Structural investigation of radiation grafted and sulfonated poly(vinylidene fluoride), PVDF, membranes

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Radiation grafted and sulfonated poly(vinylidene fluoride), PVDF, membranes have been studied by thermal analysis and X-ray diffraction to determine the changes in membrane crystallinity and structure during preparation. Commercial PVDF films were irradiated with an electron beam, grafted with styrene and finally sulfonated. Both the crystallinity and the size of the crystallites of PVDF decrease in the grafting reaction. A further decrease in crystallinity is observed in the sulfonation reaction. The residual crystallinity of PVDF was considerable (10–20%) even in membranes which had been subjected to severe reaction conditions. These results can be explained by assuming that the grafting takes place mainly in the amorphous region of the PVDF, and close to the surfaces of the crystals, but that grafts do not penetrate into the crystals. The proton conductivity of the grafted and sulfonated PVDF membranes reached values comparable to those of Nafion membranes.

Membranes with high protonic conductivity are potentially useful as separators and electrolytes in electrochemical cells such as fuel cells. Among the first proton-conducting membranes used in fuel cells were sulfonated, crosslinked polystyrenes.[1] In recent years Nafion films have been extensively studied as proton-conducting membranes[2] for use in fuel cells. Nafion is, however, a very expensive material, and other materials are being sought.

In the development of new membranes, functionalisation of a preformed polymer material offers many advantages, in particular with respect to the price and the mechanical properties of the matrix material. Functionalisation is possible by grafting. Among many grafting techniques available, radiation-initiated grafting is one of the most useful.[3,4] The electron beam pre-irradiation method is useful due to its simplicity and short irradiation times, which makes the method attractive for scale-up production. Radiation grafting methods have been extensively studied.[3–5]

Many studies have been reported on grafting different monomers onto fluorine-containing polymers by the radiation-induced grafting technique.[6–14] In order to obtain proton exchange membranes, styrene is usually grafted onto a fluoropolymer and the graft copolymer is subsequently functionalised with sulfonic acid groups.[15] Because of the chemical stability needed, the backbone polymers have been limited to the fully fluorinated polymers poly(tetrafluoroethylene), PTFE, or poly(tetrafluoroethylene-*co*-hexafluoropropylene), FEP. Styrene together with divinylbenzene, DVB, has been grafted onto FEP followed by sulfonation. In fuel cells these membranes show good performance and stability.[6,7] Poly(vinylidene fluoride), PVDF, is an interesting alternative, which apart from good stability also has a competitive price. Partially fluorinated membranes that fulfil the stability requirements in electrolysis cells have been described.[16]

We have recently reported the preparation and characterisation of proton-conducting membranes with porous poly(vinylidene fluoride), PVDF, films as matrices.[14] The preparation involves the pre-irradiation of PVDF film with an electron beam, graft polymerisation of styrene monomer into the matrix and sulfonation of the grafted film. The degree of grafting and degree of sulfonation are controlled by the reaction time and conditions. Proton conductivities corresponding to values measured for Nafion were reached. It was found that the proton conductivity of the new membranes depended on several factors, among them the crystallinity of the matrix polymer, and of the resulting graft, respectively. Residual crystallinity was found in membranes which had been subject even to the most severe reaction conditions, hence the resulting membranes are inhomogeneous. Inherent inhomogeneity also results from the preparation in which the macromolecules of the original film act as the backbone with long branches formed by the grafts. Because of the incompatibility of the two polymers the grafts are probably present as microdomains. The bulk properties of the modified film, in this case most importantly the proton conductivity, will depend on polymer–polymer and polymer–water interactions, and on the distribution and the phase separation of the grafts, as well as on the crystallinity.[17]

The introduction of the styrene grafts and of the hydrophilic sulfonic acid groups into the strongly hydrophobic PVDF matrix produces a very complex structure with the sulfonated grafts mainly in the amorphous region of the PVDF.[14] In the present investigation the melting behaviour and the crystallinity of the matrix material, the styrene grafted membranes, and of the sulfonated membranes, respectively, have been studied with thermal analysis, and with X-ray diffraction, in order to evaluate the role of the grafting conditions, and of the sulfonation, on the microstructure of the membrane. The matrix polymer is a non-porous film of PVDF, and the resulting styrene grafted and sulfonated membranes are proton conducting in wet conditions.

Experimental

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

PVDF was supplied by Goodfellow as 80 µm thick films made by melt processing. Proton-conducting films were prepared in a three-step procedure.[14] Pre-irradiated films (electron beam under nitrogen gas, dose 100 kGy) were grafted in a solution of styrene in tetrahydrofuran (80:20, *v/v*) at 67 °C, or in a solution of styrene in toluene (50:50, *v/v*) at 70 °C, to various degrees. The membrane with degree of grafting (d.o.g.) = 2%

was prepared at ambient temperature, reaction time 4 h. The grafting time varied from 0.5 to 12 h at 67 °C. The grafted membranes were dried to constant mass and the d.o.g. was determined gravimetrically, using eqn. (1)

$$\text{d.o.g.} = [(m_1 - m_0)/m_0] \times 100\% \qquad (1)$$

where m_0 is the mass of the original film and m_1 the mass of the grafted membrane. The grafted membranes were fully sulfonated [degree of sulfonation (d.o.s.) = 100%] with 0.5 M chlorosulfonic acid in 1,2-dichlorethane for 24 h. The sulfonation occurred mainly at the *para* position of the phenyl rings.[18]

Thermal analysis by differential scanning calorimetry (DSC)

Thermograms of films with d.o.g. between 2 and 100% were measured with a Perkin-Elmer DSC-7 calorimeter with a heating rate of 20 °C min^{-1} in the temperature range −50 to 200 °C. The samples were dried for 7 days at 50 °C *in vacuo* prior to the measurement, after drying the membranes were kept in a desiccator at ambient temperature. The measurement was repeated three times for each sample in order to determine the effect of annealing on the shape of the melting peak, and on the melting temperature. The overall percentage crystallinity of the sample (X_c) was evaluated from the heat of fusion of the sample [eqn. (2)]

$$X_c(\%) = \Delta H_f / \Delta H_{100} \times 100\% \qquad (2)$$

where ΔH_f is the measured enthalpy of fusion of the sample, ΔH_{100} is the enthalpy of fusion of the 100% crystalline sample = 104.7 J g^{-1}.[19]

Because of the amorphous nature of the polystyrene the measured enthalpy of fusion can be attributed to the PVDF crystallites in the membranes. The mass fraction of PVDF in the grafted membranes is given by eqn. (3)

$$W_{\text{PVDF}} = m_{\text{PVDF}} / (m_{\text{PVDF}} + m_{\text{styr}}) \qquad (3)$$

where m_{PVDF} is the mass of the PVDF, m_{styr} the mass of polystyrene grafts and W_{PVDF} the mass fraction of PVDF. The crystallinity of the PVDF is then obtained [eqn. (4)]

$$X_{\text{PVDF}}(\%) = \Delta H_f / W_{\text{PVDF}} \times 100\% \qquad (4)$$

The following relationship [eqn. (5)] was used for the grafted and sulfonated membranes

$$W_{\text{PVDF}} = \frac{m_{\text{PVDF}}}{m_{\text{PVDF}} + m_{\text{styr}} + m_{\text{SO}_3^-}} \qquad (5)$$

where $m_{\text{SO}_3^-}$ is the mass of sulfonic acid groups. The mass of sulfonic acid groups was calculated from the amount of styrene. The crystallinity of PVDF in the PVDF-g-PSSA membranes was then calculated according to eqn. (4).

Thermogravimetry (TG)

The thermal degradation of the PVDF-g-PSSA membranes was measured with a Mettler TG-50 thermobalance in the temperature range 50–250 °C with a heating rate of 10 °C min^{-1}. Samples of 5–8 mg were dried *in vacuo* at 50 °C for 18 h prior to measurement.

X-Ray diffraction measurements

The PVDF-g-PSSA membranes were measured at ambient temperature in symmetrical transmission and reflection geometries with Cu-Kα radiation (1.542 Å), using a θ–2θ diffractometer. The Cu-Kα radiation was monochromated with a quartz monochromator in the incident beam. To reduce the effects of preferred orientation the sample was rotated during the measurement. The background was measured separately and subtracted from the intensity curves of the membranes. The intensity curves were also corrected for absorption and background due to air scattering. The original PVDF film was measured with Mo-Kα_1 radiation, monochromated with a silicon monochromator crystal in the incident beam, at ambient temperature and at 170 °C with annealing in vacuum. A θ–θ diffractometer with a high-temperature chamber was used in symmetrical transmission mode. The heated sample was measured again after 12 h at ambient temperature and after a few weeks. The scattered intensities were measured with a scintillation counter. 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 (MBraun 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 minimise background scattering. The beam height at the sample was approximately 10 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 experimental smearing due to the vertical instrument function.

Results and Discussion

PVDF films have been chosen as matrix materials for functionalised membranes due to their high reactivity in electron beam irradiation grafting. Our previous results showed that very efficient grafting and sulfonation can be achieved in porous PVDF films, and considerable proton conductivity is obtained.[14] The grafting and sulfonation of non-porous films of PVDF requires longer reaction times, and the d.o.g. in these films is therefore generally lower. Several membranes of non-porous PVDF grafted with styrene were prepared. The degree of grafting varied between 2 and 100%. The grafted membranes were fully sulfonated,[14,18] and the proton conductivity was measured with ac impedance spectroscopy. The proton conductivity at room temperature increased with increasing d.o.g. reaching values around 100 mS cm^{-1} for d.o.g. around 100%. The chemical and the electrochemical characterisation of these membranes will be published elsewhere.[19,20] In the following we report the effects of the reaction conditions in the membrane preparation on the melting behaviour and crystallinity of the PVDF-g-PSSA membranes with non-porous matrices.

The melting behaviour of pure PVDF has been extensively studied.[21,22] The partial crystallinity of this material has been described as the result of two factors; the polymer is inherently easy to crystallise because of the simple structure of the repeating unit, but complete crystallisation is inhibited due to the presence of head-to-head bonds in the polymer backbone. The crystalline phase in a solution-cast PVDF film shows a double endotherm in the melting region characteristic of α form crystals. Results from DSC measurements at different heating rates and electron microscopy indicated that the two endotherms were caused by a temperature dependent bimodal distribution of lamellar thicknesses. The lower melting peak is attributed to melting of crystals originally present, and the higher melting peak is attributed to melting of crystals reorganised on heating. According to Nakagawa and Ishida[19] lamellar thickening occurs in the larger crystals during the heating process, and the smaller crystals melt out. The material formed by the partial melting is proposed to recrystallise in the cooling process. This is proposed to be the reason for the double endotherm observed in the melting region of the α form on

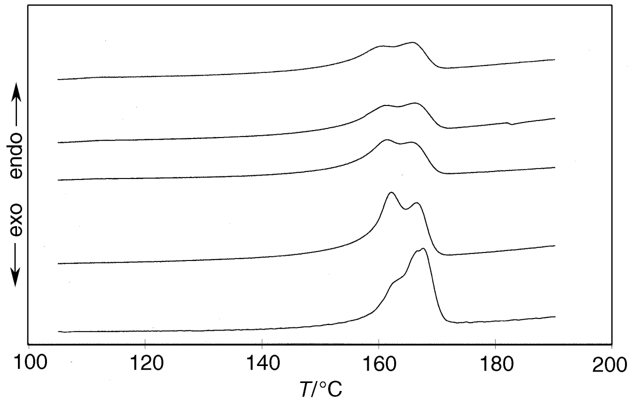

Fig. 1 Melting thermograms, second scan, of pre-irradiated styrene grafted PVDF membranes, heating rate 20 °C min^{-1}. From bottom: original PVDF, d.o.g. 23%, 54%, 83% and 100%, respectively.

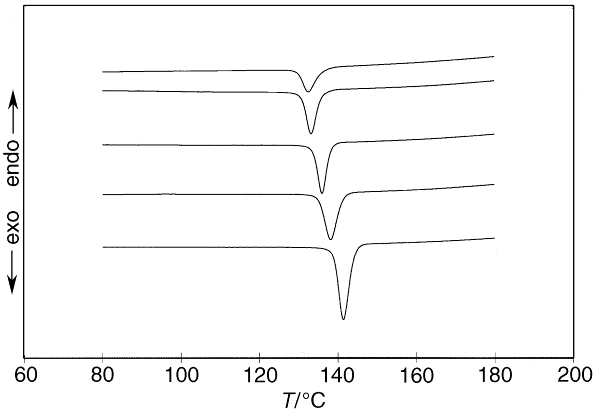

Fig. 2 Cooling thermograms, second scan, of pre-irradiated styrene grafted PVDF membranes, cooling rate 20 °C min^{-1}. From bottom: original PVDF, d.o.g. 23%, 54%, 83% and 100%, respectively.

repeated heating.[20] In this study X-ray scattering was measured from samples of PVDF at ambient temperature and at 170 °C. A change in the WAXS pattern was observed, and the new pattern was still observed from the sample after 24 h at room temperature. The original pattern of the monoclinic α form was recorded after the sample had been standing for several weeks.[23] The conclusion is drawn that heat annealing produces a crystalline phase which is not thermally stable at room temperature.

The thermal behaviour of the PVDF film, the grafted membranes, and of the PVDF-g-PSSA membranes, respectively, were studied by differential scanning calorimetry and thermogravimetry. The thermal behaviour of the styrene grafted membranes will be discussed first. Typical melting thermograms of the second scans from these samples are presented in Fig. 1. Melting thermograms were recorded in three subsequent scans. The glass transition of PVDF at −40 °C[24] could not be detected in the grafted PVDF. A bimodal melting endotherm is seen in all the thermograms. The shape of the bimodal melting endotherm changed when the samples were reheated so that the area under the lower melting peak increased and the area under the higher melting peak decreased. The change in the total enthalpy of fusion in subsequent scans of PVDF, and of grafted membranes, was very small. The melting temperatures were the same in the different samples irrespective of d.o.g., and of number of heating cycles, and they were *ca.* 163 and 167 °C.

The shape of the bimodal melting peak of the grafted membranes resembles that of pure PVDF, and changes slightly with d.o.g. The melting range broadens as the d.o.g. increases. The melting peak of the reorganised thicker lamellae decreases with increasing d.o.g. Hence, the lamellar growth in the melting region is inhibited with formation of the polystyrene grafts. The conclusion is drawn that the grafting takes place in the entire amorphous region, also in areas very close to the crystallite surfaces of the lamellae. Cooling thermograms of the grafted PVDF membranes are shown in Fig. 2. The crystallisation temperature decreases slightly with increasing d.o.g., possibly indicating mixing of polystyrene grafts into the crystallisable part of the PVDF melt. However, the polystyrene grafts are not miscible with the matrix PVDF polymer, most probably they form a separated phase within the amorphous region of the styrene grafted PVDF.[7] A very weak transition around 100 °C[24] which can be attributed to the glass transition of polystyrene, can be observed in the first DSC scans of grafted PVDF membranes with high d.o.g. The transition is obscured in calorimetric studies of the grafts with low d.o.g. because of the annealing effect of the sample drying process (7 days at 70 °C) immediately before the measurement.

The crystallinity of the grafted PVDF and the PVDF-g-PSSA membranes was calculated from the enthalpies of fusion. Results are collected in Fig. 3 and 4. It is seen that the crystallinity of the PVDF matrix is only slightly affected by the grafting process, and the decrease in crystallinity at higher d.o.g. is a few per cent, see Fig. 4. Thus we conclude that the irradiation has not formed reactive radical sites inside the crystallites. The decrease in the overall crystallinity of the grafted membranes is therefore mostly an effect of dilution, see Fig. 3. It is also noteworthy that the degree of crystallisation, as calculated from the enthalpies of fusion, does not change with repeated heating cycles, hence the ordered part of PVDF

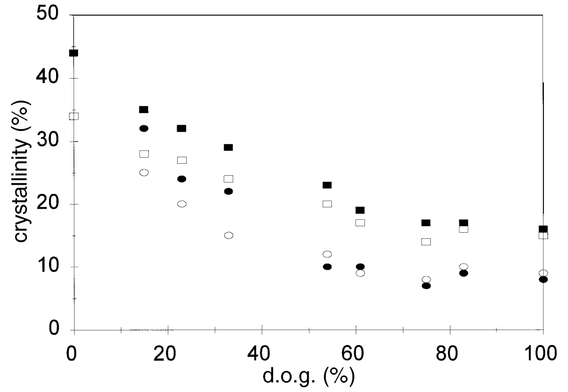

Fig. 3 Overall crystallinity of membranes as a function of the d.o.g. Styrene grafted PVDF membranes from calorimetric measurements (□), and from WAXS measurements (■), PVDF-g-PSSA membranes from calorimetric measurements (○), and from WAXS measurements (●). Calorimetric data from second scan.

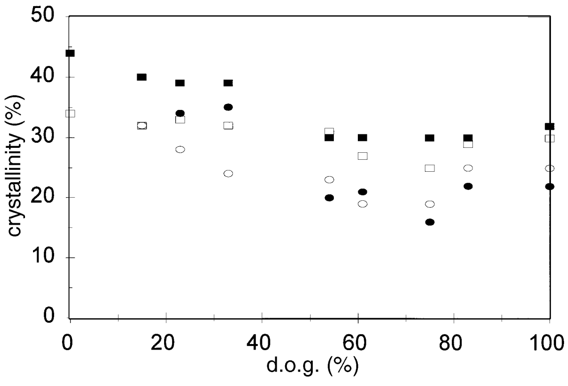

Fig. 4 Crystallinity of the PVDF moiety in membranes as a function of the d.o.g. Styrene grafted PVDF membranes from calorimetric measurements (□), and from WAXS measurements (■), PVDF-g-PSSA membranes from calorimetric measurements (○), and from WAXS measurements (●). Calorimetric data from second scan.

is changing very little in the grafting process. This is in accordance with results obtained by Gupta and Scherer[25] in investigations of proton-conducting membranes prepared by γ-irradiation induced styrene grafting of perfluorinated polymer films.

The crystallinity of the PVDF, of the grafted PVDF membranes, and of the PVDF-g-PSSA membranes was studied with wide angle X-ray scattering (WAXS) measurements. The estimation of the crystallinity from the X-ray diffraction pattern is based on the assumption that the measured scattering intensity is a linear combination of the intensities from the crystalline and from the amorphous regions.[26] The X-ray diffraction patterns are shown in Fig. 6 and 7, and the results of the crystallinity calculations are included in Fig. 3 and 4. The intensity curve from totally amorphous polystyrene has been used as the amorphous background, and the intensity of crystalline PVDF is calculated from the atomic coordinates.[27]

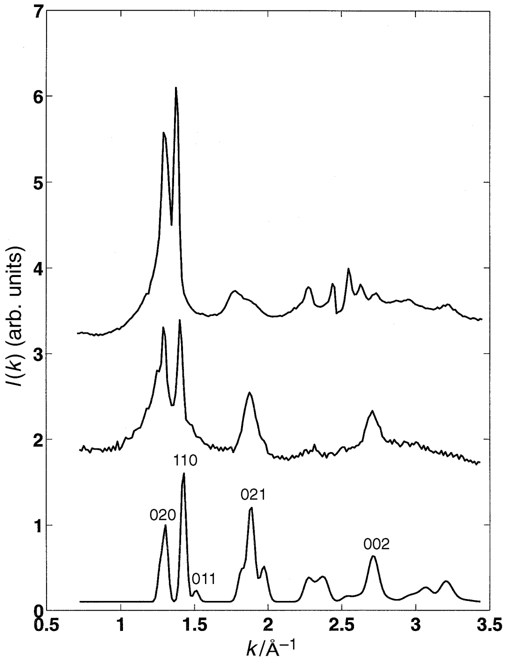

Fig. 5 WAXS intensity curves of PVDF membranes. The intensity curves from top: measured in symmetrical reflection geometry, in symmetrical transmission geometry, and calculated intensity curve for the α form.

The well known Debye formula was used, since the crystal size is small. By fitting the intensities of crystalline PVDF and amorphous material to the experimental intensity curves, the crystallinity of the polymer is obtained as the ratio of the integrals of the intensity of the amorphous component and the studied sample. Owing to the uncertainty in the determination of the model intensity of the amorphous material, however, the precision of the crystallinity is only 10%. By this method a crystallinity of 44% was obtained for the PVDF film using integration limits of $10 \leqslant 2\theta \leqslant 50°$.

Another method to determine the crystallinity from X-ray data is to present the scattering intensity of the crystalline material as a sum of Gaussians or other suitable functions.[28] The sum of these functions and a chosen background is fitted to the intensity curve. We applied this method by calculating the powder diffraction pattern of PVDF by presenting the reflections as Gaussians, and adjusting their widths to match the experimental ones.[29] For PVDF this method gave a crystallinity of 35%, and for the calculated intensity of perfectly crystalline PVDF a crystallinity of *ca.* 60% was obtained. This model underestimates the diffuse background due to the small crystal size, and thus also the crystallinity.

The results of the analysis of the crystallinity from WAXS measurements lead us to believe that the first described method is the more accurate, and this method is therefore used in the present investigation.

The diffraction patterns measured by reflection and transmission geometries do not match perfectly due to preferred orientation of the crystallites, Fig. 5. The 020 and 110 reflections are very intense in the diffraction pattern measured with reflection geometry, but weak when measured with transmission geometry. On the other hand, the 021 and 002 reflections are intense in the pattern measured with transmission geometry but weak when measured with reflection geometry. The precision in crystallinity is *ca.* 10% for pure PVDF.

The size of the PVDF crystallites in the membranes was determined from the WAXS measurements. In untreated PVDF film, the measured average crystal size is around 15 nm, which is larger than the size of the crystallites in the porous PVDF membranes, 11 nm.[14] With grafting a decrease in crystal size is observed, at d.o.g. around 50% the crystallite size is 10 nm in grafted membranes, and at 100% d.o.g. it is *ca.* 8 nm; sulfonation does not alter the crystallite size.

Thus, the WAXS results indicate decrease both in crystallinity and in crystallite size with increasing d.o.g. The decrease

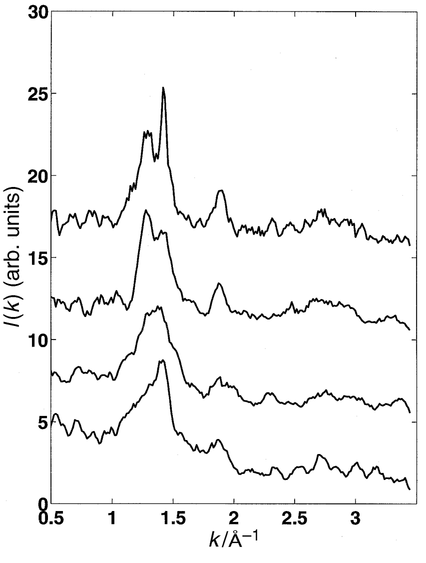

Fig. 6 WAXS intensity curves of styrene grafted PVDF membranes. From top: d.o.g. 23%, 54%, 83% and 100%, respectively.

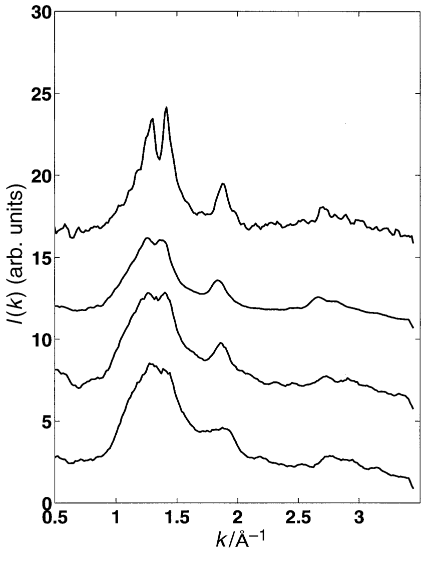

Fig. 7 WAXS intensity curves of PVDF-g-PSSA membranes. From top: d.o.g. 23%, 54%, 83% and 100%, respectively.

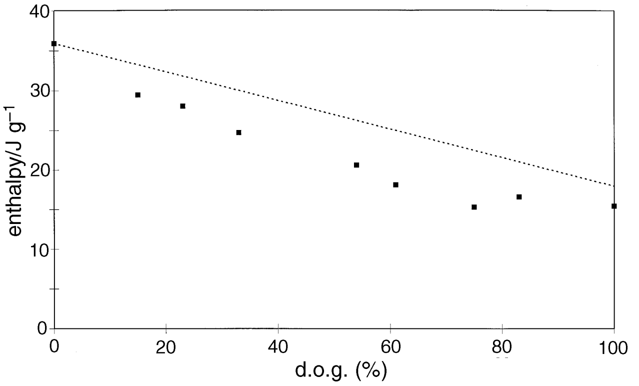

Fig. 8 Enthalpy of fusion of styrene grafted PVDF membranes as a function of the d.o.g. The line denotes values of the enthalpy of fusion, assuming that no decrease in crystallinity takes place during the grafting.

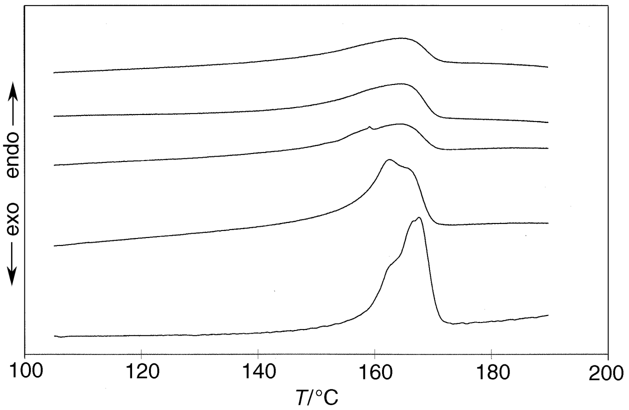

Fig. 9 Melting thermograms, second scan, of PVDF-g-PSSA membranes. Heating rate 20 °C min^{-1}. From bottom: original PVDF, d.o.g. 23%, 54%, 83% and 100%, respectively.

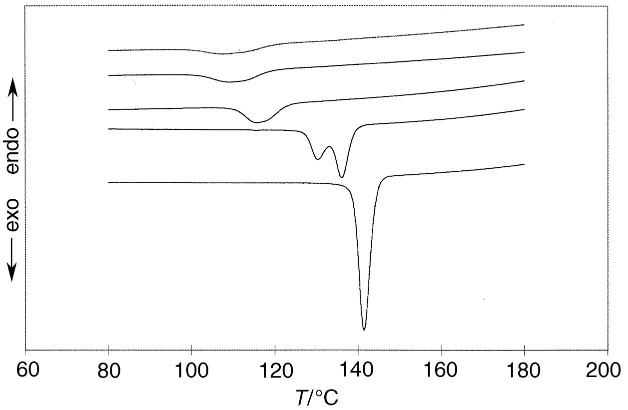

Fig. 10 Cooling thermograms, second scan, of PVDF-g-PSSA membranes. Cooling rate 20 °C min^{-1}. From bottom: original PVDF, d.o.g. 23%, 54%, 83% and 100%, respectively.

in crystallinity is steeper as measured from X-ray diffraction data than from calorimetric measurements, Fig. 3 and 4. The change in melting enthalpy corresponds to a dilution effect by the grafts in the membrane at low d.o.g., but with increasing d.o.g. the crystallinity seems to decrease more, Fig. 8. The straight line represents the enthalpy of fusion of the grafted membranes *vs.* the d.o.g. when the decrease in crystallinity is caused by dilution only. A similar effect has been reported for grafting of polyethylene, where crystal disruption is detected with d.o.g. of over 30%.[30]

Results reported by Gebel *et al.*[31] are somewhat contradictory. They studied styrene grafted and sulfonated PVDF membranes prepared after γ-irradiation. The irradiation dose was relatively low, 1–100 kGy, generally lower doses than used in the present investigation, and the matrix material consisted of only 25 μm thick films. The authors concluded from results of WAXS and SAXS measurements that the grafting reaction takes place in amorphous zones without disturbing the crystalline texture.

An explanation of the discrepancy between results in the present work from calorimetric measurements and from X-ray measurements is that X-ray scattering has its origin from highly ordered and crystalline areas in the PVDF membranes. In layers close to the crystallite surfaces the grafting has caused a decrease in the lamellar thickness, but chain ends and loops present are not ordered enough to contribute to the melting enthalpy registered in the calorimetric measurements. Owing to uncertainties in the estimation of the melting enthalpies of the partly crystalline polymers, and the base line in the thermograms, the precision in crystallinity measurements by thermal analysis is relatively low, around 10%. From these observations, the conclusion is drawn that the grafting reaction occurs mainly in the amorphous regions of the PVDF, but can occur very close to the surfaces of the crystallites in the matrix polymer so breaking up partly ordered chain structures. The styrene monomer has not acted as a solvent of PVDF, but has diffused into the mobile amorphous regions to the reactive sites.

Next we turn to the effect of sulfonation on the thermal behaviour and the crystallinity of the membranes. Typical second scan heating thermograms of PVDF-g-PSSA membranes are seen in Fig. 9, the corresponding cooling scans are seen in Fig. 10. The melting behaviour of the PVDF-g-PSSA membranes resembles that of the polystyrene grafted PVDF membranes. The bimodal melting peak is detectable in all the samples. The form of the endotherm differs slightly with the intensity of the first melting peak increasing relative to the second. There is a considerable decrease in the total melting enthalpy as the d.o.g. increases. This means that possible order remaining after the grafting reaction has been partly broken up on sulfonation. The crystallisation in the PVDF-g-PSSA membranes occurs at lower temperatures than in grafted samples, indicating the restrictive impact of the polyelectrolyte chains on the mobility and ability to crystallise of the unsubstituted PVDF blocks in the chain. A bimodal crystallisation endotherm is clearly seen at d.o.g. *ca.* 20%. We conclude that crystallisable parts of the PVDF chains are present in two different surroundings at this d.o.g. which can be detected calorimetrically. A portion of the PVDF crystallises close to the surface of the membranes where the graft density is large, while the remainder crystallises in the inner parts of the membrane, into which the sulfonated grafts have not yet penetrated. Using energy dispersive X-ray analysis we have shown that polystyrene sulfonic acid grafts become evenly distributed throughout the membrane at d.o.g. $>$*ca.* 30%.[14]

An exothermic enthalpy change over a wide temperature range (100–200 °C) is detected in the first heating scan of the PVDF-g-PSSA membranes and this effect is very pronounced at high d.o.g. The behaviour was not found in the second and subsequent scans, but was found again after storage of the membranes under ambient conditions. This behaviour is probably due to the hygroscopic properties of the PVDF-g-PSSA membranes, which bind water to the sulfonic acid groups. Not even drying at 100 °C for long periods could remove all the water. This was also confirmed with thermogravimetry, where the mass loss from the PVDF-g-PSSA membranes (dried at 50 °C for 18 h) was constant between 100 and 200 °C. Loss of sulfonic acid groups or degradation of polystyrene is not probable in this temperature range, as shown in thermogravimetry measurements.

WAXS measurements were made of the PVDF-g-PSSA

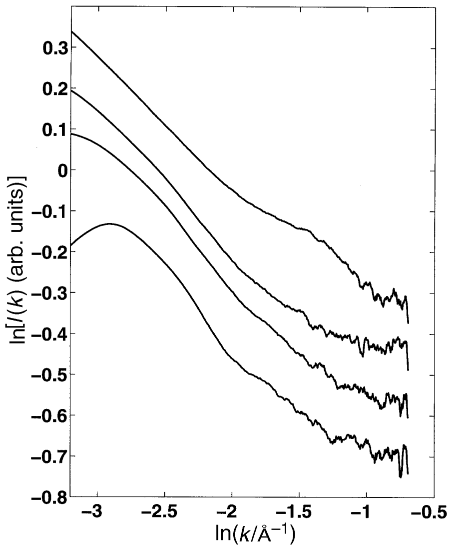

Fig. 11 SAXS intensity curves for (bottom to top) PVDF film, and hydrated PVDF-g-PSSA membranes with d.o.g. 23%, 54% and 100%, respectively

membranes at ambient temperature, see Fig. 7. The crystallinity determined from these measurements is included in Fig. 3 and 4. It is evident that the sulfonation further decreases the crystallinity. The decrease is more dramatic at low d.o.g. and levels out at higher d.o.g. This reduction in crystallinity correlates quite well with the increase in electric conductivity found for PVDF-g-PSSA membranes when d.o.g. is above 20–30%.[21] We assume that the number of grafts attached to the PVDF is rather similar in all these membranes, since the radiation dose is the same in all cases. As the polystyrene graft chains become longer the effect of the hydrophilic sulfonic acid groups on the crystallites of PVDF becomes smaller. The size of the crystallites is not much affected by the sulfonation, as judged from WAXS results. This seems to indicate that whole crystallites are destroyed in the sulfonation. This may be a result of the extremely strong interaction between the hydrophilic sulfonic acid groups and the hydrophobic PVDF matrix, which can cause crystal disruption.[30] The complex, multiphase composition of the hydrated PVDF-g-PSSA membranes, consisting of crystallites and amorphous regions of PVDF, and hydrophilic sulfonated regions of polystyrene is further evidenced with SAXS diffraction measurements, Fig. 11. A distinct feature in the SAXS pattern is the interference maximum at $k \approx 0.24\ \text{Å}^{-1}$, corresponding to a Bragg spacing of 2.5 nm, which indicates supramolecular order. In our previous report[14] this was attributed to water–sulfonic acid clusters, supposed to be the active sites for the proton conduction in the membranes. The detailed structure and the state of water in the hydrated PVDF-g-PSSA is currently being studied in our laboratory.

Conclusion

PVDF-g-PSSA membranes prepared by the three-step procedure of electron beam irradiation, grafting and sulfonation undergo changes in crystallinity under the reaction conditions. The crystallinity of the membranes decreases not only by the dilution effect of the grafted polystyrene in the amorphous regions of the PVDF matrix, but also by the disordering effect of the grafts of the lamellar surfaces. Crystal disruption can not be excluded. The sulfonation of the grafted membranes further deteriorates the crystalline region of PVDF. Slightly differing values of the crystallinity are obtained by calorimetric analysis and by X-ray diffraction analysis. This is due to formation of slightly ordered structures close to the lamellar surface of the PVDF which do not contribute to the melting enthalpy, but which are seen in X-ray diffraction.

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References

1 L. W. Niedrach, W. T. Grubb, in *Fuel Cells*, ed. W. Mitchell, Academic Press, New York, 1963, ch. 3.
2 *Fuel Cell Handbook*, ed. A. J. Appleby and R. L. Foulkes, Van Nostrand, New York, 1989, pp. 277–295.
3 L. Mandelkern, in *The Radiation Chemistry of Macromolecules*, ed. M. Dole, Academic Press, New York, 1972, vol. 1, ch. 13.
4 D. O. Geymer, in *The Radiation Chemistry of Macromolecules*, ed. M. Dole, Academic Press, New York, 1973, vol. 1, ch. 1.
5 J. L. Garnett, *Radiat. Phys. Chem.*, 1979, **14**, 79.
6 B. Gupta, F. N. Büchi and G. G. Scherer, *J. Polym. Sci., Part A: Polym. Chem.*, 1994, **32**, 1931.
7 B. Gupta and G. G. Scherer, *Chimia*, 1994, **48**, 127.
8 F. Vigo, G. Capanelli, C. Uliana and S. Munari, *Desalination*, 1981, **36**, 63.
9 E.-S. A. Hegazy, I. Ishigaki, A. M. Dessouki, A. Rabie and J. Okamoto, *J. Appl. Polym. Sci.*, 1982, **27**, 535.
10 A. Niemöller and G. Ellinghorst, *Makromol. Chem.*, 1987, **148**, 1.
11 F. Büchi, B. Gupta, M. Rouilly, P. C. Hauser, A. Chapiro and G. G. Scherer, *Proc. 27th IECEC Conf., San Diego, August 1992*, Society of Automotive Engineers, San Diego, CA, 1992, vol. 3, p. 419.
12 N. Betz, A. Le Moël, J. P. Durand, E. Balanzat and C. Darnez, *Macromolecules*, 1992, **25**, 213.
13 A. Elmidaoui, A. T. Cherif, J. Brunea, F. Duclert, T. Cohen and C. Gavach, *J. Membr. Sci.*, 1992, **67**, 263.
14 S. Holmberg, T. Lehtinen, J. Näsman, D. Ostrovskii, M. Paronen, R. Serimaa, F. Sundholm, G. Sundholm, L. Torell and M. Torkkeli, *J. Mater. Chem.*, 1996, **6**, 1309.
15 G. G. Scherer, *Ber. Bunsen-Ges. Phys. Chem.*, 1990, **94**, 1008.
16 G. G. Scherer, E. Killer and D. Grman, *Int. J. Hydrog. Energy*, 1992, **17**, 115.
17 A. Chapiro and A. M. Jedrychowska-Bonamour, *Eur. Polym. J.*, 1984, **20**, 1079.
18 M. V. Rouilly, R. Kötz, O. Haas, G. G. Scherer and A. Chapiro, *J. Membr. Sci.*, 1993, **81**, 89.
19 T. Lehtinen, F. Sundholm, G. Sundholm, P. Björnbom and M. Bursell, *Electrochim. Acta*, submitted.
20 S. Hietala, M. Karjalainen, T. Lehtinen, D. Ostrovskii, M. Paronen, R. Serimaa, F. Sundholm and G. Sundholm, *Appl. Macromol. Chem. Phys.*, submitted.
21 K. Nagakawa and Y. Ishida, *J. Polym. Sci., Phys. Edn.*, 1973, **11**, 2153.
22 E. Benedetti, S. Catanorchi, A. D'Alessio, G. Moggi, P. Vergamini, M. Pracella and F. Ciardelli, *Polym. Int.*, 1996, **41**, 35.
23 R. Serimaa and S. Vahvaselkä, unpublished work.
24 J. Brandrup and E. H. Immergut, *Polymer Handbook*, Wiley, New York, 3rd edn., 1989, p. VI-226 and VI-258.
25 B. Gupta and G. G. Scherer, *Makromol. Chem.*, 1993, **210**, 151.
26 F. J. Baltá-Calleja and C. G. Vonk, *X-Ray Scattering of Synthetic Polymers*, Elsevier, Amsterdam, 1989, pp. 175–204.
27 R. Hasegawa, Y. Takahashi, Y. Chatani and H. Tadukuro, *Polymer J.*, 1972, **3**, 600.
28 L. D. Majdanac, D. Poleti and M. J. Teodorovic, *Acta Polymerica*, 1991, **42**, 351.
29 W. Kraus and G. Nolze, the computer program Powder Cell, version 1.8.
30 R. Y. M. Huang and P. J. F. Kanitz, *J. Appl. Polym. Sci.*, 1969, **13**, 669.
31 G. Gebel, E. Ottomani, J. J. Allegraud, N. Betz and A. Le Moël, *Nucl. Instrum. Meth. Phys. Res. B*, 1995, **105**, 145.

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