

Sulfonation of Styrene-Grafted Poly(vinylidene fluoride) Films

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ABSTRACT: Electron-beam irradiated and styrene-grafted poly(vinylidene fluoride) films are sulfonated with chlorosulfonic acid in dichloroethane under various conditions. The impact of the reaction time, the concentration of the sulfonating agent, and the reaction temperature on the properties of the sulfonated film is examined. Sulfonation proceeds via a reaction front mechanism. Sulfonation of surface-grafted films is incomplete at room temperature. The number of side reactions taking place appears to be linearly dependent on the concentration of the sulfonation solution. Dimensional changes suggest that sulfone crosslinking is significant at higher concentrations. This reduces the ion-exchange capacity and proton conductivity of the films but increases the resistance to oxidation in a H₂O₂ solution. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 81: 1572–1580, 2001

Key words: sulfonation; chlorosulfonic acid; radiation-grafted membranes; ionomers

INTRODUCTION

The increasing interest in fuel cells as environmentally friendly power sources has encouraged research into the different components. A key part of the low temperature polymer electrolyte fuel cell is the proton conducting polymer membrane. Currently available perfluorinated membranes such as DuPont's Nafion[®] and W.L. Gore's Gore Select[®] are expensive and contribute significantly to the overall cost of the cell. Much research has been devoted to developing cheaper alternatives. One approach is to modify preformed partially fluorinated films by radiation grafting. The initial film provides the mechanical

properties, and the sulfonated grafts bestow proton conductivity. Our group has investigated the structure and properties of sulfonated, styrene-grafted poly(vinylidene fluoride) (PVDF) films^{1–3} and is at present studying the synthesis steps in order to improve the membrane properties. A previous article investigates the irradiation and grafting steps.⁴ Here we report work done on the sulfonation of the styrene-grafted membranes.

EXPERIMENTAL

Reagents

Chlorosulfonic acid (reagent grade, Merck), dichloroethane (reagent grade, Acros), styrene (reagent grade, Acros), and propanol (technical grade) were used as received.

Grafting

The details of the grafting reaction can be found elsewhere.⁴ Briefly, samples of 80- μ m PVDF films

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(Goodfellow) were irradiated at room temperature under N_2 with an absorbed dose of 25 kGy (175-kV acceleration voltage) by means of an Electrocurtain[®] accelerator (Energy Sciences Inc.). The irradiated films were immediately immersed in N_2 purged 50/50 vol % styrene/propanol grafting solutions at 70°C. After grafting, the films were Soxhlet extracted with chloroform and dried to constant mass and the degree of grafting was determined. The degree of grafting (DOG) was defined as follows:

$$\text{DOG} = \frac{m_{\text{grafted}} - m_{\text{initial}}}{m_{\text{initial}}} \times 100\%$$

Sulfonation

Sulfonation was carried out in a closed system of chlorosulfonic acid in dichloroethane. Nitrogen was bubbled through the dichloroethane for 30 min beforehand, and samples were preswollen in the solvent. The volumes of solution used ensured a less than 5% difference in the concentration of chlorosulfonic acid during the reaction. After sulfonation the samples were soaked for several hours in ethanol, then in aqueous NaOH (0.1 mol/L), and finally in aqueous HCl (0.1 mol/L). Samples were then boiled in distilled water for at least 2 h.

Characterization

Elemental sulfur profiles across the membrane were obtained with a Zeiss DSM 962 scanning electron microscope combined with a Link Isis energy dispersive X-ray spectrometer. The counterion profiles (Na^+) were similar to that of sulfur and therefore are not shown.

The dry weight of all samples was determined after drying the samples in a desiccator over P_2O_5 to constant mass. To measure the water uptake, samples were boiled in water for at least an hour and then left to equilibrate at room temperature. After the excess water had been removed by blotting the surface, the samples were immediately weighed and the ratio of the mass of water absorbed to the mass of the dry sample was calculated.

The ion-exchange capacity was determined by immersing samples in a known volume of NaOH and titrating the excess NaOH a day later. The success of the sulfonation reaction was evaluated from the ion-exchange capacity. A degree of sulfonation (DOS) of 100% is defined as an ion-ex-

change capacity (IEC) equivalent to one $-SO_3H$ group per aromatic ring.

$$\text{DOS} = \frac{\text{IEC}_{\text{exp1}}}{\text{IEC}_{\text{theor}}} \times 100\%$$

where $\text{IEC}_{\text{theor}}$ is the ion-exchange capacity calculated from the degree of grafting.

The conductivity of samples in the swollen state was measured at room temperature in a humidified nitrogen-purged two electrode cell by the impedance method using a 5–50 kHz frequency range. The membrane resistance was obtained by extrapolation of the linear part of the spectrum to the real axis. The conductivity was calculated from the membrane resistance and thickness (determined with a micrometer).³

To evaluate the differences in the oxidative stability of membranes sulfonated in different ways, samples were exposed to a 10% H_2O_2 solution at room temperature for 48 h followed by 3 h at 55°C. Samples were boiled in water for an hour beforehand and left to equilibrate at room temperature. After exposure the membranes were soaked in water for several hours and then dried, and the mass loss in the dry state was calculated.

RESULTS AND DISCUSSION

The sulfonation of polystyrene (PS) is a common procedure in the manufacture of ion-exchange materials, membranes, and plasticizers. The sulfonating agents used include sulfuric acid, oleum, sulfur trioxide, chlorosulfonic acid, and acetyl sulfate. The $-SO_3H$ is added to the aromatic ring by electrophilic substitution. Several side reactions can occur, notably the formation of sulfonyl chlorides and crosslinking by sulfone formation.⁵ Styrene-grafted polymer films are also sulfonated to obtain ion-exchange membranes. The conditions of sulfonation of these systems vary considerably and examples of different approaches^{6–8} are given in Table I. No detailed investigation of the influence of experimental parameters has been published. Here we examine the effect of some of the main parameters on the ion-exchange capacity and on the ultimate properties of the membrane. Tests with ungrafted PVDF showed that, within the concentration range discussed, no observable sulfonation even of the surface of the film took place at room temperature, suggesting that with grafted mem-

Table I Approaches to Sulfonation of Styrene-Grafted Fluoropolymers

Polymer Backbone	Ref.	Sulfonation Conditions	Reported Degree of Sulfonation	Determination Method
Teflon-FEP	6	30% ClSO ₃ H 95°C, 5 h	100%	?
PTFE	7	10% ClSO ₃ H added dropwise at 10°C, 3 h at 20°C	100%	Mass increase during sulfonation
PVDF	8	98% H ₂ SO ₄ refluxed under N ₂ at 95°C, 3 h	Not given IEC = 1.7/meq/g for DOG = 30 ($Q_o = 1.88$)	

PTFE, poly(tetrafluoroethylene).

branes sulfonation of the PVDF backbone is not a major reaction. The reaction mechanisms are assumed to be similar to those reported for the sulfonation of PS and nonpolymeric aromatic compounds.^{9,10}

Influence of Degree of Grafting

Radiation grafting of styrene to fluoropolymers is known to proceed by a front mechanism: grafting takes place initially on the surface of the film, then penetrates further.¹¹ At length the grafting fronts meet, and the film is “grafted through.” The degree of grafting at this point depends on the irradiation and grafting conditions. We found in this work that the efficiency of the sulfonation reaction depends to a large extent on whether or not the membrane is grafted through. In samples

possessing a core of ungrafted PVDF, sulfonation was incomplete at room temperature. This can be seen in Figure 1, where samples sulfonated in 0.2 mol/L ClSO₃H at room temperature for 24 h are shown. The grafting conditions we used led to grafting through at a degree of grafting of 25–30%. The sample below that threshold, which had a degree of grafting of 19% and an ungrafted center, had an ion-exchange capacity corresponding to a degree of sulfonation of only 39%; the sample with a degree of grafting of 33%, which was grafted throughout the thickness, was 100% sulfonated. Full sulfonation of surface-grafted samples can be achieved at higher temperatures. The lack of success at room temperature may be attributable to the inability of the dichloroethane solvent to swell these samples sufficiently, hindering the diffusion of the sulfonating agent.

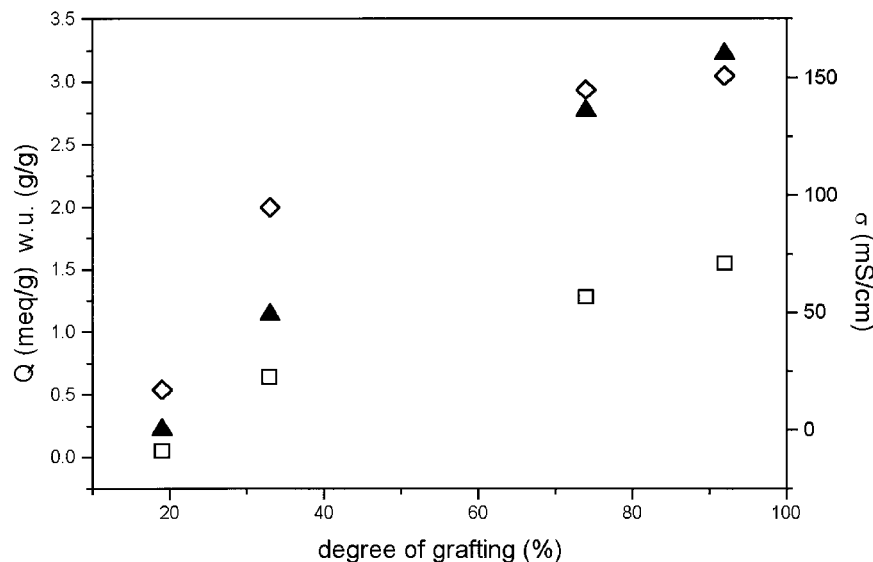


Figure 1 (◇) The ion-exchange capacity, (□) water uptake, and (▲) conductivity versus the degree of grafting. The sulfonation was in 0.2M ClSO₃H at room temperature for 24 h.

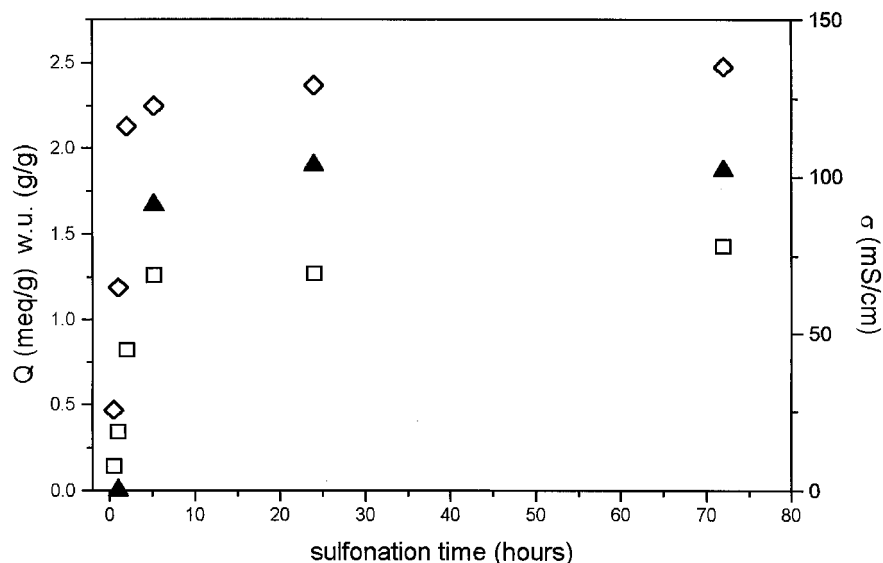


Figure 2 (◇) The ion-exchange capacity, (□) water uptake, and (▲) conductivity versus the reaction time. The sulfonation was in 0.2M ClSO₃H at room temperature.

The grafting reaction can be pursued beyond the level where the two grafting fronts meet until a saturation degree of grafting is reached. Because there is more PS present at higher degrees of grafting, more sulfonic acid groups can be added to the membrane and the ion-exchange capacity increases. This in turn induces a higher water uptake in terms of grams of water per gram of membrane and in terms of the number of molecules of water per sulfonic acid group. This intrinsic increase in the water uptake was explained by the increase in the hydrophilicity of the environment.¹² As shown in Figure 1, the conductivity of the membrane, after a dramatic improvement when the grafting fronts meet, follows the trend of ion-exchange capacity and water uptake. The experiments that follow were carried out on samples with a degree of grafting of 60–70% and an even PS profile across the bulk of the film.

Influence of Conditions of Sulfonation

Several attempts were made to sulfonate samples in concentrated sulfuric acid at various temperatures (21–95°C) and in acetyl sulfate/dichloroethane solutions (50°C). Sulfonation with these reagents and conditions was always restricted to the surface. The failure of the sulfonation reaction in concentrated sulfuric acid may have been due to the inability of sulfuric acid to penetrate the hydrophobic matrix. Moreover, the reactivity

of both of these sulfonating agents may have been insufficient for the sulfonation of the solid grafted membrane.

With chlorosulfonic acid three main parameters influence the sulfonation: the reaction time, the concentration of the sulfonating agent, and the reaction temperature. The impact of the reaction time can be seen in Figure 2. In a 0.2 mol/L ClSO₃H solution at room temperature a reaction time of 24 h resulted in a saturation ion-exchange capacity, water uptake, and proton conductivity. Pursuing the reaction further led to no further changes in the properties. The sulfur profiles given in Figure 3 show that the sulfonation reaction proceeded via a front mechanism, and the grafts at the surface sulfonated first. The reaction rate was therefore dependent on the diffusion of sulfonating agent into the membrane. At room temperature and 0.2 mol/L ClSO₃H a reaction time of 5 h ensured an even sulfur profile.

An increase in the concentration accelerated the reaction: the sulfur profiles showed that, after 24 h, sulfonation was restricted to the surface when a 0.06 mol/L solution was used whereas the profile was even after 5 h in 0.2 mol/L. As can be seen from Figure 4, however, at high concentrations the ion-exchange capacity, water uptake, and proton conductivity decreased as the concentration increased. Another effect not quantified in this work was the increase in brittleness with increasing concentration. Sulfonation in a 3.2

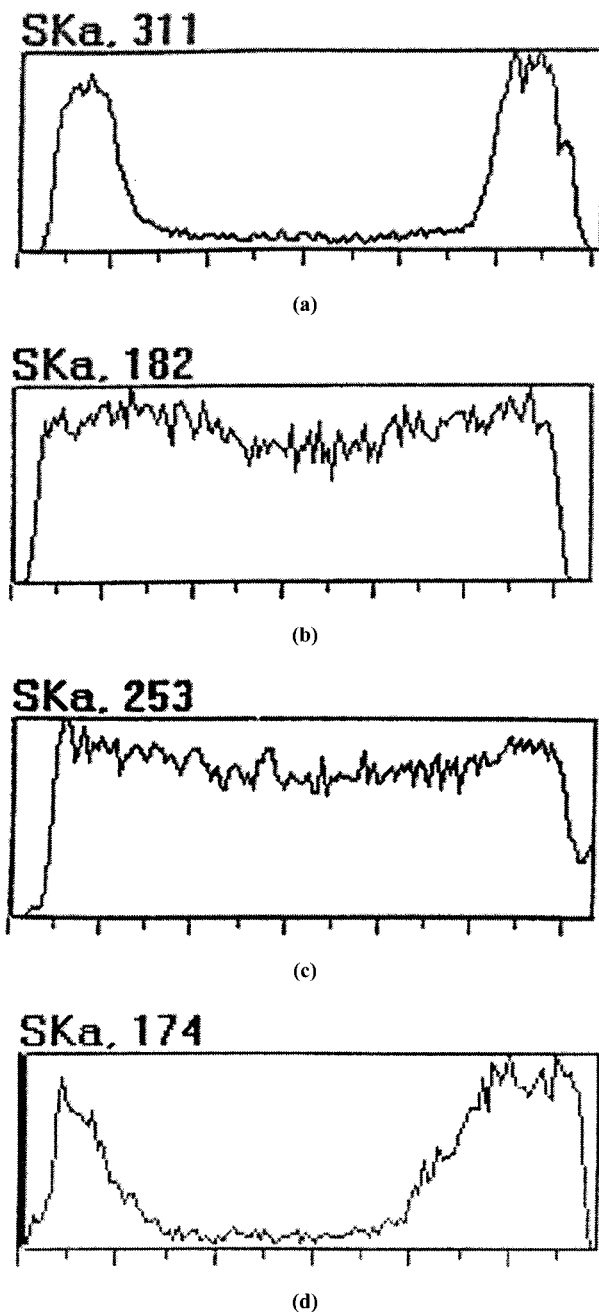


Figure 3 The elemental sulfur profiles of cross sections of films. The samples were sulfonated at room temperature in (a) 0.2 mol/L ClSO_3H for 1 h, (b) 0.2 mol/L ClSO_3H for 5 h, (c) 0.2 mol/L ClSO_3H for 72 h or (d) 0.06 mol/L ClSO_3H for 24 h.

mol/L ClSO_3H solution resulted in a membrane that broke readily even in the wet state.

The deterioration of certain properties at high concentrations of sulfonating agent suggested an increase in the number of side reactions taking place under these conditions, probably including

some reactions affecting the PVDF backbone. The occurrence of side reactions was obvious from the aspect of the sulfonated films. Fully sulfonated films varied in color from a pale translucent yellow when mild conditions were used to dark amber or brown when the conditions were harsher. In order to estimate the number of side reactions taking place, the experimental ion-exchange capacity was compared with the ion-exchange capacity suggested by the mass increase incurred by sulfonation. Any mass increase unaccounted for by a corresponding increase in ion-exchange capacity was attributed to side reactions. In this approach the possibility of sulfonic acid groups inaccessible to ion exchange was considered unlikely and not taken into account. Samples sulfonated in 0.06 and 0.1 mol/L ClSO_3H had a higher ion-exchange capacity than anticipated from the mass increase, pointing to a loss of some PS grafts and/or PVDF during the sulfonation reaction. Any such mass loss was masked when higher concentrations of acid were used, because a greater number of side reactions then occurred; the net effect was an increase in mass greater than the mass of ion-exchanging groups. In Figure 5 the difference between the ion-exchange capacity determined by titration and the ion-exchange capacity calculated from the mass increase is plotted against the concentration of the sulfonating agent. The linear dependence obtained suggested that the number of side reactions was proportional to the concentration of the sulfonating solution. The nature of the side reactions was difficult to ascertain. Van Albada and Cerfontain reported the sulfonation of aromatic compounds in dichloromethane. They found that an increasing amount of arenesulfonyl chlorides was formed with increasing $[\text{ClSO}_3\text{H}]_0/[\text{ArH}]_0$ and an increasing amount of diarylsulfones were formed with increasing reaction time and $[\text{ClSO}_3\text{H}]_0$. With a deficiency of chlorosulfonic acid, the amounts of both secondary products formed were very small.⁵ The postreaction treatment of our membranes here should ensure the hydrolysis of any sulfonyl chlorides,⁹ which leaves sulfones as probable secondary products. This interpretation was supported by measurements of the thickness of water swollen samples and the number of water molecules per sulfonic acid group as a function of the concentration (Fig. 6). The decrease in the thickness and water content when the chlorosulfonic concentration was high and the number of side reactions great was consistent with crosslinking of the sample, which

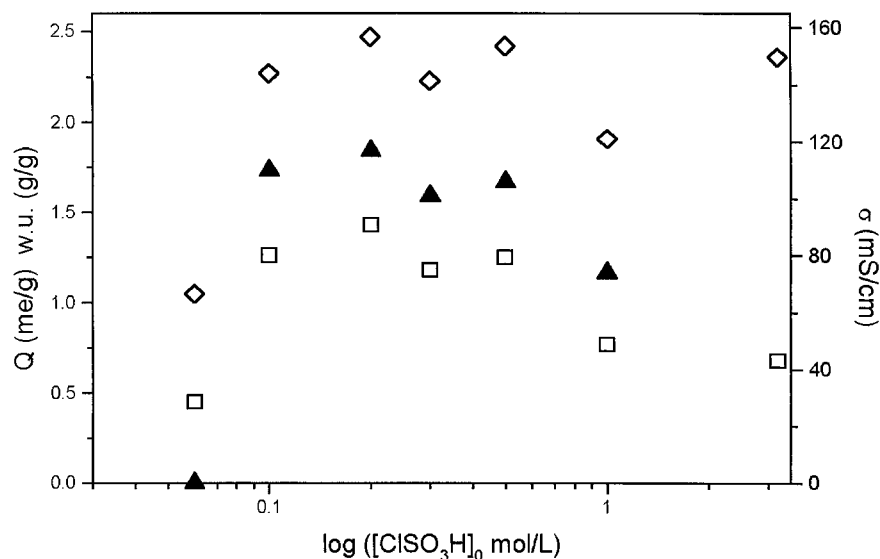


Figure 4 (◇) The ion-exchange capacity, (□) water uptake, and (▲) conductivity versus the log ClSO₃H concentration. The sulfonation was at room temperature for 24 h.

would increase the density and restrict the swelling. The formation of non-ion-exchanging sulfone bridges by combination of two sulfonic acid groups seemed likely and would account for the reduced water uptake and conductivity.

Varying the temperature again illustrated the existence of optimal conditions for a maximum ion-exchange capacity. A period of 24 h in a 0.2 mol/L chlorosulfonic acid in dichloroethane solu-

tion resulted in an only partially successful reaction at 0°C, whereas at 50°C side reactions reduced the ion-exchange capacity (Fig. 7).

Oxidative Stability

The harsh and complex environment of a fuel cell is difficult to simulate. However, Büchi et al. suggested that the degradation of grafted mem-

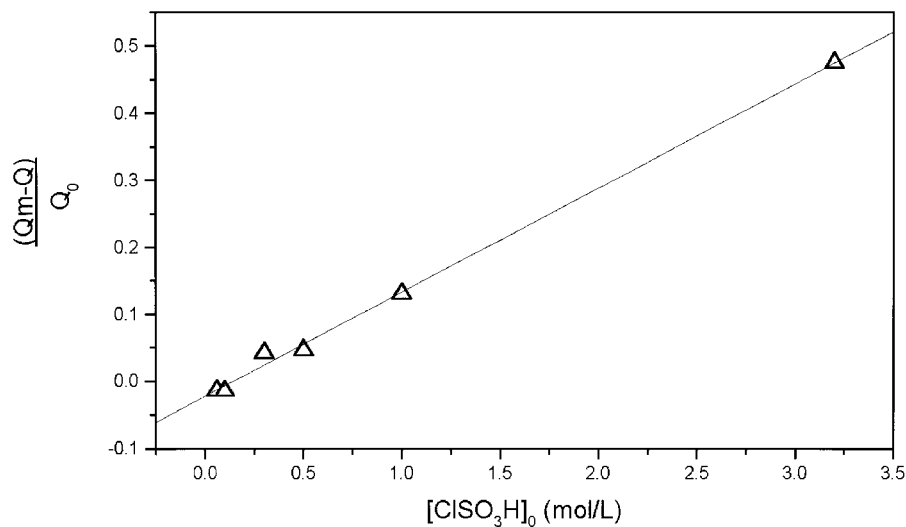


Figure 5 The difference between the ion-exchange capacity suggested by the mass increase and the ion exchange determined experimentally, divided by the theoretical ion-exchange capacity (from the degree of grafting), versus the ClSO₃H concentration. The sulfonation was at room temperature for 24 h.

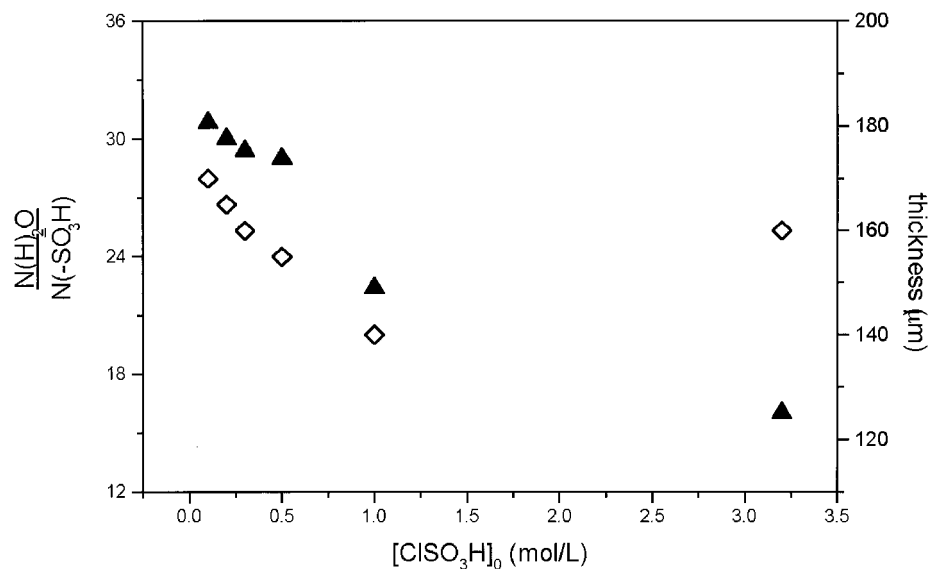


Figure 6 (◇) The thickness of the water swollen samples and (▲) number of water molecules per sulfonic acid group versus the ClSO₃H concentration.

branes is caused by oxygen diffusing through the membrane to the anode and recombining with hydrogen to form HOO· radicals.¹³ These attack the tertiary hydrogen in the PS and lead to considerable degradation.¹⁴ Although far from the exact simulation of actual conditions in a cell, soaking membranes in hydrogen peroxide solutions yields interesting data on the relative oxidative stability of samples. Hogdon first reported a screening of membranes by this method,¹⁵ and

later Guzman-Garcia et al. used a similar test to differentiate between radiation-grafted Raipore membranes with different polymer backbones.¹⁶

Our purpose here was to observe whether varying the sulfonation conditions had any effect on the oxidative stability of the system. The FTIR spectra of samples before and after exposure to a hydrogen peroxide solution showed no additional features. However, a mass loss was observed for all samples, suggesting that chain scission and solubilization of

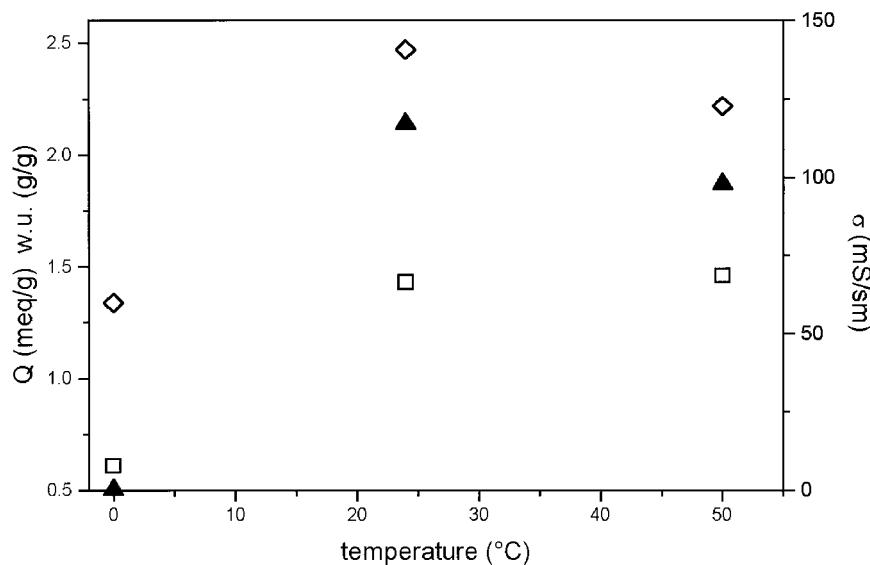


Figure 7 (◇) The ion-exchange capacity, (□) water uptake, and (▲) conductivity versus the reaction temperature. The sulfonation was in 0.2M ClSO₃H for 24 h.

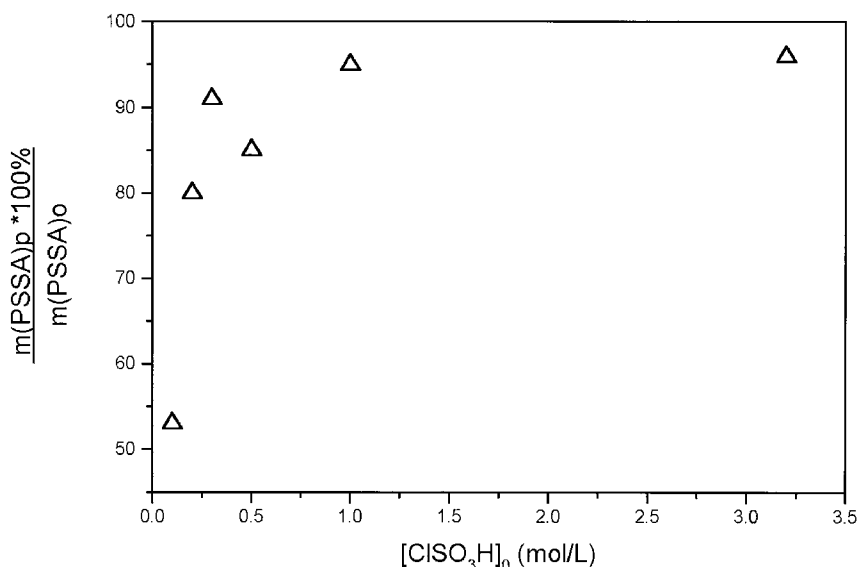


Figure 8 The remaining mass percentage of PSSA after exposure to a 10% H₂O₂ solution versus the ClHSO₃H concentration.

the PS sulfonic acid (PSSA) grafts was the major reaction. As a working hypothesis the mass loss was attributed wholly to a loss of PSSA grafts. The PVDF backbone was assumed to be more stable. Figure 8 shows the mass of remaining PSSA as a percentage of the original for samples sulfonated in solutions of different concentrations. The sample sulfonated under the mildest conditions lost approximately half its mass of PSSA during the treatment. However, as the concentration of chlorosulfonic acid in the sulfonating solution was increased, the samples became more resistant to the hydrogen peroxide solution. Samples sulfonated in 1 or 3.2 mol/L ClSO₃H solutions suffered only a 5% PSSA mass loss. It was likely that the sulfone formation taking place as a side reaction at higher concentrations stabilized the PSSA.

CONCLUSION

The efficiency of the sulfonation of styrene-grafted PVDF films in chlorosulfonic acid/dichloroethane solutions depends on whether PS is present throughout the bulk of the film. Sulfonation of films with an ungrafted core is incomplete at room temperature. In saturation grafted films sulfonation proceeds by a reaction front mechanism. Sulfonation conditions also affect the reaction. Increases in the concentration of the sulfonating agent and the reaction temperature accelerate the reaction but also favor side reactions. These lead to a de-

crease in the ion-exchange capacity, water uptake, and proton conductivity. The number of side reactions taking place appears to be linearly related to the concentration of chlorosulfonic acid. The data are consistent with the formation of sulfone bridges. Exposure to a H₂O₂ solution results in a considerable mass loss for samples where few side reactions occur but only a small mass loss for samples where many sulfone crosslinks may be formed. The use of harsher sulfonation conditions therefore offers advantages in terms of the speed of the sulfonation process and oxidative stability, but it reduces the ion-exchange capacity, water uptake, and proton conductivity and increases the brittleness of the membrane. It may be useful to favor, to some extent, the formation of sulfone bridges because it seems to restrict swelling and degradation of grafted membranes.

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