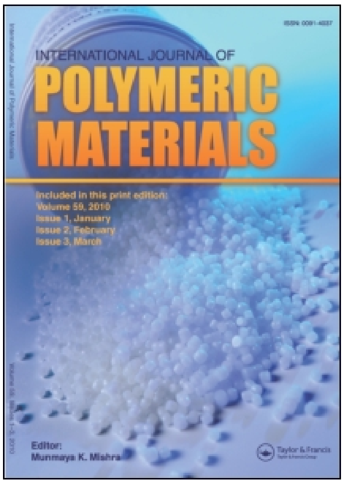

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STRUCTURE OF POLYETHYLENE-GRAFT-POLYSTYRENE SULFONIC ACID MEMBRANES PREPARED BY RADIATION-INDUCED GRAFTING

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STRUCTURE OF POLYETHYLENE-GRAFT-POLYSTYRENE SULFONIC ACID MEMBRANES PREPARED BY RADIATION-INDUCED GRAFTING

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Structural behavior of polyethylene-graft-*polystyrene sulfonic acid (PE*-g-*PSSA) membranes prepared by simultaneous radiation-induced grafting of styrene onto low density polyethylene (PE) films followed by sulfonation was investigated. FTIR, X-ray diffraction (XRD) and differential scanning calorimetry (DSC) were used to monitor the changes in the morphology and the crystallinity taking place in the membranes during the applied two step preparation procedure (grafting and sulfonation) and the variation of the degree of grafting. Thermal properties such as melting temperature (T_m) and the heat of melting (ΔH_m) were also studied. The membranes showed a chemical structure of strongly hydrophilic nature due to the presence of (SO_3^-) groups with their associated water molecules. Both grafting and subsequent sulfonation were found to induce significant structural changes in the PE matrix. The overall crystallinity of the membranes was found to decrease with the increase in the degree of grafting and that is attributed to the cumulative effect of dilution and partial disruption of the inherent crystallites of the PE films.*

Keywords: radiation grafted PE-*g*-PSSA membranes, structural behavior, FTIR, XRD, DSC

INTRODUCTION

Ion exchange membranes have attracted increasing attention in a wide number of applications of industrial interest such as water electrolysis, electrolytic desalination of bioproducts, batteries, sensors, and fuel cells [1–2]. Preparation of these membranes requires grafting

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of functional ionizable groups on a trunk polymer, which has to be subsequently, shaped into a thin foil. Grafting can be chemically, photochemically, and radiochemically initiated [3]. Of all methods, radiation-induced grafting is a flexible technique that addresses the ion exchange membranes property needs through imparting functional characteristics of a polar monomer to a pre-existing nonpolar polymer already in a film form with an easy control over the composition by variation of the grafting parameters [4–5].

In this method, grafting is initiated by generating free radicals in a film through exposing it to high-energy radiation (e.g., γ-rays, electron radiation, and ion radiation). Contacting the irradiated films during the irradiation step or after it with monomer units leads to the formation of macro-radicals, which subsequently propagate to form side chain grafts that can be activated by a post-grafting chemical reaction such as sulfonation, unless the grafted monomer already contains a functional group such as acrylic acid [4].

Polyethylene (PE) films have been frequently used as base polymers for preparation of various ion exchange membranes. This is because of their saturated structure, cheapness, high radiation resistance, and excellent mechanical properties. However, most of the attention was given to the development of membranes having weakly acidic characters by grafting functional monomers such as acrylic acid [6–14]. Nevertheless, membranes having strongly acidic exchange groups such as sulfonic acid were also developed to obtain higher stability and wider practical pH ranges, in several occasions [15–20].

Applying radiation-induced grafting is well known to cause structural changes in the polymer matrix. Crystallinity, melting temperature, and thermal resistance are among the most important parameters that vary during the development of the microstructure and the morphology of the membranes. The impact of the variation of such parameters on the membranes most crucial properties such as water uptake, ionic conductivity, and mechanical stability is so influential that the overall performance of the membranes during operation in a separation system is affected. Therefore, it is of utmost importance to understand the structure developed in the radiation grafted membranes and its effect on their physical properties.

In the authors, previous studies, styrene was grafted onto low density PE films by simultaneous irradiation technique [21]. The grafted films were chemically activated by introducing sulfonic acid groups in a post-grafting reaction (sulfonation) [22]. The membrane's physical and chemical properties were found to be strongly dependent on the degree of grafting. As for the present study, the membranes are further characterized by studying their structural behavior in terms of chemical composition, crystallinity, and the relevant thermal characteristics in correlation with the membrane preparation procedure and the variation of the degree of grafting using XRD and DSC.

EXPERIMENTAL PART

Materials

Low density, PE films of 60 μm thickness were obtained from Al Nasr Co., Egypt. Styrene of purity more than 99% was purchased from Fluka (Switzerland) and used without any further purification. Chlorosulfonic acid of analytical grade (Fluka) was used. Solvents: Toluene (J.T. Baker, USA) 1,2-dichloromethane (J.T. Baker), and 1,1,2,2-tetrachloroethane (Fluka) were reagent grades and used as received.

Membrane Preparation

The membranes were prepared following the two-step procedure shown in Figure 1. Kinetics of the grafting reactions and the effect of

Step 1: Grafting

- The film was cut into 5cm × 5cm pieces, washed with acetone, dried in a vacuum oven and placed in a glass ampoule containing styrene of known concentration (20-60 vol %) diluted with dichloromethane. 0.1M H_2SO_4 solution was added to the grafting mixture.
- The ampoule was flushed with purified N_2 for 10 minutes, sealed and irradiated by γ-rays from a Co-60 source with a dose rate of 1.32 kGy/h to total dose of 20 kGy at 30°C .
- The grafted film was washed with toluene several times and soaked therein over night and subsequently dried in the vacuum oven at 60°C overnight.

Step 2: Sulfonation

- The grafted films were sulfonated in a glass reactor using 10% chlorosulfonic acid in 1,1,2,2-tetrachloroethane mixture at room temperature for 1 h. The sulfonated membranes were treated with 0.5 M KOH solution and regenerated with 1 M HCl solution then washed acid free using deionized water and eventually stored under deionized water.

FIGURE 1 Schematic representation of the preparation steps of PE-*g*-PSSA membranes.

various grafting parameters on the degree of grafting were reported elsewhere [21]. The degree of grafting was determined as the weight gain according to the following equation:

$$\text{Degree of grafting } (\%) = \frac{W_g - W_0}{W_0} \times 100 \qquad (1)$$

where, W_g and W_0 are the weights of pre-grafted and grafted PE films, respectively. More details on the sulfonation process can be found in Reference [22].

FTIR Spectral Analysis

FTIR analysis was conducted using a Perkin Elmer Spectrum 2000 Explorer spectrophotometer at ambient conditions in transmittance mode. The spectra were detected by ATR accessory equipped with Zn Sn lens at fixed angle of 45°.

X-Ray Diffraction (XRD)

XRD measurements were performed using Philips, PW 1830, X-ray diffractometer. The diffractograms were measured at ambient temperature and 2θ in the range of 5–50° by means Cu-Kα radiation ($\lambda = 1.54$) monochromated by means of nickel filter.

Differential Scanning Calorimetry (DSC)

Perkin Elmer, Pyris-1 DSC was used to obtain the thermograms of the membranes. The membrane samples were initially dried at 60°C in a vacuum oven (10^{-4} torr) for 24 h and stored in a desiccator over fresh silica gel prior to DSC runs. The samples were analyzed over a temperature range of 50–180°C at a constant programmed heating rate of 20°C min^{-1} and under nitrogen atmosphere.

Calculations of the Degree of Crystallinity

The degree of crytallinity of the original PE (as received) film was calculated using Eq. 2.

$$\text{Degree of crystallinity } (\%) = \frac{\Delta H_m}{\Delta H_{m100}} \times 100 \qquad (2)$$

where, ΔH_m is the heat of melting of PE film and ΔH_{m100} is the heat of melting of 100% crystalline PE polymer, which equals 290 J/g [23].

Because the incorporated polystyrene has an amorphous nature, the crystallinity in the grafted PE films (PE-*g*-PS) and in the final sulfonated membranes (PE-*g*-PSSA) is always referred to the fraction of PE matrix.

The crystallinity of PE-*g*-PS films is calculated using Eq. 2 after correcting the recorded ΔH_m by dividing over the weight fraction of PE in the grafted film [$W_{PE(PE\text{-}g\text{-}PS)}$] obtained from Eq. 3:

$$W_{PE(PE\text{-}g\text{-}PS)} = m_{PE}/(m_{PE} + m_{PS}) \tag{3}$$

where, m_{PE} and m_{PS} are the weight fractions of PE and grafted polystyrene, respectively. Similarly, the degree of crystallinity of PE-*g*-PSSA membranes is calculated using Eq. 2 after taking into the account the weight fraction of PE in the membranes [$W_{PE(PE\text{-}g\text{-}PSSA)}$] calculated using Eq. 4:

$$W_{PE(PE\text{-}g\text{-}PSSA)} = m_{PE}/(m_{PE} + m_{PSSA}) \tag{4}$$

where, m_{PSSA} is weight of sulfonated polystyrene grafts, which equals $m_{PS} + m_{\bar{S}O3} + m_{H_2O}$.

RESULTS AND DISCUSSION

Polyethylene-*graft*-polystyrene sulfonic acid (PE-*g*-PSSA) membranes with degrees of grafting in the range of 7–60% were prepared using the previously described experimental procedure. The degree of grafting was varied by changing the monomer concentration in the range of 10–50 vol% in presence of 0.1 M sulfuric acid whereas the rest of grafting parameters were kept unvaried to identify the source causing structural changes and to maintain a high degree of accuracy. A tentative molecular structure of PE-*g*-PSSA membranes is shown in Figure 2 and a summary of their physico-chemical properties is presented in Table 1.

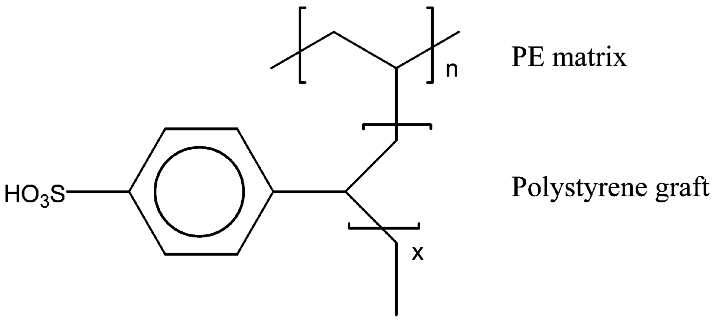

FIGURE 2 A tentative molecular structure of PE-*g*-PSSA membrane.

TABLE 1 Summary of the Physico-Chemical Properties of PE-*g*-PSSA Membranes

Degree of grafting (%)	Water uptake (wt %)	Ion exchange capacity (mmol/g)	Ionic conductivity (Ω^{-1} cm^{-1})
7	15	0.7	9.2×10^{-4}
24	40	1.8	3.9×10^{-2}
42	61	2.4	4.4×10^{-2}
60	74	2.8	4.9×10^{-2}

Grafting of polystyrene onto PE films and its subsequent sulfonation were confirmed by FTIR spectral analysis. Typical FTIR spectra of the membrane (60% degree of grafting) and its corresponding grafted and original PE films are shown in Figure 3. Compared to original PE film (Figure 3A), the spectrum of the polystyrene grafted PE (PE-*g*-PS) films (Figure 3C), contains additional peaks representing benzene ring features at 3050 cm^{-1}, 1500 cm^{-1} and 1600 cm^{-1}. The presence of aromatic out-of-plane C-H deformation band at 860 cm^{-1} and C–H bending overtone and combination bands in the region of 1660–2000 cm^{-1} is due to mono-substitution of benzene ring. The size of the characteristic peaks of benzene ring increases with the increase in the degree of grafting as clearly seen from the spectra of 7% of PE-*g*-PS film (Figure 3B) when compared to that of 60% one (Figure 3C). The sulfonated membrane (PE-*g*-PSSA) (Figure 3D) was characterized by the emergence of three new sharp bands at 1126, 1034, and 1007 cm^{-1} representing SO_3^- groups. The broad band at 3200–3600 is due to the OH groups of water molecules strongly bound to SO_3^- groups by hydrogen bonding. These results confirm that grafting and subsequent sulfonation permanently modified the chemical structure of the PE matrix by introducing sulfonated polystyrene grafts and the final membranes have a strong hydrophilic nature.

To have a preliminary idea on the structural changes that took place in the PE film upon grafting and subsequent sulfonation, XRD qualitative analysis was conducted on PE-*g*-PS film and PE-*g*-PSSA membrane, both of which posses the same degree of grafting. Original PE film was used as a reference. Figure 4 shows typical X-ray diffraction patterns of original PE film and 60% grafted PE-*g*-PS film and its counterpart PE-*g*-PSSA membrane. The diffractogram of the original PE film (A) shows a typical morphology of semicrystalline polymer where two regions representing the crystalline (strong peaks) and the amorphous (flat peaks) fractions, can be recognized. Grafting is found to reduce the degree of crystallinity and so does the sulfonation

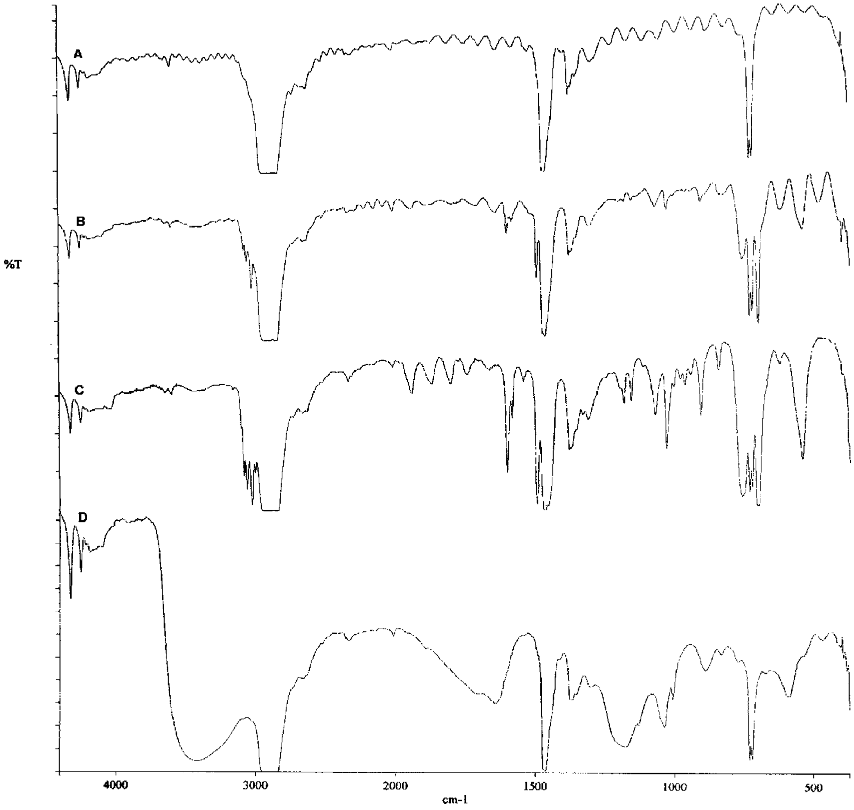

FIGURE 3 FTIR spectra of (A) original PE film; (B) 7% grafted PE-*g*-PS film; (C) 60% grafted PE-g-PS film and (D) 60% grafted PE-*g*-PSSA membrane.

as indicated by the reduction of the relevant crystallinity peak size shown in diffractogams B and C, respectively. However, the diffraction angle (2θ) records no remarkable shift indicating the absence of any significant changes in the crystalline structure of the PE films and no new phase formed during grafting and subsequent sulfonation. These results suggest that both grafting and sulfonation affected the crystalline structure of the PE films by a dilution effect and polystyrene grafting took place in the entire amorphous region without penetrating the crystallites.

To further elucidate the effect of variation of the degree of grafting on the crystallinity of the membranes, XRD measurements were also conducted on membrane samples having various degrees of grafting. Figure 5 shows typical X-ray diffractograms of PE-*g*-PSSA membranes

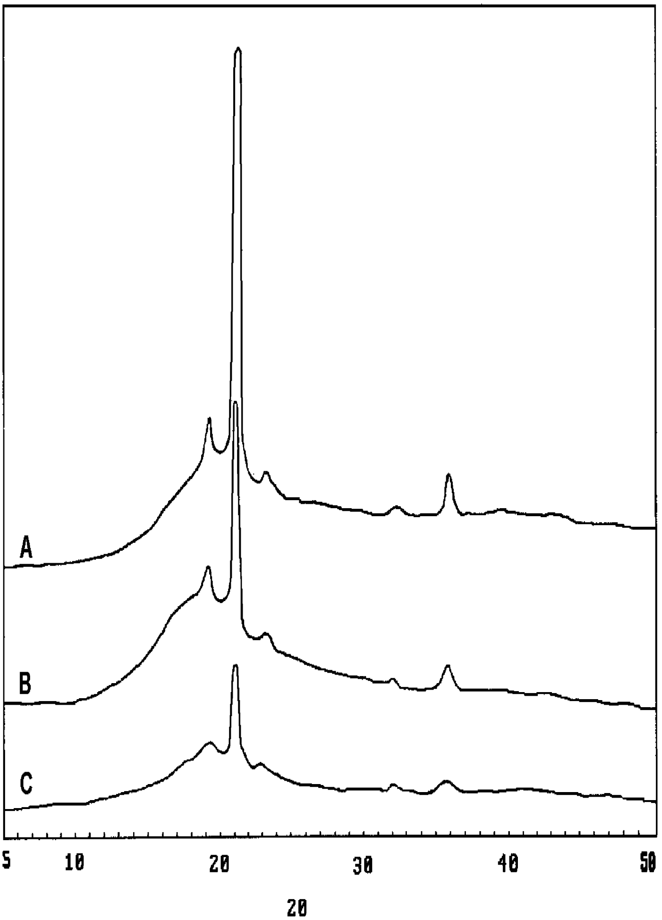

FIGURE 4 X-ray diffractograms of: (A) original PE film; (B) 60% grafted PE-*g*-PS film and (C) 60% grafted PE-*g*-PSSA membrane.

having various degrees of grafting. It is obvious that the peak intensity decreases with the increase in the degree of grafting indicating that the reduction in the degree of crystallinity is a function of the degree of grafting. Also, there is no remarkable shift in Bragg's angle (2θ). These results indicate that the reduction in the crystallinity of the membranes is mainly due to the dilution of the crystalline structure with the amorphous polystyrene grafts, which increase gradually with the degree of grafting. Nevertheless, XRD qualitative analysis alone does not provide any decisive information on the structural changes that took place in the membranes prepared in this work.

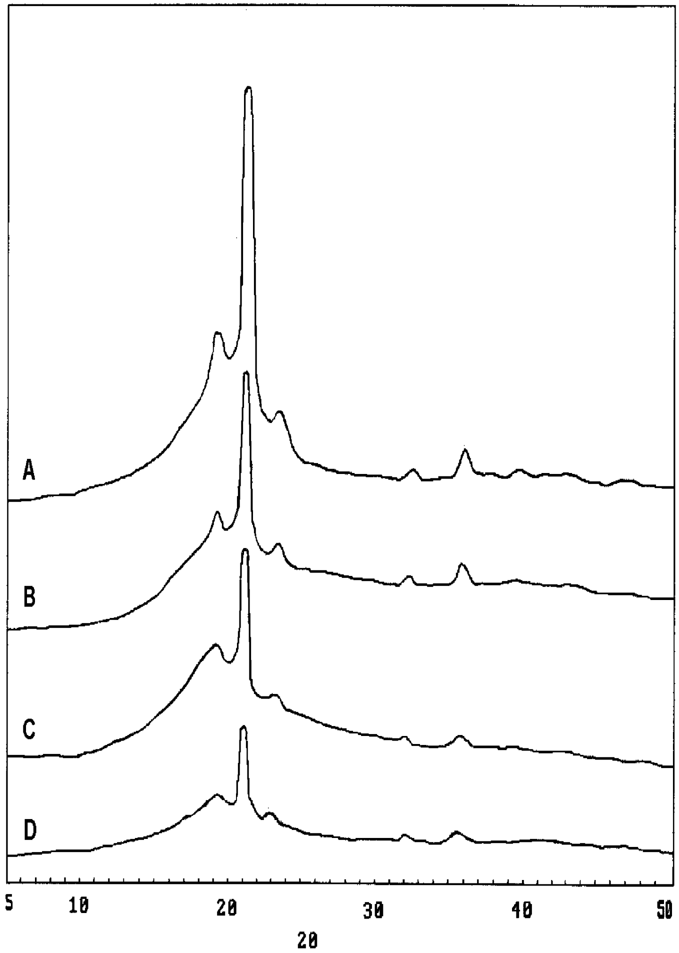

FIGURE 5 X-ray diffractograms of PE-*g*-PSSA membranes having various degrees of grafting: (A) 7%; (B) 24%; (C) 42% and (D) 60%.

Thus, further exploration on the nature of the structural changes in the membranes and quantitative analysis including crystallinity calculations are sought. Calculation of the degree of crystallinity in the polymer is important because crysallinity affects most of the physical properties. To achieve this, DSC measurements were conducted on samples similar to those used for XRD measurements and the analysis included the determination of the thermal properties, that is, melting temperature and heat of melting in correlation with preparation procedure and the variation of the degree of grafting.

Figure 6 shows DSC thermograms of the original (pre-grafted) PE film and 60% PE-*g*-PS film and 60% grafted PE-*g*-PSSA membrane. As can be seen, the original PE film shows a single melting endothermal peak at 107.0°C. The shape of this peak remains unchanged after grafting and subsequent sulfonation despite the reduction in its area, which seems to be highly dependent on sulfonation as depicted in Figure 6 (A–C). Moreover, the melting temperature (T_m) of PE-*g*-PS film was not affected by grafting and remained at 107.0° C unlike that of PE-*g*-PSSA membrane, which was marginally decreased to 106.2° C. In addition, the heat of melting (ΔH_m) obtained from the area under the melting peaks and the calculated degree of crystallinity obtained from Eq. 2 were reduced by grafting and the subsequent sulfonation. For instance, ΔH_m was reduced from 63.2 to 32.8 J/g by grafting (60% polystyrene) and to 6.1 J/g by sulfonation whereas, the degree of crystallinity of the same samples decreased from 21.8 to 11.3 and 2.3, by grafting and the followed sulfonation, respectively.

The decrease in the ΔH_m and the degree of crystallinity by grafting can be explained based on the fact that grafting reaction was carried out at a temperature of 30°C, which is far below the T_m of low density PE film that has a very low swelling tendency hindering the diffusion of most of the monomers at room temperature according to Ishigaki et al. [7] and Gupta and Chapiro [10]. Consequently, it can be suggested that styrene diffuses only through the amorphous part of the PE

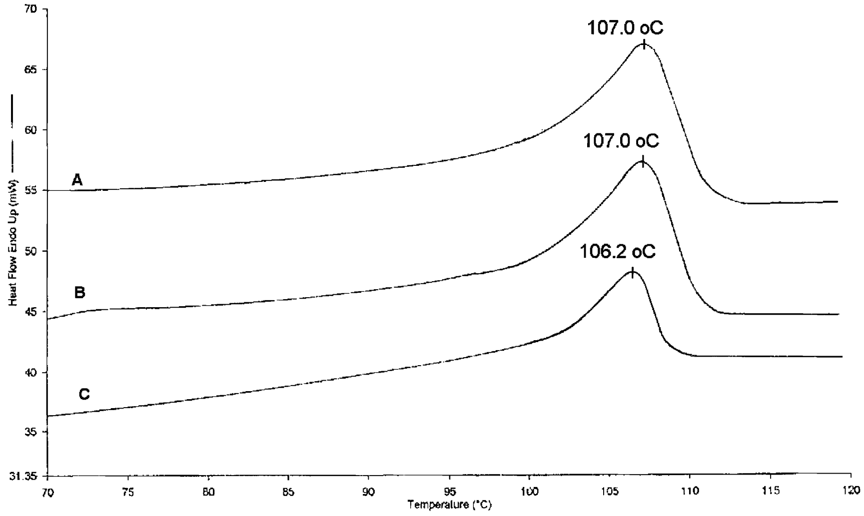

FIGURE 6 DSC thermograms of: (A) original PE film; (B) 60% grafted PE-*g*-PS film and (C) 60% grafted PE-*g*-PSSA membrane.

matrix causing no swelling to the crystallites and forms polystyrene grafts in the entire amorphous region and at the surface of the crystallites despite the presence of the radicals in both crystalline and amorphous regions. This leads to a remarkable increase in the amorphous content, which exerts a dilution effect on the crystalline structure of the film without any significant disruption in the inherent crystallites of PE matrix. This explanation is supported by the absence of any variation in the T_m upon grafting, indicating the original crystal size distribution in PE film has not been affected. It is also in accordance with the fact that grafting of styrene diluted with 1,2-dichloromethane in the present system is a diffusion-controlled process whereby grafting proceeds by front mechanism [21]. Similar results were reported for grafting of styrene onto poly(vinylidene fluoride) (PVDF) films upon preparing similar ion exchange membranes using gamma rays [24].

The reduction in the ΔH_m and the degree of crystallinity with sulfonation, which was accompanied by a marginal reduction in the T_m, reflects the existence of not only an additional dilution effect but also a partial disruption in the crystallites of the PE matrix. The additional dilution is believed to be due to the increase in the amorphous fraction by the incorporation of sulfonic acid groups. The partial disruption may be attributed to the penetration of the crystallites by some grafts under the influence of the aggressiveness of sulfonation process and the hydrophilic/hydrophobic stress at grafts-lamellae interface. The latter is a result of the strongly hydrophilic nature of sulfonic acid groups, which prompts it where grafts are attached to the surface of the lamellae causing some of polystyrene grafts to split off and partial disruption occurs in the crystallites when the membrane swells. It can be concluded that the cumulative effect of the dilution of the crystalline structure with the amorphous polystyrene and the crystal partial disruption caused by the possible penetration of some grafts during sulfonation and the rupture in the crystallites during the hydration account for the changes in the heat of melting and the degree of crystallinity of the PE-*g*-PSSA membrane. Chlorosulfonation of PE films reported by Zevin and Messalem [25] and Konishi et al. [26] showed similar results. The disruptions in the crystallinity taking place in PE matrix under the current membranes preparation procedure are also similar to those reported for poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [27], (PVDF) [28], and poly(tetrafluoroethylene) (PTFE) [29] film when they were radiochemically grafted with polystyrene and subsequently sulfonated using chlorosulfonic acid. Such similarity in the structural-induced changes is most likely due to the similarity in the mechanism by which grafting proceeds in these films despite the differences in their nature and structure.

To discriminate the role of the dilution effect from that of the crystal disruption during the structural changes taking place upon grafting and sulfonation, DSC measurements were conducted on grafted films (PE-*g*-PS) with various degrees of grafting and their respective sulfonated membranes (PE-*g*-PSSA). Figures 7 and 8, respectively, show typical DSC thermograms of PE-*g*-PS films having various degrees of grafting and their corresponding PE-*g*-PSSA membranes. The melting peaks shape of PE-*g*-PS films remains almost similar, with the area under each peak decreasing with the increase in the degree of grafting, as shown in Figure 7. This coincides with the absence of any change in the T_m reflecting no changes in the crystal size. These results confirm that the polystyrene grafts are introduced to the noncrystalline regions of the PE matrix and the amorphous fraction increases with the increase in the degree of grafting.

Like PE-*g*-PS films, all the melting endotherms of PE-*g*-PSSA membranes (Fig. 8) show peaks of similar shape despite the differences in the beginning of each peak, whereas the area under them steeply decreases in an inverse relationship to the degree of grafting. This was coupled by a tiny down shift in the T_m of the membranes with the increase in the degree of grafting. This decreasing trend can be clearly seen in Figure 9 in which T_m of the membranes was plotted

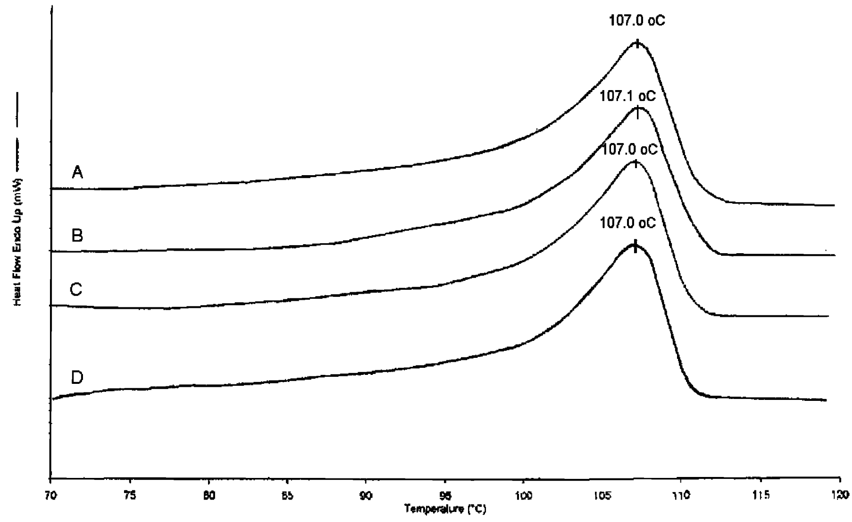

FIGURE 7 DSC thermograms of PE-*g*-PS films having degrees of grafting of (A) 7%; (B) 24%; (C) 42% and (D) 60%.

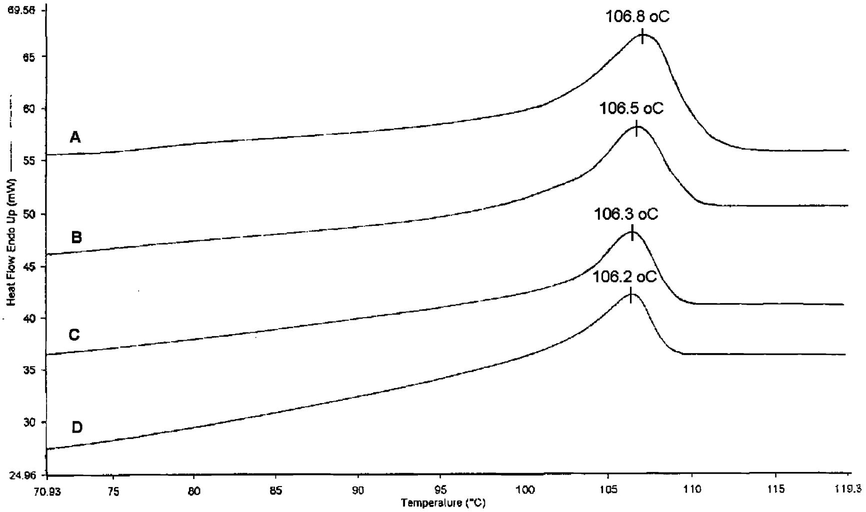

FIGURE 8 DSC thermograms of PE-*g*-PSSA membranes having degrees of grafting of (A) 7%; (B) 24%; (C) 42% and (D) 60%.

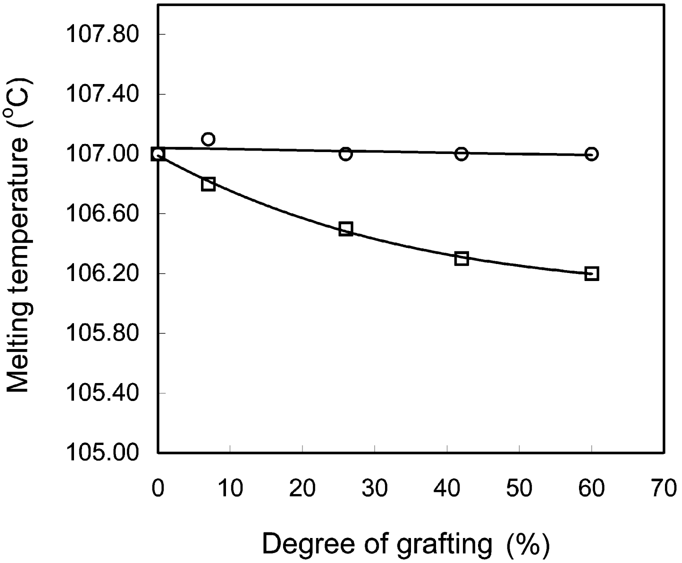

FIGURE 9 The relationship between the melting temperature (T_m) and the degree of grafting for (○) PE-g-PS films and (□) PE-*g*-PSSA membranes.

against the degree of grafting. The straight line is representing the T_m of PE-*g*-PS films. The slight reduction in T_m with the increase in the degree of grafting is caused by some disorder in the crystalline structure (reduction in the crystal size) mostly arising from the disruption in the crystallites by the incorporation of sulfonic acid groups in the membranes. The reduction in the crystal size increases with the increase in the degree of grafting due to the introduction of more sulfonic acid groups.

The changes in the peak areas of both grafted films and final membranes were also reflected in a form of a continuous decrease in the ΔH_m with the increase in the degree of grafting as depicted from correlations presented in Figure 10. However, the decreasing trend of ΔH_m in the grafted film is linear and that in membranes is nonlinear. The former confirms that the incorporated polystyrene exerts only dilution effect on the crystalline structure of PE films at all grafting levels and the variation in the heat of melting is a function of the fraction of PE matrix in the grafted films, whereas, the latter confirms

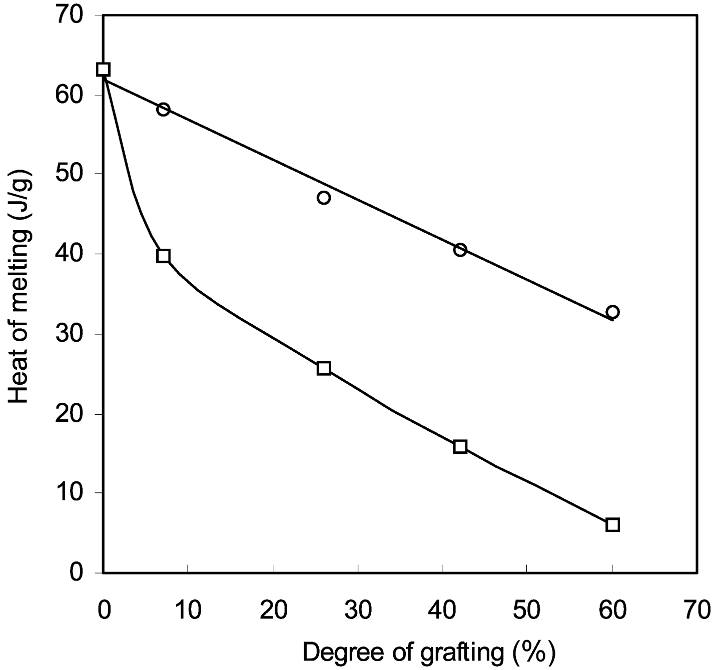

FIGURE 10 The variation of the heat of melting (ΔH_m) with the degree of grafting for (○) PE-*g*-PS films and (□) PE-*g*-PSSA membranes.

that the dilution effect is not the only factor affecting the crystalline structure but also, the partial disruption taking place in the crystallites as a result of introducing sulfonic acid groups, which increases with the increase in the sulfonic acid content. It can be stated that both dilution and partial disruption affect the heat of melting of the membranes simultaneously but in an independent manner.

The variation in the degree of crystallinity of the membranes with the degree of grafting compared to that of the grafted films is shown in Figure 11. All the grafted films and the membranes show continuous decrease in the degree of crystallinity, which is linear in PE-*g*-PS films and nonlinear in PE-*g*-PSSA membranes. This behavior is in line with the recorded variation in the ΔH_m and can be attributed to the dilution effect in case of PE-*g*-PS films and to the cumulative effect of the dilution and the partial disruption in the inherent crystallinity of PE-*g*-PSSA membranes. The conclusion that can be drawn is that despite the changes in the structural and the thermal properties of PE-*g*-PSSA membranes with the variation of the content of polystyrene sulfonic acid, their crystallinity remains confined to the PE fraction. The DSC analysis results explain the part of the structural behavior that could not be seen by XRD qualitative analysis in which the

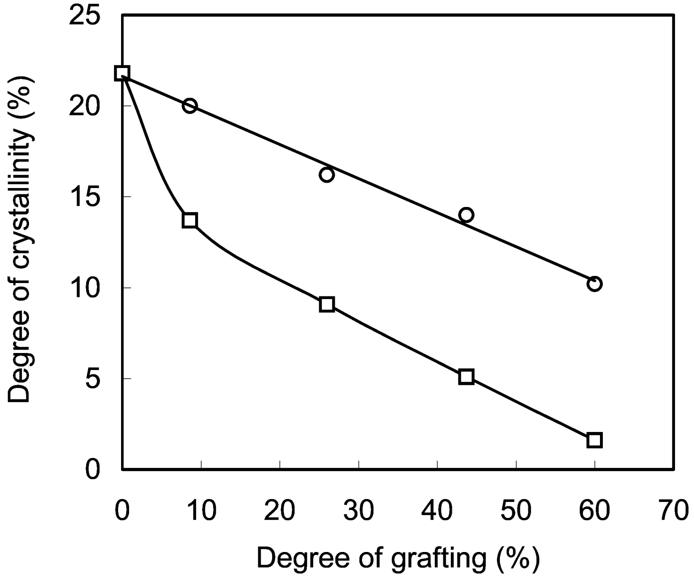

FIGURE 11 The variation of the degree of crystallinity with the degree of grafting for (○) PE-*g*-PS films and (□) PE-*g*-PSSA membranes.

intensity of the crystalline reflection peaks were found to decrease with the increase in the degree of grafting and was only attributed to dilution effect.

CONCLUSIONS

PE-*g*-PSSA membranes prepared by simultaneous radiation-induced grafting of styrene onto low-density polyethylene (PE) films followed by sulfonation were found to undergo structural changes under the effect of preparation procedure. Grafting was found to impose a dilution effect on the crystallinity by incorporating amorphous polystyrene entirely in noncrystalline region of PE matrix without causing any disruption in the crystalline structure as indicated by the absence of changes in T_m at all grafting levels. Sulfonation induces a combined dilution and partial disruption effects to the inherent crystallinity of PE films under the influence of crystalline penetration by some grafts and hydrophilic/hydrophobic stress at grafts-lamellae interface, which ruptures the crystallites upon hydration. The increase in the degree of grafting increases the content of sulfonic acid groups and consequently the degree of crystallinity decreases. The crystalline fraction in PE film represents the overall crystallinity of these membranes.

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