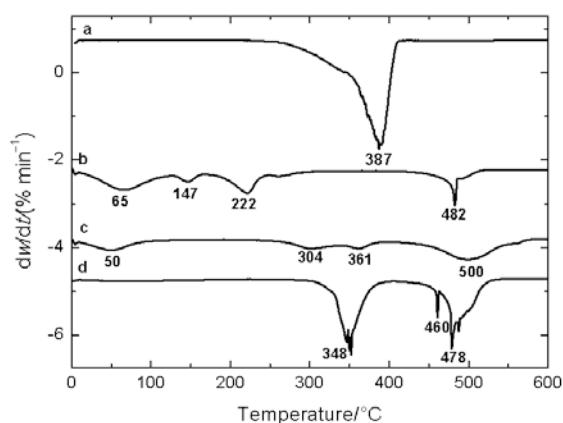
The elemental analysis results are illustrated in Table 1. The presence of  $11.55\%$  of sulfur in the sulfonated sample indicates a successful sulfonation reaction. The presence of  $1.72\%$  of nitrogen in the PSS-PPDI polymer confirms the success of grafting of the 1,4-phenylene diisocyanate group on PSS. In the PSS-PPDI-DETA polymer,  $5.76\%$  of nitrogen were found. The increase of nitrogen concentration in the sample of PSS-PPDI-DETA confirms the grafting of the diethylenetriamine group on PSS-PPDI. Oxygen concentration was considered due to the retained water in the sample (hygroscopic nature of PSS).



**Fig. 9.** DTA curves of PS (a), PSS (b), PSS-PPDI (c) and PSS-PPDI-DETA (d).



**Fig. 10.** TGA curves of PS (a), PSS (b), PSS-PPDI (c) and PSS-PPDI-DETA (d).



**Fig. 11.** DTG curves of PS (a), PSS (b), PSS-PPDI (c) and PSS-PPDI-DETA (d).

### DTA, TGA and DTG analyses

DTA, TGA and DTG curves for PS, PSS, PSS-PPDI and PSS-PPDI-DETA are presented in Figs. 9,

**Table 2.** Thermogravimetric data for polystyrene and its substituted derivatives, mass loss and temperature range

| Sample        | No. | w/%   | $\Delta T/^\circ\text{C}$ |
|---------------|-----|-------|---------------------------|
| PS            | I   | 99.17 | 270–420                   |
| PSS           | I   | 37.82 | 50–150                    |
|               | II  | 24.00 | 150–190                   |
|               | III | 8.70  | 190–265                   |
|               | IV  | 8.60  | 265–370                   |
|               | V   | 19.75 | 370–550                   |
| PSS-PPDI      | I   | 20.29 | 25–200                    |
|               | II  | 9.50  | 200–350                   |
|               | III | 18.30 | 350–405                   |
|               | IV  | 49.16 | 405–600                   |
| PSS-PPDI-DETA | I   | 7.51  | 50–180                    |
|               | II  | 46.44 | 180–405                   |
|               | III | 44.89 | 405–600                   |

10 and 11, respectively. Fig. 9 shows that the degradation process was carried out in a single step for PS and in three steps for PSS; in the last case, the first step was the evaporation of water present in the polymer structure, the second step is the decomposition of sulfonic acid groups and the third step is the final decomposition of the polymer. The degradation process was carried out in three steps for PSS-PPDI and in four steps for PSS-PPDI-DETA (Fig. 9). These results are also an indirect evidence for the existence of the  $-\text{SO}_3\text{H}$ , PPDI and the DETA component in the synthesized polymers. The results showed that the thermal stability decreases in the following order (from the left): PSS-PPDI-DETA, PS, PSS-PPDI, PSS (Figs. 10 and 11, Table 2).

TGA curves (Fig. 10) showed that each polymer exhibits a different decomposition temperature. The final product showed three stages of mass loss up to  $600^\circ\text{C}$ : in the first stage, the mass loss of 7.51 % at  $180^\circ\text{C}$  seems to be due to water evaporation; the second mass loss started after  $200^\circ\text{C}$  and corresponds to the first decomposition stage of PPDI started at around  $365^\circ\text{C}$ ; and the third mass loss started after  $400^\circ\text{C}$  corresponding to the first decomposition stage of DETA started at around  $464^\circ\text{C}$ . The presence of a water molecule in this polymer matrix showed that PSS-PPDI-DETA is more hydrophilic than the starting solid support (PS). Therefore, the transfer rate of a metal ion from solution to the chelating polymer increased (Prabhakaran & Subramanian, 2003). These results indicate successful PSS-PPDI-DETA synthesis.

### Adsorption of some metallic cations

Extraction efficiency of the synthesized polymers for some metal cations is summarized in Table 3. The

**Table 3.** Comparison of the sorption capacities of PSS–PPDI and PSS–PPDI–DETA with other functionalized polystyrene in aqueous solutions

| Chelating ligand  | Initial concentration/M | Extraction/% |        |        | Reference               |
|---|-------------------------|--------------|--------|--------|-------------------------|
|   |                         | Cd(II)       | Zn(II) | Co(II) |                         |
| <i>p</i> -Phenylene diisocyanate                        | $2 \times 10^{-4}$      | 80           | 81     | 88     | This work               |
| <i>p</i> -Phenylene diisocyanate and diethylenetriamine | $2 \times 10^{-4}$      | 92           | 97     | 94     | This work               |
| Sorption capacity/(mmol g <sup>-1</sup> )               |                         |              |        |        |                         |
| Iminodiacetamides                                       | 0.15                    | 0.0          | 0.0    | –      | Sonmez et al. (2003)    |
| Ureasulfonamide   | 0.15                    | 0.05         | 0.04   | –      | Senkal and Yavuz (2006) |
| Thiol containing sulfonamide                            | 0.15                    | 1.5          | –      | –      | Yavuz et al. (2009)     |
| Acetyl sulfonamide                                      | 0.15                    | 0.05         | 0.04   | –      |                         |
| Methanesulfonyl sulfonamide                             | 0.15                    | 0.1          | 0.07   | –      | Senkal and Yavuz (2007) |

selectivity order of the synthesized polymers towards metallic cations depends on the nature of the functional group of the chelating agent. The PSS–PPDI–DETA polymer provided better results than the PSS–PPDI polymer in the extraction of Cd<sup>2+</sup>, Zn<sup>2+</sup> and Co<sup>2+</sup> cations. The different extraction efficiencies for each metal ion can be explained by the hard soft acid base principle. Intermediate cations Co(II) and Zn(II) have affinities for both hard and soft ligands. Then, PSS–PPDI and PSS–PPDI–DETA are considered as ligands containing electrons donor atoms such as nitrogen and sulfur as soft ligands and oxygen atoms as hard ligands. However, Cd(II) tends to form partial covalent bonds and possesses higher affinity to the borderline (nitrogen atom) and soft (sulfur atom) ligands, which characterize it as a soft Lewis acid; in consequence, the chelating agent preferentially binds, according the level of affinity, to Co(II) or Zn(II) and finally to Cd(II). The selectivity order (from left) of PSS–PPDI is thus: Cd<sup>2+</sup>, Zn<sup>2+</sup>, Co<sup>2+</sup> and it is shifted to Cd<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup> for the PSS–PPDI–DETA. The studied polymers can be used as complexing agents that can be simply filtered and reused repeatedly after simple washing with a solution of diluted hydrochloric acid (10<sup>-2</sup> M) and with distilled water.

## Conclusions

Functionalized sulfonated polystyrene with 1,4-phenylene diisocyanate and diethylenetriamine as chelating agents was successfully validated by the ATR-FTIR spectroscopy and elemental analysis. Thermal stability of the obtained products was investigated by the thermogravimetric analysis. The presented study shows that PSS–PPDI and PSS–PPDI–DETA are effective adsorbents for the removal of Co<sup>2+</sup>, Cd<sup>2+</sup> and Zn<sup>2+</sup> ions from aqueous solutions, exhibiting high adsorption capacities and high selectivity for Co(II) and Zn(II), while PSS–PPDI–DETA showed higher maximum adsorption capacities for Zn<sup>2+</sup>, Co<sup>2+</sup> and Cd<sup>2+</sup> than PSS–PPDI. Moreover,

the studied polymers are easily synthesized and they can be reused repeatedly in the extraction of metallic cations after simple washing with a solution of diluted hydrochloric acid (10<sup>-2</sup> M).

*Acknowledgements.* The authors would like to thank the Tunisia Ministry (Research Unit: 05/UR/12-05) for financing this project.

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