JOURNAL OF
Materials
CHEMISTRY

Thermal stability of styrene grafted and sulfonated proton conducting membranes based on poly(vinylidene fluoride)

Sami Hietala,[a] Mihkel Koel,[b] Eivind Skou,[c] Matti Elomaa,[a] and Franciska Sundholm*[a]

[a]*Laboratory of Polymer Chemistry, University of Helsinki, PB 55, FIN-00014 Helsinki, Finland*
[b]*Institute of Chemistry, Estonian Academy of Science, Akadeemia tee 15, EE-0026 Tallinn, Estonia*
[c]*Department of Chemistry, University of Odense, DK-2530 Odense M, Denmark*

The thermal stability of styrene grafted and sulfonated poly(vinylidene fluoride), PVDF-g-PSSA, proton conducting membranes has been studied using thermal gravimetric analysis in combination with mass spectrometry and thermochromatography. The matrix polymer, PVDF, and the non-sulfonated counterpart, PVDF-g-PS, were studied as reference materials. It was found that the degradation of the PVDF-g-PS membrane proceeds in two steps starting at *ca.* 340 °C with the evolution of degradation products typical of polystyrene. The PVDF-g-PSSA membranes are stable to around 270 °C even in a strongly oxidising atmosphere. The degradation starts with the simultaneous evolution of water and sulfur dioxide. The polystyrene grafts start decomposing at 340 °C in the PVDF-g-PSSA membranes. Thus the membranes are suitable for tests in electrochemical applications at elevated temperatures.

Polymeric separator materials for use in electrochemical cells and fuel cells have to meet a combination of conditions: high ion conductivity, excellent electrochemical and chemical long term compatibility with the reducing and oxidative reagents at the electrocatalysts, reasonable mechanical stability including a defined swelling behaviour in the presence of water are among the most important requirements.[1] Thermal stability is of crucial importance for membrane materials. Polyanskii and Tulupov[2] have published a detailed review on the thermal properties of polymer electrolytes.

In the development of new polymer electrolyte materials proton exchange membranes have been made by radiation-induced graft polymerisation.[3–9] The process involves the polymerisation of a monomer in the presence of a preformed polymer film. The preparation of cation exchange membranes by the simultaneous radiation grafting of styrene monomer onto poly(tetrafluoroethylene-*co*-hexafluoropropylene) (FEP) films has been reported by Rouilly *et al.*[10] The grafted films were sulfonated to introduce the ion exchange groups. A three step pattern in the thermal degradation of these membranes was attributed to dehydration, desulfonation and degradation of the FEP backbone.[11] A detailed study of the thermal properties of FEP based membranes has been done with thermal gravimetric analysis[11] and with a combination of thermogravimetry, FT IR and mass spectrometry.[12]

The preparation of proton exchange membranes by pre-irradiation induced styrene grafting onto poly(vinylidene fluoride) (PVDF) films followed by sulfonation has been reported previously.[13,14] It was found that the grafting occurs mainly in the amorphous regions of the PVDF in which polystyrene domains are formed.[14] In the sulfonation sulfonic acid groups are introduced in the polystyrene chains thus forming hydrophilic domains in the hydrophobic matrix polymer. The crystallinity of the matrix polymer changes only slightly during the grafting and sulfonation.[14] Good ion conductivities were found for membranes based on PVDF.[15] High conductivity, although an important factor, is not sufficient to make the polymer electrolyte suitable for demanding applications, such as fuel cells. The clear identification of the degradation products formed at various temperatures offers the possibility of understanding the mechanisms of the thermal degradation of the membranes. This paper contains the results of an investigation in the temperature range 20–650 °C in an inert gas atmosphere, and in oxygen atmosphere of the thermal degradation of PVDF based membranes. In addition the influence of crosslinking the styrene grafts with two different crosslinkers, divinylbenzene, DVB, and bis(vinylphenyl)ethane, BVPE, on the thermal properties of the membranes was studied. The evolved gaseous products were analysed by mass spectrometry and with thermochromatography to correlate mass losses at different temperatures with the formation of low molar mass degradation products related to the structure of the membranes. Nafion 117 membranes were used as reference materials in the thermal degradation experiments.

Experimental

Materials

The matrix material was PVDF film supplied by Goodfellow (Cambridge) as melt processed 80 μm sheets. Pre-irradiated films (electron beam under nitrogen gas, 100 kGy) were grafted in styrene (Fluka) solution and subsequently sulfonated with chlorosulfonic acid (Merck) in a three step procedure which has been described in detail previously.[13,14] Membranes with degrees of grafting, d.o.g., of 18, 32, 48, 60, 73 and 100%, respectively, (PVDF-g-PS membranes), were fully sulfonated (PVDF-g-PSSA membranes). Part of the membranes were crosslinked in the grafting step with either DVB (Fluka, isomeric mixture in ethylvinylbenzene) or BVPE (isomeric mixture) as has been previously described.[16]

The original PVDF film and the irradiated film were measured without further treatment. The PVDF-g-PS samples were measured as received, after drying *in vacuo* at 80 °C for 20 h, and after a second drying period *in vacuo* at 120 °C for 20 h. The PVDF-g-PSSA membranes were treated for 1 h in boiling water and dried *in vacuo* at 80 °C for 20 h before measurement. The Nafion 117 membrane was boiled for 0.5 h in 3% aqueous H_2O_2, 0.5 h in water, 0.5 h in 1 M aqueous H_2SO_4, 0.5 h in water and finally dried *in vacuo* at 80 °C for 20 h before measurement. The samples were stored in plastic bags in ambient conditions. 5–10 mg pieces of membrane were cut for the measurements.

Measurements

The thermal analyses were done with a Setaram 92-12 thermobalance connected to a Varian CH 7A mass spectrometer through a flow meter and a heated tube, approximately 40 cm in length. The samples were typically 4–6 mg. The inlet to the mass spectrometer was through a membrane inlet using a silicone rubber membrane, SR 606 by Radiometer Copenhagen, thickness 25 µm. Excess gases were directed out through holes in the inlet.

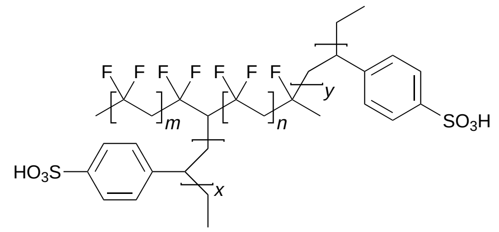
The samples were weighed on the thermobalance without any gas flow. Before the measurement the furnace was purged with a nitrogen flow of 150 ml min^{-1} (high flow) for 10 min. The gas flow was then changed to 25 ml min^{-1} (low flow) for 1 min to stabilise the balance, after which the balance was tared. For measurements in an O_2–N_2 atmosphere this stabilisation was made accordingly with a 50:50 mixture flowing at 50 ml min^{-1}. The samples were heated from 20–650 °C with a heating rate of 10 K min^{-1} under a nitrogen flow of 25 ml min^{-1}, and the thermograms were recorded. The samples were kept at 650 °C for 10 min, then the residue was burned by flowing the O_2–N_2 mixture through for 2 min. During measurements in an O_2–N_2 atmosphere the heating procedure was the same, but the gas atmosphere was kept constant. The results were corrected by subtracting a baseline measurement with an empty crucible.

Mass spectra were recorded every 60 s. The scanning was started 5 min before the gas purging and the actual measurement to check the mass spectrometer stability and record the intensity of atmospheric air for comparison. The mass spectrometer responded quickly to weight losses and changes in the gas composition. However, due to the large volume of the oven and condensation of high molar mass products in the tubing the decay of some peaks was slow and occasionally produced a constant background for several mass peaks. The accuracy of the mass data is one mass unit for masses below *m/z* 100, and two units for masses over *m/z* 100. The accuracy is adequate for this kind of mass trace analysis.

The thermochromatographic (ThGC)[17,18] analysis was done with a gas chromatograph (Carlo Erba 4200) equipped with a pyrolysis oven, a sampling valve, a capillary column [NSW-Plot (HNU Nordion), inner diameter 0.53 mm and length 25 m] and a thermal conductivity detector (Model 430). The pyrolysis oven was a quartz tube with an inner diameter of 4 mm and length of 250 mm having a centrally located 25 mm long quartz sample vessel. The sample size was around 5 mg. The samples were conditioned to constant mass in a constant relative humidity of 75% over a saturated aqueous solution of sodium nitrate at room temperature before the analysis. The heater for the pyrolysis consisted of a copper block with resistor heating elements surrounding the quartz tube. Temperature calibration was achieved by placing a thermocouple in the sample vessel in place of a sample. The heating ramp could be repeated with a measured precision of ±1 °C. The sampling valve consisted of a Deans' type valve[19] inside the column oven run by a three way solenoid valve outside the oven. A microcomputer was used to control both the heating of the pyrolysis oven and the timed sampling of the evolved gases in the pyrolyser tube head space. The sample was heated from 70–400 °C with a heating rate of 5 K min^{-1}. Helium gas (99.99%) was used to purge the pyrolyser at a rate of 10 ml min^{-1} and through the column at a rate of 4 ml min^{-1}. An injection period of 1 s was repeated at 110 s intervals. The design of the device permitted efficient, rapid separation of low boiling point components of the pyrolysate at a constant column-oven temperaure of 70 °C.

Results and Discussion

The tentative chemical structure of the PVDF-g-PSSA membranes is shown:



Tentative structure of the styrene grafted and sulfonated poly(vinylidene fluoride), PVDF-g-PSSA

The supermolecular structure of the system forms a very complex system of crystalline and amorphous domains of PVDF, in which the sulfonated polystyrene grafts form hydrophilic domains within the amorphous parts of the hydrophobic PVDF.[14] It was found that the ion conductivity at 20 °C in the PVDF-g-PSSA membranes is of the same order of magnitude as measured for Nafion 117. The ion conductivities were measured with impedance spectroscopy. The values varied with d.o.g. and were typically around 100 mS cm^{-1}.[15] The hydrogen and helium gas permeabilities through the membranes were measured with a mass spectrometric leak detector, and gas permeabilities equal to or lower than those for Nafion 117 were found.[20] The detailed structural analysis of the PVDF-g-PSSA membranes is still in progress in our laboratory.

The thermal degradation of the matrix polymer PVDF, the grafted PVDF-g-PS membranes, and the sulfonated PVDF-g-PSSA membranes were studied in a nitrogen atmosphere, and in a nitrogen–oxygen (1::1) atmosphere.

It was found that the PVDF is very stable to around 420 °C in a nitrogen atmosphere, and to around 410 °C in the presence of oxygen which is to be expected for a fluorinated polymer backbone. The thermal stability is slightly lower than for fully fluorinated vinyl polymers like FEP in which the degradation starts at around 450 °C in a helium atmosphere, according to a report by Gupta *et al.*[12] In another report by the same group the ungrafted FEP was shown to be stable up to 490 °C in a nitrogen atmosphere.[21] The degradation products of FEP were determined using mass spectrometry. The main products in the decomposition correspond to the splitting of fragments of the main monomer, C_2F_4, and the comonomer, C_3F_6.[12] In PVDF, the degradation caused formation of fragments corresponding to dimers, monomers and oligomers of vinylidene fluoride (*m/z* = 129, 130, 63, 64, 65 and larger fragments). Some typical mass traces from degradation products of PVDF are shown in Fig. 1. The irradiated PVDF film (radiation dose 100 kGy) showed the same fragmentation pattern as the untreated film, but the onset of the degradation was about 5 °C lower. When heated in an inert atmosphere only a charred residue of almost 30% was left of the PVDF at 650 °C. In the presence of oxygen the whole sample was burned to gaseous products at around 530 °C, see Fig. 2.

Thermograms measured in an inert atmosphere of an ungrafted and several grafted PVDF-g-PS films are shown in Fig. 3. The grafted films show mainly a two step degradation. The first degradation occurs at 390 °C in the non-crosslinked grafted films. In the crosslinked films the first degradation step occurs at 10–15 °C lower temperatures than in the non-crosslinked films. Thermograms of samples crosslinked with 5% BVPE and 5% DVB, respectively, are shown in Fig. 4. The degradation in the PVDF-g-PS film crosslinked with DVB starts at the lowest temperature. The second degradation step occurs in all these samples at around 420 °C and corresponds to the degradation of PVDF. This is clearly illustrated in Fig. 5 which shows the mass trace for typical degradation products from polystyrene (*m/z* 103, 104) and from PVDF (*m/z* 130) as a function of temperature, recorded during the thermal analysis.

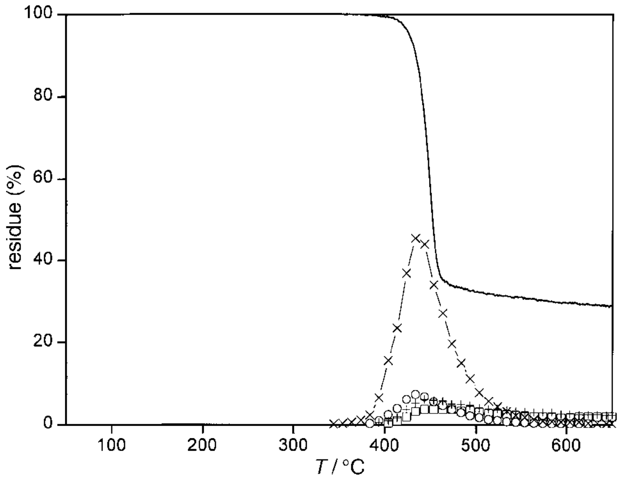


Fig. 1 The thermal degradation of poly(vinylidene fluoride), PVDF. Mass trace of the evolution of fragments with *m/z* 63–65 (□), 80 (o), 115 (+) and 130 (×).

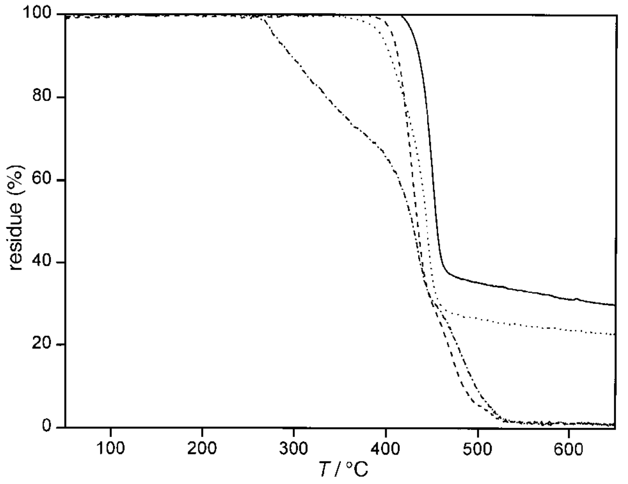


Fig. 2 The thermal degradation of PVDF in a nitrogen atmosphere (—) and in an O_2–N_2 atmosphere (---), and of styrene grafted PVDF, PVDF-g-PS in a nitrogen atmosphere (....) and in an O_2–N_2 atmosphere (-.-.-). Degree of grafting, d.o.g., 48%.

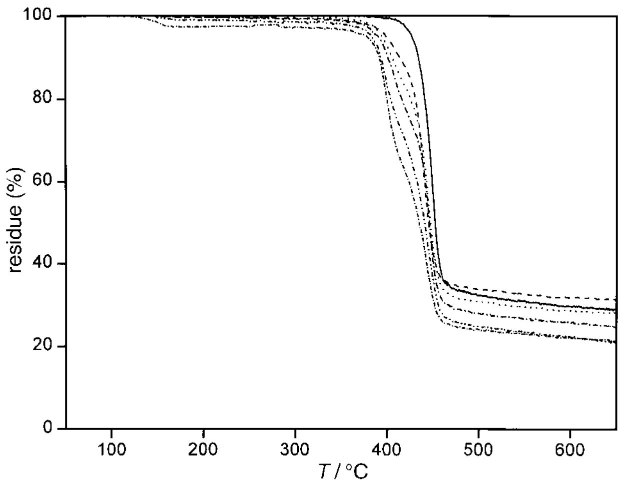


Fig. 3 The thermal degradation of PVDF (—) and PVDF-g-PS membranes with d.o.g. 18% (---), 32% (....), 48% (—.—.), 68% (-..-) and 73% (-.-.) in a nitrogen atmosphere

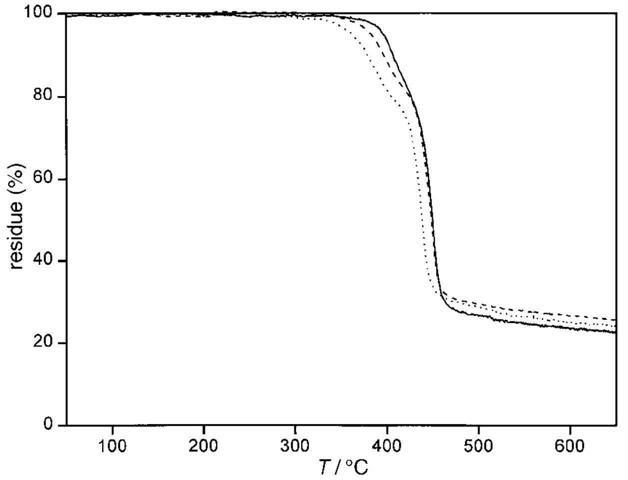


Fig. 4 The thermal degradation of non-crosslinked PVDF-g-PS (—), and of PVDF-g-PS crosslinked with 5% BVPE (---) and with 5% DVB (....) in a nitrogen atmosphere. The d.o.g. is 32%, 30% and 31%, respectively.

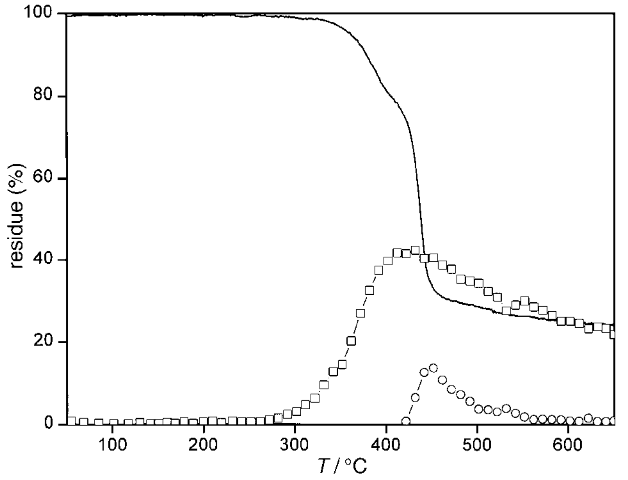


Fig. 5 The thermal degradation of PVDF-g-PS crosslinked with 5% DVB. Mass trace of the evolution of fragments with *m/z* 104–105 (□) from polystyrene grafts and 130 (o) from the PVDF matrix.

Thus the conclusion is drawn that the matrix polymer remains unchanged in the grafted samples and the polystyrene grafts do not alter the inherent decomposition of the PVDF. The two components, PVDF and PS, undergo fragmentation separately. Once the decomposition of the polystyrene grafts is completed, it leaves behind the more stable PVDF backbone which decomposes above 430 °C. This is in accordance with the view that the polystyrene grafts are incompatible with the PVDF matrix and form phase separated microdomains in the grafted polymer,[13] and behave as a distinct two phase system on thermal degradation. Similar observations have been made by Momose *et al.*[22] for the decomposition of α,β,β-trifluoroethylenesulfonyl fluoride grafted onto polyethylene film. Furthermore, Gupta *et al.*[12,21] conclude that the introduction of polystyrene onto FEP films introduces a two step degradation behaviour in the thermograms of copolymer films where both the polystyrene and FEP components undergo degradation in separate steps.

The decreased thermal stability of the crosslinked PVDF-g-PS membranes with respect to the non-crosslinked is somewhat surprising, since it has been shown that crosslinks stabilise the polymer structure.[23,24] These studies were concerned with styrene grafted and sulfonated FEP membranes crosslinked with DVB or triallyl cyanurate. It was shown that the grafting of FEP was considerably reduced by the presence of the crosslinker, and that the rate and the final d.o.g. were decreased. In the present case it was found that both crosslinkers, DVB and BVPE, increase the final d.o.g. dramatically.[16] Thus the grafting reactions in PVDF and in FEP differ in mechanism. Higher d.o.g. can be achieved in PVDF than in FEP under similar reaction conditions. One possible explanation is the difference in glass transition temperatures, T_g, which for FEP is 55 °C[21] and for PVDF is −40 °C.[25] Thus the FEP is close to its glassy state during the grafting, whereas the grafting of the PVDF takes place in the rubbery state. The diffusion of the styrene and the crosslinkers into the irradiated matrix is influenced by the difference in mobility of the polymer matrices. The difference between the two crosslinkers, DVB and BVPE, on the other hand is explained by the very large difference in their reactivities compared with the reactivity of styrene.[16,26] DVB has a much higher reactivity than styrene which results in the formation of highly crosslinked stiff areas close to the grafting points. The product of the reactivity ratios r_1/r_2 of BVPE and styrene is close to 1, hence the reaction results in a more homogeneously and randomly crosslinked membrane.[16]

The degradation pattern of the PVDF-g-PS films is slightly dependent on the preceding drying procedure. In samples dried at 120 °C the thermograms show only the two degradation steps of the polystyrene grafts and the matrix polymer, see Fig. 2 and 3. Samples which were measured as received, or had been dried *in vacuo* at 80 °C, showed a small mass loss around 120 °C. The mass loss is about 1% at d.o.g. = 18%, and it increases to about 4% at d.o.g. = 73%. Mass spectra recorded of the evolving gases at 120 °C do not, however, indicate evaporation of residual solvents or reagents from the membranes. The fragmentation trace points to chain end fragmentation in the PVDF matrix; the peaks in the mass spectrum can be attributed to fragments of type CH_xCF_y. There is no indication of fragmentation of the polystyrene grafts at this temperature. Since it was found that the PVDF and the irradiated PVDF are stable at 120 °C the conclusion is drawn that the styrene grafting reaction has caused some decomposition of the PVDF matrix.

The mass losses from PVDF-g-PS films with various d.o.g. at 420 °C are seen in Fig. 6. The polystyrene content of the PVDF-g-PS films was calculated from the d.o.g. {d.o.g. % = $[(W-W_0)/W_0]\times 100$, polystyrene content = [d.o.g./(d.o.g. + 100)] × 100% where W is the mass of the grafted membrane and W_0 is the mass of the ungrafted membrane, respectively}. It is seen that the mass loss at the temperature of the onset of decomposition of PVDF, 420 °C, increases with increasing d.o.g. However, in the grafted films there is a polystyrene residue of 4–10% left at this temperature. This implies that the mechanism of degradation of the polystyrene changes as the decomposition of the chains approaches the graft points. The polystyrene decomposition becomes linked to the decomposition of the PVDF when small amounts of the grafts are left. The residue at 650 °C decreases with increasing d.o.g. on heating in a nitrogen atmosphere, from around 30 to only 20% in PVDF in films with d.o.g. = 75%, which further points to some synchronous degradation mechanism of PVDF and short residual polystyrene grafts in the films. If all the polystyrene were to decompose, the residue would be about 17% for the sample with d.o.g. = 75% at 650 °C.

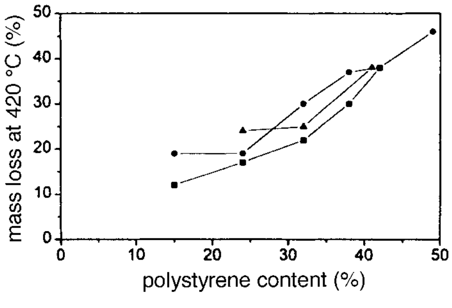


Fig. 6 Mass loss at 420 °C from PVDF-g-PS membranes as a function of the mass% styrene in the membrane, non-crosslinked (■), crosslinked with 5% BVPE (●) and crosslinked with 5% DVB (▲), respectively

The thermal degradation of the PVDF-g-PS films in the presence of oxygen is illustrated in Fig. 2. The mass loss curve shows the onset of the degradation of the PVDF part at slightly lower temperatures than in the ungrafted film. The degradation of the styrene grafts starts at around 270 °C, the mass loss in the interval 270–420 °C is of the same order of magnitude as for the PVDF-g-PS sample in a nitrogen atmosphere in the interval 390–410 °C. The degradation of the sample in the presence of oxygen is complete at around 530 °C.

The sulfonation of the polystyrene grafts in PVDF-g-PS produces a strongly acidic polyelectrolyte membrane, PVDF-g-PSSA. The thermograms of the degradation of the PVDF-g-PSSA membranes in an inert atmosphere are shown in Fig. 7. The decomposition reaction differs from the one in the PVDF-g-PS membranes since the residue at 650 °C increases with increasing d.o.g. This is probably due to an increase in char formation of the polystyrene grafts in the presence of sulfur dioxide (and other acidic fragmentation products originating from the sulfonic acid groups) and water during the thermal degradation. Similar effects have been reported in the thermal degradation of polystyrene in the presence of sulfuric acid or Lewis acids.[27,28]

The first stage in the thermal degradation of the PVDF-g-PSSA membranes is a mass decrease of 1–10% depending on d.o.g. between 100 and 180 °C. This mass decrease is due to loss of bound water in the membranes. The introduction of the hydrophilic sulfonic acid group in the membrane makes it hygroscopic. Part of the water becomes hydrogen bonded to the sulfonic acid groups, and remains in the membrane even after drying *in vacuo* at 80 °C. Similar behaviour has been observed in the FEP based proton exchange membranes[12] and in commercial membranes.[29]

Massive degradation of the membranes starts at 220 °C. Fig. 8 shows the mass trace of the thermal degradation of a PVDF-g-PSSA membrane with d.o.g. 48%. The mass trace shows that there is a simultaneous increase in water formation and onset of formation of sulfur dioxide at 220 °C. The evolution of sulfur dioxide is clearly seen from the mass spectra. Evidence of the formation of sulfur oxide and sulfur trioxide

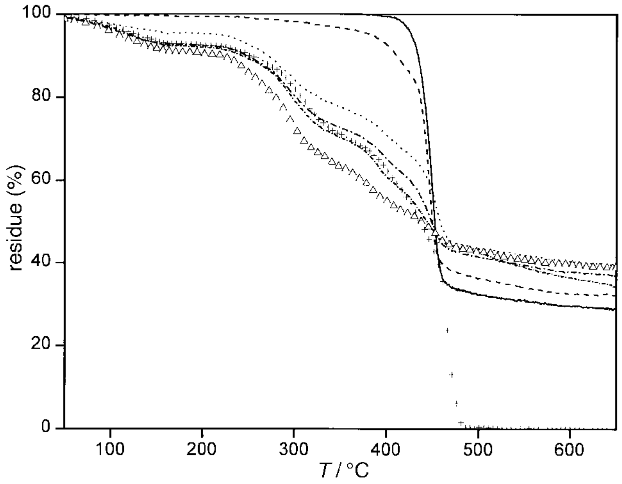


Fig. 7 The thermal degradation of PVDF-g-PSSA membranes with d.o.g. 18% (--), 32% (....), 48% (.—.—) and 73% (-.-.-.) in a nitrogen atmosphere. The thermogram of pure PVDF (—) is included as a reference, as is the degradation of a PVDF-g-PSSA membrane with d.o.g. 70% and crosslinked with 5% DVB (△) and the degradation of a PVDF-g-PSSA membrane, d.o.g. 60%, in an O_2–N_2 atmosphere (+ + +).

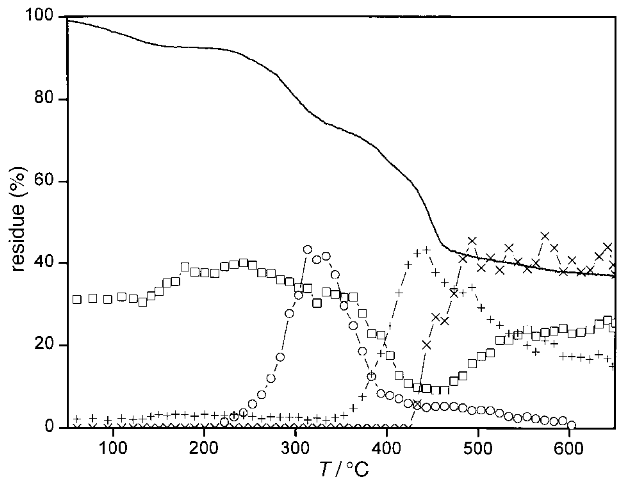


Fig. 8 The thermal degradation of PVDF-g-PSSA membrane with d.o.g. 48%. Mass traces of evolving fragments *m/z* 18 (water □), 64 (SO_2 o), 104 (styrene +) and 117 (×) are shown.

was also seen in the mass trace. Desulfonation is at its maximum around 320 °C. Depolymerisation of the polystyrene grafts occurs after this in the interval 390–410 °C, and degradation of the PVDF matrix sets in at 430 °C as in the PVDF-g-PS membranes. The desulfonation temperature, the decomposition temperatures of the polystyrene grafts and of the PVDF backbone are unaffected by the degree of grafting. The crosslinkers DVB and BVPE shift the degradation to lower temperatures, DVB more than BVPE. The degradation trace for a PVDF-g-PSSA membrane crosslinked with 5% DVB is included in Fig. 7. The onset of the formation of sulfur dioxide is as low as 200 °C. The degradation pattern of the PVDF-g-PSSA membranes resembles the degradation trace obtained under similar conditions from styrene grafted and sulfonated FEP membranes.[11,12] The main difference is that the degradation of the PVDF-g-PSSA membranes starts at lower temperatures. Since the chemical composition of the FEP based and the PVDF based membranes is very similar this marked difference could be due to different mechanisms of formation due to the very different T_g values of the matrix materials leading to differences in morphologies in the products. Further studies are in progress.

The mass loss due to evolution of sulfur dioxide from the PVDF-g-PSSA membranes correlates with measured values of the ion exchange capacity, *Q*, giving further evidence for the loss of sulfonic acid groups from the membrane at elevated temperatures. The measurements of *Q* have been reported previously.[30] The mass loss in the PVDF-g-PSSA membranes in the temperature interval 220–320 °C as a function of d.o.g. is shown in Fig. 9.

The formation of water in the degradation of the PVDF-g-PSSA films is not very clearly seen from the mass trace because of the high water background. This is because some atmospheric water is present in the ionisation chamber, and because of the hydrophobic nature of the silicone membrane in the spectrometer inlet; water does not pass the membrane at rates corresponding to the evolution of water in the degradation. Therefore the thermal degradation of the PVDF-g-PSSA membranes was analysed with thermochromatography. The two dimensional picture of gas evolution as a function of temperature is shown in Fig. 10. The thermogram shows a secondary background peak seen as a front at retention time 43 s. This peak is due to secondary degradation products formed from degradation products in previous heating cycles. The evaporation of strongly bound non-freezing water is clearly seen after 63 s at around 100 °C, as is water formed as a degradation product from the sulfonate groups at around 63 s above 200 °C. The formation of sulfur dioxide is seen in thermograms of a PVDF-g-PSSA membranes; an example with d.o.g. 48% is seen in Fig. 10, with a maximum around 135 s at 300 °C. The evaporation of the strongly bound water in the range 70–180 °C as a function of d.o.g. is illustrated in Fig. 11. Formation of water and sulfur dioxide in the range 180–400 °C as a function of d.o.g. is included in the same figure. The conclusion is drawn that water evaporates in two distinct fractions, and the water formation in the higher temperature range is accompanied by the simultaneous formation of sulfur dioxide. Thus the results from the thermal analysis with gas leak detection and from the thermochromatography are in excellent agreement.

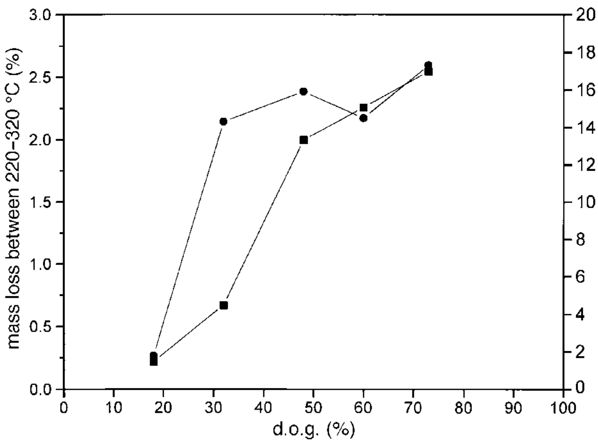


Fig. 9 The mass loss from PVDF-g-PSSA membranes between 220 °C and 320 °C (●) and the ion exchange capacity Q (■) as a function of d.o.g.

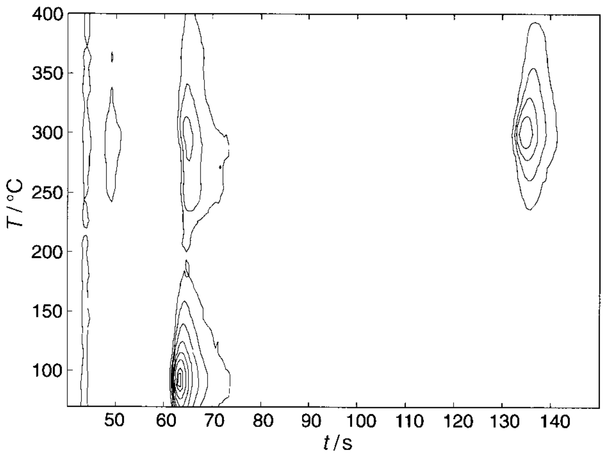


Fig. 10 Thermochromatogram showing the evolution of water (retention time 60–70 s) and sulfur dioxide (retention time 130–140 s) from a PVDF-g-PSSA membrane as a function of temperature. D.o.g. 48%.

The degradation of the PVDF-g-PSSA membranes in the presence of oxygen is very similar to the degradation in nitrogen atmosphere. In the oxidising environment the degradation of the PVDF component starts at a lower temperature than in the nitrogen atmosphere, see Fig. 7. The membrane is completely combusted at 480 °C in the oxidising environment.

Conclusion

The matrix polymer, PVDF, is thermally stable to 420 °C in an inert atmosphere, and to 400 °C in the presence of oxygen. In the PVDF-g-PS films the degradation of the polystyrene grafts at lower temperatures than the PVDF is evident. Crosslinking of the grafts decreases the thermal stability of the grafted polymers. The PVDF-g-PSSA membranes are stable to 370 °C in an inert atmosphere, and to 270 °C in a highly oxidising atmosphere. The degradation starts with the splitting

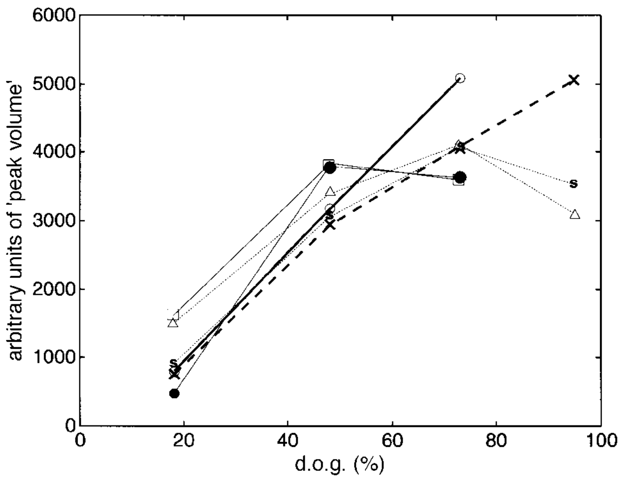


Fig. 11 The evolution of water and sulfur dioxide as a function of d.o.g. Water evolved in the range 100–180 °C from a PVDF-*g*-PSSA membrane (o), and from a BVPE crosslinked (5 mol%) PVDF-*g*-PSSA membrane (×). Water evolved in the range 180–400 °C from a PVDF-*g*-PSSA membrane (□), and from a BVPE crosslinked (5 mol%) PVDF-*g*-PSSA membrane (△). Sulfur dioxide evolved in the range 180–400 °C from a PVDF-*g*-PSSA membrane (●), and from a BVPE crosslinked (5 mol%) PVDF-*g*-PSSA membrane (**s**) .

of the sulfonic acid groups as water and mainly sulfur dioxide. The degradation of the polystyrene grafts start at 390 °C. Crosslinking of the grafts decreases the thermal stability of the membranes. Thus the PVDF-g-PSSA membranes can be regarded as suitable for tests as polyelectrolyte membranes in applications at elevated temperatures up to 200 °C.

S.H. and M.E. are indebted to the Nordic Energy Research Programme (NEFP) for grants. F.S. acknowledges research funding from The Academy of Finland. The authors are well aware that without the assistance with the syntheses by Svante Holmberg and Jan Näsman, Åbo Akademi University, this study would not have been possible.

References

1 *Fuel Cell Handbook*, ed. A. J. Appleby and R. L. Foulkes, Van Nostrand, New York, 1989, G. G. Scherer, *Ber. Bunsenges. Phys. Chem.*, 1990, **94**, 1008.
2 N. G. Polyanskii and P. E. Tulupov, *Russ. Chem. Rev.*, 1971, **40**, 1030.
3 A. Bozzi and A. Chapiro, *Eur. Polym. J.*, 1987, **23**, 255.
4 A. Chapiro, *Radiat. Phys. Chem.*, 1979, **9**, 55.
5 A. Bozzi and A. Chapiro, *Radiat. Phys. Chem.*, 1988, **32**, 193.
6 B. D. Gupta and A. Chapiro, *Eur. Polym. J.*, 1989, **11**, 1137.
7 B. D. Gupta and A. Chapiro, *Eur. Polym. J.*, 1989, **11**, 1145.
8 E. A. Hegazy, I. Ishigaki, A. M. Dessouki, A. Rabie and J. Okamoto, *J. Appl. Polym. Sci.*, 1982, **27**, 535.
9 A. Chapiro and A. M. Jedrychowska-Bonamour, *Eur. Polym. J.*, 1984, **20**, 1079.
10 M. V. Rouilly, R. Kötz, O. Haas, G. G. Scherer and A. Chapiro, *J. Membr. Sci.*, 1993, **81**, 89.
11 B. Gupta and G. G. Scherer, *J. Appl. Polym. Sci.*, 1993, **50**, 2129.
12 B. Gupta, J. G. Highfield and G. G. Scherer, *J Appl. Polym. Sci.*, 1994, **51**, 1659.
13 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.
14 S. Hietala, S. Holmberg, M. Karjalainen, J. Näsman, M. Paronen, R. Serimaa, F. Sundholm and S. Vahvaselkä, *J. Mater. Chem.*, 1997, **7**, 721.
15 T. Lehtinen, F. Sundholm, G. Sundholm, P. Björnbom and M. Bursell, *Electrochim. Acta*, accepted.
16 S. Holmberg, J. H. Näsman and F. Sundholm, *Polym. Adv. Technol.*, accepted.
17 M. Kaljurand and M. Koel, *Computerized Multiple Input Chromatography,* Ellis Horwood, Chichester 1989, p. 139.
18 M. Elomaa, PhD Thesis, University of Helsinki, Helsinki 1991.
19 D. R. Deans, *J. Chromatogr.* 1984, **289**, 43.
20 S. Hietala, E. Skou and F. Sundholm, submitted to *Polymer.*
21 B. Gupta and G. G. Scherer, *Angew. Makromol. Chem.*, 1993, **210**, 151.
22 T. Momose, I. Ishigaki and J. Okamoto, *J. Appl. Polym. Sci.*, 1988, **36**, 669.
23 F. N. Büchi, B. Gupta, O. Haas and G. G. Scherer, *J. Electrochem. Soc.*, 1995, **142**, 3044.
24 F. N. Büchi, B. Gupta, O. Haas and G. G. Scherer, *Electrochim. Acta*, 1995, **40**, 345.
25 J. Brandrup and E. H. Immergut, *Polymer Handbook,* Wiley, New York, 3rd edn., 1989, p. VI-226 and VI-258.
26 R. Wiley and G. Mayberry, *J. Polym. Sci. A,* 1963, **1**, 217.
27 C. F. Cullis and M. M. Hirschler, *The Combustion of Organic Polymers*, Clarendon, Oxford, 1981, pp. 229–230.
28 X. Zhu, M. Elomaa, F. Sundholm and C. H. Lochmüller, *Macromol. Chem. Phys.* 1997, **198**, 3137.
29 T. A. Zawodzinski, Jr., M. Neeman, L. O. Sillerud and S. Gottesfeld, *J. Phys. Chem.*, 1991, **95**, 6040.
30 S. Hietala, S. Holmberg, J. Näsman, D. Ostrovskii, M. Paronen, R. Serimaa, F. Sundholm, L. Torell and M Torkkeli, *Appl. Macromol. Chem. Phys.,* 1997, **253** 151.

Paper 7/08288F; *Received* 18*th November*, 1997