Surface Modification of Radiation-Grafted Polymer Films and Membranes by Crosslinking

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ABSTRACT: The surface composition of radiation-grafted FEP-*g*-poly(styrene-*co*-divinylbenzene) films and its sulfonated analogues was investigated by X-ray photoelectron spectroscopy. These investigations demonstrate that the surface composition is strongly influenced by the degree of crosslinking of the polystyrene phase. In the absence of a crosslinker, the surface concentration of the grafting component was high and could even exceed the calculated average concentration in the volume of the polymer. With increasing crosslinker concentration, the surface concentration of the grafting component decreased rapidly and became close to zero for crosslinker concentrations above 2% in the monomer mixture. The effect was most pronounced in the case of grafted films and weaker in the case of sulfonated membranes. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1973–1978, 2007

Key words: crosslinking; ESCA/XPS; FEP; fuel cell; membranes; polystyrene; radiation grafting; surface

INTRODUCTION

Radiation grafting with ionizing radiation is an established method for introducing a second polymeric component into the volume of a prefabricated polymer film. Materials prepared in this way have been considered for many years as membranes for various applications, such as polymer electrolyte fuel cells.[1,2] Mainly for reasons of costs and availability, sulfonated polystyrene is probably the most commonly used grafting component for this purpose.

Since the early times of radiation grafting, crosslinking by either intensified irradiation or by copolymerization of multifunctional monomers has been used to modify the bulk properties of the resulting grafted polymer films and membranes.[3–16] These properties include in particular the microstructure, the mechanical and chemical stability, the degree of swelling when contacted with liquid media, and (related to this) the gas permeability and ionic conductivity. With increased crosslinking, membranes tend to become more brittle but at the same time chemically much more resistant. Additionally, the swelling, the gas-permeability, and the ionic conductivity decrease with increased crosslinking. Although some of these effects are rather unfavorable, crosslinked membranes have altogether clearly superior properties (e.g., for fuel cell applications) as compared with membranes without crosslinking.[7,12]

Recently, we have reported that the performance in fuel cells of our own crosslinked poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) and poly(styrenesulfonic acid) based membranes suffers from a very hydrophobic surface that is depleted in ionic groups.[11] Contrary to this, Nasef et al. have determined for similar—but noncrosslinked—materials a significant surface enrichment of the sulfonated and nonsulfonated polystyrene grafts over a wide range of graft levels.[17–19] These diverging results stimulated us to investigate more closely the effect of crosslinking on the surface properties of radiation-grafted membranes, a parameter that had been ignored in earlier investigations (e.g.,[17–20]). Only very recently, while this manuscript was still in preparation, Li et al. have reported on the surface analysis of radiation-crosslinked poly(tetrafluoroethylene) (PTFE) grafted with styrene and divinylbenzene (DVB).[21] They have demonstrated significant differences in surface composition for samples prepared with 0, 4, and 10% DVB, respectively, both before and after sulfonation of the grafting component.

An ideal method to investigate surface properties is X-ray photoelectron spectroscopy (XPS). This method provides quantitative information on the elemental composition of surface layers with a thickness of only a few nanometer. It was therefore the preferred tool for our work.

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EXPERIMENTAL

Radiation-grafted polymer films and membranes were prepared by the preirradiation method as described previously in much detail.[11,22,23] About 25-μm-thin Teflon FEP 100-A films (Du Pont) were activated by electron-beam irradiation under air with doses of either 3 or 30 kGy. After inserting the irradiated films into a solution of styrene (Fluka, 99%) and DVB (Fluka, 56.3% meta-isomer, 24.4% para-isomer), the solution was deoxygenated by purging with N_2 and heated to 60°C for 1–24 h. Smaller-size films were prepared by grafting with a solution of 50 vol % monomer in isopropanol in cylindrical glass reactors, whereas larger films (that were subsequently converted into polyelectrolyte membranes) were grafted with a solution of 20 vol % monomer in isopropanol/water in a home-built rectangular stainless-steel reactor. Films with different degrees of crosslinking were prepared by adding different amounts of DVB to the grafting solution, ranging from 0 to 10 vol % relative to the total amount of monomer. The reaction time was decreased for samples with lower degrees of crosslinking or higher irradiation dose, to correct for the increasing grafting rate.[22,23] The grafted films were washed with toluene and dried under vacuum. The degree of grafting of each film was determined by weighing the pristine and the grafted film; it is given as the relative weight increase due to grafting, this is, as the weight ratio of poly(styrene-co-DVB) to FEP. The degrees of grafting amounted to ~30% for the nonsulfonated samples and ~20% for the sulfonated ones, which represents typical degrees of grafting for materials of practical relevance. Since sulfonation results in an additional weight increase of the grafting component, its weight fraction after sulfonation amounted to ~30% as well.

Sulfonation of the grafted films was carried out by contacting them with 2 vol % chlorosulfonic acid in dichloromethane at r.t. for 5 h. Following this, the polymer films were treated with 0.1M NaOH for the hydrolysis of sulfonyl chloride groups. The polymer electrolyte membranes were reacidified with 2M H_2SO_4 and finally washed with deionized water. Degrees of sulfonation of ≥0.9 sulfonic acid groups per phenyl ring were confirmed by potentiometric titration of membrane samples with 0.05M KOH in 0.5M KCl solution.

XPS spectra were recorded with an ESCALAB 220i XL (Thermo VG Scientific) photoelectron spectrometer. The photoelectron spectrometer was equipped with a magnesium X-ray source ($h\nu$ = 1253.6 eV). In our spectrometer configuration the analyzer was placed normal to the sample surface, measuring the photoelectron leaving the sample mainly at an angle of 90°. To reduce the degradation of the samples, the source was operated at a power of only 100 W. The samples were investigated without any additional cleaning. XPS spectra were recorded in the CAE-Mode with an analyzer pass energy of 50 eV for the survey scan and 20 eV for the detail scans of C 1s, O 1s, F 1s, F 2s, and S 2p. The assignment of the XPS signals was made according to earlier reports.[24–26] During the measurement a constant charging in the order of a few eV was noticed. To correct for this, the resulting binding energies were referred to the CF_2 peak in the C 1s spectrum at 292.5 eV, corresponding to the literature value for pure FEP.[24] Since the spectrum for the noncrosslinked film showed almost no signal for fluorine-bound carbon (CF_x with x ranging from 1 to 3), this spectrum was charge corrected by assuming the binding energy of the main peak to be at 284.6 eV, corresponding to the carbon of polystyrene (CH_x with x ranging from 0 to 2). After the correction, the related F 1s peak was always at 689.8 eV. The composition of the samples was determined by quantitative analysis, using the cross sections of Scofield.[27]

RESULTS AND DISCUSSION

The surfaces of a series of FEP-g-polystyrene films as well as a series of FEP-g-poly(styrenesulfonic acid) membranes with different degrees of crosslinking were analyzed by XPS, and the elemental composition of the surfaces was derived from these spectra.

The XPS results for the nonsulfonated FEP-g-polystyrene films are given in Table I together with the theoretical composition of these films. This theoretical composition was calculated from the degree of grafting under the assumption of a homogeneous distribution of the grafting component (polystyrene-co-DVB) throughout the film thickness; the styrene/DVB ratio, and the tetrafluoroethylene/hexafluoropropylene ratio have no influence on this theoretical composition since the C/H ratios for styrene and DVB and the C/F ratios for tetrafluoroethylene and hexafluoropropylene are each identical.

The carbon C 1s signals from the XPS analysis of the grafted films are represented in addition in Figure 1. The spectrum for the noncrosslinked film shows a strong signal for carbon that is coordinated to other carbon atoms or hydrogen (CH_x with x ranging from 0 to 2) whereas the signal for fluorine-bound carbon (CF_x with x ranging from 1 to 3) is very weak. If the surface and the bulk material had the same composition, the ratio of the two corresponding peak areas would be almost 1 : 1 (CH_x ~ 26.5 atom %, CF_x ~ 24.5 atom %, cf. Table I). A weak signal near 291 eV in the spectrum of the DVB-free film can be attributed to the characteristic shake-up line for carbon in aromatic compounds,

TABLE I
Surface Composition in Atom % of Radiation-Grafted FEP-*g*-Poly(styrene-*co*-DVB) Films with Different Degree of Crosslinking

Irradiation dose (kGy)	Degree of grafting (wt %)	Cross linker concentration[a] (vol %)	F	CF_x	CH_x	O
3	27.2	0	15.5	6.9	75.7	1.8
3	28.8	0.5	50.2	24.3	24.6	1.0
3	29.4	1	60.0	28.9	10.7	0.4
3	28.2	2	64.8	30.2	4.3	0.6
3	29.7	5	66.6	32.3	1.0	0.1
3	28.1	10	66.6	31.9	0.5	0.9
Calculated values for a homogeneous film						
—	27–30	Any	49.6–48.2	24.8–24.1	25.7–27.8	0.0

[a] Concentration of DVB relative to the total amount of monomer in the grafting solution.

which results from the $\pi \rightarrow \pi^*$ transition. (In the spectra of the other samples this feature overlaps with the more intense CF_x peak and cannot be detected even if present.)

With increasing DVB concentration in the grafting solution, the intensity of the CH_x signal in the spectrum decreases and the intensity of the CF_x signal increases, until the former has almost completely disappeared at a DVB concentration of 5 vol %. In

Figure 1 C 1s XPS spectra for radiation-grafted FEP-*g*-poly(styrene-*co*-DVB) films with different degrees of crosslinking. CF_x indicates the signal of the fluorine-bound carbon atoms, whereas CH_x indicates the signal of the fluorine-free carbon atoms. The DVB concentration refers to the concentration in bulk solution relative to the total monomer concentration. The dashed line is a 10-fold magnification of the spectrum for the sample without DVB.
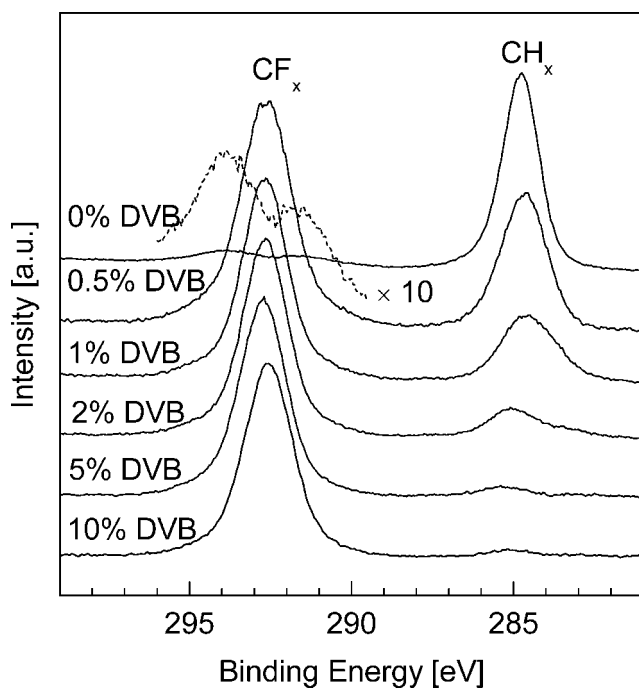
addition to these changes in intensity, a shift of the CH_x signal by about 0.5 eV to higher energy with increased crosslinking was observed for the spectra in Figure 1. Chemical shifts are related to a change of the electronic properties or to differential charging. Most likely, this particular shift was due to a different extent of charging of the polystyrene domains depending on their size and distribution within the FEP matrix.

The F 1s signal follows the same trend as the CF_x part of the C 1s spectrum (Table I), and the F(F 1s)/CF_x(C 1s) atomic ratio amounts to an almost constant value of 2.1–2.2 for all degrees of crosslinking, as would be expected from the chemical structure of FEP. A very similar F/CF_x ratio of 1.8–1.9 is determined from the F 2s spectra (not shown here).

Besides the expected elements C and F, a small amount of oxygen (~1 atom %) was detected on the surface of all samples (Table I). This oxygen content is most likely due to oxidation as a consequence of electron-beam and X-ray irradiation.

The almost complete absence of hydrocarbon at the surface at high degrees of crosslinking was only marginally influenced by the irradiation dose, as can be seen from a comparison of films with 3 and 30 kGy irradiation dose in Figure 2 and Table II. This suggests that the low surface modification that was observed at high degrees of crosslinking has other causes than a deficit in initiator sites at (or near) the surface of the film.

The XPS results indicate that under the given preparation conditions the formation of a film surface consisting of polystyrene is energetically preferred and kinetically accessible, as long as the polystyrene chains are highly flexible. Since the CF_x signal is suppressed to a large extent for the noncrosslinked sample, the thickness of the polystyrene layer has to approach at least 5–10 nm, which is the typical information depth of XPS measurements. Crosslinking of polystyrene apparently limits the dimensions of phase separation between the two
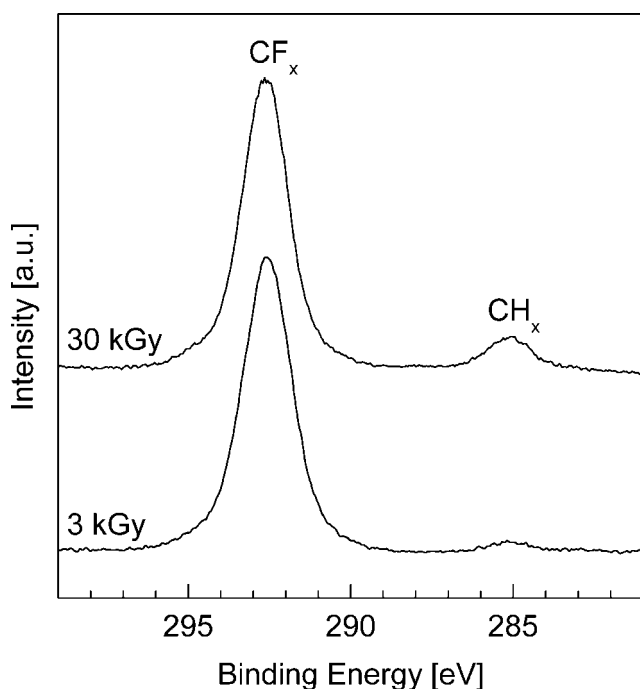
Figure 2 C 1s XPS spectra for radiation-grafted, cross-linked FEP-*g*-poly(styrene-*co*-DVB) films prepared with different irradiation dose. CF_x indicates the signal of the fluorine-bound carbon atoms, whereas CH_x indicates the signal of the fluorine-free carbon atoms.

polymers and prevents polystyrene from efficiently spreading on top of FEP. As a result, more FEP becomes exposed to the surface. Again, the thickness of this surface layer, which is enriched in FEP, has to approach at least 5–10 nm for the highest DVB concentrations. It is noteworthy that the most pronounced changes in surface composition occur at very low crosslinker concentrations. Apparently, amounts of crosslinker of less than 1 vol % relative to styrene in the grafting solution are sufficient to significantly modify the grafting component to hinder the polystyrene from spreading at the film surface.

The results of analogous XPS measurements on sulfonated membranes are shown in Figure 3 and Table III. Similar to the FEP-*g*-poly(styrene-*co*-DVB) films, the amount of sulfonated polystyrene at the

surface decreased rapidly with increasing DVB content. However, the starting point at 0% DVB was much lower than in the case of nonsulfonated polystyrene. Even in the case of the DVB-free sample, the surface was depleted in poly(styrenesulfonic acid) as compared with the calculated average composition, and a significant part of the XPS carbon signal originated from FEP. Reasons for this could be the higher polarity of sulfonated polystyrene, which increases its surface energy in contact with air or vacuum, some possible crosslinking by sulfone bridges during sulfonation, and degradation of surface-bound polystyrene chains during sulfonation. Despite this smaller variation of the XPS signals with crosslinking, the wetting properties of crosslinked and noncrosslinked membranes still differed markedly. While noncrosslinked samples readily immersed in water, samples prepared with 5 or 10 vol % DVB content in the monomer mixture rejected to submerge although their density is clearly above the one of water.

Like for the nonsulfonated samples, the most pronounced change in surface composition occurred at low degrees of crosslinking. From the application point of view it has to be noted that the critical crosslinker concentrations are far below those values that are required for a significant modification of the bulk properties of the polymer.[7,12] (We have typically used crosslinker concentrations of 10 vol % for the preparation of membranes.[11]) As a consequence, it appears to be impossible to optimize both, the surface and the bulk properties of the films, by simply adjusting the DVB content of the polystyrene phase. Contrary to this, one may even speculate that the low concentration of crosslinked polystyrene at the film surface contributes to the electrochemical stability of the membranes in fuel cell applications because it reduces the direct contact between the Pt electro-catalyst and the hydrocarbon fraction of the membrane.

Similar to the crosslinked films, a shift of the CH_x signal to slightly higher energy was visible for all sulfonated samples. Again, this can be explained by different degrees of charging of FEP and sulfonated polystyrene.

The measured binding energy of the S 2p level at ~168 eV confirmed the presence of sulfonated poly-

TABLE II
Surface Composition in Atom % of Radiation-Grafted, Cross Linked FEP-*g*-Poly(styrene-*co*-DVB) Films Prepared with Different Irradiation Dose, but the Same Cross Linker Concentration of 10 vol % DVB

Irradiation dose (kGy)	Degree of grafting (wt %)	Cross-linker concentration[a] (vol %)	F	CF_x	CH_x	O
3	28.1	10	66.6	31.9	0.5	0.9
30	32.0	10	66.3	30.0	2.9	0.7
Calculated values for a homogeneous film						
—	28–32	Any	49.1–47.3	24.5–23.6	26.4–29.1	0.0

[a] Concentration of DVB relative to the total amount of monomer in the grafting solution.
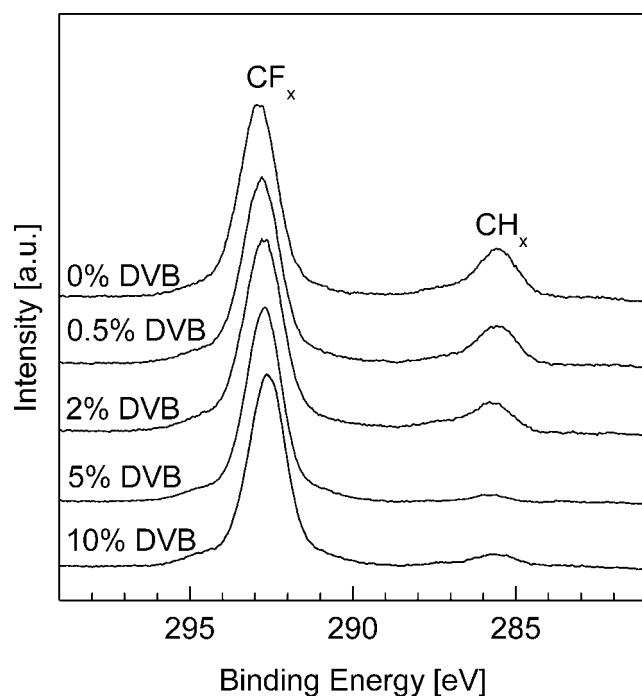
Figure 3 C 1s XPS spectra for radiation-grafted FEP-*g*-poly(styrenesulfonic acid) membranes with different degrees of crosslinking. CF_x indicates the signal of the fluorine-bound carbon atoms, whereas CH_x indicates the signal of the fluorine-free carbon atoms. The DVB concentration refers to the concentration in bulk solution relative to the total monomer concentration.

styrene at the surface for all membranes. The determined sulfur contents related to sulfonated polystyrene are lower than the calculated values (Table III), but correlate well with the carbon contents assigned to poly(styrene-*co*-DVB). Comparing the sulfur and the oxygen contents in Table III indicates, that the oxygen content is always higher than the expected value for the sulfonic acid group ($-SO_3$). This additional oxygen content (0.2–1.3 atom %) is similar to the oxygen content that was observed for the grafted film and may again be attributed to a weak oxidation of the membrane surface.

The ratios of the atomic concentrations F(F 1s)/CF_x(C 1s) and F(F 2s)/CF_x(C 1s) are equivalent to those of the grafted films before sulfonation and amount again to values of 1.8–2.2.

Qualitatively very similar XPS results were recently reported for radiation crosslinked PTFE films grafted with styrene and DVB.[21] Quantitative differences consist in higher amounts of fluorine-free carbon at the surface of samples with a high DVB content. In addition, contrary to our results, a surface enrichment of the grafting component was also observed for noncrosslinked poly(styrenesulfonic acid). The most obvious explanation for these differences is that the radiation-crosslinking of the fluorinated matrix hinders the grafting component from withdrawing from the surface. As a consequence, it seems to be a reasonable assumption that crosslinking of the fluorinated matrix is an option to force more sulfonated poly(styrene-*co*-DVB) to the surface. In addition, Li et al.[21] pointed out that hydrocarbon residues might have been generated by covalent attachment of surfactant molecules and by defluorination during radiation crosslinking. This latter assumption finds support by the fact that the S/C ratio of the DVB-free samples amounts to little more than half of the expected value. This indicates that part of the hydrocarbons at the surface does not belong to sulfonated polystyrene. The same is most likely valid for the noncrosslinked samples of Nasef et al.[17–19] These authors too, reported high surface concentrations of poly(styrenesulfonic acid) and at the same time S/C ratios that are significantly below the theoretical values. In addition to this, the different grafting technique of Nasef et al. (simultaneous instead of preirradiation grafting) may have contributed to the differences as well.

CONCLUSIONS

The surface composition of radiation-grafted FEP-*g*-polystyrene films and FEP-*g*-poly(styrenesulfonic acid) membranes is strongly influenced by the

TABLE III
Surface Composition in Atom % of Radiation-Grafted FEP-*g*-Poly(styrenesulfonic acid) Membranes with Different Degree of Cross Linking

Irradiation dose (kGy)	Degree of grafting (wt %)	Cross-linker concentration[a] (vol %)	F	CF_x	CH_x	O	S
3	18.6	0	61.4	27.4	7.2	3.3	0.8
3	21.8	0.5	62.6	28.5	6.1	2.3	0.5
3	20.6	2	63.6	27.9	5.1	2.8	0.5
3	20.7	5	67.2	30.8	0.9	0.8	0.2
3	18.2	10	66.4	30.1	1.9	1.4	0.2
Calculated values for a homogeneous film (90% sulfonation assumed)							
—	18–22	0	50.0–47.1	25.0–23.5	17.3–19.9	5.8–7.1	1.9–2.4

[a] Concentration of DVB relative to the total amount of monomer in the grafting solution.

degree of crosslinking of the polystyrene phase. While high surface concentrations of the grafting component are observed in the absence of cross-linker, the surface is almost exclusively composed of FEP at high crosslinker concentrations. The most pronounced changes occur at DVB concentrations below 5 vol %. A comparison with results from literature indicates that the surface concentration of poly(styrenesulfonic acid) might also be influenced by crosslinking of the fluorinated base material and by the grafting method.

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