

Proton Exchange Membranes by Radiation Grafting of Styrene onto FEP Films. I. Thermal Characteristics of Copolymer Membranes

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SYNOPSIS

Thermal behavior of radiation-grafted and sulfonated poly(tetrafluoroethylene-hexafluoropropylene)-*g*-polystyrene membranes was evaluated using thermogravimetric analysis. A three-step degradation pattern was observed from thermograms of all the membranes and was attributed to the dehydration, desulfonation, and degradation of the FEP backbone. The evidence for desulfonation was reflected in the loss in ion exchange capacity of the heat-treated samples. The membranes were found to undergo loss in ion exchange capacity beyond $\sim 200^{\circ}\text{C}$. No trace of sulfonic acid groups as the ion exchange sites was found above $\sim 350^{\circ}\text{C}$. The swelling of heat-treated membranes was also reduced considerably. However, the loss in swelling was much higher than that in the ion exchange capacity of the corresponding membrane. The results were explained in terms of cross-linking reaction occurring in the membrane matrix during the desulfonation process that imparts rigidity in the membrane matrix. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Ion exchange membranes have generated considerable interest in a number of applications of industrial importance that range from dialysis and electro dialysis to the fuel cell and other electrochemical applications.¹⁻⁷ The stability of a membrane depends on its chemical and physical nature that in turn influences the overall performance of such membrane-based systems. In particular, when the membrane is subjected to severe thermal, chemical, and mechanical effects, a partial breakdown in the membrane matrix may occur. Efforts have been made to produce membranes suitable for such environments by careful manipulation of the chemical structure of the matrix. A detailed review on the thermal behavior of various ion exchange membranes has been made by Polyanskii and Tulupov.⁸

The radiation grafting of vinyl and acrylic monomers onto polymeric films is an attractive way to prepare ion exchange membranes because of its ver-

satility in controlling the graft composition by careful variation of the dose and dose rate of irradiation.⁹⁻¹⁵ During such a process, the monomer is polymerized in the presence of a preformed polymer film so that the modified polymer acquires some additional properties of the grafted moiety.¹⁶ We have prepared cation exchange membranes by the simultaneous radiation grafting of styrene monomer onto poly(tetrafluoroethylene-hexafluoropropylene) (FEP) films.^{5,17} The grafted films were sulfonated so as to introduce ion exchange groups into the grafted matrix. A detailed study on the thermal behavior of the polystyrene grafted FEP films (FEP-*g*-PST) has been carried out.¹⁸ The grafted films showed that the degradation of the polystyrene component starts at 400°C , which is followed by the degradation of FEP matrix.¹⁸ However, membranes obtained by the sulfonation of these grafted films may be expected to alter the degradation pattern of the polymer matrix due to the presence of polar sulfonic acid groups. It is therefore interesting to determine the thermal stability of these polystyrene grafted FEP membranes (FEP-*g*-PSTS) as a function of the degree of grafting.

The present investigation has been carried out to

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study the thermal behavior of membranes with an emphasis on their ion exchange capacity at elevated temperatures.

EXPERIMENTAL

Materials

The membranes were obtained by the radiation grafting of styrene onto FEP films using the simultaneous irradiation technique, followed by their sulfonation as reported earlier.¹⁷ The degree of sulfonation in these membranes was found to be $\sim 95\%$. Membranes with the degree of grafting in the range of 6.5–40% were evaluated for their thermal behavior. The degree of grafting refers to the percent increase in the weight of the FEP film by the grafted polystyrene component.

$$\text{degree of grafting} = \frac{W_g - W_0}{W_g} \times 100$$

where, W_0 and W_g are the weight of ungrafted and grafted films, respectively.

Thermogravimetric Analysis (TGA) Studies

TGA studies were made to evaluate degradation behavior of membranes containing various degrees of grafting. Membranes were dried at 80°C under vacuum (1 Torr) for 24 h and stored under ambient conditions before analyzing them. TGA runs were made using Perkin-Elmer TGA-7, in the temperature range of 50–650°C under nitrogen atmosphere. The heating rate was kept at 20°C/min for all the experiments.

Heat Treatment

The heat treatment of membranes was carried out using an oven (Nabertherm) being purged with argon for various periods at different temperatures. The loss of sulfonic acid groups as active sites was represented in terms of the corresponding variation in the ion exchange capacity of membranes.

Ion Exchange Capacity

The ion exchange capacity (IEC) of membranes was determined by immersing them in water at 80°C for 6 h to enable complete swelling of the matrix.¹⁷ These swollen membranes were placed in 0.5 M KCl solution for 6 h. The amount of protons released

into the medium during the ion exchange process was determined by titration against 0.05 M KOH solution using Metrohm 702 SM Titrimo. The IEC was represented as meq/g of the dry sulfonated membrane. After the titration, membranes were regenerated into the proton form by putting them in 2.5 M hydrochloric acid for 6 h at 80°C.

Swelling Measurements

Swelling measurements on membranes were carried out by putting vacuum-dried membranes (1 Torr at 80°C) in Millipore water for 24 h and boiling them for 6 h. The water adhering to the membrane surface was removed by blotting with an adsorbent paper. The equilibrium swelling was obtained from the increase in the weight of the membrane as follows.

$$\text{Equilibrium swelling (\%)} = \frac{W_s - W_d}{W_d} \times 100$$

where, W_d and W_s are the weight of dry and swollen membranes, respectively.

RESULTS AND DISCUSSION

The radiation grafting of styrene onto FEP films followed by the sulfonation produces membranes that exhibit similar degradation patterns for the whole range of degree of grafting, 6.5–40%. A closer view of the systematic influence of the grafting and subsequent sulfonation on the degradation of FEP membranes may be seen from TGA thermograms presented in Figure 1. Ungrafted FEP has a per-

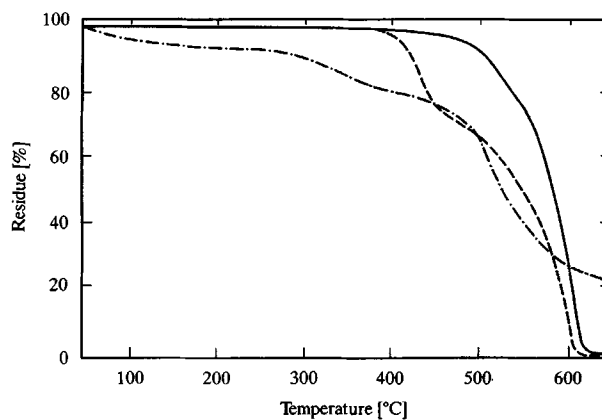


Figure 1 TGA thermograms of (—) ungrafted FEP film; (---) FEP-g-PST film, degree of grafting 40%; (- · -) FEP-g-PSTS membrane, degree of grafting 40%.

fluorinated structure and remains stable up to 490°C (curve A). The incorporation of polystyrene grafts into the FEP backbone introduces a two-step degradation pattern where both moieties show a distinct degradation temperature (curve B). The polystyrene moiety starts degradation at 400°C and continues up to 460°C, followed by the degradation of FEP component at ~ 490°C. The sulfonation of this grafted film brings about further alteration in the degradation pattern of the membrane. The weight loss starts well below 100°C and proceeds up to 180°C (step I). This is followed by another degradation at ~ 300°C (step II). In the final stage (step III), the degradation begins at ~ 490°C. Looking at these degradation patterns, one can understand that while the weight loss at 490°C is the degradation of the backbone polymer, the loss at 300°C is due to the elimination of sulfonic acid groups from the membrane matrix. The weight loss in step I (~ 100°C) may therefore be attributed to the loss of moisture present in the membrane. In the sulfonated samples, it is difficult to have clear demarcation between the desulfonation and decomposition of polystyrene chains. Instead, the thermogram showed a continuous loss in the range of 300–460°C.

The above observations suggest that the sulfonation of polystyrene grafted FEP film makes the membrane more susceptible toward thermal degradation and advances the degradation of copolymer membrane to a considerable extent as compared to the nonsulfonated film. However, from these thermograms, it may be stated that the membranes are thermally stable up to ~ 300°C under the present experimental conditions.

The TGA thermograms for membranes with different degrees of grafting have been presented in

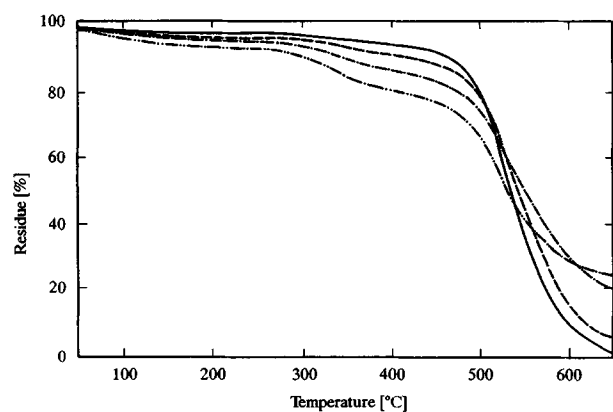


Figure 2 TGA Thermograms of FEP-g-PSTS membranes with different degree of grafting: (—) 6.5%; (---) 15%; (- · - ·) 26%; (- · · -) 40%.

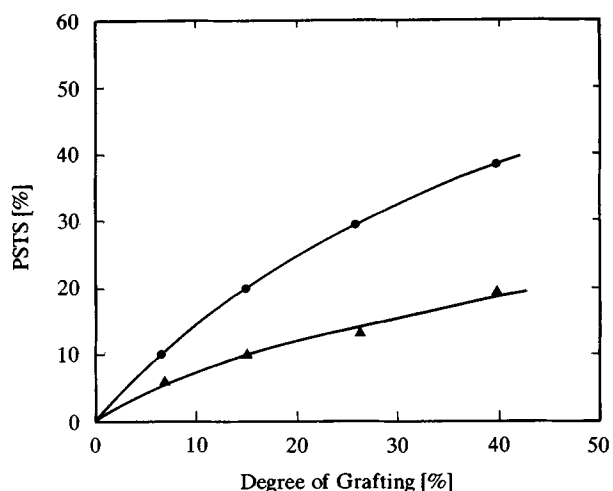


Figure 3 Variation of cumulative weight fraction of polystyrene and sulfonic acid (PSTS) in membranes: (●) initial weight; (▲) loss in the range of 200–470°C.

Figure 2. All the membranes show multi-step degradation pattern where the weight loss was found to be a function of the degree of grafting. The interesting behavior visible from thermograms is that the membranes do not undergo complete degradation in contrast to the nonsulfonated copolymer films. Instead, some of the residue is left behind at the end of the thermogram. It may be seen that the residual weight increases with the increase in the amount of the sulfonated polystyrene moiety in membranes. Such behavior indicated that the sulfonic acid groups play an important role during the degradation of the membrane in such a way that it leads to the formation of thermally stable structures in the matrix and contributes to the residue formation at the end of the thermogram.

The desulfonation temperature (310°C) and the initial decomposition temperature of FEP backbone (490°C) remain unaffected for all the membranes with different grafted polystyrene content. These results indicate that the desulfonation is an independent process and does not interfere with the degradation of the backbone skeleton in all the membranes. The thermograms in Figure 2 show a continuous loss in the range of 300–460°C. Keeping the two processes of desulfonation and dearomatization together, the weight loss in the range of 200–470°C was determined from thermograms and has been represented as PSTS in Figure 3. The loss in weight was found to be much lower than the calculated values. These observations suggest that a significant part of the aromatic moiety is left behind after the dearomatization process. Notably, these units may not contain sulfonic acid groups as evident

from the IEC measurements on the heat-treated membranes as discussed later.

The moisture content of the membrane was obtained from the loss in TGA thermograms in the range of 50–180°C (step I). The interesting part of thermograms is that the dehydration process continues up to 180°C. This indicates a strong interaction of water molecules with sulfonic acid groups.¹⁹ The variation of moisture content of membranes against degree of grafting has been plotted in Figure 4. The membranes show an increase in the moisture content with the degree of grafting. Essentially, this is due to the incorporation of polar sulfonic acid groups into the membrane that interact with the water molecules. In other words, sulfonic acid groups impart hydrophilicity in the membrane matrix. As the grafting increases, the relative number of sulfonic acid groups into the membrane also increases. The molar ratio of water to sulfonic acid groups for various graft levels in membranes was determined from the moisture content in thermograms. It was found that the membranes have nearly 1.6–2.0 molecules of water associated with each sulfonic acid group in the dry state depending upon the degree of grafting. The perfluorinated membrane, Nafion, has also been found to retain one molecule of water per ion exchange site after drying the membrane at 10^{-10} Torr and 20°C.²⁰

In order to investigate the desulfonation behavior, membranes were heated at different temperatures for various periods under inert atmosphere. The sulfonic acid groups in such membranes were estimated in terms of IEC measurements on the heat-treated samples. The influence of the heat treatment at 310°C for 20 min on the IEC of membranes is

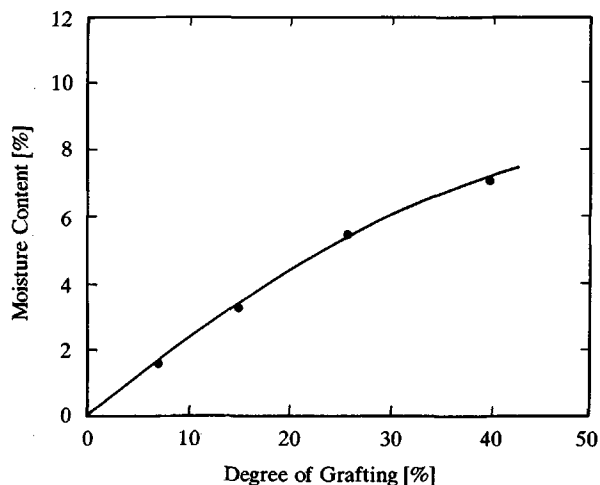


Figure 4 Variation of moisture content with degree of grafting in membranes.

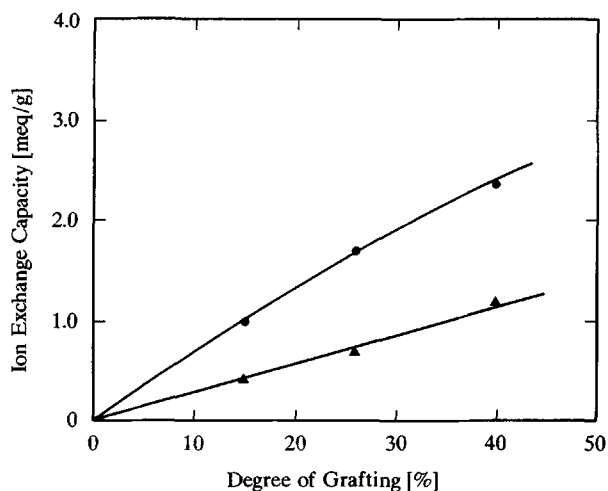


Figure 5 Relation between ion exchange capacity and degree of grafting: (●) before heat treatment; (▲) after heat treatment at 310°C for 20 min.

shown in Figure 5. Membranes lost nearly half of their original IEC after the heating process. The fraction of the retained IEC was nearly constant for all three membranes with different degrees of grafting. Such behavior has been found to be characteristic of sulfonated polystyrene resins.^{19,21} Karpov et al.¹⁹ carried out the elemental analysis of a sulfonated polystyrene resin heated to 305°C and found that half of the sulfonic acid groups were lost by the heat treatment. Our studies on the grafted membranes are in accordance with these observations.

The decrease in IEC with the time of heating for a membrane with 40% degree of grafting has been presented in Figure 6. The results show that the desulfonation is a time-dependent process. The capacity shows a continuous decrease with the heating period and reaches almost zero within 3 h, suggesting a complete loss of sulfonic acid groups in the membrane. Similar observations have been made by Bothe et al.²¹ during the degradation of sulfonated polystyrene divinylbenzene resins where a sharp loss in the capacity with the heating time was observed. The temperature of the heat treatment also influences the capacity of the membrane. The samples did not show any change up to 200°C, beyond which a sharp decrease in the IEC was observed. The capacity dropped to nearly zero at 350°C (Fig. 7). These studies indicate that the degradation of the membrane at 310°C as shown by TGA in Figure 1 does not represent the true desulfonation temperature. Instead, the loss of sulfonic acid groups is already initiated above 200°C.

The relation between the IEC and the equilibrium swelling retained during the heat treatment of a 40%

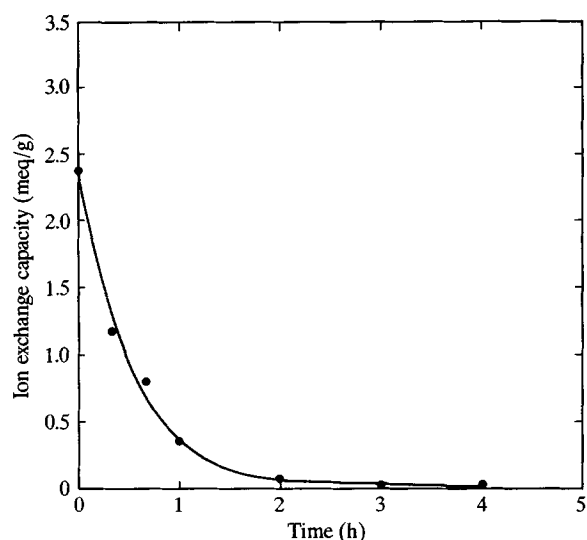


Figure 6 Variation of ion exchange capacity with time of heat treatment: degree of grafting 40%; heating temperature 310°C.

grafted membrane at various temperatures has been presented in Figure 7. The trend in the variation in swelling was found to follow that of the IEC. However, the fraction of swelling retained was much smaller than the IEC for the corresponding sample. Because the swelling of a membrane is a function of the hydrophilic sulfonic acid groups in its matrix, any variation in IEC should be accompanied by the corresponding alteration in the swelling behavior of the membrane as well. The higher degree of loss in swelling as compared to the IEC leads to the conclusion that the desulfonation process is accompanied by certain structural changes in the membrane

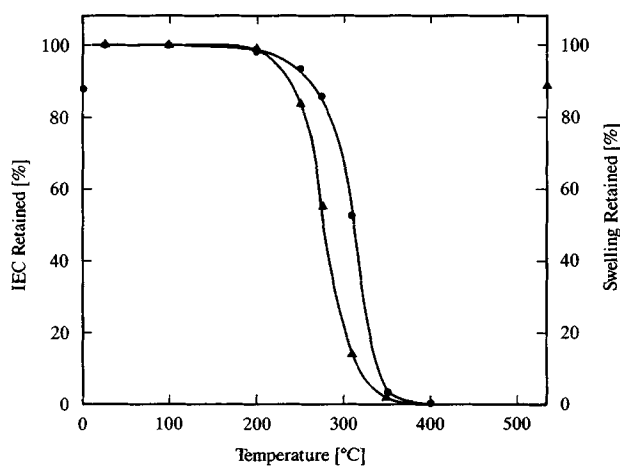


Figure 7 Variation of retained (●) ion exchange capacity and (▲) residual swelling with temperature of heat treatment; degree of grafting 40%.

matrix that are associated with the decrease in the swelling of the sample. These changes may be in the form of increase in the hydrophobicity of the membrane due to the decrease in the number of sulfonic acid groups or cross-linking of molecular chains during the desulfonation involving two adjacent polystyrene graft chains. The latter imparts restrictions to the mobility of molecular chains during the swelling process, thereby decreasing the sorption of water, an effect that is in addition to the contribution of decreasing content of sulfonic acid groups in membranes.

Further evidence for the desulfonation-induced cross-linking in membranes is visible from Figure 8. Plot A shows the relationship between swelling and IEC of the membrane obtained by the desulfonation at various temperatures. On the other hand, plot B represents the swelling behavior of the membrane with similar graft composition, but prepared by partial sulfonation of a 40% grafted film. In principle, both the membranes should be similar with respect to the graft composition and sulfonic acid groups, but show a marked difference in the swelling pattern. These results could be understood from the fact that the desulfonation should produce a structure where a fraction of the styrene units remain sulfonated. In the second membrane (B), a part of the styrene units are sulfonated (sulfonation for different time intervals). The high level of difference

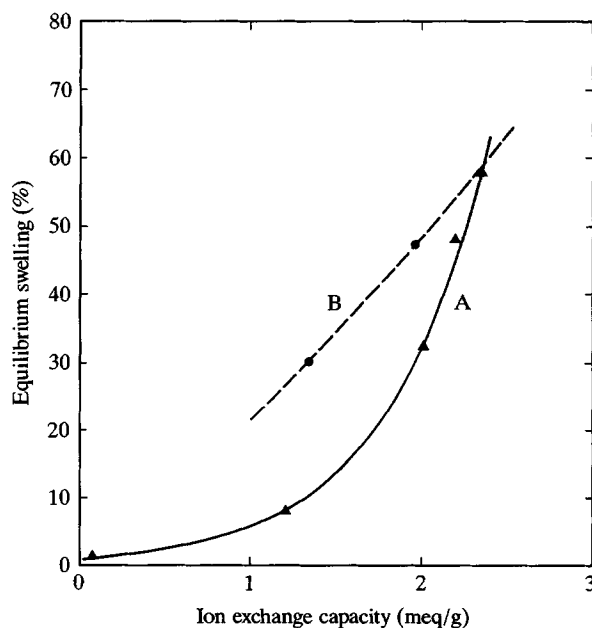


Figure 8 Relation between swelling and ion exchange capacity: (A) heat-treated membrane (degree of grafting 40%); (B) membranes after partial sulfonation of grafted film (degree of grafting 40%).

in the swelling of two membranes with similar IEC indicates that the desulfonated membranes have a more rigid structure that prevents the easy passage of water during the swelling process. This structure should be due to the formation of cross-links during desulfonation, which are absent when the film is obtained by partial sulfonation. The cross-linking takes place in the form of the interaction of two sulfonic acid groups from the adjacent polystyrene chains. The formation of cross-links is well supported by the studies of Leiken et al.²² on sulfonated polystyrene-divinylbenzene resin heated at 333°C. It was found that bispolystyrenesulfones are formed as a result of desulfonation. A more detailed investigation into the possible mechanism of the degradation of membranes using TGA/FTIR/MS has been carried out in the subsequent study.²³

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