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The state of water and the nature of ion clusters in crosslinked proton conducting membranes of styrene grafted and sulfonated poly(vinylidene fluoride)

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Proton conducting membranes were prepared by irradiation grafting with styrene followed by sulfonation on matrices of poly(vinylidene fluoride), PVDF. Membranes crosslinked with divinylbenzene and/or bis(vinylphenyl)ethane were compared to non-crosslinked membranes. The ion conductivity of the crosslinked membranes is lower than that of the non-crosslinked membranes. This is due partly to the very inefficient sulfonation of the crosslinked membranes below the graft penetration level, which in turn leads to a low water uptake at low degrees of grafting. The graft penetration level is lower in crosslinked membranes than in non-crosslinked membranes. This leads to a more compact structure of the crosslinked grafts within the matrix. The lower ion conductivity in the crosslinked membranes is therefore partly also due to restricted mobility of the ion clusters necessary for ion and water transport in the membranes.

Introduction

Proton conduction in solid polymers is studied because of important potential applications of such membranes as separators in electrochemical cells and fuel cells.[1,2] Much of the work in the literature is concerned with the commercially available Nafion® and Dow membranes. These membranes readily incorporate water, the presence of which is essential for proton conduction. Adequate control of water content of the ionomeric material is necessary in applications. A central question in the evaluation of membranes for electrochemical cells has thus been the analysis of the structural water and the water uptake characteristics in relation to the proton conductivity. Yeo *et al.*[3] showed that ion aggregates form in perfluorinated polymer sulfonic acids. These aggregates effectively act as crosslinkers in the membranes adding mechanical strength to the thin membranes. Evidence for the formation of ion aggregates in Nafion® has been derived from wide angle and small angle X-ray measurements (WAXS and SAXS).[4,5] Structural models have been developed describing these membranes as phase separated systems with two or more phases. The existence of the clusters is generally agreed upon, but the details of their arrangement and connectivity are still under debate.[2,6]

Although the perfluorinated commercial membranes are noted for their stability and good performance, the high cost of these membranes has focused interest on the syntheses of new proton conducting materials. Steck[7] reports on successful work on sulfonated polyaromatic polymers in which it was shown that the ion clustered regular morphology of the perfluorinated sulfonic acid membranes is not a prerequisite to good fuel cell performance.

Radiation induced graft copolymerisation has proved to be an efficient way to develop proton exchange membranes based on fluorinated or partly fluorinated polymers. In this method a film forming polymer with suitable morphology and physical properties is chosen as matrix material. Reactive sites, free radicals, are introduced in the matrix by irradiation. In the presence of vinyl monomers the free radicals can initiate graft copolymerisation. The various types of radiation and the radiation chemistry of polymeric materials have recently been reviewed by Heger.[8] Irradiation methods have been used in the development of strongly acidic membranes for use in fuel cells. Gupta *et al.* have reported the graft copolymerisation of styrene into films of poly(tetrafluoroethylene-*co*-hexafluoropropylene), FEP, with subsequent sulfonation after γ-irradiation.[9–12] Membranes with good chemical stability and ion conductivity were achieved. Correlations between the degree of grafting (dog), and the physical properties of the resulting membranes were found. FEP was chosen as matrix material because of its high resistance to radiation damage.

Irradiation with electron beams is a useful method due to its simplicity and short irradiation times, which makes the method feasible also for large scale production of graft copolymers. Various types of cation exchange membranes have been prepared by electron beam irradiation followed by grafting reactions.[13] A sulfonic acid group containing membrane was prepared by grafting glycidyl methacrylate onto an ethylene–tetrafluoroethylene copolymer with subsequent sulfonation. The ion conductivity of the membrane was comparable to that of Nafion®.[14] Poly(vinylidene fluoride), PVDF, has been used as matrix polymer in the preparation of polymer membranes for low temperature fuel cells.[15] We have recently reported the preparation and characterisation of proton conducting membranes with PVDF films as matrices. The preparation involves the irradiation of the PVDF film with an electron beam followed by graft polymerisation of styrene into the matrix and sulfonation of the grafted film.[16] The characterisation of the resulting membranes, PVDF-g-PSSA membranes, involved thermal analysis,[17] X-ray diffraction (WAXS and SAXS)

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measurements,[18] gas permeation determinations[19] and electrochemical measurements.[20,21] Preliminary fuel cell tests show promise for the development of these membranes. Gupta *et al.* have reported better performance of similar membranes after chemical crosslinking.[9–12] In the present study two different crosslinkers, divinylbenzene, DVB, and 1,2-bis(vinylphenyl)-ethane, BVPE, were introduced in the grafting reaction, and the influence of the crosslinking on the properties of the membranes was investigated. The objectives of the work in the present paper were to compare the graft penetration, the degree of sulfonation, the swelling, the binding of the water and the ion conductivity in the non-crosslinked and the crosslinked membranes, and ultimately, to test the fuel cell performance of the membranes, tests that are still in progress.

The polymer electrolyte membranes are ion conductive only when swelled with water. The factors dominating the transport of protons and water in proton conducting polymer membranes are closely related to the local interactions of sulfonic acid moieties and solvating water molecules, especially the water molecules in the first solvating sphere around the sulfonic acid.[22] Molecular level understanding of the structural and dynamic properties governing the transport processes, which would improve the design of new membranes, is still incomplete. Most of the experimental work has concentrated on Nafion.[23–26] We have reported results of studies of the binding of water,[17] the water sorption and the diffusion coefficients of protons and water[27] in non-crosslinked PVDF-g-PSSA membranes. The following main conclusions have been drawn: the water self diffusion coefficient increases with increasing water content in the membrane, and the proton conductivity increases to a certain limiting value with increasing water content.

Experimental

Preparation of the crosslinked styrene grafted and sulfonated PVDF membranes, PVDF-g-PSSA

The matrix polymer films were melt processed 80 μm thick films of PVDF from Goodfellow. The divinylbenzene (65% isomeric mixture in ethylvinylbenzene, Fluka) was distilled prior to use. The bis(vinylphenyl)ethane was prepared from vinylbenzyl chloride (isomeric mixture containing 70% of the *meta*- and 30% of the *para*-isomer, Dow) in 67% yield and 95% purity according to a method described by Li *et al.*[28] This synthesis has been described in detail elsewhere.[16] Styrene (Fluka), chlorosulfonic acid (Merck), 1,2-dichloroethane (Merck) and toluene (LabScan) were reagent grade and used as received.

The proton conducting membranes for this study were prepared by electron beam irradiation of PVDF membranes followed by grafting with styrene, or styrene in the presence of two different crosslinkers, DVB and BVPE, respectively. The grafting was followed by sulfonation with chlorosulfonic acid.[16] PVDF was chosen as the matrix material as it is commercially available in thin films, has suitable mechanical properties and has a low glass transition temperature, T_g, around −40 °C. Svarfvar *et al.* have shown that PVDF becomes very active towards vinyl monomers as a result of the irradiation.[29] The results showed that the effects of the crosslinkers could well be described using measurements with membranes containing 0 and 5 mol% of the two crosslinkers, respectively, and therefore mainly these results are included in the present report. The properties of some typical crosslinked membranes are collected in Table 1; non-crosslinked membranes are included as references. The graft penetration limit of the membranes was determined by energy dispersive X-ray measurements of the fluorine and sulfur distribution in the transverse plane of the grafted and sulfonated membranes. These measurements have been described in detail.[30] The penetration limit is defined as the lowest degree of grafting at which the sulfur is evenly distributed through the membrane.

Irradiation was carried out with an Electrocurtain accelerator (Energy Sciences Inc.) under nitrogen atmosphere (<200 ppm O_2) at an acceleration voltage of 175 kV. The absorbed dose was 100 kGy. The irradiated films were immediately immersed in the 1 : 1 (v/v) monomer solution containing styrene and 0, 2.5, 5 or 10 mol% of the crosslinker, respectively, and toluene. The monomer solution was purged with nitrogen before and during the reaction. The reaction temperature was 70 °C. The sulfonation reaction was carried out at ambient temperature for 24 h in a solution of 0.5 M chlorosulfonic acid in 1,2-dichloroethane. The degree of grafting was determined gravimetrically as $((m_1 - m_0)/m_0)) \times 100\%$ where m_0 is the mass of the original membrane and m_1 is the mass of the grafted membrane. The details of the preparation of the styrene grafted PVDF membranes, PVDF-g-PS, and the sulfonated membranes, PVDF-g-PSSA, have been described elsewhere.[16]

Water uptake, equilibrium swelling, cation exchange

The water uptake of the membranes, defined as the ratio of the mass of the hydrated membrane to that of the dry membrane, was determined by equilibrating the membranes in water. The excess water was blotted with filter paper from the membrane surface before weighing. The dry mass of a membrane was determined after drying over P_2O_5 in a desiccator for one week at ambient temperature. The proton was exchanged to caesium or zinc ions by soaking the membranes in a large excess of a 20 mM aqueous solution of the appropriate metal chloride for 4 d, followed by rinsing with water and drying as described.

Ion exchange capacity, *Q*

The ion exchange capacity was determined by back titration with aqueous hydrochloric acid after soaking the membranes in sodium hydroxide solution for several days.

Ion conductivity

The ionic conductivity of the PVDF-g-PSSA membranes was determined by the ac impedance method using a frequency range of 5 to 50 kHz. The measurements were done in a solid two-electrode cell connected to a Solartron 1270 frequency response analyser and a microcomputer. The membrane resistance was obtained by extrapolating the data to infinite frequency. The conductivity was calculated from the electrode area of the cell and the thickness of the membrane. Prior to the measurements the membranes were equilibrated with water vapour in a closed vessel for a minimum of three days. The conductivity measurements have been discussed in great detail elsewhere.[18]

Thermal analysis

Thermograms of the membranes were measured with a Perkin-Elmer DSC 7 calorimeter with a heating rate of 20 °C in the temperature range −50 °C to 200 °C. The calorimeter was calibrated with indium and water. The measurements were repeated three times in order to determine the influence of annealing on the melting process. The overall percentage crystallinity of the sample was evaluated from the heat of fusion of the sample in the usual way with a value of 104.7 J g^{-1} for the enthalpy of fusion of the fully crystalline PVDF.[31] The freezing bound water in the PVDF-g-PSSA membranes was determined from cooling thermograms. The samples were closed in aluminium pans and cooled in the calorimeter sample chamber. The temperature of the calorimeter block was −80 °C. Thermograms were registered between −50 °C and 10 °C, with a heating rate of

Table 1 Composition and properties of PVDF-g-PSSA membranes

			Water uptake			
Crosslinker	Dog/%	Q/mequiv g^{-1}	w/w	nH$_2$O/nSO$_3$H	Non-freezing nH$_2$O/nSO$_3$H	σ/mS cm^{-1}
—	18	0.30	0.06	9–11	9–10	<0.1
—	32	0.90	0.22	9–15	9–10	<0.1
—	48	2.01	0.90	25	11	108
—	60	2.26	1.43	35	11	107
—	73	2.55	1.39	30	10	117
5 mol% BVPE	18	0.48	0.06	7–9[a]	7–9	<0.1
5 mol% BVPE	30	0.43	0.08	10[a]	7–9	<0.1
5 mol% BVPE	48	2.24	0.08	3–5[a]	3–5	<0.1
5 mol% BVPE	60	2.29	1.14	28	11	100
5 mol% BVPE	73	2.51	1.12	29	12	77
5 mol% DVB	95	2.78	1.30	30	11	130
5 mol% DVB	19	0.19	0.02	3–5[a]	3–5	<0.1
5 mol% DVB	31	0.18	0.03	5–7[a]	5–7	<0.1
5 mol% DVB	49	0.66	0.07	15	10	<0.1
5 mol% DVB	70	2.53	0.62	13–15	8–10	45
5 mol% DVB	103	2.95	0.59	21	8–10	68

[a] The precision in these measurements is not very high due to the inhomogeneity of the membranes and the roughness of their surface.

5 °C min^{-1}. The freezing water in the membranes was estimated using the value 330 J g^{-1} for the melting enthalpy of water. The non-freezing water was calculated from the total water loss obtained by heating the membranes after the cooling cycle to over 100 °C.

X-Ray diffraction measurements. WAXS

The PVDF-g-PSSA membranes were measured in caesium or zinc form at ambient temperature in symmetrical transmission and symmetrical reflection geometries with Cu-Kα radiation 1.542 Å, using a θ–2θ diffractometer. The radiation was monochromated with a quartz monochromator in the incident beam. The intensity curves were corrected for absorption and background due to air scattering. The original PVDF film was measured with Mo-Kα_1 radiation with a silicon monochromator crystal in the incident beam in vacuum at various temperatures. A θ–θ diffractometer with a high temperature chamber was used in symmetrical transmission mode. The scattered intensities were measured with a scintillation counter.

SAXS

The SAXS measurements were made with a sealed copper anode fine-focus X-ray tube, used in point focusing mode. The Cu-Kα_1 radiation was monochromated by means of a nickel filter and a totally reflecting glass block (Huber small angle chamber 701). The scattered radiation was measured in the horizontal direction (beam width) by a linear one-dimensional position-sensitive proportional counter (M. Braun OED-50M). The space between the sample and the detector was evacuated to 0.05 mmHg using 13 µm polyimide foils as X-ray windows. The scattering distance was 150 mm. A narrow vertical slit was used before the sample to reduce background scattering. The beam height at the sample was approximately 1.0 mm. The primary beam was narrow, FWHM < 0.002 Å^{-1}. Together with the detector height profile the FWHM of the instrumental function in the vertical direction was about 0.044 Å^{-1}. The magnitude of the scattering vector is defined as $k = (4\pi/\lambda)\sin\theta$, where θ is half of the scattering angle and λ is the wavelength. The smallest achievable k was 0.015 Å^{-1}. The experimental SAXS curves were corrected for absorption, air scattering and the experimental smearing due to the vertical instrument function. The samples were heated with a Linkam TP93 temperature controller which was connected to the sample holder. In order to prevent membrane drying during the measurement the samples were sealed between thin Mylar® foils.

Results and discussion

Degree of sulfonation, water uptake and binding of water

Recently the influence of the degreee of grafting and the crosslinking on the efficiency of the sulfonation has been studied. In contrast to what has been reported for the sulfonation of irradiation grafted FEP membranes[32] the sulfonation turns out to be incomplete in styrene grafted samples based on PVDF with low degrees of grafting, and in crosslinked samples,[33] and especially so when the sulfonation is accomplished at low temperatures. Highly grafted, non-crosslinked samples have been found to be homogeneously grafted and homogeneously sulfonated to a high degree. On the other hand, samples with low degree of grafting have been found to be inhomogeneously grafted on the surface, and they also show a variation with depth due to a front grafting mechanism.[16] In addition, it was found that the relative sulfonation varies over the surface as well as with depth into the sample. At low grafting levels the sulfonation of the DVB crosslinked samples was considerably less efficient than in samples crosslinked with BVPE. For high grafting levels the addition of crosslinker does not have a significant impact on the achieved sulfonation.[32] The incomplete sulfonation therefore is most probably one of the main reasons for the low water uptake and the low ion conductivity. In a previous paper[21] we have attributed the differences in ion conductivity between crosslinked and non-crosslinked PVDF-g-PSSA membranes to differences in the graft penetration, *i.e.* in all the samples the penetration limit is lower in non-crosslinked samples than in crosslinked, although this effect is much more pronounced in membranes crosslinked with DVB. Obviously incomplete graft penetration leads to a low degree of sulfonation and an unfavourable distribution of the hydrophilic domains necessary for ion transport. The grafting and the sulfonation are the subject of further investigations in our group.[34]

The bulk properties of proton conducting membranes, in this case most importantly the ion conductivity, will depend on hydrophobic–hydrophilic interactions, and thus, on the distribution of water and grafts in the membranes. For proton transport to occur, the water uptake of the material has to exceed a certain treshold value. In Nafion® 117 the minimum water content for conduction was shown to be 6–7 molecules of water per sulfonic acid group.[35,36] We have recently reported[30] that the minimum water content for ion conductivity in the non-crosslinked PVDF-g-PSSA membranes is around 10 molecules of water per sulfonic acid group, which are considered to form the primary hydration shell around the sulfonic acid groups, but do not alone form the aqueous domains necessary for efficient ion and water transport.

The total water uptake of the crosslinked PVDF-g-PSSA membranes was determined gravimetrically. The results are collected in Fig. 1 which shows the total water uptake in molecules per sulfonic acid group as a function of the degree of grafting. It is seen that the water uptake is very low in membranes with the degree of grafting below the graft penetration limit, in particular in membranes crosslinked with DVB, *cf.* Fig. 1 and Table 1. In previous studies we saw a similar effect of the degree of grafting and crosslinker on the ion conductivity in the membranes.[21,37] This was attributed mainly to the different reactivities of the crosslinkers, resulting in networks of disparate nature with different diffusion rates and different mobilities of the macroradicals in the membranes.[38] DVB reacts faster than styrene leading to highly crosslinked domains inside the membrane.[39] The grafting with styrene in the presence of BVPE results in a randomly crosslinked polymer with a more even crosslink distribution since the product of the reactivity ratios r_1r_2 is close to 1 for styrene copolymerising with BVPE.[37] The looser structure of the BVPE crosslinked membrane favours the sulfonation reaction which, however, is less complete in all the crosslinked samples than in the noncrosslinked ones. With a less complete sulfonation the water uptake stays low.

The binding of the water in the PVDF-g-PSSA membranes was studied with thermal analysis. A large portion of the total water uptake accounts for the formation of the primary solvation shell of the sulfonic acid groups. This portion is the non-freezing water, the phase transition of which could not be detected down to −50 °C. The less closely associated water in the PVDF-g-PSSA membranes is detected as melting/crystallisation peaks, with supercooling. The thermograms in Fig. 2 show the thermograms for crosslinked and non-crosslinked PVDF-g-PSSA membranes, respectively, with approximately the same degrees of grafting. Supercooling freezing water is found in non-crosslinked membranes.[36] Since the water uptake is low in the crosslinked membanes to a degree of grafting >50% peaks of freezing bound water are clearly detectable only in samples with high degree of grafting. In samples crosslinked with 10 mol% DVB no peak for freezable bound water could be reliably detected.

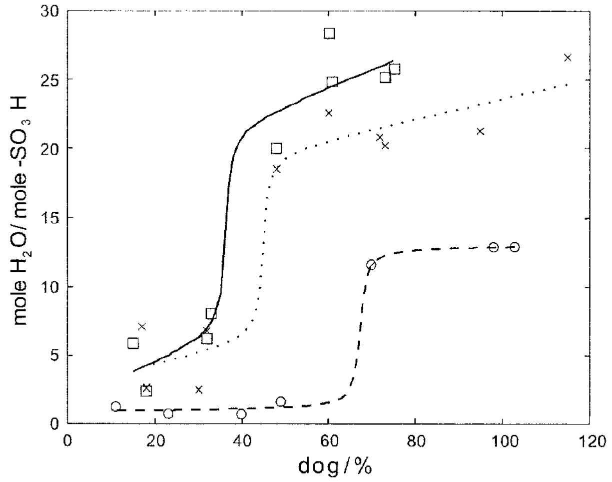

Fig. 1 The total water uptake of the PVDF-g-PSSA membranes as moles of water per mole of sulfonic acid as a function of degree of grafting, dog. (□) non-crosslinked membranes, (×) membranes crosslinked with 5 mol% of BVPE, (○) membranes crosslinked with 5 mol% of DVB.

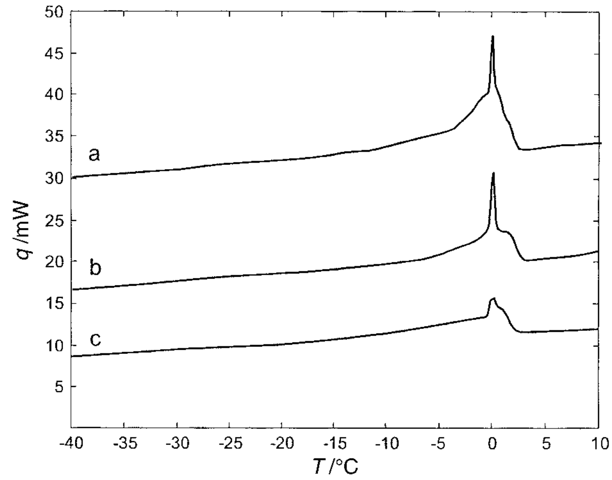

Fig. 2 Thermograms of PVDF-g-PSSA membranes with a degree of grafting of around 70%. a) non-crosslinked membrane, b) membrane crosslinked with 5 mol% of BVPE, and c) membrane crosslinked with 5 mol% of DVB.

In non-crosslinked samples two melting peaks for water are seen, one close to 0 °C, and one between −5 °C and −10 °C.[36] Both peaks are broadened indicating water bound to pores or sites of a wide distribution of sizes. The conclusion was drawn that the fully hydrated membranes contain water of three different types associated with the polymer; non-freezing water bound to the sulfonic acid groups, freezing bound water weakly bound to the ionic groups and the polymer matrix, and freezing free water.[36]

The membranes crosslinked with BVPE show a broad bimodal melting peak from −15 °C to −2 °C. The bimodal peak develops at higher degrees of grafting (around 50%) in the BVPE crosslinked membranes than in the non-crosslinked. In the membranes crosslinked with 5 mol% DVB a small peak of freezing water can be detected at a degree of grafting around 70%, see Fig. 2. The depression of the freezing point of the freezable water in the membranes with respect to pure water is explained by assuming that the water is associated with the polymer backbone. The amount of freezable water in the membranes was calculated from the total change in enthalpy of the water melting peaks. The difference between the total water uptake and the freezable water gives the amount of non-freezable water in the membranes which is included in Table 1. In non-crosslinked samples this is around 10 molecules of water per sulfonic acid group, a number which is nearly independent of the degree of grafting.[36] In the crosslinked membranes the total water uptake stays below 10 molecules of water per sulfonic acid group at low degrees of grafting, see Table 1. Only a little freezable water is detectable in the crosslinked membranes, in fact no freezable water was detected in the crosslinked membranes below a degree of grafting of around 50%, and the total water uptake remained below 10 molecules of water per sulfonic acid group. Thus the stiffened crosslinked grafts are less able to accommodate hydration water than the noncrosslinked structures. This is obvious in particular in membranes crosslinked with DVB in which the total water uptake stays low (10–15 molecules of water per sulfonic acid group) also at high degrees of grafting.

Ion exchange capacity and ion conductivity

The ion exchange capacity, *Q*, of the PVDF-g-PSSA is a measure of the concentration of the active ion exchange sites in the membranes. The *Q* values of the PVDF-g-PSSA membranes are plotted against degree of grafting in Fig. 3. The values of *Q* are low in membranes below the graft penetration

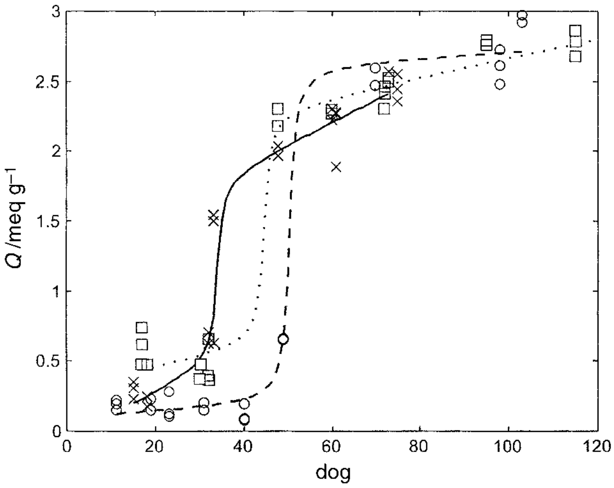

Fig. 3 The ion exchange capacity of PVDF-g-PSSA membranes as a function of dog (×) non-crosslinked membrane, (□) membrane crosslinked with 5 mol% of BVPE, and (○) membrane crosslinked with 5 mol% of DVB.

limit, <0.5 mequiv g^{-1}; especially this is the case with the membranes crosslinked with DVB, see Table 1. Q reaches values >2 mequiv g^{-1} over the graft penetration level where the degree of sulfonation is high. The low Q values also correspond to membranes in which the water uptake stays low, see Table 1. Nafion 117 was measured as a reference, and values of $Q = 0.7$–0.9 mequiv g^{-1} were found.[36] The dependence of Q on the degree of grafting was studied with the Nelder–Mead simplex non-linear optimisation method.[40] The ion exchange data were fitted to the equation $a + bx + c$ arctan$(x - d)$. Results of this optimisation are included in Fig. 3, and they clearly show that there is a rapid increase in the Q at a threshold value of the degree of grafting which is lowest for the non-crosslinked membranes and highest for the DVB crosslinked membranes. This corresponds to the parameter d in the equation, and is the turning point of the arctan function giving the degree of grafting at which there is a rapid increase in Q. This is in agreement with the finding that the sulfonation is incomplete and inhomogeneous at low degrees of grafting and, in particular, in the presence of crosslinkers.[29] The values of Q are also rather low in the presence of crosslinkers at low degrees of grafting, as a consequence of the incomplete and inhomogeneous sulfonation. Obviously the sulfonation proceeds *via* a front mechanism, and the penetration of the sulfonating agent is considerably hindered in the crosslinked membranes. Low Q values indicate inefficient diffusion of ions in the membranes, thus also implying that the hydrated sulfonic acid groups are isolated in the interior of the membrane, the hydrophobic matrix governing the transport. The Nelder–Mead simplex non-linear optimisation method was used also for the dependence of the water uptake on the degree of grafting, the results are included as full lines in Fig. 1.

The ion conduction, σ, of the crosslinked PVDF-g-PSSA membranes has been discussed in detail elsewhere.[21,36] From Table 1 it is seen that σ is lower in the crosslinked membranes than in the non-crosslinked, and reaches practically useful values as the water uptake and Q increase beyond the graft penetration limit. As conductivity depends both on the number of charge carriers and their mobility the lower ionic conductivity measured in the crosslinked membranes must be due to restrictions in the mobility of the ionic aggregates. To differentiate between the effect of the number of sulfonic acid groups and the reduced mobility of the aggregates further detailed experiments are needed. Some details are revealed, however, in the X-ray diffraction measurents as discussed below.

Water and ion clustering

The formation of ion clusters in the PVDF-g-PSSA membranes was studied with X-ray diffraction in low angle scattering experiments. The experimental SAXS intensity curves are typical for ionomers.[41,42] They include an ionic peak at around $k = 0.36$ Å^{-1} with an upturn towards $k \rightarrow 0$ in dried membranes in the caesium or zinc form. The PVDF lamellae cause an intensity maximum at $k = 0.06$ Å^{-1}, corresponding to a Bragg distance of 105 Å. Changes in the intensity curves due to the preferred orientation of the lamellar structures were observed by rotating the samples in the plane perpendicular to the primary beam. By comparing the results of the orientation studies by WAXS and SAXS it was concluded that the lamellae have the same orientation as the PVDF chains. The intensity curves did not indicate any preferred orientation of the ionic aggregates.[43]

The ionic peak is seen at 0.36 Å^{-1} in the PVDF-g-PSSA membranes in the wet state, see Fig. 4. This corresponds to a Bragg distance of 17 Å. This peak was not observed in dry membranes, hence it is due to the sulfonic acid–water aggregates in the membrane. Such a SAXS peak is typical for ionomers but in most cases a larger Bragg distance has been observed.[43] The Bragg distance is considerably smaller than in Nafion 117, in which it is 30–50 Å.[4,5] We believe that the difference is due to the degree of sulfonation which in our case is higher than in most previous studies. Furthermore, the ionic peak of the PVDF-g-PSSA samples moves to higher k values as the sulfonation level increases.

Heating of the PVDF-g-PSSA membranes affects both the PVDF lamellae and the ionic aggregates. The membranes in

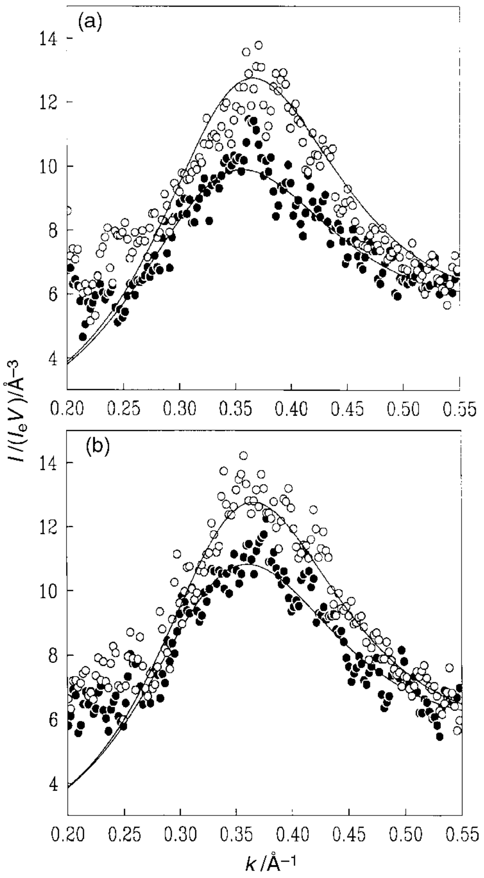

Fig. 4 The experimental SAXS intensities of PVDF-g-PSSA membranes, and the intensities fitted to the Yarusso liquid-like hard sphere model.[44] a) non-crosslinked membrane with a degree of grafting of 48%, and b) membrane with a degree of grafting of 73% crosslinked with 5 mol% BVPE. (■) measured at room temperature, and (□) measured at 90 °C.

Table 2 The fitting parameters determined by using the Yarusso liquid-like hard sphere model.[43]

	Degree of grafting 48%			Degree of grafting 73%		
	Non-crosslinked			Crosslinked		
Temp./C	ρ_1/Å^{-3}	R_1/Å	R_2/Å	ρ_1/Å^{-3}	R_1/Å	R_2/Å
RT	5.4 ± 0.6	2.5 ± 0.1	8.1 ± 0.3	3.9 ± 0.2	2.8 ± 0.1	8.1 ± 0.3
50	3.3 ± 0.6	2.8 ± 0.1	8.1 ± 0.3	3.4 ± 0.2	3.0 ± 0.1	8.1 ± 0.3
70	2.8 ± 0.3	3.2 ± 0.1	8.0 ± 0.3	2.5 ± 0.2	3.3 ± 0.1	7.8 ± 0.3
90	2.5 ± 0.3	3.3 ± 0.1	8.0 ± 0.3	2.3 ± 0.1	3.4 ± 0.1	7.8 ± 0.3

caesium form were heated in the sample holder to 30 °C, 50 °C, 70 °C and 90 °C, respectively. The intensity maximum of the PVDF lamellae increased and sharpened as a result of the heating indicating rearrangement of the structure. These changes in the diffraction pictures are most noticeable in the crosslinked membranes. The intensity of the ionic peak of all the membranes increased with increasing temperature. In the non-crosslinked membrane with a degree of grafting of 73% the ionic peak shifted to higher k values with increasing temperature. At room temperature the ionic peak of the crosslinked membranes was more symmetric than that of the non-crosslinked membranes. The different thermal behaviour of the ionic aggregates in the non-crosslinked and the crosslinked membranes indicates that crosslinking influences the structure of the ionic aggregates.

WAXS measurements at various temperatures show that crosslinking decreases the thermal stability of the membranes. Both the size of the crystallites and the preferred orientation diminished in crosslinked membranes with increasing temperature. In contrast, the preferred orientation increased on heating, and the size of the crystallites decreased less in the non-crosslinked membranes, most probably due to increased mobility of the grafted chains on heating. The crosslinked and sulfonated polystyrene grafts form a rigid structure within the PVDF matrix[18] which affects the structure and restricts the mobility of the ionic aggregates.

The structure of ionic aggregates has been described by the Yarusso liquid-like hard sphere model.[44] The Percus–Yevic structure factor was used.[41] The model assumes a spherical shape for the aggregates. The radius of the aggregate is denoted R_1 and the radius of closest approach of the aggregates is R_2. R_2 can be considerably larger than the aggregate diameter $2R_1$. The scattered intensity $I(k)$ is given by

$$I(k) = [(I_e V)/v_p] v_1^2 \rho_1^2 \Phi^2(k, R_1) S(k, R_2, v_p) \qquad (1)$$

where $\Phi(k, R_1)$ is the form factor of the sphere, $S(k)$ is the structure factor and $v_1 = 4/3\pi R_1{}^3$. I_e is the intensity scattered by a single electron under the experimental conditions and V is the illuminated volume of the sample. The electron density difference between the aggregates and the matrix is ρ_1 and the average sample volume per aggregate is v_p. The measurements were scaled to absolute intensities with the aid of the intensity of water.[45] Fitting of eqn. (1) to experimental results gives optimal values for the four parameters ρ_1, R_1, R_2 and v_p. Fig. 4 shows examples of the fitting to the model of the experimental intensity curves of a non-crosslinked sample with a degree of grafting of 48%, and a crosslinked sample with degree of grafting of 73% at two different temperatures. Although the agreement is good in both cases, it is slightly better for the crosslinked sample. The fitting parameters are collected in Table 2. Similar results were obtained for other membranes at various temperatures. The volume $v_p = (1.3 \pm 0.1) \times 10^4$ Å^3 did not change upon annealing.

The electron density difference between the ionic aggregates and the matrix decreased and the radius of the aggregates increased with increasing temperature. When the aggregates grow the border between the aggregates and the matrix disappears which decreases the electron density difference. However, heating affected neither the distance between two aggregates R_2 nor the volume v_p, hence the number of ionic aggregates did not change as a result of heating.

Conclusion

Crosslinked membranes of PVDF-g-PSSA were prepared. With divinylbenzene as a crosslinker a tighter structure is formed which hinders graft penetration to a higher degree of grafting than with bis(vinylphenyl)ethane as a crosslinker. Below the graft penetration limit sulfonation is ineffective in all the membranes. The low degree of sulfonation at low degrees of grafting and the crosslinked structures restrict the formation of ion clusters for proton transport. The hydration of the polymer structure to a level of powerful ion conduction is also severely restricted in the crosslinked structures. The ion conductivity of the crosslinked membranes is lower than in the non-crosslinked membranes. Aggregates of water and ionic sites with a Bragg distance of 17 Å were determined. Heating decreases the preferred orientation of the lamellae in the membranes; the effect is more pronounced in the crosslinked membranes than in the non-crosslinked membranes. Heating also affects the short range order of the membranes. The intensity of the ionic peak increases with temperature. Heating affected neither the distance between ionic aggregates nor their volume, hence there is no change in the number of aggregates on heating. The lower ion conductivity in the crosslinked membranes is therefore due to restricted mobility of the ion clusters.

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