# Structure of Sulfonated Poly(vinyl fluoride)

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ABSTRACT: Sulfonated poly(vinyl fluoride) (PVF-SA) has been made by chemical sulfonation or radiation-induced sulfonation of commercial poly(vinyl fluoride) (PVF) films. The effects of the irradiation treatment and sulfonation on sulfonic acid distribution, crystallinity, state of water, and molecular organization have been examined. The results indicate that proton irradiation and subsequent sulfonation produce a structure that is different from the ones produced by the sulfonation of nonirradiated or electron beam (EB)-irradiated samples. The water uptake is higher in proton-irradiated samples than in the other samples. In addition, the portion of nonfreezing water is highest in proton-irradiated samples. Infrared spectra of the sulfonated samples indicate that a large part of the freezing bound water is associated with the hydrophobic polymer backbone. However, this portion was smaller in the proton-irradiated sample than in the EB-irradiated sample. The proton-irradiated samples had a small-angle X-ray diffraction maximum with a corresponding Bragg spacing of 70 Å, which was taken as evidence for the formation of ion-water cluster domains in the protonirradiated samples. The ion conductivity was slightly lower in nonirradiated and in EB-irradiated membranes than in the proton-irradiated sulfonated samples in which the highest values were 10-20 mS/cm. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 1273-1284, 1999

**Key words:** poly(vinyl fluoride); irradiation; sulfonation; proton conductivity; fuel cell

## **INTRODUCTION**

Direct sulfonation of aliphatic polymers is an attractive method for the preparation of proton conducting materials. The additional word "direct" is used in this context to stress that this method does not include any grafting or other assisting routes to make the sulfonation of the polymer easier. Thus, problems that arise from film processing of already sulfonated polymers<sup>1</sup> as well as from several stages of preparation as, for example, in the case in the grafting method,<sup>2</sup> can be avoided. Also, the possibility to be able to direct

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sulfonate fluoropolymers is a tempting alternative when seeking new and chemically stable materials for fuel cells and electrochemical devices.

As reported previously,<sup>3</sup> poly(vinyl fluoride), PVF, can be activated for sulfonation by irradiation with ionizing radiation. On the basis of the characteristic behavior of different types of radiation in the irradiated medium, energy absorption occurs either randomly or highly selectively. For example, the energy absorption of accelerated electrons occurs mainly via the collisions with the electrons of the irradiated material. Thus, the collisions occur between particles with equal mass. Because of this, the energy dissipation is fast, and the direction of the original electron as well as of the secondary electrons is almost random. This has the effect that the positions of the energy absorption spread very efficiently inside the matrix. In contrast to this, the paths of protons and other ions are rectilinear, and they produce cylindrical tracks of reaction products. Thus, the ion irradiation activation of the matrix for the sulfonation reaction guides sulfonation to proceed along linear paths. This method was shown to promote introduction of ion conductivity in insulating matrices.<sup>3</sup>

An analysis of the structure of the directly sulfonated poly(vinyl fluoride) is presented in this work. Samples that were sulfonated without irradiation or after irradiation either with electron beam or protons are compared. Attention is paid to the amount and the various ways of binding of water, the sulphur and the counter ion distribution across the matrix film, and the details of the structure that can be achieved with small- and wide-angle X-ray scattering analyses (SAXS and WAXS). These results are related further to the ion exchange capacity and the ion conductivity of the membranes. On the basis of this, reasons for the enhancement in ion conductivity in membranes sulfonated after proton irradiation is presented. In addition, some general rules for the dependence of ion conductivity on ion-exchange capacity, the state and the amount of water, and sulfonic acid-water cluster formation are proposed.

## **EXPERIMENTAL**

The sample preparation, ion exchange capacity analysis, and measurement of ion conductivity have been described in detail.<sup>3</sup> Briefly, the the original PVF film (Tedlar, Du Pont), with the measured thickness of 31  $\mu$ m, was sulfonated with chlorosulfonic acid (2.5 vol % in dichloro ethane; O<sub>2</sub> free) either directly or after irradiation with an electron beam or a proton beam. The ion exchange capacity was determined by back titration of the excess NaOH after the equilibrium. Ion conductivity was determined by the impedance method.

#### X-ray Analysis

X-ray diffraction methods were used to study the effects of irradiation and sulfonation on the crystallinity and morphology of the samples. The crystallinity of the sulfonated samples was analyzed with wide-angle X-ray scattering (WAXS). The samples were analyzed both in proton and cesium form, and prior to the measurement the samples were alloved to dry at ambient conditions. The experiments were performed in symmetrical transmission and reflection geometries with Cu- $K\alpha_1$  radiation (1.54 Å), which was monochromated with a quartz monochromator in the incident beam. The scattered intensities were measured with a scintillation counter. An angular step of 0.2° and a measuring time of 20 s per point were used. The background scattering was measured separately and subtracted from the intensity curves of the samples, which were also corrected for absorption.

The average crystal sizes were estimated using the well-known Scherrer formula. The precision of the determination for well resolved reflections was about 5 Å. The estimation of the crystallinity by means of the X-ray diffraction method is based on the two-phase model of the polymer structure: the measured intensity is a linear combination of the intensities from the crystalline and the amorphous regions.<sup>4</sup> The intensity curve from the amorphous sample 7 (400 kGy proton irradiation, 19 h sulfonation) was used as the amorphous background.

The intensities of the wide-angle diffraction from the pristine PVF film and from the amorphous material were fitted to the intensity curves of the samples. By this procedure the change in the crystallinity in the samples was obtained as the ratio of the integrals of the intensities of the crystalline component and the studied sample. The integration limit was  $10^{\circ} < 2\Theta < 50^{\circ}$ .

The SAXS measurements were made with a sealed copper anode fine focus X-ray tube. The Cu-K $\alpha$  radiation was monocromated by means of a nickel filter and a totally reflecting glass block

(Huber small angle chamber). The intensity patterns were recorded using a linear position sensitive detector (MBraun OED50M). The distance from the sample to the detector was 160 mm. The beam had a narrow profile: the vertical instrument function had a fwhm of 0.54  $\text{\AA}^{-1}$ , while in the horizontal direction the instrumental function had a fwhm of 0.008  $Å^{-1}$ . The magnitude of the scattering vector is defined as  $k = 4 \sin \Theta \lambda^{-1}$ . where  $\Theta$  is half of the scattering angle and  $\lambda$  is the wavelength. Thus, the obtained k-range in this setup was 0.03 Å<sup>-1</sup> < k < 0.8 Å<sup>-1</sup>. The background scattering was measured separately and subtracted from the intensity curves. The unsmeared intensity curves were sought using the iterative procedure of Lake.<sup>5</sup>

The SAXS measurements were done on the membranes in cesium form. The counter ion was exchanged from proton to cesium ion by equilibrating the samples in 0.01 M CsCl solution for 4 days, followed by rinsing with deionized water. The samples were inserted in the measuring frame in the following way. Two pieces of each sample were supported inside a sealed and 1 mmthick frame for the direct transmission measurement. Two 2- $\mu$ m Mylar films were used as X-ray windows. The samples were measured under ambient conditions. In addition, in the measurements of the samples in a humid state water was injected to the bottom of the cavity to achieve a 100% relative humidity inside the frame.

#### **Energy Dispersive X-ray Analysis**

The sulphur and cesium concentration profiles across the samples were analyzed with a Zeiss DSM 962 scanning electron microscope combined with a Link Isis energy dispersive X-ray spectrometer. Samples were embedded in epoxy resin (LX 112, Ladd Research Industries Inc.), and the blocks were trimmed with an ultramicrotome to obtain a clean cross-section.

#### **Thermal Analysis**

The state and the amount of different forms of water in the samples was analyzed calorimetrically. Thermograms of the samples were measured with a Perkin-Elmer DSC-7 calorimeter. Samples were boiled in distilled water for 1 h and stored for 1 week in water at room temperature prior to the measurements. Because the membranes are very sensitive to drying in ambient conditions, the sample preparation was done in a glove box, the atmosphere of which was saturated with water vapor. The surfaces of the sample pieces were blotted with humid paper. The sample pieces were closed in aluminium pans and weighed. The temperature of the calorimeter block was  $-80^{\circ}$ C. The temperature was held at  $-50^{\circ}$ C for 10 min before the measurement. Thermograms were registered between -50 and  $10^{\circ}$ C, with a heating rate of  $5^{\circ}$ C min<sup>-1</sup>. Water and indium were used as standards.

#### Water Uptake

The water uptake of the samples was determined after the DSC measurement. The sample pans were pricked with a pin to allow drying. The drying was done in a vacuum desiccator at  $70^{\circ}$ C to constant mass. After drying, the desiccator was filled with nitrogen gas via a cold finger to avoid condensation of water onto the surface of the sample pans and absorption of water into the samples. Finally, the samples were weighed.

#### **IR** Analysis

IR spectra were recorded with a Bruker IFS-66v FTIR spectrometer. The spectral resolution was 2  $cm^{-1}$ . The samples were studied both in H<sub>2</sub>O and  $D_2O$  hydrated forms. The deuterated samples were prepared as follows: the membranes were dried in vacuum ( $\sim 10^{-4}$  mbar) for 24 h at  $\sim 80^{\circ}$ C, then equilibrated with D<sub>2</sub>O (Aldrich, 99.9% D) at ambient temperature for 2-3 h, dried as described, and finally equilibrated 2-3 h in  $D_2O$ . To investigate the changes in the state of water with a degree of hydration "drying dynamics" measurements were applied. The samples were equilibrated with water (or heavy water) and placed in a semisealed chamber that was in the evacuated sample compartment of the spectrometer. Subsequent spectra were measured with different time delays allowing partial evaporation of the hydration water from the membrane. The multicomponent IR absorptions were analyzed in terms of frequency positions and integrated intensities of the spectral components using commercially available software (LabCalc, PeakFit). The standard error of the frequencies and the intensities obtained in curve fitting was less than 0.2%.

### **RESULTS AND DISCUSSION**

A sample series of approximately 40 samples has been used in this article. Ion exchange capacities

Sample	Irradiation	Dose/ kGy	Sulfonation Time/h	$egin{array}{c} Q \ { m quiv} \ \cdot { m g}^{-1} \end{array}$	$\sigma { m mS/} { m cm}$	cryst. dec. %	c.s. (110) Å	wut N(H <sub>2</sub> O)/ $SO_3H$
PVF	_		_	_	n.m.	_	166	n.m.
PVF	$\mathbf{EB}$	400	_	_	n.m.	10	133	n.m.
PVF	EB	1000	_		n.m.	18	142	n.m.
PVF	$\mathrm{H}^+$	400	_		n.m.	10	128	n.m.
1	_	0	1	1.2	1.1	56	73	9
2		0	26	3.7	n.m.	95	u.a.p.	5
3	$\mathbf{EB}$	400	1	1.2	0.2	66	43	7
4	$\mathbf{EB}$	1000	5	3.1	2.2	93	u.a.p.	6
5	$\mathrm{H}^+$	400	1	1.3	1.8	76	u.a.p.	11
6	$\mathrm{H}^+$	400	5	3.1	6.8	94	u.a.p.	10
7	$\mathrm{H}^+$	400	19	3.7	7.9	100	u.a.p.	10

Table I Sample Preparation Parameters and Numerical Values of the Results of Ion Exchange Capacity (Q), Ion Conductivity  $(\sigma)$ , Decrease in Crystallinity (cryst. dec.), Crystal Size (c.s.), and Total Water Uptake (wut) Analyses

The precision of the crystallinity value and ion conductivity is  $\pm 20\%$ . Ungiven values: under analysis precision (u.a.p.), not measured (n.m.).

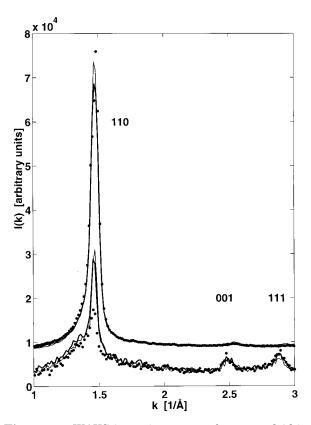
and ion conductivities of all of these samples were analyzed. On the basis of these partially published results<sup>3</sup> a narrower sample selection was made to study further the structural differences between the samples, and especially to investigate the reasons for the significant differences in ion conductivities. Thus, seven different directly sulfonated membranes are analyzed in this work with respect to results for X-ray measurements, elemental distribution analysis, and binding of water. These seven samples represent three different alternatives of matrix films to be sulfonated: pristine PVF (two samples), EB irradiated PVF (two samples), and proton irradiated PVF (three samples).

The ion exchange capacities, Q, of the seven selected samples are collected in Table I. The interpretation of the dependence of Q on the irradiation method and on the absorbed dose has been discussed in detail previously.<sup>3</sup> The samples in this presentation are divided into three groups on the basis of the Q: 1.2 mEq.  $g^{-1}$ , 3.1 mEq.  $g^{-1}$ , and  $3.7 \text{ mEq. g}^{-1}$ . In addition, each group contains one proton irradiated and sulfonated sample in addition to either a nonirradiated or EBirradiated and sulfonated sample. The purpose of this sample clustering is to compare membranes prepared in different ways with respect to irradiation treatment but having similar values of Q. In this way, one of the variables can be excluded when discussing the dependence of ion conductivity on the treatment before the sulfonation.

The conclusion is drawn that a regioselective sulfonation is achieved by means of proton irra-

diation. This conclusion is based on the facts that proton irradiation forms linear energy absorption tracks into the membrane, and irradiation treatment increases the sulfonation rate both with EB and proton irradiation.<sup>3</sup> Thus, the proton irradiated samples have two to three times higher conductivities than the respective nonirradiated or EB-irradiated samples. The practical meaning of this is that with proton irradiation the necessary ion conductivity can be achived for practical applications of this material. In other words, the measured conductivities of the EB irradiated and also of the nonirradiated samples remain on a level that is not enough for fuel cell application. The ion conductivity can be taken to be essentially dependent on both the overall amount of acid groups and also on the mutual location and organization of the acid groups. The samples studied give possibilities to analyze this more precisely, because the original material can be modified by irradiation, which further effects the location of the sulfonation reactions. The role of the sample morphology on Q and ion conductivity includes the study of crystallinity.

The crystallinity and the crystal sizes of the samples, both of which change due to irradiation and the sulfonation reaction, were determined by wide-angle X-ray scattering (WAXS) analysis. Figure 1 presents the diffraction patterns of the untreated, the EB-irradiated and the proton-irradiated PVF films, respectively, measured with symmetrical reflection and with transmission geometries. The differences of the diffraction patterns measured with reflection and transmission



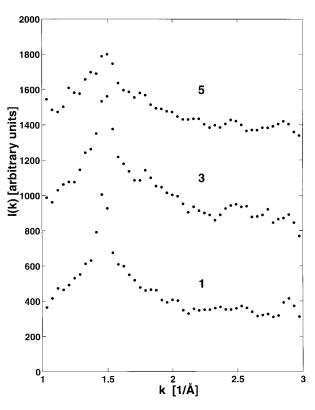
**Figure 1** WAXS intensity curves of untreated (thin line), electron beam (dotted line), and proton-irradiated films (thick line) measured with symmetrical transmission (lower curves) and reflection geometries (upper curves).

geometries are explained by the preferred orientation of polymer chains parallel to the surface of the film. The crystallinity was determined similar to our previous study of grafted and sulfonated poly(vinylidene fluoride) membranes,<sup>6</sup> but the effect of preferred orientation of the crystallites was taken into account.<sup>7,8</sup> Because of the preferred orientation, the precision of the crystallinity index is 20%. The results from the pristine PVF are in good agreement with previously published results.<sup>9–12</sup> The crystallinity of the pristine PVF was about 53%. The average crystal sizes determined with the well-known Scherrer formula were about 166, 72, and 77 Å for reflections 110, 001, and 111, respectively.

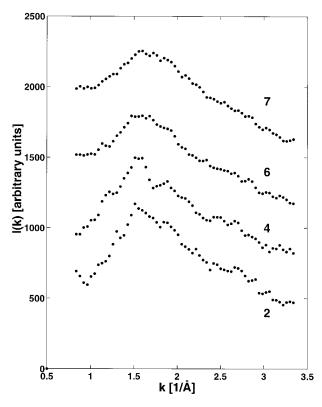
The diffraction patterns of the EB and proton irradiated films were slightly different than that of the original PVF. Irradiation treatment increased the preferred orientation. This result is in accord with the results reported by Pae et al.<sup>13</sup> and Torrisi et al.,<sup>14</sup> who also observed the same phenomenon both with EB- and ion-irradiated PVDF. The crystallinity decreased about 10% due to the irradiation with both EB and protons, respectively, with the absorbed dose of 400 kGy. The decrease was about 18% with 1000-kGy EB irradiation. This result is on the line with the results of Chailley et al.,<sup>15</sup> who noticed the same effect in poly(vinylidene fluoride) (PVDF). However, Pae et al.<sup>13</sup> have reported an increase in crystallinity in PVDF based on both the WAXS and DSC results.

The diffraction patterns of the sulfonated samples are presented in Figures 2 and 3. The samples with 1-h sulfonation time and partial crystallinity are presented in Figure 2. The samples with longer sulfonation times and high amorphicity are presented in Figure 3. The crystallinity has decreased in all the samples due to the sulfonation. The decrease arises both from the disruption of the crystallites and from the dilution of the matrix due to the inclusion of sulfonic acid groups.

Samples 1 and 2 were sulfonated without irradiation. The decrease in crystallinity in sample 1 was 56%. The average crystal dimensions were about 73 and 60 Å for reflections 110 and 111,



**Figure 2** WAXS intensity curves of the semicrystalline samples 1, 3, and 5.



**Figure 3** WAXS intensity curves of the amorphous samples 2, 4, 6, and 7.

respectively, after sulfonation. Sample 2 was highly amorphous; i.e., the decrease in crystallinity was estimated to be 95%. It had been subjected to the longest sulfonation time of all the samples (see Table I).

The exchange of the counter ion from proton to cesium in the sulfonated membrane was used in this work to increase the contrast between sulfonic acid-rich and -poor areas in the matrix, and also to evaluate the distribution of the ion exchange active groups across the membranes. The effects of the ion-exchange reaction and counter ion on the crystallinity was studied with sample 1. This sample in cesium form showed a 64% decrease in crystallinity (56% in proton form), and the average crystal size was 80 Å in the 110 reflection (73 Å in proton form). Thus, within the measuring precision the exchange reaction did not further diminish the size of the PVF crystallites or the overall crystallinity.

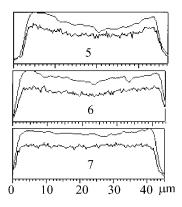
The EB-irradiated and sulfonated sample 3 showed a 66% decrease in crystallinity, and the average crystal size was 43 Å in the 110 reflection. The other EB-irradiated but more strongly sulfonated sample 4 was amorphous. The most mildly sulfonated proton-irradiated sample 5 had a 76% decrease in crystallinity. The crystal size could not reliably be determined. The other proton beam-irradiated samples, 6 and 7, were largely amorphous.

Comparison of the WAXS results for samples 1, 3, and 5 shows that the sulfonation decreased the crystallinity equally and irrespective of the pretreament; thus, the sulfonation is the main cause of the decrease in crystallinity.

The distribution of the sulfonic acid groups in the membranes was studied by measuring the sulphur and cesium profiles across the sample membranes with energy dispersive X-ray analysis. An example of the results of these analyses is seen in Figure 4, which shows the distribution of sulfur and cesium across samples 5, 6, and 7. These samples represent the three Q values, on the basis of which the studied samples were selected. Similar sulphur and cesium distributions with the respective Q values were found in all samples. In other words, the irradiation treatment did not effect on the consentrations of sulphur and cesium.

The sample with the lowest Q has about 20% lower sulphur and cesium content in the middle of the membrane than close to the surfaces. The profiles of the sample with Q around 3.1 mEq. g<sup>-1</sup> show only a slight decrease of sulphur and cesium content in the middle of the membranes. The samples with the highest value of Q (3.7 mEq. g<sup>-1</sup>) show sulphur and cesium profiles, indicating even distribution of the ion exchange groups throughout the sample.

The cesium profiles in the samples follow the respective sulphur profiles. Differences in the sulphur and cesium profiles could indicate formation



**Figure 4** Sulphur (upper curves) and cesium (lower curves) profiles across samples 5, 6, and 7. Sample thicknesses 32, 40, and 40  $\mu$ m, respectively.

of functional groups other than sulfonic acid groups, such as sulfone bridges.<sup>16</sup> The similarity of the distribution curves shows that the sulfonic acid groups are evenly distributed in the membranes after long sulfonation times. Swelling of the film during the sulfonation was also noticed, and as can be seen in Figure 4. The thickness increases with increasing the ion exchange capacity. This is due to both the increased solvent uptake of the matrix and naturally also due to the increased mass due to the sulfonation reaction.

Because the proton conductivity is critically dependent on the water content of the membranes,<sup>17</sup> the water uptake and the binding of water were studied in detail. The total water uptake in the samples expressed as number of water molecules/sulfonic acid group  $\{N(H_2O)/(SO_3H)\}$  is presented in Table I. The content of sulfonic acid groups in the membranes was taken to be equal to the experimental values of Q. The total water uptake of both of the EB-irradiated samples and also of the nonirradiated sample with Q = 3.7mEq.  $g^{-1}$  was low, five to seven water molecules per sulfonic acid. In contrast to this, the water content of all proton-iradiated samples and also of the nonirradiated sample with Q = 1.2 mEq. g<sup>-1</sup> was higher, and of the order of 9-12 water molecules per sulfonic acid. The total water uptake in all these membranes is still lower than in the styrene-grafted and sulfonated-fluorinated membranes.<sup>18–20</sup> The hydrophilicity of the membranes is dependent on the sulfonic acid content, but obviously also on the distribution of the sulfonic acid groups in the matrix. Thus, structural differences in the membranes cause differences in water absorption; in nonirradiated and in EB-irradiated samples the hydrophilic sulfonic acid groups occur more isolated from each other, and the surrounding hydrophobic matrix prevented efficient hydration. In addition, irradiation of PVF mainly causes formation of crosslinks instead of chain scission,<sup>21</sup> which in turn, makes the matrix less swellable. In proton-irradiated samples the hydrophilic groups occur in near proximity to each other along cylindrical channels in the matrix, which facilitates the formation of larger water clusters. Thus, we conclude that despite the similar concentration of hydrophilic groups the homogenously crosslinked material (i.e., EB-irradiated film) is unable to absorb as much water as a nonrosslinked or proton-irradiated material.

The binding of the water in the membranes was further studied by thermal analysis. The pri-

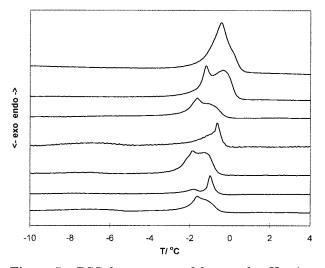
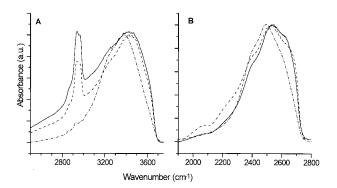


Figure 5 DSC thermograms of the samples. Heating rate  $5^{\circ}$ C min<sup>-1</sup>. Samples 1–7 from below.

mary solvation shell associated with the sulfonic acid groups comprises the nonfreezing water, for which no phase transition could be detected down to  $-50^{\circ}$ C. Thermograms showing the melting endotherms of water in the samples are shown in Figure 5. The freezable bound water was calculated from the enthalpies of fusion. This portion of the water is seen in the thermograms as melting/ crystallization peaks, with supercooling. Assuming thermodynamic equilibrium is reached, the freezable bound water must be bound with an energy exceeding  $6.03 \text{ kJ mol}^{-1}$ , otherwise it would freeze in the form of ice crystals at 0°C. All of the samples show similar DSC thermograms, despite the differences in pretreatment and sulfonation times (see Fig. 5). The thermograms have a bimodal peak in the region -3 to  $-1^{\circ}$ C, with a fairly broad appearance. The intensity of this double peak is generally higher in protonirradiated samples than in the others, thus indicating structural differences between proton-irradiated and EB- or nonirradiated samples. The right part of this bimodal peak propably arises partially from the water loosely bound on the rough membrane surface. It is unlikely that the drying of the membrane by blotting leaves with exactly the same proportion of surface water in every case. Hence, the melting peaks are not exactly comparable.

The amount of nonfreezing water in the sulfonated samples was further calculated from the difference of total water uptake and freezing water. We found that the amount of nonfreezing water was five to seven molecules per sulfonic

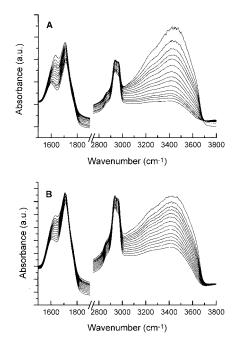


**Figure 6** FTIR spectra of different polymer based proton conductors in the frequency region of OH (plot A) and OD (plot B) stretching vibrations. Spectra of PVDF-based material was recorded with the ATR technique. Proton-irradiated and sulfonated sample (---), electron beam-irradiated and sulfonated sample (-), and a PVDF-g-PSSA sample (---).

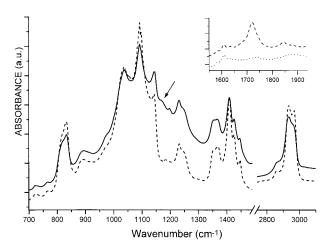
acid group in nonirradiated and EB-irradiated samples, because the portion of freezable bound water in these membranes is very small—<0.5water per sulfonic acid group. On the other hand, in proton-irradiated samples the freezable bound water was 0.5-2.5 water molecules per sulfonic acid group, leaving 9-11 nonfreezing water per sulfonic acid group in the membrane. On the basis of these results PVF membranes can be described as a totally hydrophobic matrix with embedded hydrophilic sites, which form a less continuous hydrophilic subsystem in nonirradiated or EBirradiated samples, but form a better ion conducting and more continuous hydrophilic phase in proton-irradiated samples.

The state of water in the membranes has been further studied with infrared spectroscopy. Figure 6 presents the FTIR spectra of membranes in the frequency region characteristic of the OH and OD stretching vibrations. Spectra measured from PVDF-g-PSSA membranes are included for comparison. The difference in the state of water of these two types of membranes is immediately seen. The PVF membranes show a high frequency shoulder around  $3600 \text{ cm}^{-1}$  (2600 cm<sup>-1</sup> in deuterated samples), which can be attributed to vibrations of free OH (OD) groups<sup>22</sup> and also to water molecules connected with the hydrophobic part of the material.<sup>23</sup> Thus, the conclusion is drawn that part of the water molecules in the PVF membranes is in a state different from bulk-like, and a number of water molecules are connected with the hydrophobic backbone. The situation is different from the one in the PVDF-g-PSSA membranes, where the contribution of hydrophobically bound water is much smaller.

Furthermore, the effect of drying on the state of water in the samples was studied with FTIR. The results of these measurements for the protonirradiated sample 6 and the EB-irradiated sample 4, both swelled in  $H_2O$ , are seen in Figure 7. It is seen that the total band shape remains the same; the intensities decrease monotonously as the water content decreases. A very thorough curve-fitting procedure was used to analyze the process of drying. Three spectral components, around 3460 cm<sup>-1</sup>, 3560 cm<sup>-1</sup>, and 3625 cm<sup>-1</sup>, were chosen for that purpose. The most intense component, at about  $3460 \text{ cm}^{-1}$ , is assigned as the  $\nu_1(H_2O)$  vibration of bulk water.<sup>22</sup> The two other components can have several different assignments, such as  $\nu_3(H_2O)$  of bulk-like water,<sup>22</sup>  $\nu_1(H_2O)$  or  $\nu_3(H_2O)$  of water not bulk-like.<sup>23,24</sup> Fermi resonance and overtones can influence the intensities of these bands, as can contributions of  $\nu_3(H_2O)$  vibrations in the  $\nu_1(H_2O)$  band.<sup>23</sup> Taking these into account, the comparison of the bands with respect to their intensities reveal that the highest frequency spectral component is larger in the case of the proton-irradiated sample. This means that proton irradiation and subsequent



**Figure 7** FTIR of irradiated and sulfonated samples at different degrees of hydration in the frequency range characteristic for OH vibration. Plot A is for electron beam-irradiated sample 4, and plot B for the protonirradiated sample 6.



**Figure 8** FTIR spectra of original PVF  $(\cdots \cdots)$ , proton-irradiated (1 MGy) PVF (---), and proton-irradiated and sulfonated (1 MGy, 1 h) PVF (---). An arrow marks the frequency position of the antisymmetric SO<sub>3</sub><sup>-</sup> vibration.

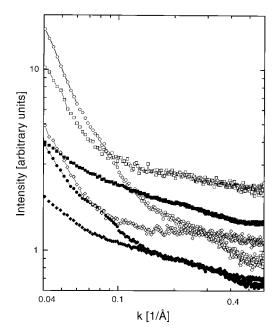
sulfonation create some extra space in the host matrix where water molecules can be bound, i.e., the regions of the cylindrical paths of protons with high sulfonic acid consentration. Analysis of the bands in the spectra of the deuterated samples support the conclusions drawn. The proton irradiation and subsequent sulfonation produces some hydrophilic sites that are missing both in the nonirradiated sulfonated and in the EB-irradiated and sulfonated samples. This result is further supported by the thermal analysis, which showed a greater ability to bind water for the proton-irradiated samples.

Figure 8 shows the IR absorption spectra of a PVF membrane at different steps of the material treatment. It is immediately seen from the spectra that proton irradiation, even at absorbed doses about 1 MGy, causes only minor changes in the material structure (see insert in Fig. 8). The two new spectral bands, around 1720 and 1845  $cm^{-1}$ , appearing after irradiation, can be assigned to the vibrations of C=O, C=C, or COOH— groups, which may be formed during the irradiation procedure.<sup>25</sup> It should be stressed that the intensities of these two bands are very weak compared to those of polymer skeleton, which shows that amount of the created complexes is rather small. Subsequent 1-h sulfonation of the irradiated membrane results in the appearance of an intense wide band centered at  $1174 \text{ cm}^{-1}$  in the IR spectra (marked with an arrow in Fig. 8). This spectral feature can readily

be assigned to the asymmetric stretching vibrations of the  $SO_3^-$  groups.<sup>22,24</sup> Moreover, comparing the spectra in Figure 8, one may note some characteristic changes in the band intensities with sulfonation. For instance, the intensities of the bands at 825 and 2950 cm<sup>-1</sup>, assigned to the rocking and stretching vibrations of the CH<sub>2</sub> groups, respectively,<sup>26</sup> decrease with sulfonation, whereas the intensity of the spectral band at 1035 cm<sup>-1</sup>, which is attributed to the CF stretching vibrations,<sup>26</sup> remains unchanged. This finding supposed that sulfonic groups are mostly connected to the carbon atoms from the CH<sub>2</sub> groups of PVF.

Structural features such as water and ion clustering in the membranes were further studied with small-angle X-ray scattering, SAXS, measurements. SAXS experiments give information on inhomogeneities of electron density on the length scale 10-1000 Å. The inhomogeneites that exist in the investigated samples are crystalline lamellae, sulfonated areas, and pores in the polymer matrix. SAXS experiments give information on their size and orientation in addition to the to the nature of the interphase boundaries. SAXS intensity curves of the proton-irradiated and sulfonated samples are presented in Figure 9.

Lamellar structures and ion aggregates are expected to give Bragg peaks or shoulders in the



**Figure 9** SAXS intensity curves of the proton-irradiated and sulfonated samples  $5(\bigcirc)$ ,  $6(\Box)$ , and  $7(\diamondsuit)$  in dry (open symbols) and wet state (filled symbols).

intensity curve, and an upturn of the intensity curve towards zero k gives information on the size of the scattering objects (Guinier approximation) and on the interphase surfaces (power law behavior).<sup>27</sup> In our case, such small k values where the Guinier approximation would hold was not reached, but the power law behavior was observed. To determinate the power law exponent the unsmeared intensity curves were fitted to the function

$$I(k) = I_0 k^{\alpha} + \text{constant}$$

where  $\alpha$  is the power law exponent. For irregular two-phase systems with sharp interphase boundaries the power law exponent is -4. For thin platelets and rods with sharp interphase boundaries the exponents -2 and -1, respectively, are obtained. Higher exponents than -4 are also obtained for fractal systems. If the surfaces are rough, then the exponent is between -3 and -4. Exponents between -2 and -3 are obtained for mass fractal objects like disordered fractal aggregates.

The SAXS intensity curves of dry and humid pristine PVF films are essentially the same, which is in accord with the low water absorption of PVF. The intensity curves increase towards zero k and obey a power law with the exponent of -4 when 0.06 Å<sup>-1</sup> < k < 0.12 Å<sup>-1</sup>. It is suggested that the scattering arises from pores in the membrane. The power law exponent of -4 indicates that the interphase boundaries are sharp. Similar behavior was also noticed in the EB- or protonirradiated samples. WAXS results showed that PVF films are anisotropically oriented. To see whether this had any effect on the pores, the sample was measured from angles perpendicular to each other, but no changes in the intensity curves were observed. The result indicates that the pore structures are isotropic. A very weak diffraction maximum at  $k = 0.038 \text{ Å}^{-1}$  was observed using an eight times larger sample to detector distance. This scattering component arises from lamellar structures and thus has a strong directional dependence.

The SAXS intensity curves of the sulfonated samples 1–7, both in the dry and in the humid state, also increases towards k = 0, but they differ from those of pristine PVF. The intensity curve of the humid sample 1 is closest to that of PVF. The intensity for  $k < 0.06 \text{ Å}^{-1}$  of the humid sulfonated samples is smaller than that of the dry films.

Such a change was not observed in the case of pristine PVF film. The change is probably caused by the increased water uptake of the sulfonated samples. The result may also indicate that the SAXS intensity of samples 1–7 partly arises from scattering of voids filled with water that are caused by the sulfonation process.

The intensity curves of the sulfonated nonirradiated samples 1 and 2 obey the power law in the range 0.04 Å<sup>-1</sup> < k < 0.12 Å<sup>-1</sup>. Exponents of -4 and-3.5 were obtained for the dry samples, and an exponent of about -3.5 was obtained for the humid samples. The decrease in the power law exponent compared to pristine PVF indicates that the sulfonation increases the roughness of the interphase boundaries. No maxima were observed in the intensity curves of either dry or humid samples 1 and 2, which indicates that the sulfonic acid groups are distributed randomly in the matrix.

From the point of view of the SAXS experiment, exchange of the counter ion to cesium ion is advantageous because it increases the electron density difference between the polymer matrix and the ionic groups. Sample 1 was measured both in proton and cesium form. The SAXS results resembled each other closely, and cesium labelling did not affect the interphase structure, as the power law exponent did not change.

The SAXS intensity curve of the electron beam irradiated and sulfonated sample 3 obey the power law in the range 0.06 Å<sup>-1</sup> < k < 0.12 Å<sup>-1</sup>. Power law exponents of about -3.5 and -3.3 were obtained for the dry and humid samples, respectively. The intensity curve of sample 4 did not obey any power law. No scattering maxima were observed in samples 3 and 4, indicating that the sulfonic acid groups are distributed randomly in the matrices.

Figure 9 shows the SAXS intensity curves of the proton-irradiated and sulfonated samples. The intensity curve of sample 5 did not follow any power law, and those of the more sulfonated proton-irradiated samples 6 and 7 obey the power law only in humid form. The k range is only 0.06  $Å^{-1} < k < 0.09 Å^{-1}$ . The exponent was -2, and this may be attributed to the scattering from lamellar structures. This further indicates that some kind of ordered structures are also present in the amorphous sample 7.

Two different shoulders can be seen in the intensity curves. One shoulder is seen in the k range of 0.14 Å<sup>-1</sup> < k < 0.4 Å<sup>-1</sup>. This shoulder could be seen in all the other samples as well as in

the original film. The other shoulder is at k = 0.09 $Å^{-1}$ , and could be observed only in the SAXS intensity curves of sample 5, both in the humid and wet state. This corresponds to a Bragg distance of about 70 Å. Because no similar shoulder was observed in the other sulfonated samples or in the nonsulfonated membranes, this shoulder is taken to arise from ionic clusters that are located along the paths of the protons. This result is in good agreement with the result that PVF can be activated for sulfonation by irradiating with ionizing radiation.<sup>3</sup> The absence of this feature in the other proton-irradiated and more strongly sulfonated samples 6 and 7 is possibly due to the decrease of contrast, i.e., the clusters are present in the samples but are not visible in the SAXS intensity patterns. Also, the experimental setup did not favor the visibility of the clusters; in the measurements the scattering vector laid in the plane of the membrane and thus perpendicular to the tracks. Because of this, the clusters that are located along the same proton tracks were weakly visible.

The above results point towards the existence of water-binding channels through the membranes made by proton irradiation. The water uptake is higher in proton-irradiated samples than in nonirradiated or EB-irradiated samples. SAXS intensities of the proton-irradiated samples exhibit features that can be taken to arise from ion clusters. The reason for this result is possibly the formation of microvoids along the paths of protons. Volatile radiolysis products are formed in organic materials upon irradiation. Depending on the type of irradiation, the position of the formation of these products can be homogenous or heterogeneous.<sup>2</sup> In ion irradiation the local dose reaches extremely high values, with the consequence of the cumulation of the radiolysis products along the tracks, and possibly the formation of microvoids. The formation of microvoids has been established, for example, by Ouano,<sup>28</sup> Besmann et al.,<sup>29</sup> and Komaki et al.<sup>30</sup> Ouano has proposed that in poly(methyl methacrylate) microvoids are formed due to the irradiation, which increases etchability and solvent penetration.<sup>28</sup> Besmann et al. concluded that upon  $\gamma$ -irradiation of polyethylene volatile radiolysis products are accumulating in less dense areas in the matrix polymer.<sup>29</sup> Komaki et al.<sup>30</sup> studied ion irradiation effects on poly(vinylidene fluoride) and came to the conclusion that ion irradiation generates microvoids of a size of several tens of an Å along the tracks of the passed ions. The arrays of the microvoids makes the sulfonation reaction easier, thus facilitating water penetration and ion transport.

## **CONCLUSIONS**

A detailed analysis of the structure of the directly sulfonated poly(vinyl fluoride) has been performed. Sulfonated samples with the same ion exchange capacity but different irradiation treatment had significantly diverse properties with respect to water uptake, portion of different forms of water, and ion conductivity. Proton irradiated and sulfonated samples had higher water uptake than the nonirradiated and sulfonated or the electron beam-irradiated and sulfonated samples. In addition, the portion of the hydrophobically bound water was lower in proton-irradiated and sulfonated sample than in the respective electron beam-irradiated and sulfonated sample. This result, together with ion conductivities, agree well with with generally accepted idea that hydrophobically bound water is excluded from the proton transport process.<sup>23,31–33</sup> SAXS experiments showed features of ion cluster formation in one of the proton irradiated samples. Because proton irradiation forms cylindrical tracks and enhances the sulfonation reaction, the overall product can be taken as being a sort of phase-separated structure of sulfonated and unreacted PVF. Thus, these results indicate that phase separation and aggregation of the ionic groups favor or is tightly related to the enhanced ion conductivity. This conclusion is in line with conclusions drawn for the grafted membranes like PDVF-g-PSSA,<sup>20</sup> which have even higher ion conductivity with lower ion exchange capacity. The inherent regular morphology of the Nafion membranes is not a prequisite for high ion conductivity, but the present work shows that continuous hydrophilic domains are necessary for ion and water transport. In addition, the selection of the irradiation method gives new alternatives to prepare, modify, and improve properties of proton-conductive polymer membranes.

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