

XPS Studies of Radiation Grafted PTFE-g-polystyrene Sulfonic Acid Membranes

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ABSTRACT: Structural investigations of PTFE-g-polystyrene sulfonic acid membranes prepared by radiation grafting of styrene onto PTFE were conducted by X-ray photoelectron spectroscopy (XPS). The analyzed materials included original PTFE film as a reference material, grafted film, and sulfonated membrane samples having various degrees of grafting. Interest is focused on C1s, F1s, O1s, and S2p of narrow XPS spectra as the basic elemental components of the membrane. The original PTFE film was found to undergo structural changes in terms of chemical composition and shifting in binding energy induced by incorporation of sulfonated polystyrene grafts, and the amount of such changes depends on the degree of grafting. The atomic ratio of F/C was found to decrease with the increase in the degree of grafting, while that for S/C and O/C were found to increase. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 336–349, 2000

Key words: XPS studies; radiation grafted PTFE-g-polystyrene sulfonic acid membranes

INTRODUCTION

Cation exchange membranes have shown a potential to be used in various fields of separation science and technology.^{1,2} Particularly, perfluorinated sulfonic acid cation exchange membranes have been proposed for electrochemical applications such as fuel cells where higher current density is required. This is due to their sulfonic acid groups complete dissociation, better stability, and higher conductivity.³

Radiation-induced grafting offers an attractive method to prepare cation exchange membranes

through chemical modification of existing polymers already having the physical shape of the membranes.^{4,5} The reliability of this method relies on the ability to closely control the composition of the membrane by proper selection of grafting conditions.^{6,7}

Radiation-grafted sulfonic acid membranes have been prepared by grafting of styrene or its derivatives onto different base polymers.^{8–17} However, fluorocarbon polymers are commonly used as base polymers, owing to their excellent chemical inertness and mechanical integrity.¹⁸

Irradiation of the base polymers by the ionizing radiation generates free radical sites, which are capable of initiating polymerization reaction with styrene molecules to form polystyrene graft copolymers. The properties of the obtained membrane depend on the percentage of styrene grafted

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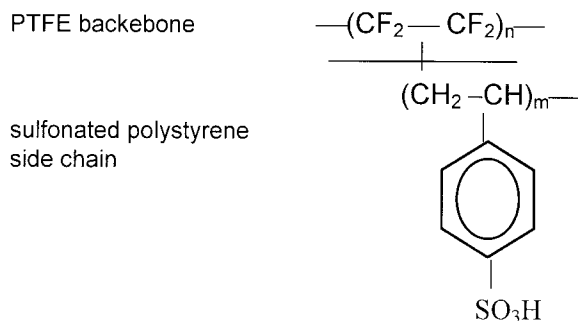


Figure 1 An idealized structure of the PTFE-*g*-poly(styrene sulfonic acid) membrane.

thereon (degree of grafting) when subsequently sulfonated.

X-ray photoelectron spectroscopy (XPS) offers a powerful technique to characterize the radiation grafted membranes. It allows quantitative determination of surface chemical composition and chemical bonding on the surface by measuring the chemical shift of the electron-binding energies of the surface elements. It also provides information about the surface chemical structure with a spatial resolution of a few millimeters in the system used and a depth resolution of about 5 nm, depending on the take-off angle.¹⁹

In our previous study, we prepared cation exchange membrane by grafting of styrene onto PTFE and subsequent sulfonation.²⁰ In the present work, we report the characterization of these membranes by XPS to monitor the structural changes enhanced by styrene grafting and subsequent sulfonation of PTFE film as well as variation of the degree of grafting of PTFE-*g*-polystyrene sulfonic acid membranes.

EXPERIMENTAL

Materials

PTFE film of 90 μm thickness (Porghof, USA) was used as a base polymer. Styrene of purity more than 99% (Fluka) was used as a grafting monomer without any further purification. Other chemicals were reagent grades, and used as received.

Graft Copolymerization

Graft copolymerization of PTFE was carried out using simultaneous irradiation technique. Clean and dried film was immersed into a known volume of monomer solution in a glass ampoule. The

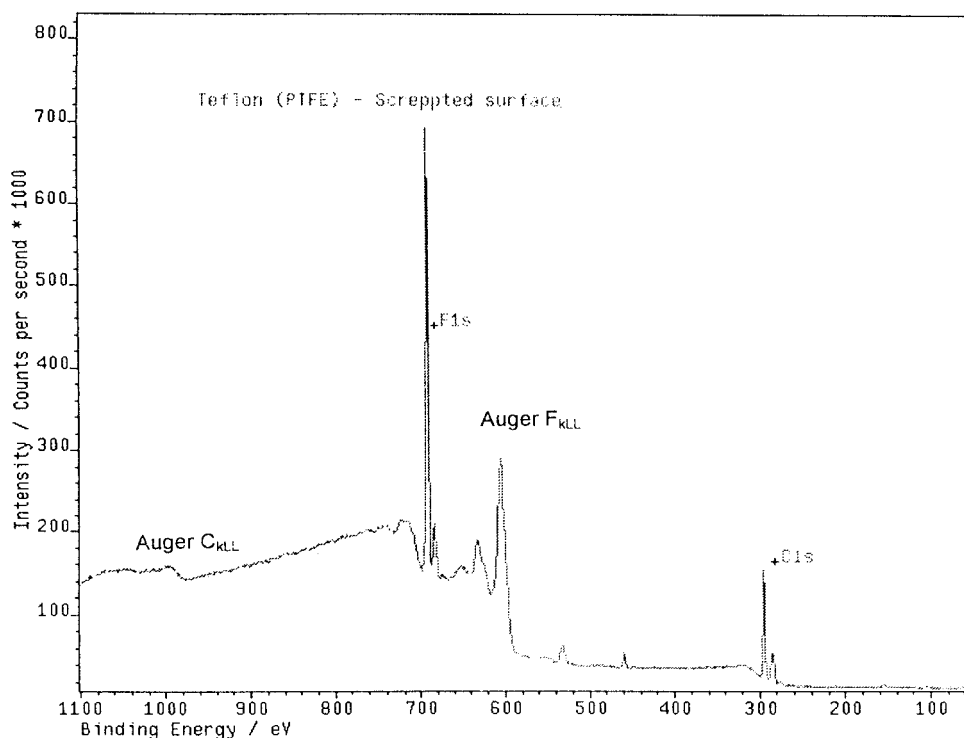


Figure 2 Survey-wide scan of ungrafted (original) PTFE film.

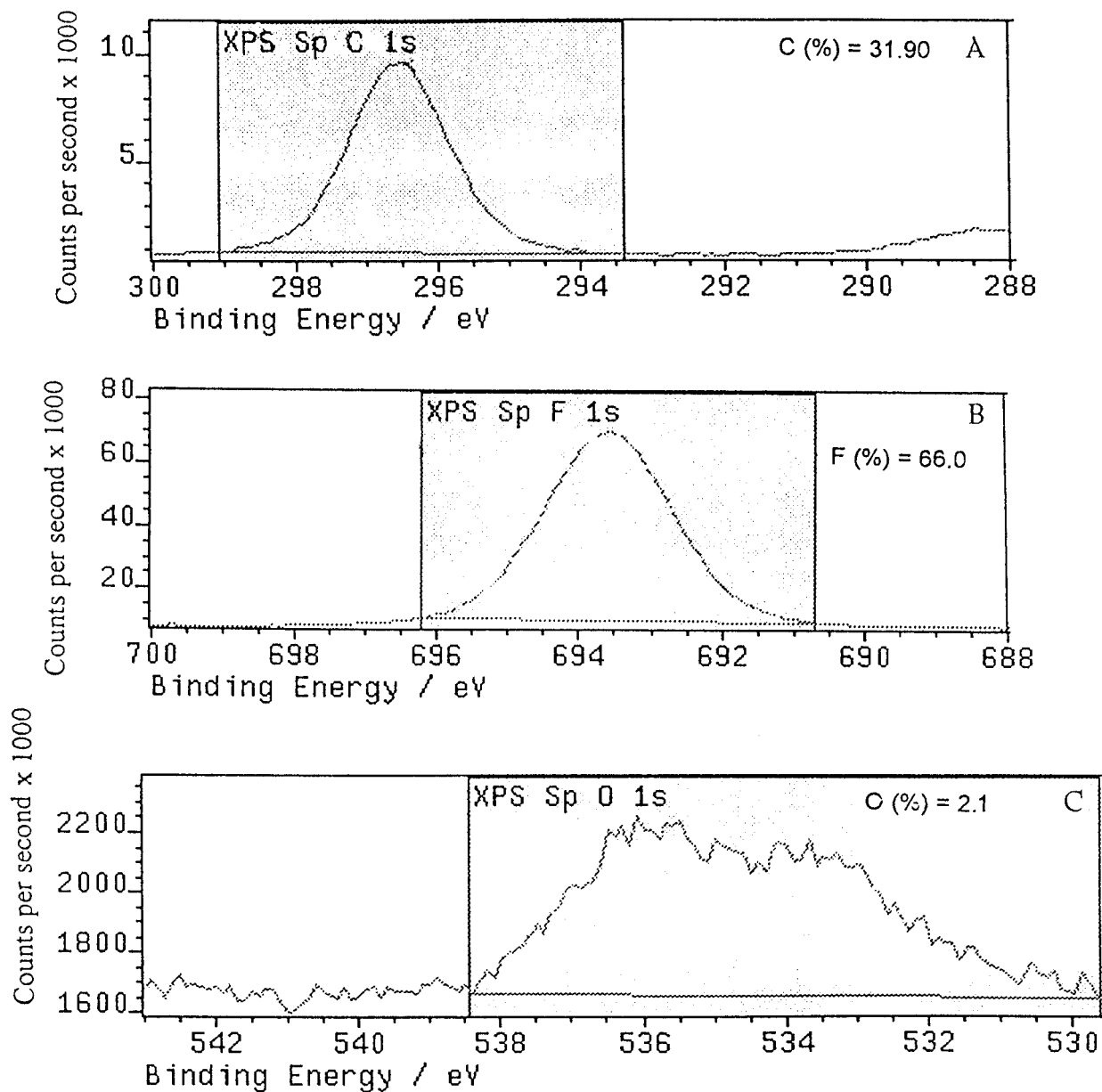


Figure 3 Spectra of a narrow scan of individual elements of ungrafted PTFE film: (A) C1s, (B) F1s, (C) O1s.

ampoule was flashed with nitrogen for 8 min to remove air, then sealed. The ampoule was subjected to γ -rays from ^{60}Co source. After irradiation, the film was washed with methyl benzene and soaked therein over night to remove the residual monomer and homopolymer occluded in the film. The grafted film was dried in the vacuum oven at 60°C until a constant weight was obtained. The degree of grafting was determined as per the following equation:

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

where, W_g and W_0 are the weights of grafted and original PTFE films, respectively.

Sulfonation

The grafted films were sulfonated by treating with chlorosulfonic acid in 1,1,2,2-tetrachloroethane mixture at 95°C for 5 h. After the reaction,

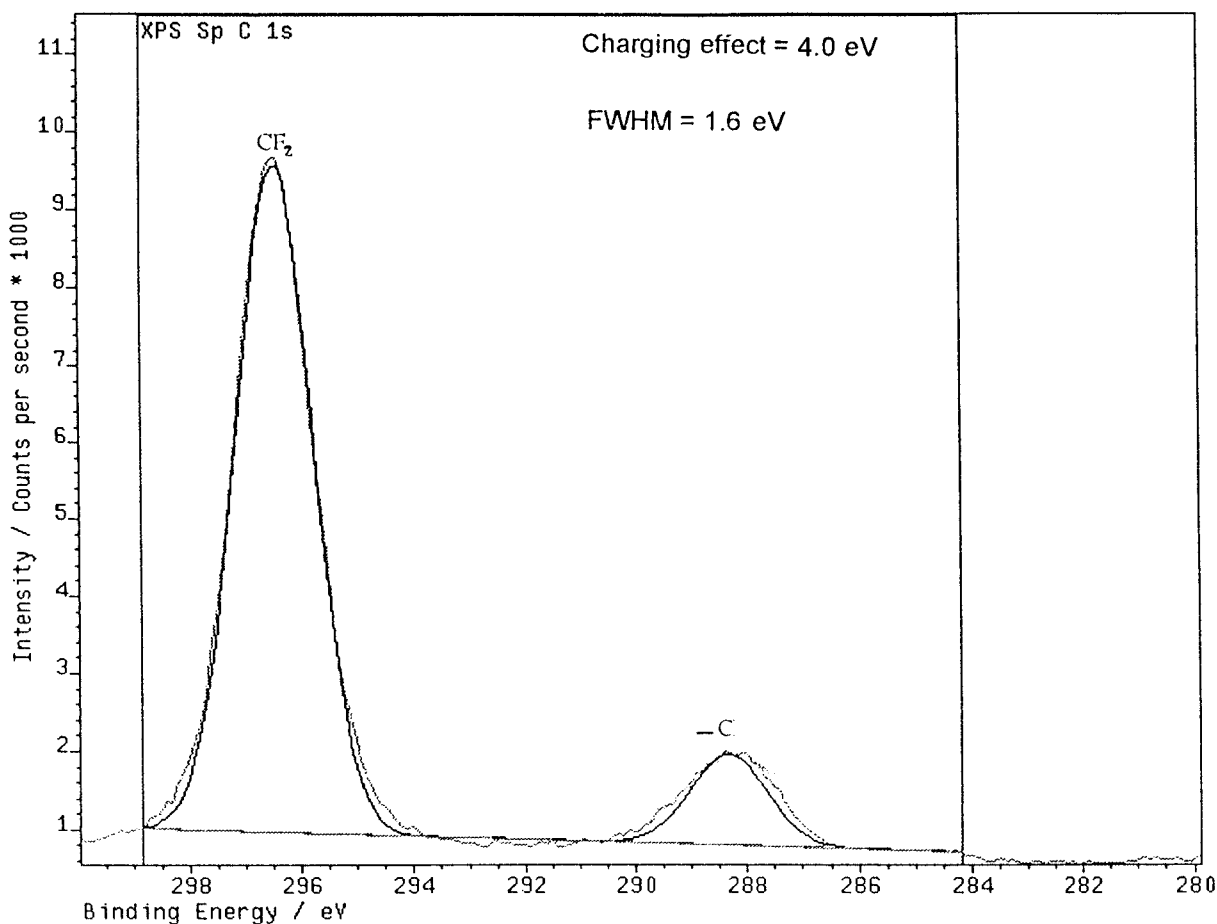


Figure 4 The narrow scan (core level spectrum) of C1s of ungrafted (original) PTFE film.

the sulfonated films were washed several times with carbon tetrachloride and dichloroethane, then dried in air. The sulfonated films were expanded to acid form by boiling in pure water for 2 h. Details of preparation procedures and characterization of the membrane will be published elsewhere.²⁰

XPS Measurements

XPS measurements were conducted on dry samples (original, grafted, and sulfonated membranes in acid form) using a Kratos XSAM-HS surface microanalyzer using an Mg K X-ray source (1253.600 eV) in a Fixed Analyzer Transmission (FAT) mode. Binding energies of the instrument were calibrated using a pure silver plate, and gives Ag $3d_{5/2}$ at 368.250 eV and Δ Ag = 6.000 eV. Low X-ray flux of the nonmonochromatized MgK

line normally operated at 10 mA and 12 kV, while the charge neutralizer was switched on to minimize the charging effect. The sample areas excited by the X-ray spot had a size of $240 \mu\text{m}^2$. The vacuum system was kept at 4.0×10^{-9} Torr. Wide scans were carried out in the range of 50 to 1150 eV, and recorded at a pass energy of 160 eV, with a step size of 1 eV and dwell time of a 0.1 s step. Narrow scans at higher resolution (at a pass energy of 20 eV with a step size of 0.050 eV and a dwell time of a 0.1 s step) were performed for the C1s, F1s, S2p, and O1s regions. Each element scanning was repeated five times to get reproducible results. Both surfaces of the samples were investigated to establish the symmetrical structure of each membrane. The Gaussian peak fitting parameter with a straight baseline was applied for peak analysis using Vision software supplied by Kratos.

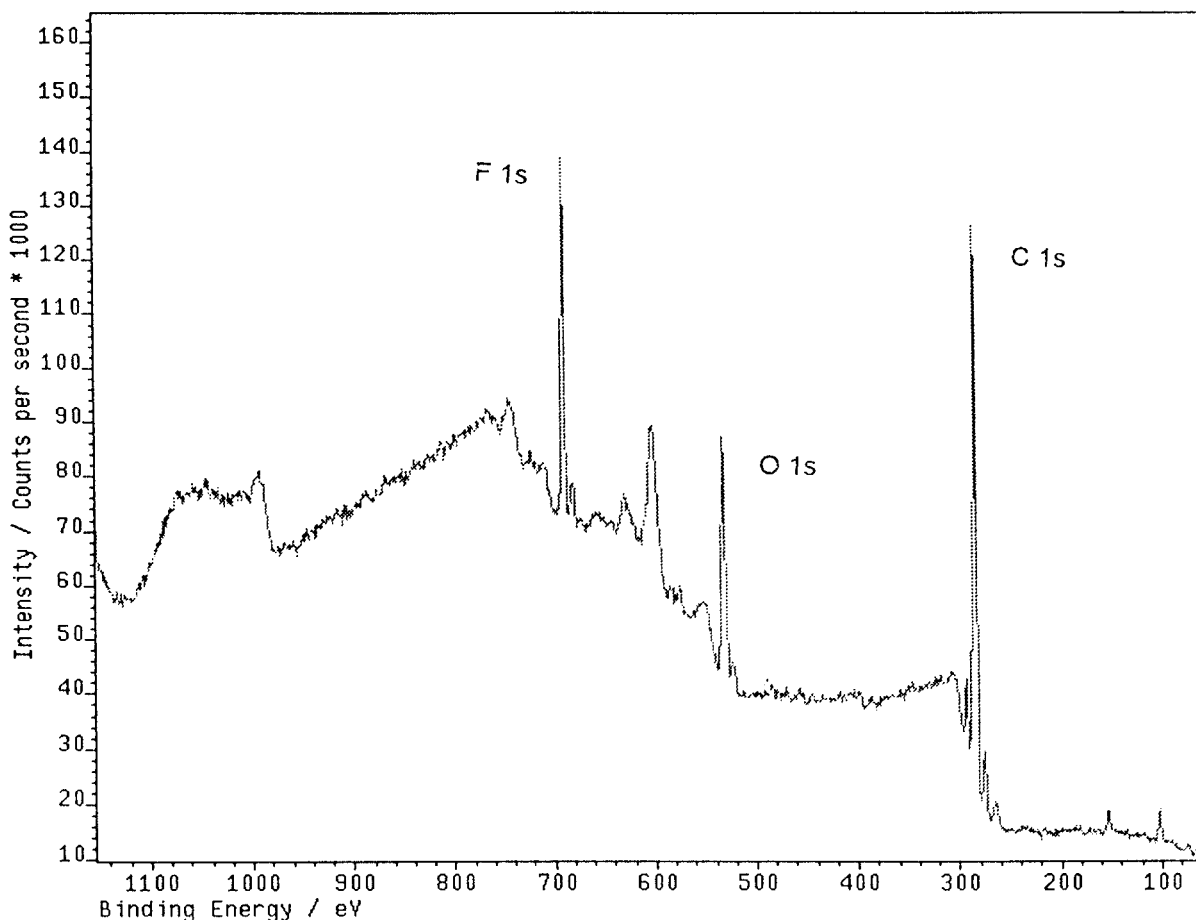


Figure 5 Survey-wide scan of PTFE-*g*-polystyrene film having a degree of grafting of 36%.

RESULTS AND DISCUSSION

Radiation grafting of styrene onto PTFE films and subsequent sulfonation of the grafted films resulted in PTFE-*g*-polystyrene sulfonic acid membranes having degrees of grafting ranging from 8–36%. An idealized structure of PTFE-*g*-polystyrene sulfonic acid membrane is given in Figure 1.

Surface Analysis of the Ungrafted Film

A survey-wide scan of ungrafted (original) PTFE film is shown in Figure 2, while the spectra of a narrow scan of individual elements are shown in Figure 3. Two major peaks can be observed clearly at 296.5 eV and at 693.6 eV, beside a very small peak at 536.1 eV (charging effect = 4.0 eV). The peak at 296.5 eV is assigned for C1s from CF,

while the peak at 693.6 eV is assigned for F1s. The shifts in the binding energy compared to the literature (284.5 eV for C—) are due to a combined effect between the chemical shift owing to the electron attraction towards fluorine atom, which equals 8.0 eV, and the charging effect, which is equal 4.0 eV.²¹ The very small peak at 536.1 eV indicates a detection of a small amount of oxygen in the film. This may be ascribed to the oxygen contamination during the polymer fabrication or to some physical/chemical interaction between the film surface with H₂O from the moisture or oxygen. From these results, it is evident that polymer film composed of carbon and fluorine and F/C ratio is found to be 2.10, which is in a good agreement with the theoretical value. The narrow scan (core level spectrum) of C1s is displayed in Figure 4. From the curve fitting, it can be clearly seen that the major peak at 296.5 eV is

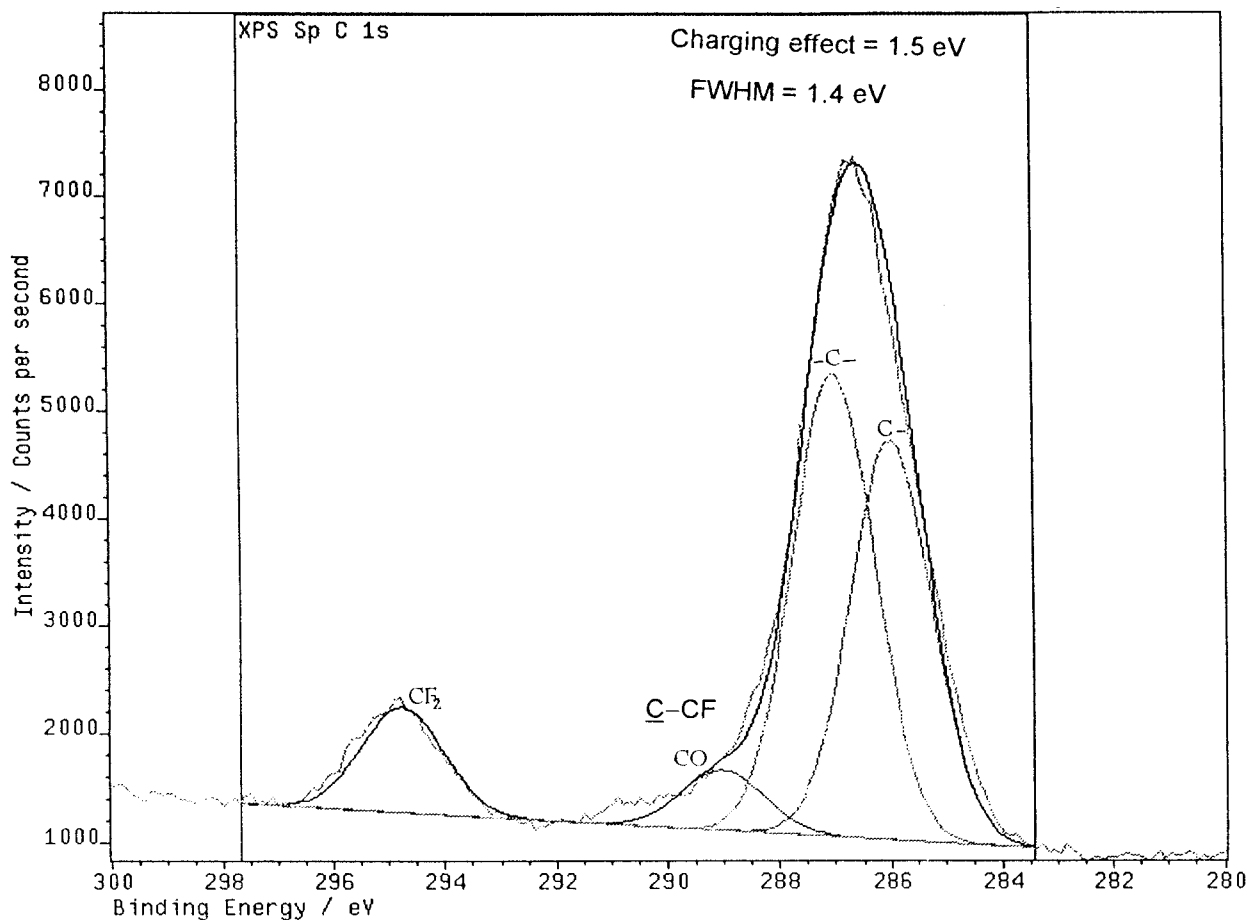


Figure 6 The narrow scan of spectrum and curve fitting of C1s of the 36% PTFE-*g*-polystyrene film.

deconvoluted into only one component peak referring to CF_2 , which constitutes the basic unit in the structure of PTFE film, whereas the minor peak at 288.5 eV is assigned for the adventitious carbon (C—).

Surface Analysis of the Grafted Film

Figure 5 shows a survey-wide scan of PTFE-*g*-polystyrene film having a degree of grafting of 36%. As can be seen, the intensity of C1s increases, while that of C1F decreases. The incorporation of polystyrene side-chain grafts enhances more rupture of —CF— bonds near the surface, and introduces hydrocarbon components in the form of aliphatic (— CH_2 —CH=) and aromatic (— C_6H_5) into the fluorinated structure of PTFE films. Consequently, a considerable increase in the intensity of C1s followed by a de-

crease in the intensity of a F1s peak takes place, and as a result, the F/C ratio falls sharply to 0.26. Meanwhile, a considerable amount of oxygen is detected in the grafted film, as can be seen from the intensity of the O1s peak. The introduction of oxygen is probably due to the reaction with the oxygen remaining in the grafting mixture during the grafting process or/and to the reaction with the atmospheric oxygen when exposed to air, leading to the formation of a carbonyl group.

Figure 6 shows the narrow scan of spectrum and curve fitting of C1s of the 36% PTFE-*g*-polystyrene film. The spectrum is deconvoluted into four component peaks having corrected binding energy of 293.3, 287.5, 285.5, and 284.5 eV representing CF_2 ; CO and C—CF; —C—; and C—, respectively. The emergence of the C—CF peak indicates that the styrene is already grafted onto the main chain of the PTFE film, which has a

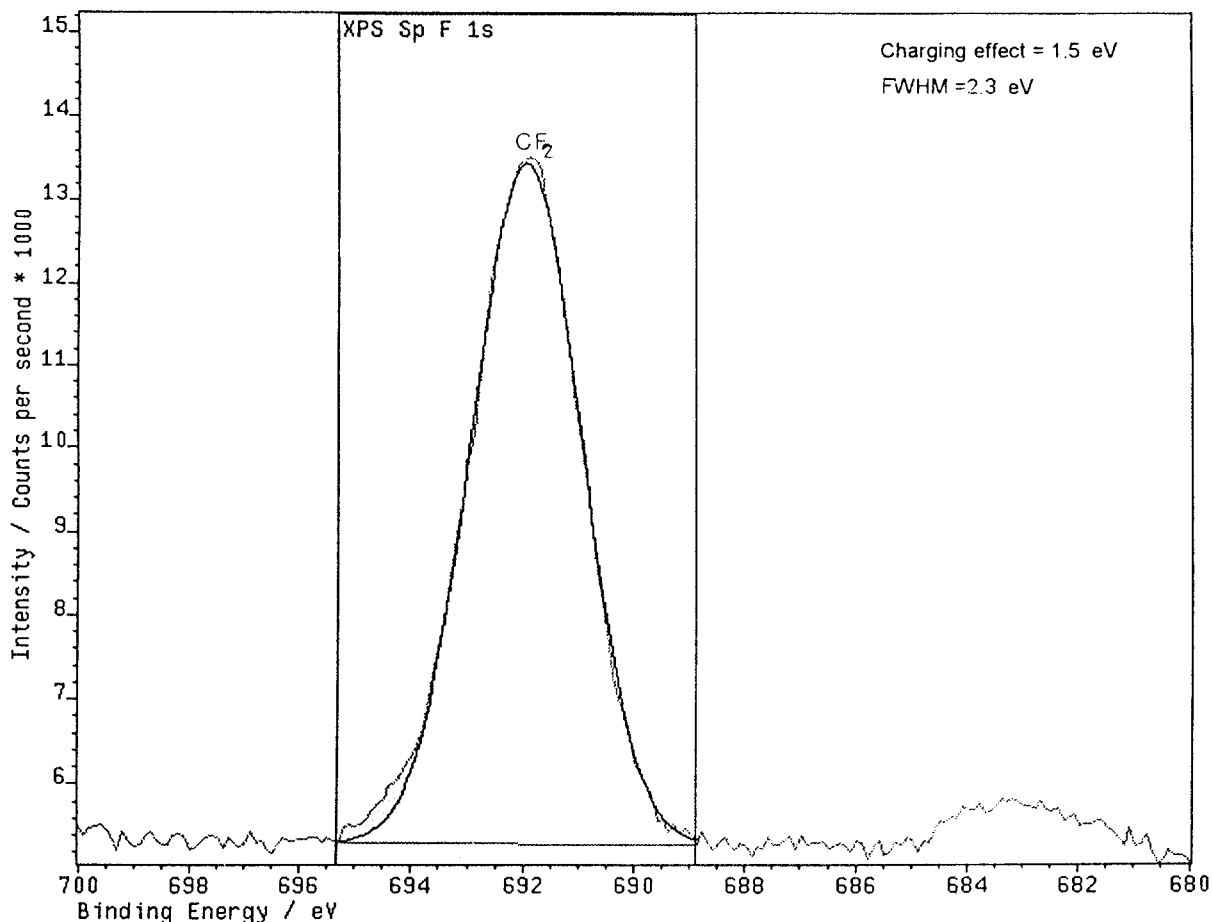


Figure 7 The narrow scan of spectrum and curve fitting of F1s of the 36% PTFE-g-polystyrene film.

—(CF₂—CF₂)_n structure by the replacement of a fluorine atom. The difficulty in the specific determination of —C— and C— of aliphatic (—CH₂—CH=) and aromatic —(C₆H₅) of the polystyrene incorporated in the grafted film is due to the minor chemical shifts in these carbon atoms.^{22,23} From the comparison of the peak intensities, it can be also seen that the contribution of —C— is higher than that of C—, while the contribution of the CO and C—CF groups is low compared to both of them.

Figure 7 shows the narrow scan of spectrum of F1s of the 36% PTFE-g-polystyrene film. As can be seen, the spectrum is deconvoluted to only one peak at 692.0 eV (charging effect = 2.1 eV), which is characteristic for the CF₂ group contained in the grafted film. It can be noticed that no shift in the binding energy of F1s occurs as a result of the styrene grafting. However, a decrease in the peak

intensity takes place, indicating that the fluorine content is reduced as a result of grafting.

From the aforementioned results, it is evident that the grafting of styrene onto PTFE films induces considerable changes into the surface structure of the PTFE film. Such changes can be monitored not only by the incorporation of a hydrocarbon component and the reduction of the F/C ratio in the film, but also by the shifting in the binding energy of the CF₂ group as well.

Surface Analysis of the Sulfonated Membrane

Figure 8 shows a survey-wide scan of a PTFE-g-polystyrene sulfonic acid membrane having a degree of grafting of 36%. It can be seen that, compared to the spectrum of the PTFE-g-polystyrene film, one additional peak appears at 168.220 eV (corrected), which can be assigned for S2p. More-

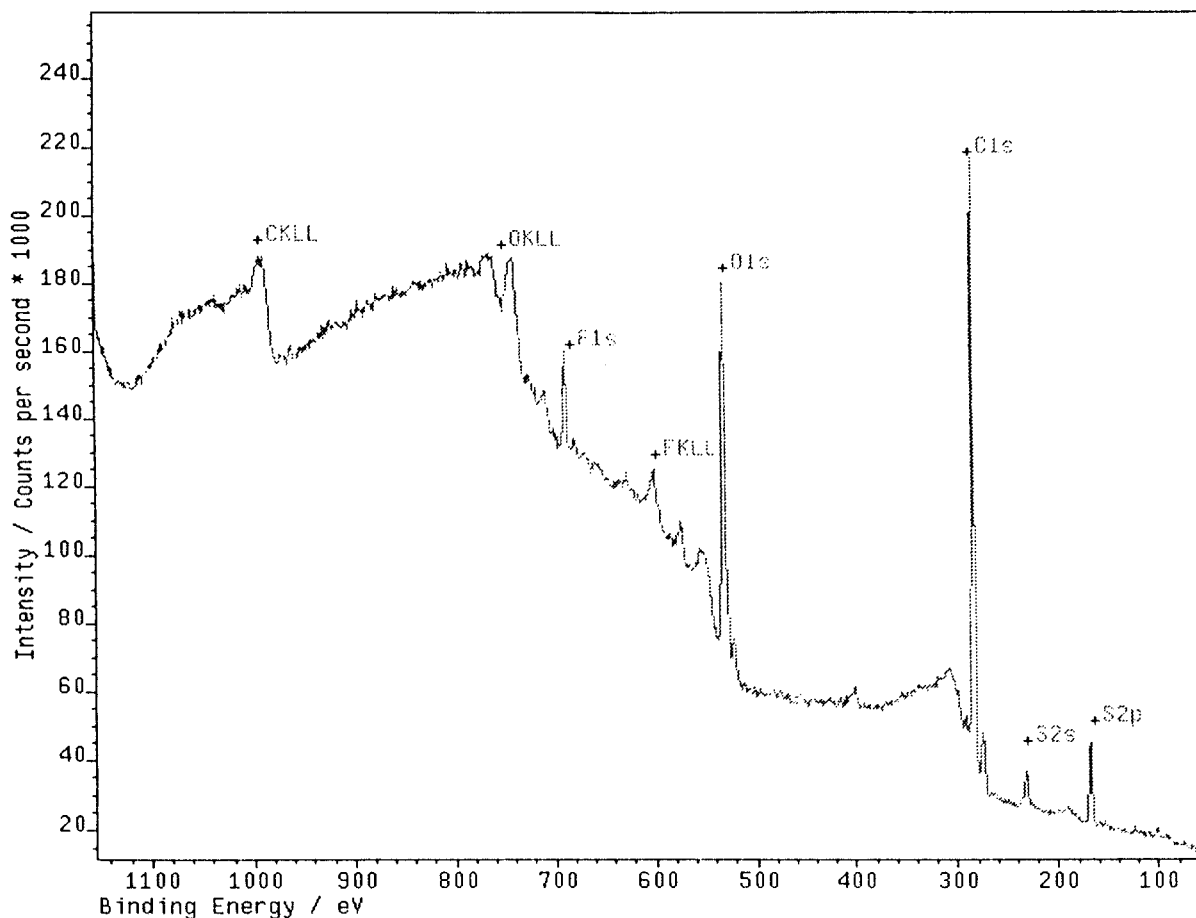


Figure 8 Survey wide scan of PTFE-g-polystyrene sulfonic acid membrane having a degree of grafting of 36%.

over, the peak intensity of O1s at 531.520 eV (corrected) increases, while that of the F1s at 692.600 eV (corrected) remarkably decreases and the F/C ratio becomes as low as 0.066. This is ascribed to the introduction of SO_3^- groups to the polystyrene side chains, which covers more CF_2 groups of the main chain located near the surface of the film, and leads to an increase in the peak intensity of O1s, beside the appearance of a new S2p peak.

Figure 9 shows the narrow scan and curve fitting of C1s of the spectrum of the 36% PTFE-g-polystyrene sulfonic acid membrane. As can be seen, the deconvoluted of the spectrum shows five peaks at 292.1, 287.5, 286.5, 285.2, and 284.5 eV (corrected). These peaks are assigned for CF_2 ; C—S; CO; C—CF; —C—; and C—, respectively. The appearance of one extra peak at 287.5 eV (corrected) compared to the spectrum of PTFE-g-polystyrene film representing C—S shows evi-

dence of the presence of a SO_3^- group introduced by sulfonation of a benzene ring of the polystyrene grafts.

It can also be observed that sulfonation of the grafted film brought very slight shifts to the binding energy of the predominant peak of $\text{C1s}_{(\text{C}-\text{H})}$ at 284.5 (corrected) and to the weak peak for $\text{C1s}_{(\text{C}-\text{F})}$ at 292.1 eV (corrected). Despite such a chemical shift, the separation of these two peaks by 7.6 eV remains in a good agreement with the difference in binding energy between CF_2 in PTFE and CH_2 in LDPE reported in the literature.²¹

A similar investigation was carried out earlier by Scherer et al.²³ on Permion 4010, a commercial cation exchange membrane during a series of investigations prior to testing of such membranes in a water electrolyzer. These membranes were reported to be prepared by radiation grafting of styrene onto PTFE followed by sulfonation.²⁴

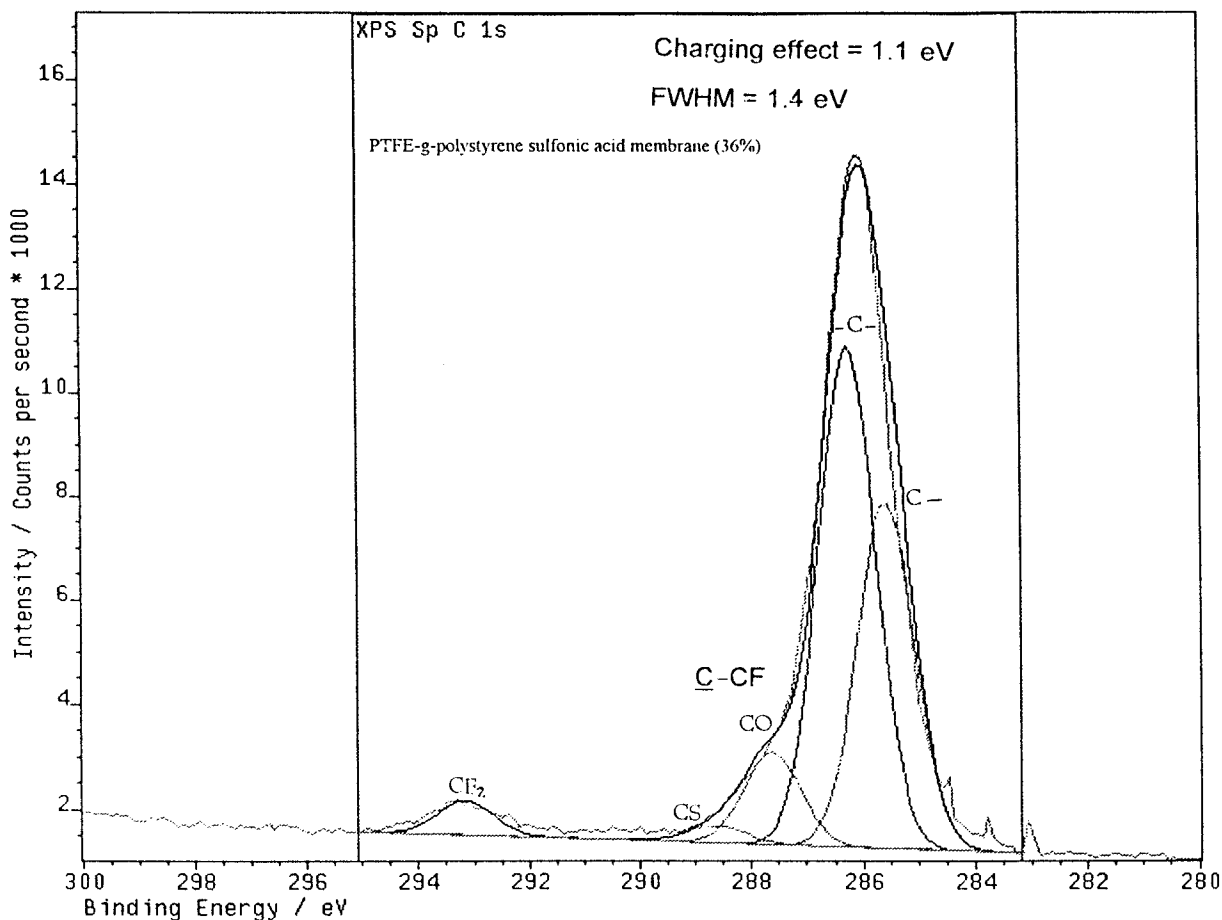


Figure 9 The narrow scan and curve fitting of C1s of the spectrum of the 36% PTFE-g-polystyrene sulfonic acid membrane.

Therefore, they have a typical structure (PTFE-g-polystyrene sulfonic acid) as that of the membranes investigated in this study. It was found that the separation between the predominant peak of C1s_(H) at 285.4 eV and the weak peak for C1s_(F) at 292.6 eV due to the chemical shift is 7.2 eV.

The curve fitting of the spectrum of F1s of the 36% PTFE-g-polystyrene sulfonic acid membrane is shown in Figure 10. As can be seen, the spectrum is deconvoluted to only one peak at 688.7 eV, which is characteristic for the CF₂ group contained in the membrane. It obviously can be seen that there is no shift in binding energy compare to that of the grafted film, due to sulfonation. However, the peak intensity is getting smaller, indicating that the fluorine content is further reduced by sulfonation.

Figure 11 shows the curve fitting of the S2p spectrum of a 36% PTFE-g-polystyrene sulfonic

acid membrane. The spectrum is deconvoluted into four peaks at 170.0, 171.1, 169.2, and 170.3 eV (charging effect = 1.9). The major two peaks at 170.0 and 171.2 eV are characteristic to 2p_{3/2} and 2p_{1/2} of the sulfur contained in the —SO₃⁻ group, which has a binding energy of 167.0 eV(±) as reported in Moulder.²² The minor peaks at 169.2 and 170.3 eV can be assigned for 2p_{3/2} and 2p_{1/2} of the sulfur contained in —SO₂, which is associated with the sulfonic acid groups. The calculated percentage of —SO₃⁻ is found equal to 86%.

Figure 12 shows the curve fitting of spectrum of O1s of a 36% PTFE-g-polystyrene sulfonic acid membrane. The spectrum is deconvoluted into three peaks at 533.4, 535.6, and 530.7 eV (charging effect = 1.9 eV). The major peak, which has a corrected value of 530.5 eV, is characteristic of the oxygen present in the —SO₃⁻ group, while minor peaks having corrected values at 533.0 and 528.8

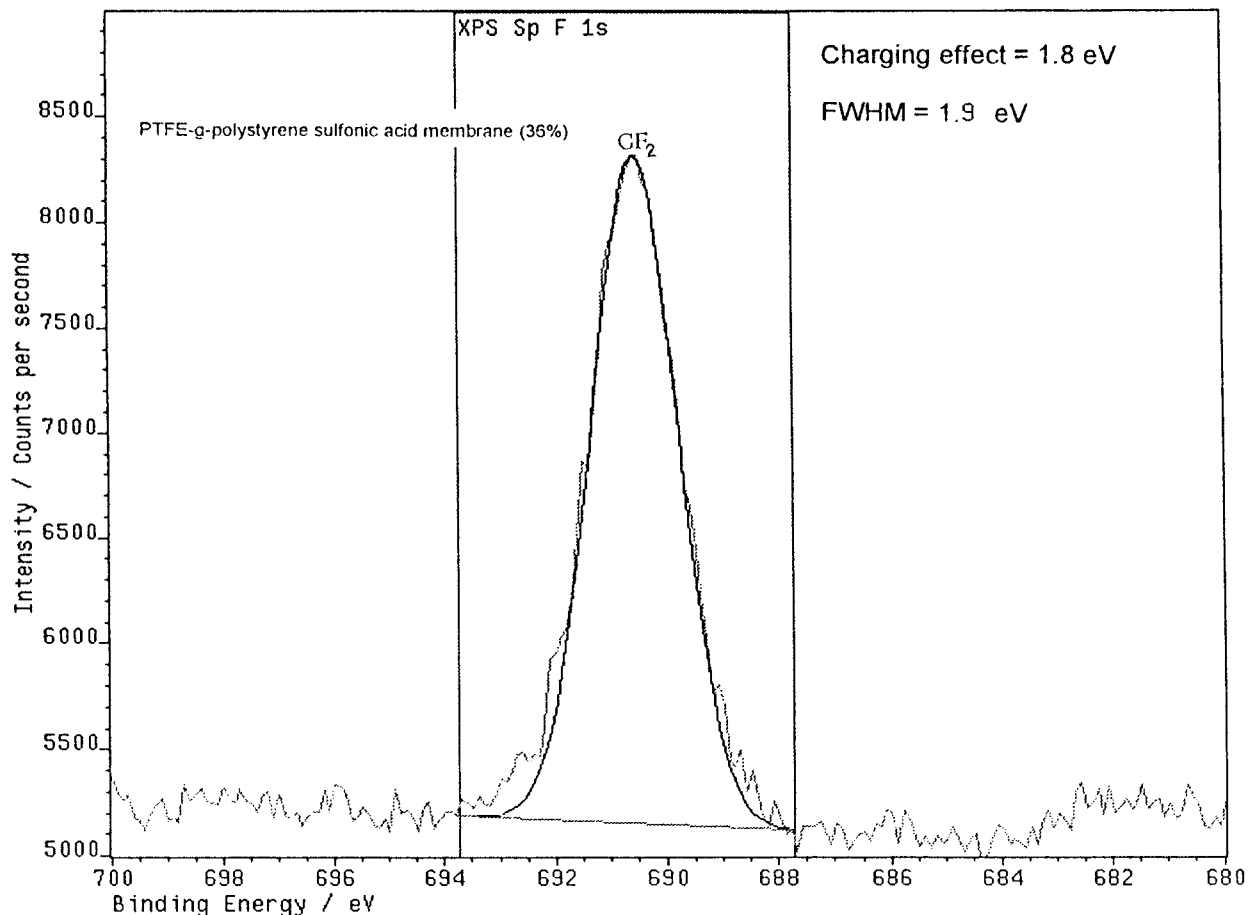


Figure 10 The narrow scan and curve fitting of spectrum of F1s of 36% PTFE-*g*-polystyrene sulfonic acid membrane.

eV can be assigned for the H_2O and $-\text{SO}_2^-$ groups, respectively. It can be concluded that sulfonation of the grafted polystyrene film brings more structural changes into the layer close to the surface in terms of chemical composition as well as binding energy.

Surface Analysis Sulfonated Membranes of Various Degrees of Grafting

Figure 13 shows the wide-scan spectra of a PTFE-*g*-polystyrene sulfonic acid membrane having various degrees of grafting. It can clearly be seen that the intensity of C1s, F1s, O1s, and S2p peaks depends on the degree of grafting. The intensities of C1s, O1s, and S1s peaks increase as the degree of grafting increases, while the intensity of F1s decreases. Such behavior can be attributed to the increase in the content of sulfonated polystyrene

side chains, at the expense of the CF_2 group in the membrane with the increase in the degree of grafting. Consequently, the content of carbon, oxygen, and sulfur increases, while that of fluorine decreases.

To obtain better understanding of the structural changes that take place in PTFE-*g*-polystyrene sulfonic acid membranes with the increase in the degree of grafting, the changes in binding energies of C1s, F1s, O1s, and S2p were investigated. Moreover, the atomic ratios: F/C, O/C, S/C, and O/S were also calculated. Table I shows the corrected binding energies of C1s, F1s, O1s, and S2p of PTFE-*g*-polystyrene sulfonic acid membranes having various degrees of grafting. It can be seen that the binding energies of C1s, F1s, O1s, and S2p peaks have almost no shifts, despite the increase in the degree of grafting within the membrane. This means that there is no changes

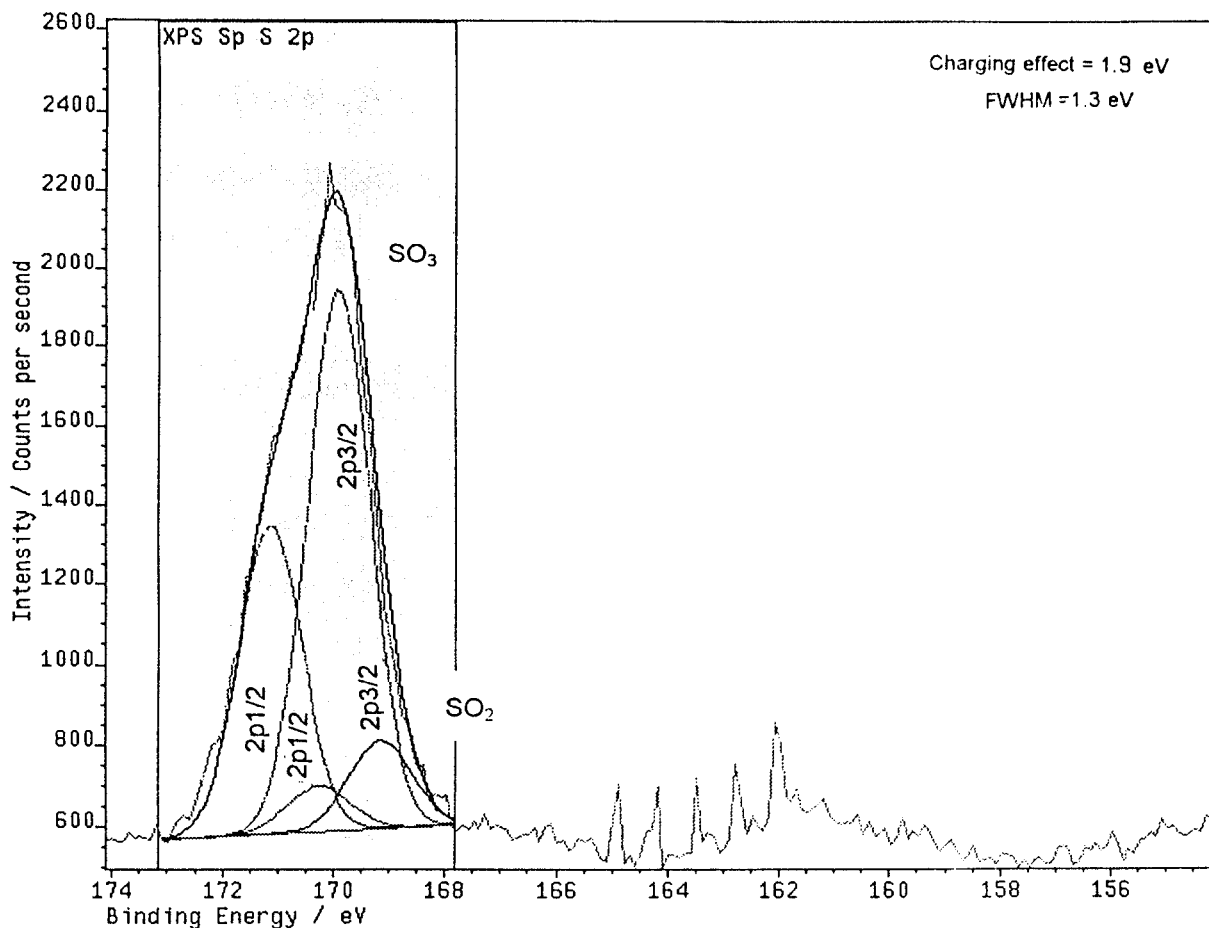


Figure 11 The narrow scan and curve fitting of S2p spectrum of 36% PTFE-*g*-polystyrene sulfonic acid membrane.

in oxidation state of the elemental components, which seem to be independent of the degree of grafting.

Table II shows the changes in ratios of the elemental components of PTFE-*g*-polystyrene sulfonic acid membranes (F/C, O/C, S/C, and O/S) as a function of the degree of the grafting. The elemental ratio of the original film is included as a reference. It can be noticed that radiation-induced grafting of styrene onto PTFE film causes a drastic decrease in the F/C ratio compare to the original film. Moreover, the F/C ratio shows a decreasing trend with an increase in grafting. The drastic decrease in the F/C ratio upon grafting is due to the rupture of the C—F bonds available at the film surface under the effect of ionizing radiation to form the radicals required to initiate the grafting in presence of styrene molecules,

whereas the continuous decrease in the F/C ratio with the increase in the degree of grafting is attributed to the increase in the ruptured C—F bonds, which leads to formation of more radicals on the PTFE backbone. Such an increase in the number of radicals considerably enhances the styrene grafting onto the PTFE backbone. Consequently, the content of polystyrene grafts increases while that of fluorine is decreased.

The second and third columns in the Table II show that the S/C as well as O/C ratios increase with the increase of the degree of grafting of the membranes. The increase in the polystyrene content provides more graft chains for sulfonation, and as a result, the sulfur and oxygen content increase with the increase in the degree of grafting. This means that the amount of sulfonic acid groups in the membrane increases with the in-

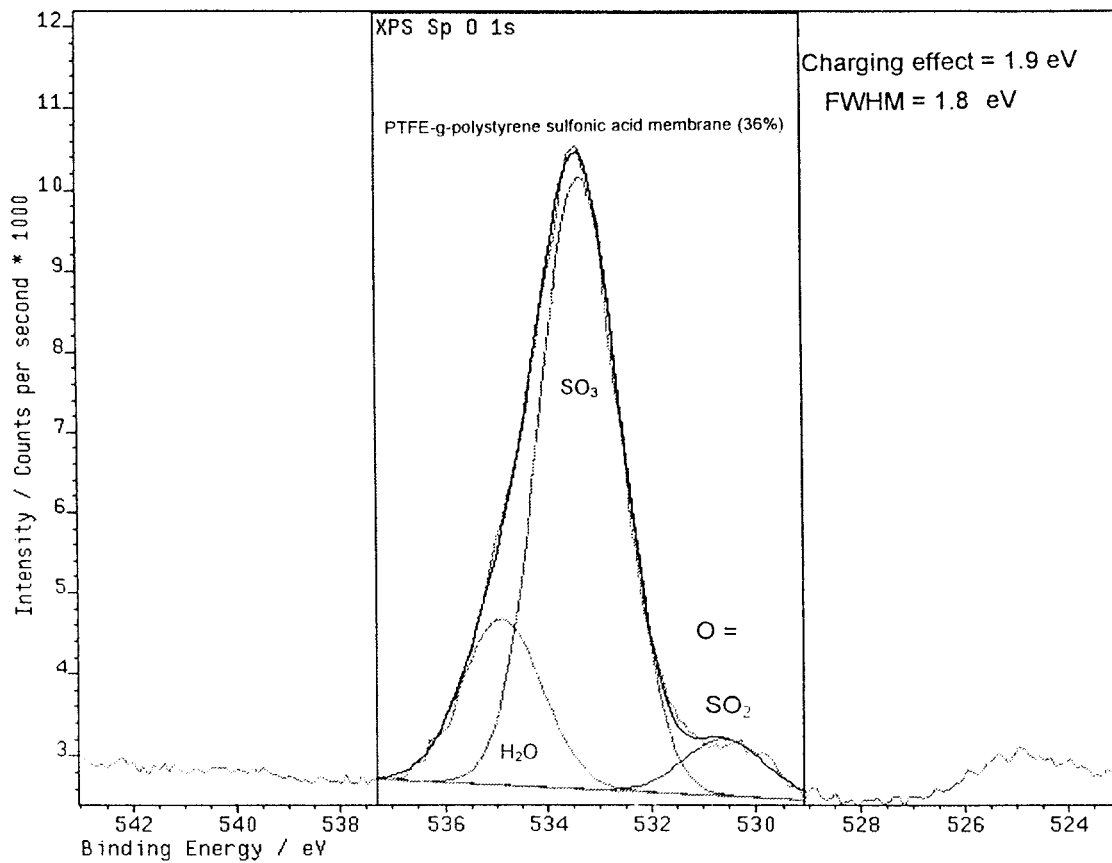


Figure 12 The narrow scan and curve fitting of spectrum of O1s of 36% PTFE-g-polystyrene sulfonic acid membrane.

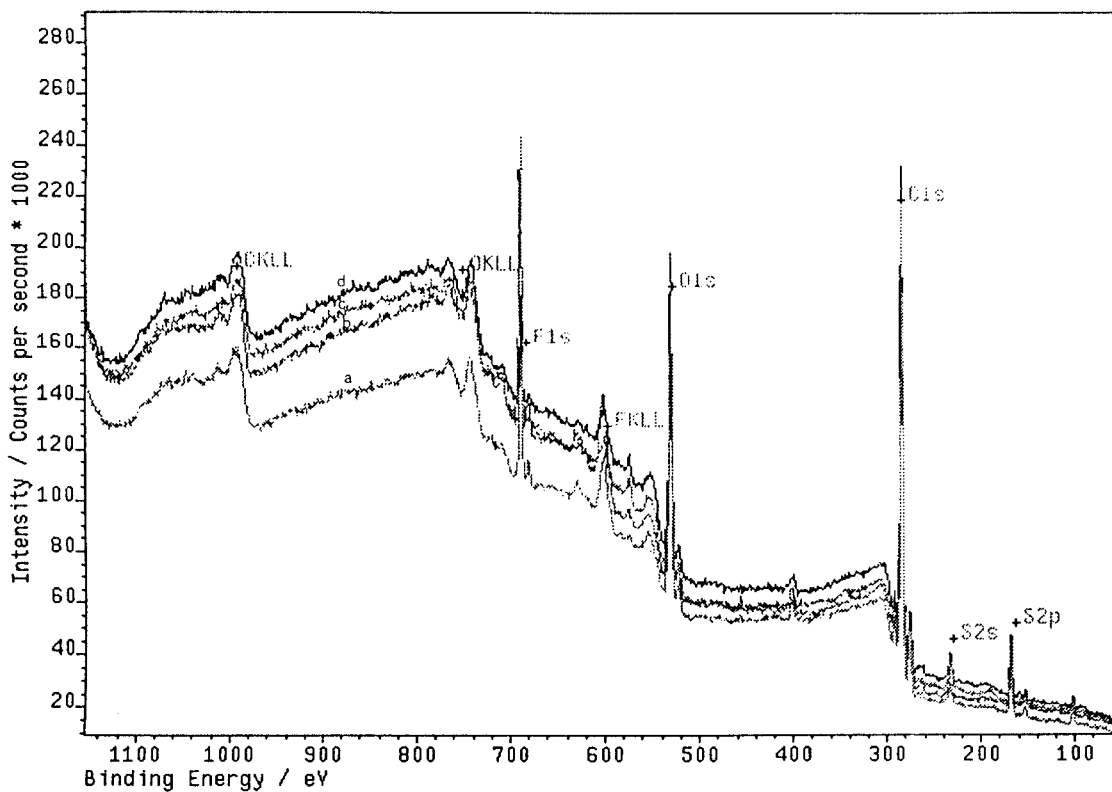


Figure 13 The wide-scan spectra of PTFE-g-polystyrene sulfonic acid membrane having various degrees of grafting: (a) 8%; (b) 12.5%; (c) 24%; (d) 36%.

Table I Corrected Binding Energy of C 1s, F 1s, O 1s, and S 2p of PTFE-g-polystyrene Sulfonic Acid Membranes Having Various Degrees of Grafting

Degree of Grafting (%)	C 1s				F 1s	H ₂ O	O 1s		S 2p			
	CF ₂	C-S	C-CF	-CO;			SO ₃ ⁻ /=O	SO ₂	(SO ₃ ⁻) 2p1/2	(SO ₃ ⁻) 2p2/3	(SO ₂) 2p1/2	(SO ₂) 2p2/3
8	292.3	288.7	287.5	285.9	688.9	534.8	532.9	529.9	169.8	168.6	168.7	167.7
13	292.1	288.6	287.2	285.7	689.0	534.8	532.8	529.8	169.4	168.4	169.7	167.5
24	292.1	288.5	287.1	285.6	689.1	534.8	532.8	529.7	169.6	168.2	168.6	167.4
36	292.1	288.4	287.1	285.6	688.7	534.6	532.7	529.6	169.3	168.1	168.4	167.3

Table II Changes in Ratios of the Elemental Components of PTFE-g-polystyrene Sulfonic Acid Membranes (F/C, O/C, S/C, and O/S) as a Function of Degree of Grafting

Degree of Grafting (%)	F/C	S/C	O/C	O/S
0	2.000	—	—	—
8	0.18	0.03	0.28	5.06
13	0.16	0.05	0.30	5.42
24	0.08	0.06	0.31	5.46
36	0.07	0.06	0.34	4.98

crease in the degree of grafting. Finally, the last column in Table II shows that O/S ratio is nearly constant for all membrane samples. However, it is higher than the expected ratio, which equal 3, referring to the structure of SO₃⁻. Such an increase in the O/S ratio is due to the increase of the oxygen content in the membranes, which can be attributed to the possible contamination of the sample by moisture and the oxygen found earlier in the grafted PTFE film.

CONCLUSIONS

A qualitative as well as quantitative correlation can be established between structural changes and degree of grafting from XPS studies of PTFE-g-polystyrene sulfonic acid membranes. The membranes were shown to have side-chain grafts of polystyrene and structures composed of carbon, fluorine, sulfur, and oxygen. The amount of each elemental component depended on amount of sulfonated polystyrene grafts incorporated (degree of grafting) in the membrane. However, the binding energies of C1s, F1s, S2p, and O1s were independent of the degree of grafting. The overall results in this study suggest that tailor-made membranes of desired structure can be prepared via controlling the degree of grafting during the membrane preparation.

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