

# Preparation and Properties of Ion-Exchange Membranes Prepared by the Radiation-Induced Grafting of a Styrene/Acrylic Acid Comonomer onto Low-Density Polyethylene

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**ABSTRACT:** The preparation of ion-exchange membranes by the direct radiation grafting of acrylic acid and styrene onto low-density polyethylene was studied. The effects of the grafting conditions, such as the comonomer composition and concentration and the irradiation dose, on the grafting yield were also investigated. The swelling behavior, ion-exchange capacity, structural changes, and thermal properties of unsulfonated and sulfonated membranes were studied. The crystallinity decreased with grafting and sulfonation, but the chemical and thermal stability was improved by sulfonation. The removal of some toxic heavy-metal ions— $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$ —was studied. Some factors that influenced the metal-ion uptake

were studied. The metal-ion-uptake results showed that the membranes could be used for the adsorption of the investigated metal ions and had an affinity toward  $\text{Pd}^{2+}$  ions in a mixture. The regeneration of the membranes was carried out by a treatment with 1M  $\text{HNO}_3$ , and the membranes were used several times with high efficiency. Thus, the membranes may be suitable for pervaporation or vapor permeation to separate wastewater because of their hydrophilicity. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 2769–2777, 2007

**Key words:** graft copolymers; ion exchangers; membranes; polyethylene (PE); radiation

## INTRODUCTION

The surface modification of polymer films by radiation-induced grafting is an advantageous technique for preparing membranes with desirable properties, particularly in terms of the ability to control the composition and properties of the membranes by the variation of the grafting parameters.<sup>1–4</sup> The influence of experimental conditions on the properties of the resulting modified materials is a particular focus of interest.<sup>5–7</sup> One of the most important properties in determining the process efficiency is the  $G$  value of the free radicals [ $G(R')$ ], that is, the radiation sensitivity of the polymer and monomer pair.  $G(R')$  of the polymer substrate must be higher than that of the grafted monomer, especially in the mutual method, and thus the proper solvent is that which reduces  $G(R')$  of the monomer by the chain-transfer effect; this leads to successive grafting and minimization of homopolymerization.<sup>8</sup> Membranes play a very important role in various separation processes such as desalting, separation of gases, separation of water from organic and inorganic mixtures, and wastewater treatment.<sup>9–21</sup>

The radiation-induced grafting of acrylic and vinyl monomers onto polyethylene provides a noble way of producing ion-exchange membranes for uses in separation science and electrochemical energy conversion.<sup>22–25</sup> Such membranes require chemical and thermal resistance.

Grafting a sulfonated monomer is very difficult because of the high incompatibility between sulfonic acid groups (strongly hydrophilic) and polymer films (strongly hydrophobic). Therefore, styrene (Sty) is often grafted onto polymer films to produce graft copolymers that can be easily sulfonated with chlorosulfonic acid.<sup>26</sup> The ion-exchange properties are improved by sulfonation, which changes the overall structure of the membranes; these structural changes may be in the form of a crystalline–amorphous ratio.<sup>20</sup> Also, membranes containing sulfonic acid groups exhibit some demerits, such as excessive water swelling, good thermal properties, and weak mechanical strength.<sup>27,28</sup> Sulfonated grafted membranes containing carboxylic and sulfonic acid groups have been considered as alternative membranes. It is expected that this type of membrane can be applied over a broad pH range.

A membrane is chemically stable if it remains intact in solutions of various pHs, organic solvents, and oxidizing agents, whereas environmental stability requires avoiding fouling by bacteria. Apart from these, membrane properties such as permeability, hyperfiltration, and pervaporation would be developed for

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different practicing fields. The membranes must retain these properties for a longer period.

The objectives of this study were the following:

1. The preparation of ion-exchange membranes by the direct radiation grafting of acrylic acid (AA) and Sty comonomers onto low-density polyethylene (LDPE). In this part, the grafting conditions were studied, such as the comonomer composition and concentration and the irradiation dose.
2. Some properties of the grafted and sulfonated membranes were investigated, such as the chemical stability, swelling behavior, thermal properties, and ion-exchange capacity (IEC).
3. The factors influencing the ion-exchange membranes for the removal of some toxic heavy-metal ions ( $\text{Cd}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Zn}^{2+}$ ) were also investigated.

## EXPERIMENTAL

### Materials

LDPE films 60  $\mu\text{m}$  thick were provided by El-Nasr Co. for Medical Supplies (Kaloubia, Egypt). Reagent-grade AA and Sty of 99% purity (Merck, Germany) were used as received. Other chemicals were reagent-grade and of the BDH type.

### Graft copolymerization and sulfonation

Direct radiation-induced grafting was used as a technique. The irradiation was carried out with  $^{60}\text{Co}$   $\gamma$  rays at a dose rate of 4.943 kGy/h in a nitrogen atmosphere. A methanol/aqueous medium was used as a solvent, and the optimum ratio is shown in Figure 1. The grafted membrane was freed from the homopolymer by extraction with methanol in a Soxhlet apparatus for 24 h. This membrane was dried in an oven at 40°C for 24 h and weighed. The degree of grafting was calculated with the following equation:

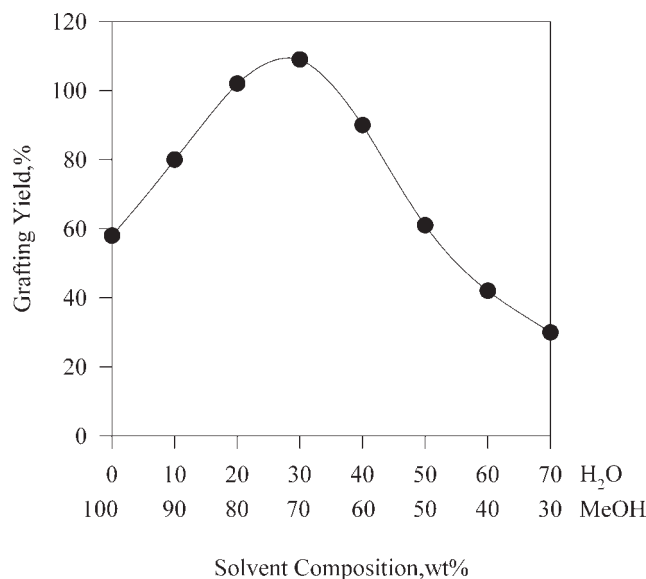
$$\text{Grafting yield}(\%) = [(W_g - W_0)/W_0] \times 100$$

where  $W_0$  and  $W_g$  represent the weights of the initial and grafted films, respectively.

The sulfonation of phenyl groups of Sty was carried out through the soaking of the grafted membrane in a mixture of chlorosulfonic acid and 1,2-dichloroethane (1 : 9 vol %) in an ice bath for 6 h. The membrane was then washed with distilled water and dried in an oven at 40°C. The polystyrene (PSty) was converted into polystyrene sulfonic acid (PSS).

### FTIR spectroscopy

A Mattson 1000 FTIR spectrophotometer (Unicam, Ltd., England) was used for the analysis by IR spectroscopy.



**Figure 1** Effect of the solvent composition on the grafting yield (comonomer composition = 1 : 1, comonomer concentration = 20 wt %, irradiation dose = 20 kGy, Moher salt concentration = 0.1 wt %).

### Swelling measurements

The membrane was swollen in deionized water at pH 7 for 24 h, the surface-attached water on the membrane was removed with filter paper, and it was weighed. The wet weight was determined by the change in the weight before and after hydration. The swelling percentage was calculated as follows:

$$\text{Swelling} (\%) = [(W_s - W_g)/W_g] \times 100$$

where  $W_g$  and  $W_s$  represent the weights of the dry and wet membranes, respectively.

### IEC

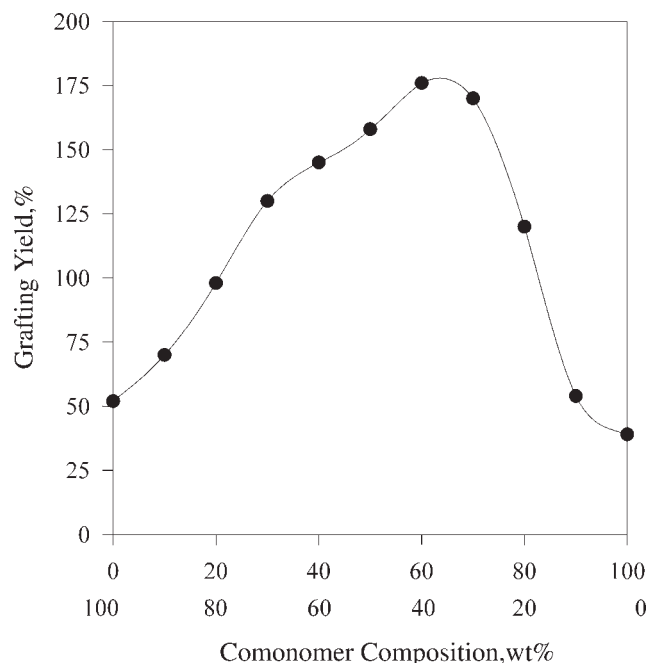
The grafted and sulfonated membranes were immersed with stirring in a solution of NaOH of a known concentration at the ambient temperature for 24 h. The exchanged solution was titrated with a 0.1M HCl solution with a phenolphthalein endpoint. The procedure was carried out in triplicate, and the results were averaged. IEC was calculated according to the following equation:

$$\text{IEC} (\text{mmol/g}) = [V_{\text{NaOH}} \times (M_1 - M_2)]/W_g$$

where  $V_{\text{NaOH}}$  is the volume of the NaOH solution (mL),  $M_1$  is the initial molarity of NaOH,  $M_2$  is the molarity after the exchange, and  $W_g$  is the weight of the membrane in the hydrogen form (g).

### Chemical stability

The grafted and sulfonated membranes were immersed in a 3%  $\text{H}_2\text{O}_2$  solution including 4 ppm



**Figure 2** Effect of the comonomer composition on the grafting yield (comonomer concentration = 20 wt %, irradiation dose = 20 kGy, solvent composition = 70/30 MeOH/H<sub>2</sub>O, Moher salt concentration = 0.1 wt %).

Fe<sup>2+</sup> at 70°C for 7 h. Then, the membranes were dried, and the weight loss was calculated.

#### Thermogravimetric analysis (TGA)

TGA for the investigated samples was performed under a nitrogen atmosphere at a flow rate of 50 mL/min for pure nitrogen gas and at a heating rate of 10°C/min from the ambient temperature up to 600°C with a Shimadzu TGA-50 thermal analysis system (Japan).

#### X-ray diffraction (XRD) analysis

Different samples were measured with a Bruker D8 Advance XRD instrument (Germany). The diffraction patterns were examined under constant operating conditions at room temperature.

#### Metal-ion-uptake measurements

The metal-ion uptake was measured by the immersion of the sulfonated membrane in metal feed solutions of various concentrations and pH values for different intervals and then removal. The remaining metal in the feed solution was determined with a PerkinElmer model 2380 atomic absorption spectrophotometer with lamps for Cd, Pb, and Zn. Merck atomic absorption standard solutions of these metals were used for the calibration process. The metal-ion uptake ( $A$ ) was calculated according to the following equation

$$A \text{ (mmol/g)} = [V(C_1 - C_2)]/W$$

where  $V$  is the volume of the solution taken for equilibration with the cation exchanger;  $C_1$  and  $C_2$  are the concentrations of the metal ions before and after the adsorption, respectively; and  $W$  is the weight of the membrane.

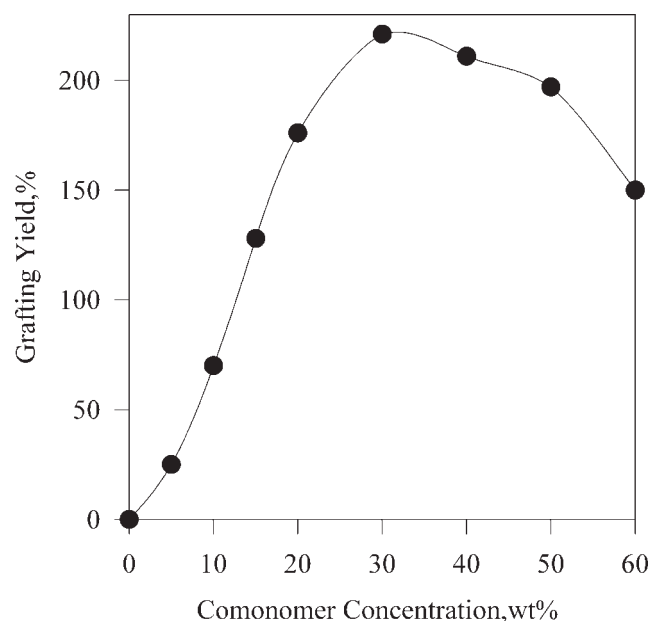
## RESULTS AND DISCUSSION

### Effect of the comonomer composition

The effect of the comonomer composition on the grafting yield is shown in Figure 2. The grafting yield increases as the Sty content increases or the AA content decreases in the grafting medium up to 60 wt %. AA shows a high tendency to homopolymerize during radiation grafting copolymerization, unlike non-active monomers such as Sty, which has less of a tendency for homopolymerization. This means that the grafting yield is enhanced in the presence of Sty, which acts as a self-inhibitor to the homopolymerization process by an energy-transfer effect caused by resonance stabilization of its phenyl ring. For monomers to be grafted, they should have a low viscosity and a small dipole strength. Thus, the presence of the Sty monomer enhances the amount and rate of monomer diffusion into the base polymer.<sup>29</sup>

### Effect of the comonomer concentration

The effect of the comonomer concentration on the grafting yield is investigated in Figure 3. The degree

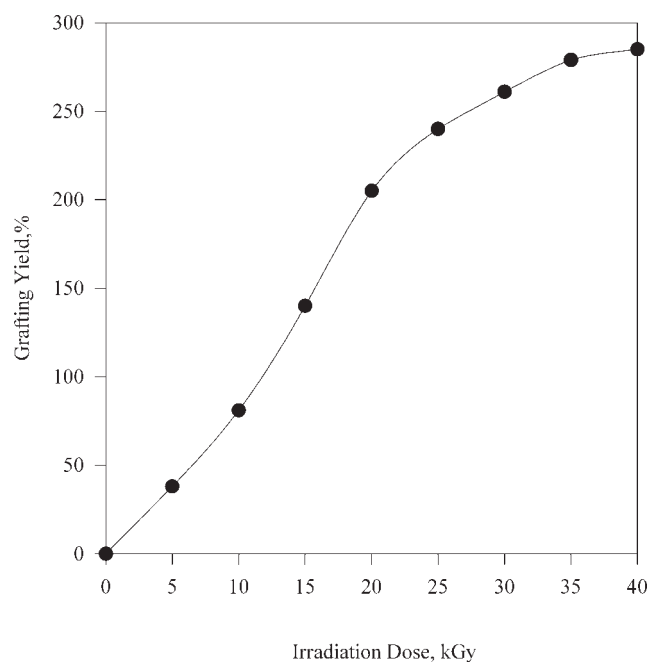


**Figure 3** Effect of the comonomer concentration on the grafting yield (comonomer composition = 60/40 w/w Sty/AA, irradiation dose = 20 kGy, solvent composition = 70/30 MeOH/H<sub>2</sub>O, Moher salt concentration = 0.1 wt %).

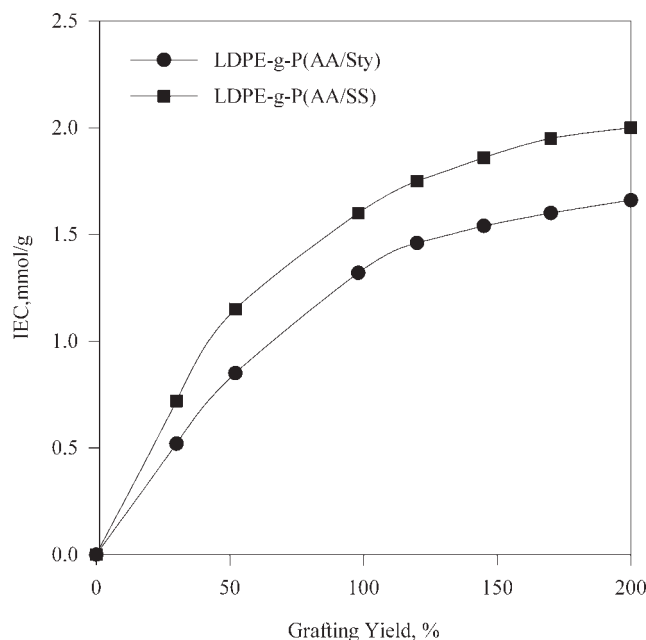
of grafting increases with increasing comonomer concentration, that is, with decreasing solvent content in the reaction medium. This is because the grafting reaction may take place via a front mechanism.<sup>30</sup> Increasing the monomer concentration leads to increasing availability of the monomer to reach the reaction sites on the polymer (up to 30 wt %). Above this concentration, the excess of the comonomer concentration causes suppression of the monomer diffusion by increasing the viscosity of the grafting mixture under the homopolymerization effect and hence reducing the probability of radicals reaching the polymer (the Trommsdorff effect).<sup>31</sup>

### Effect of the irradiation dose

The relationship between the grafting yield and irradiation dose is shown in Figure 4. The grafting yield increases with increasing irradiation dose, and the acceleration occurs at irradiation doses ranging from 5 to 20 kGy. This trend can be ascribed to the fact that the increase in the irradiation dose leads to more free-radical formation in the grafting system, and consequently, more radicals contribute to the grafting reactions, leading to an increase in the grafting yield. At high irradiation doses (>20 kGy), the rate of the grafting yield decreases above 30 kGy. At such high doses, the content of polymer crosslinking increases, and this limits the molecular motion; consequently, the rate of grafting decreases. Thus, the monomer has not



**Figure 4** Effect of the irradiation dose on the grafting yield (comonomer composition = 60/40 w/w Sty/AA, comonomer concentration = 30 wt %, solvent composition = 70/30 MeOH/H<sub>2</sub>O, Moher salt concentration = 0.1 wt %).



**Figure 5** Effect of the grafting yield on IEC of the grafted and sulfonated membranes.

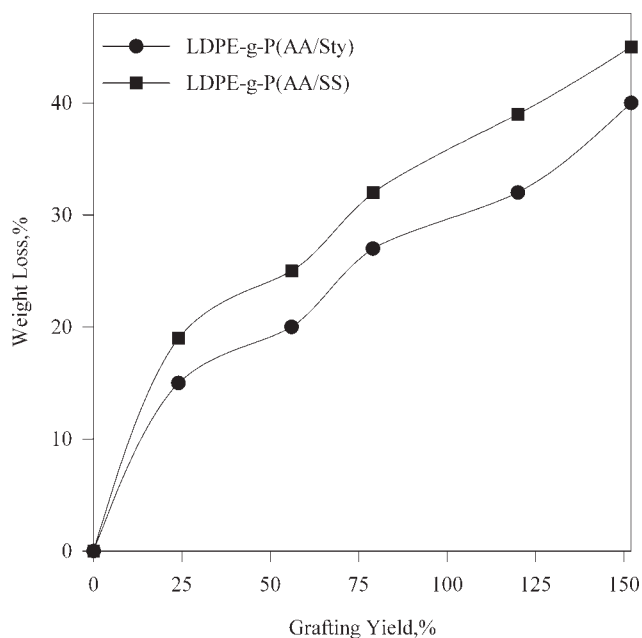
diffused sufficiently into the reaction sites, and most of it has been homopolymerized.<sup>32</sup>

The grafting has been confirmed by FTIR; the strong absorption band of the aromatic C—H of PSty and the O—H group of —COOH of poly(acrylic acid) (PAA) appears around 3000 cm<sup>-1</sup>. The characteristic absorption bands of C=O and C—O stretching of —COOH appear around 1711 and 1290 cm<sup>-1</sup>, respectively. The stretching absorption bands of C—C of PSty in the ring and out of plane appear around 1466 and 788 cm<sup>-1</sup>, respectively.

### IEC

The experimental IEC is based on the total number of fixed ionic groups. The relationship between the grafting yield and the IEC of the grafted and sulfonated membranes is shown in Figure 5. The IEC increases with increasing grafting yield because of the increase in the charged portion of the membrane, but the sulfonated membrane has a higher IEC than the unsulfonated one. This is because the fixed ionic groups of the grafted membrane are the carboxylic acid groups, but for the sulfonated one, they are the sum of the carboxylic and sulfonic acid groups. The IEC can be changed by changes in the grafting conditions in the grafting system because membranes of different IECs can be prepared.

The pK<sub>a</sub> values of the carboxylic acid group are in the range of 4–5, but that of the sulfonic acid group is below 1. Therefore, the membrane containing only carboxylic acid groups as cation-exchange sites may be applied in a limited pH range because the ioniza-



**Figure 6** Effect of the grafting yield on the chemical stability of the grafted and sulfonated membranes.

tion ability of carboxylic sites is strongly dependent on the pH condition,<sup>33</sup> but the presence of sulfonic acid groups makes the membrane applicable in a broad pH range.

### Chemical stability

The chemical resistance of grafted and sulfonated membranes having various grafting yields against the oxidation is presented in Figure 6. The weight loss increases with increasing the grafting yield because the amorphous phase increases as a result of grafting. Consequently, the diffusion and the mobility of the oxidizing solution inside the membrane matrix increases. Moreover, the weight loss of the sulfonated membrane is higher than that of the unsulfonated one; the introduction of sulfonic acid groups further increases the amorphousness of the membrane. It can be concluded that the membrane has effective resistance toward degradation.

### Swelling behavior

The swelling behavior is an important characteristic if the membrane is to be used as an ion-exchange membrane. The swelling percentages of membranes having different grafting yields and sulfonated membranes are presented in Figure 7. The water absorption increases with increasing grafting yield because of increasing hydrophilic groups ( $-\text{COOH}$  groups) of PAA by grafting. The swelling percentage of the sulfonated membrane is higher than that of the unsulfonated one because the conversion of PSty to PSS

makes the polymer membrane more hydrophilic. Thus, the swelling behavior depends on both the amount and form of the functional reactive group introduced into the polymer substrate by grafting.

At a high grafting yield ( $>125\%$ ), the rate of the increase in the water uptake decreases as a result of the rigidity of the aromatic group. In other words, the high grafting yield materials is rigid to swell when water molecules penetrate the polymer membrane.

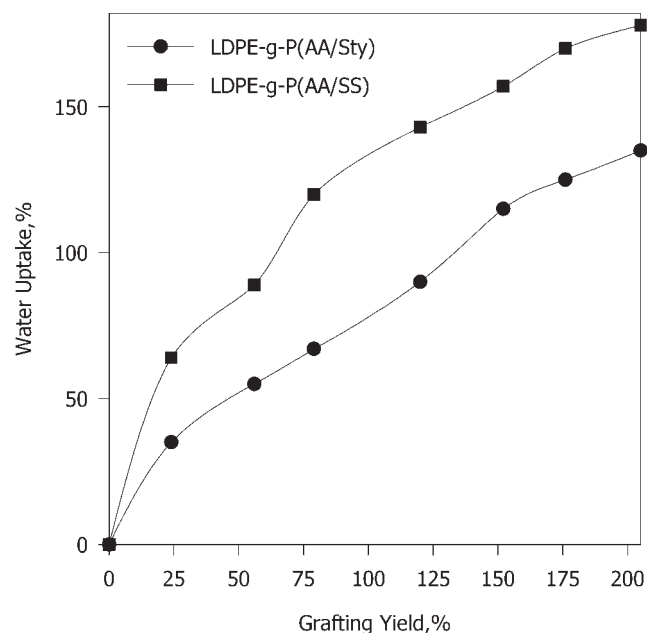
### XRD analysis

XRD analysis of the grafted and sulfonated membranes was performed, and they were compared with the base polymer to clarify the changes in their crystallinity and morphological structures caused by the grafting and sulfonation (Fig. 8). The intensity of the diffractogram, representing the crystallinity, decreases with grafting and further with sulfonation. This is due to the dilution of the crystalline fraction by the incorporation of the amorphous PAA and PSty chains into the polymer matrix and by sulfonation.<sup>34</sup>

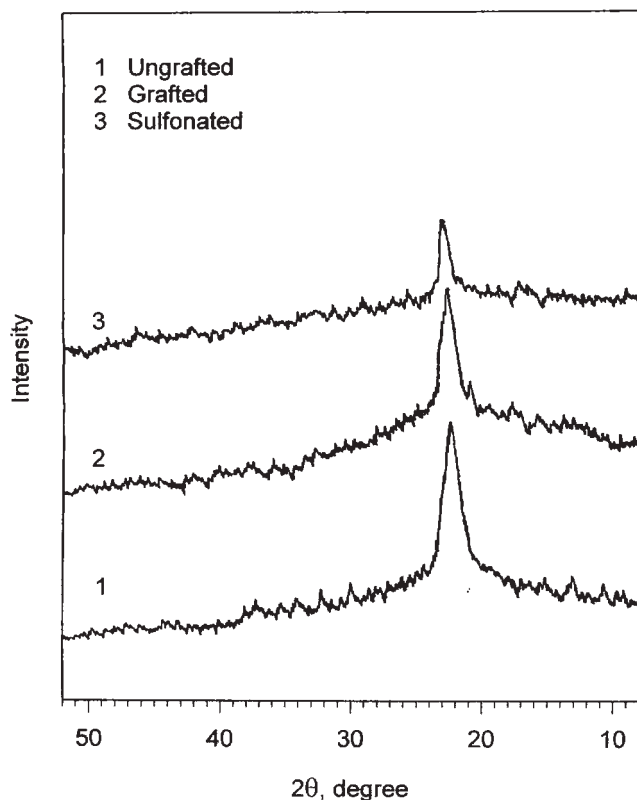
It can be concluded that the grafting occurs in the amorphous region of LDPE and in some areas close to the surfaces of the crystallites, thus breaking up partly ordered chain structures of the LDPE matrix.<sup>35</sup>

### TGA

The thermograms of the original LDPE, grafted LDPE, and sulfonated LDPE are shown in Figure 9. The ungrafted LDPE has thermal stability up to  $400^\circ\text{C}$ , followed by single-step degradation; a smooth decrease in the weight can be observed, and complete



**Figure 7** Effect of the grafting yield on the swelling percentage of the grafted and sulfonated membranes at pH 7.



**Figure 8** XRD graph of the grafted and sulfonated membranes (grafting yield = 80).

depolymerization occurs at 500°C, as depicted in Figure 9 (curve 1). The grafting of LDPE with PAA and PSty induces two degradation steps at 304 and 400°C, as observed from the thermogram Figure 9 (curve 2). The first stage of the weight loss represents the degradation of the grafted side chain, and the second stage represents the depolymerization of the backbone polymer. This shows that grafted AA-co-Sty degrades earlier than the LDPE matrix; similar behavior has been observed for Sty grafted and sulfonated onto different substrates.<sup>36,37</sup>

Three degradation pattern steps have been observed for the sulfonated grafted membrane, as shown in Figure 9 (curve 3). The first degradation step starts below 100°C and continues up to 200°C and is ascribed to the loss of water molecules associated with the sulfonic acid groups in the membrane because sulfonated membranes have strong hydrophilic character. The second step of degradation at 290°C is attributed to desulfonation, which is mostly accompanied by the evolution of SO<sub>2</sub>.<sup>38</sup> The third stage of the degradation represents the depolymerization of the backbone polymer, which begins at 400°C.

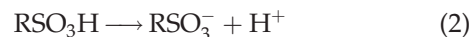
Thus, the sulfonation of PSty makes the membranes more susceptible to thermal degradation in comparison with unsulfonated ones. It can be concluded that the membranes are thermally stable up to 290°C under the same experimental conditions.

### Adsorption properties

Such sulfonated membranes possess excellent properties and may be used as ion-exchange membranes. For this purpose, some toxic heavy-metal ions that exist in wastewater—Cd<sup>2+</sup>, Pb<sup>2+</sup>, and Zn<sup>2+</sup> ions—have been studied. The factors that can affect the metal-ion uptake with the prepared membranes are as follows.

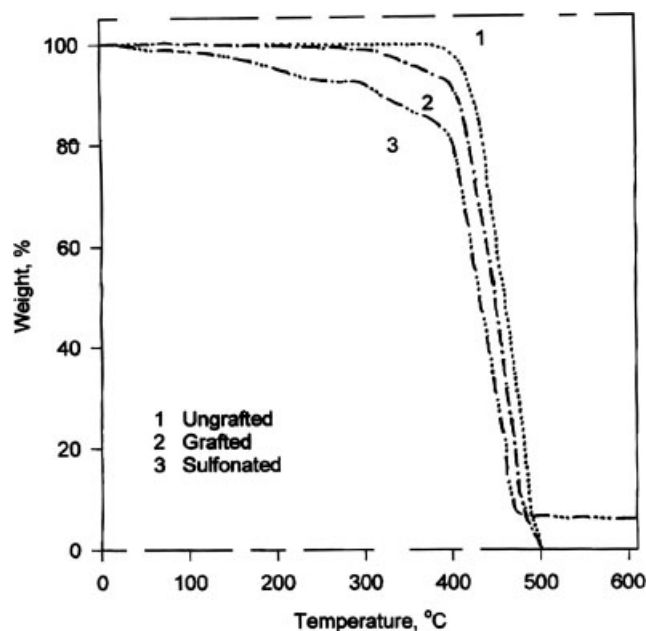
### Effect of the pH of the medium

The complexation of a heavy-metal ion by a chelating ligand strongly depends on the pH of the medium. This effect can be observed especially in the formation of the coordination bond between oxygen or sulfur and metal ions. The effect of the acidity of a medium on the metal-ion uptake is presented in Figure 10. As expected, the metal-ion uptake increases with an increasing pH value of the medium for all investigated metal ions:

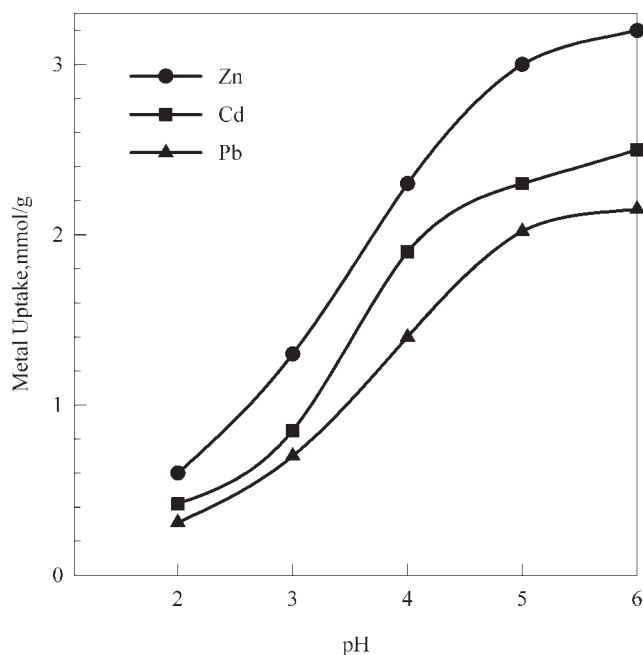


where R is the matrix of the cation exchanger.

At low pHs, eqs. (1) and (2) are displaced to the left; therefore, the concentration of ionized carboxyl or sulfonyl groups is low, and there is protonation of the lone pair of oxygen and sulfur.<sup>39</sup> However, the highly acidic medium is not favorable for the sorption of the metal (II) cation by the membrane. At high pHs, eqs. (1) and (2) are displaced to the right; there-



**Figure 9** TGA thermograms of the grafted and sulfonated membranes (grafting yield = 130).



**Figure 10** Effect of the pH on the metal uptake at the ambient temperature (initial feed concentration = 1000 ppm, treatment time = 6 h, grafting yield = 180).

fore, the concentration of ionized carboxyl or sulfonyl groups is high, and thus the probability of the interaction between them and metal ions in the solution increases. The lone pair on the oxygen and sulfur atoms of the carboxylic and sulfonic acid groups, respectively, is suitable for coordination with the metal ions to give the metal-polymer complex. The pH must not be increased up to pH 6 to avoid the precipitation of metal ions, especially  $\text{Pb}^{2+}$ , as hydroxides.

#### Effect of the treatment time

The equilibrium adsorption time of the metal ions by the adsorbent is important for practical use. For this purpose, the adsorption time of metal ions on the membrane has been investigated and is shown in Figure 11. The metal-ion adsorption increases with increasing time to reach its maximum value after 3, 5, and 6 h for  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$ , and  $\text{Zn}^{2+}$  ions, respectively; after this period, there is no significant increase in the metal-ion adsorption.

These results indicate that in the first 2 h, the membrane shows a higher affinity to  $\text{Pb}^{2+}$  than  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  ions, and the metal-ion adsorption is ordered in the following sequence:  $\text{Pb}^{2+} > \text{Cd}^{2+} > \text{Zn}^{2+}$ . This may be explained on the basis of hard and soft acids (bases theory): the hard acids bind strongly to hard bases.<sup>40</sup>  $\text{Pb}^{2+}$  ion as an acid is harder than both  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ ; thus, the  $\text{Pb}^{2+}$  ion is attached to the cation exchanger (hard base) more strongly than  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$ . On the other hand, after 2 h the metal-ion adsorption is ordered in the sequence of  $\text{Zn}^{2+} > \text{Cd}^{2+}$

$> \text{Pb}^{2+}$ , which depends on their ionic radii; the lower the ionic radii are, the higher the metal-ion adsorption is. The ionic radius of the metal ions is ordered in the sequence of  $\text{Zn}^{2+} > \text{Cd}^{2+} > \text{Pb}^{2+}$ ; therefore, the membrane shows a higher capacity for the  $\text{Zn}^{2+}$  ion than other metal ions investigated.

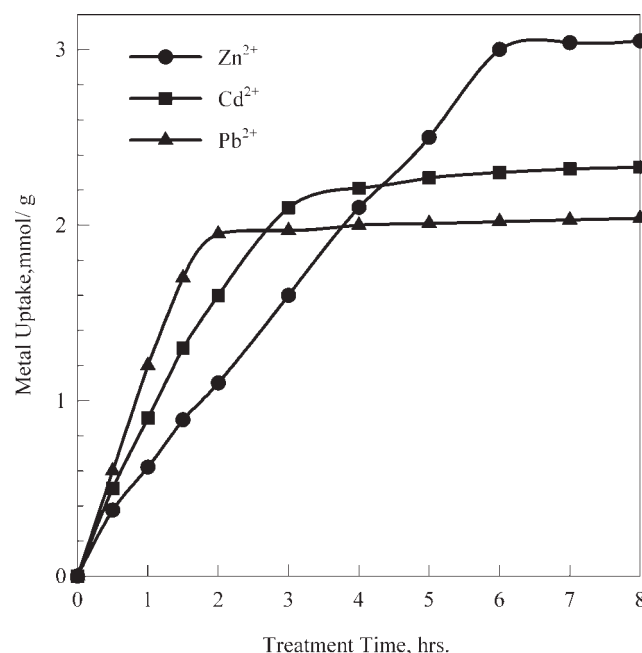
The high initial rate of metal-ion adsorption suggests that adsorption occurs mainly at the membrane surface. The mechanism of intrapore diffusion is involved in the adsorption, and it is represented by the slower adsorption rate, which can be noticed after 3 h of initial adsorption.

#### Effect of the initial concentration

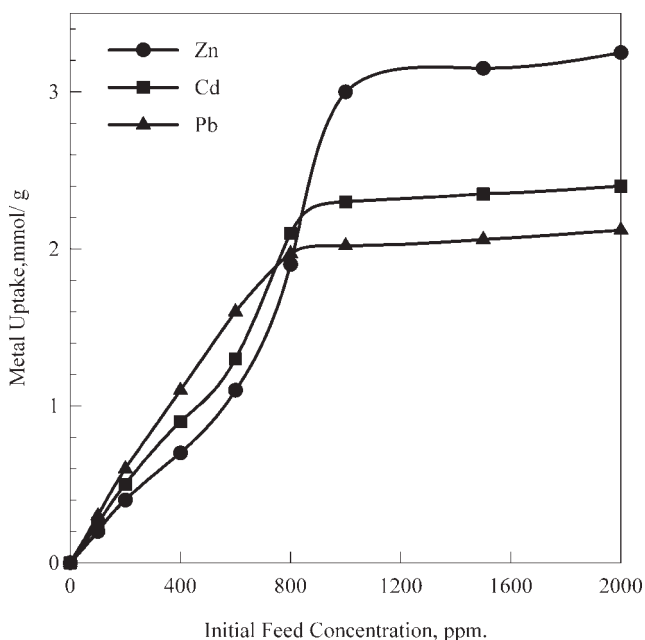
To investigate the effect of the initial concentration on metal-ion adsorption, the process was carried out at initial metal-ion concentrations ranging from 100 to 2000 ppm at room temperature. The results (Fig. 12) reveal that the metal-ion uptake increases with an increasing initial metal-ion concentration to reach a certain limiting value and tends to level off at a higher feed concentration ( $>1000$  ppm). This is because the chelating sites of the sorbent become saturated when the concentration of the feed solution reaches 1000 ppm, above which no more metal-ion uptake occurs.

#### Competitive conditions

The adsorption of a mixture of  $\text{Cd}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Zn}^{2+}$  metal ions in the same feed solution at a suitable pH

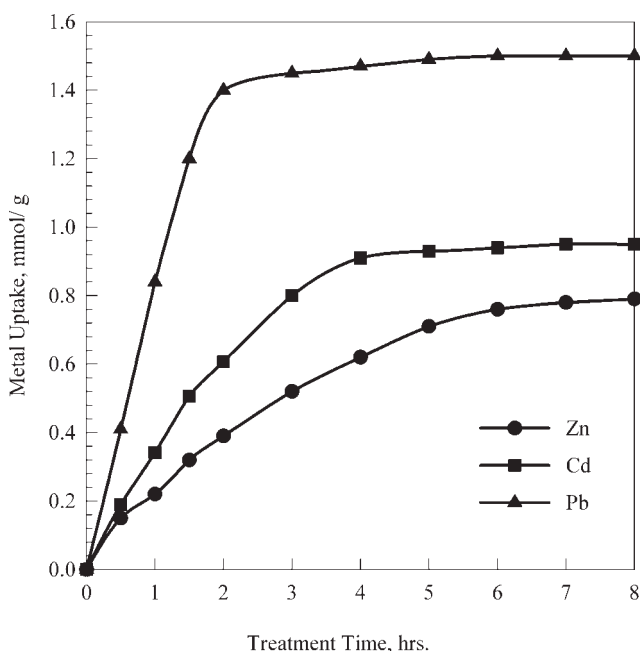


**Figure 11** Effect of the treatment time on the metal uptake at the ambient temperature (initial feed concentration = 1000 ppm, pH = 5, grafting yield = 180).



**Figure 12** Effect of the initial feed concentration on the metal uptake at the ambient temperature (pH = 5, treatment time = 6 h, grafting yield = 180).

has been studied, and the results are shown in Figure 13. The membrane has a higher affinity for  $\text{Pd}^{2+}$  than  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$ . This may be explained on the basis of the base theory, as mentioned before. Consequently, the membrane has an affinity toward  $\text{Pb}^{2+}$  ions in a mixture of the investigated metal ions.



**Figure 13** Selectivity of the membrane toward a mixture of the metal ions as a function of the treatment time at the ambient temperature (pH = 5, initial feed concentration = 1000 ppm, grafting yield = 180).

**TABLE I**  
Recycling Profile of the Ion-Exchange Membrane Toward  $\text{Cd}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Zn}^{2+}$  Ions

Cycle	Membrane efficiency (%)		
	$\text{Zn}^{2+}$	$\text{Cd}^{2+}$	$\text{Pb}^{2+}$
1	98.5	98	99
2	98	98	98
3	98	98	98

### Reuse studied

To be viable materials for practical use, modified polymers must be easily desorbed under suitable conditions and reusable. The adsorbed metal ions can be easily desorbed from the membrane through soaking in 1M  $\text{HNO}_3$ . The desorption percentage can be calculated with the following equation:

Desorption(%)

$$= \frac{\text{Amount of metal ion desorbed to the elution medium}}{\text{Amount of metal ion sorbed on the on the membrane}} \times 100$$

Table I shows that the desorbed membrane has a removal efficiency of 98% even after three cycles. Thus, the membrane can be used several times with high efficiency, and this makes it economically suitable for use.

### CONCLUSIONS

In this study, the  $\gamma$ -radiation-induced graft copolymerization of AA and Sty onto LDPE films was performed. The optimum preparation conditions for high grafting yields were studied. The IEC of the grafted membrane was improved by sulfonation. The prepared membrane had high hydrophilic, thermal, and chemical stability. The sorption capacities of the membrane toward some heavy-metal ions— $\text{Cd}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Zn}^{2+}$ —were also studied. The metal-ion uptake was found to be dependent on the pH of the medium, the adsorption time, and the initial feed concentration. The membrane had an affinity toward  $\text{Zn}^{2+}$  ions rather than  $\text{Cd}^{2+}$  and  $\text{Pd}^{2+}$  ions, but in a mixture of the three metal ions, it had an affinity toward  $\text{Pd}^{2+}$  ions. The ion-exchange membrane could be regenerated easily by treatment with 1M  $\text{HNO}_3$ . It can be concluded that the prepared membrane could be used as ion exchanger to remove  $\text{Cd}^{2+}$ ,  $\text{Pd}^{2+}$ , and  $\text{Zn}^{2+}$  ions from wastewater.

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