Proton Exchange Membranes by Radiation Grafting of Styrene onto FEP Films. III. Structural Investigation

BHUVANESH GUPTA, OTTO HAAS, and GÜNTHER G. SCHERER*

Paul Scherrer Institute, CH-5232 Villigen PSI, Switzerland

SYNOPSIS

Structural investigation on proton-exchange membranes, obtained by the radiation grafting of styrene onto FEP films and subsequent sulfonation, was carried out by differential scanning calorimetry. The membrane crystallinity was found to show a decreasing trend with increasing degree of grafting. The melting temperature of all the membranes also showed a slight decrease as compared to the ungrafted FEP. The results have been explained in terms of the cumulative effect of the decrease in the crystalline/amorphous ratio by the incorporation of amorphous polystyrene grafts and of disruption of spherulitic crystallites of the FEP component in the membranes. The glass transition temperature of the membranes with different water contents was also evaluated. A correlation of the glass transition temperature with the residual water in dried membranes was established. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Radiation-induced graft copolymerization of monomers into fluorine-containing polymers has been widely studied to produce membranes for various purposes, such as in separation science and electrochemical applications.[1-8] These studies have been carried out to correlate the performance of such membranes with the degree of grafting in these systems. The various steps involved in the membrane-preparation process may influence the overall structure of membranes depending upon the nature, amount, and distribution of the grafted component. These changes may be in the form of a crystalline–amorphous ratio, lamellar defects, and domain formation of the grafted component in the membrane matrix. The crystallinity has been found to exert strong influence over the transport behavior of molecules through grafted films.[9-12] Huang and Kenitz,[12] e.g., found that the styrene grafting into polyethylene films results in the partial disruption of crystalline regions and correlated them with the permeation behavior of gases through copolymer films.

Radiation-induced grafting of vinyl and acrylic monomers onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films has been investigated by several workers in the recent past.[13-22] However, an extensive study to investigate the grafting-induced structural changes in copolymer membranes has not been made. In our recent study, the preparation of proton-exchange membranes was carried out by the simultaneous radiation grafting of styrene onto FEP films, followed by the sulfonation.[23] A correlation between structural changes occurring in the membrane and some of the membrane properties, such as degree of swelling and ionic resistivity, was established.[24] These membranes have been found to show good thermal stability as evaluated by TGA in combination with FTIR/MS, as discussed in our previous communications.[25,26]

From the DSC studies on nonsulfonated FEP-g-polystyrene graft copolymer films, it was observed that the polystyrene grafts are incorporated in the amorphous region of the FEP film.[27] The inherent crystallites in the film remain intact for the whole range of graft levels. These studies indicated that the grafted chains are amorphous in nature and form independent domains within the perfluorinated FEP matrix.[27] However, the second step of membrane preparation, i.e., sulfonation of the polystyrene-grafted FEP film, may induce certain crystalline/

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* To whom correspondence should be addressed.

amorphous changes in the membrane matrix that should have a profound influence over membrane properties. In the first part of this investigation, an attempt was made to evaluate the changes occurring in the crystalline region of these proton-exchange membranes, using differential scanning calorimetry. In the second part, the glass transition temperature of membranes with different water contents was evaluated.

EXPERIMENTAL

Materials

Proton-exchange membranes were prepared by a two-step procedure as reported earlier.[23] In the first step, radiation grafting of styrene onto FEP [poly(tetrafluoroethylene-co-hexafluoropropylene)] films was carried out using a simultaneous irradiation technique, which resulted in the formation of FEP-g-polystyrene graft copolymer films with different degrees of grafting. The degree of grafting in graft copolymer films was obtained from the following relationship:

Degree of grafting (%)

$$= [(W_g - W_0)/W_0] \times 100 \quad (1)$$

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

In the second step, copolymer films were sulfonated to produce FEP-g-polystyrene sulfonic acid (FEP-g-PSA) membranes. The degree of sulfonation in membranes was found to be $\sim$ 95%.[23]

Differential Scanning Calorimetry (DSC)

Membranes with a degree of grafting in the range of 6.5–40% were analyzed for their structural changes occurring as a result of the sulfonation process. DSC studies on membranes were made using a Perkin-Elmer DSC-7 system. A known weight of the membrane was taken and dried at 50°C overnight prior to the DSC run. The drying of the sample was necessary in order to eliminate the possible interference of moisture on the melting thermogram (water in membranes has a strong endothermic transition in the temperature range of 60–160°C). This drying process enables one to obtain a precise determination of enthalpic changes in membranes. Thermograms were obtained in the temperature range of 100–300°C under a nitrogen atmosphere. The heating rate during the run was kept constant

at 20 K/min. The heat of fusion values of membranes $\Delta H_{f(mem)}$ were obtained from the area under the melting thermograms.

The weight fraction of the FEP component (W_x) in the membranes was obtained from the following relationship:

$$W_x = \frac{F}{[F + G]} \quad (2)$$

where F is the weight of the FEP component, and G, the cumulative weight of the sulfonated polystyrene (PSA) grafts and water associated with ionic sites in a membrane. The cumulative weight fraction of PSA and water may, therefore, be represented as $(1 - W_x)$.

Since the weight fraction of the FEP component in a membrane decreases as the grafting increases, the heat of fusion of the FEP component, $\Delta H_{f(fep)}$, was obtained by correcting $\Delta H_{f(mem)}$ for the FEP fraction in a membrane as per the following equation:

$$\Delta H_{f(fep)} = \frac{\Delta H_{f(mem)}}{W_x} \quad (3)$$

The crystallinity in the membranes was obtained from the heat of fusion values of the corresponding membranes according to the following equation:

$$\text{Crystallinity (\%)} = \frac{\Delta H_{f(mem)}}{\Delta H_{f(crys)}} \times 100 \quad (4)$$

where $\Delta H_{f(crys)}$ is the crystallinity of the 100% crystalline FEP polymer, which was taken as 87.9 J/g.[28]

For glass transition temperature measurements, DSC thermograms were obtained in the temperature range of 40–180°C under a nitrogen atmosphere. The heating rate was maintained at 20 K/min. For T_g determination, membranes were dried at different temperatures under vacuum ($\sim$ 1 Torr) just before the DSC measurements.

RESULTS AND DISCUSSION

Crystallinity in Membranes

DSC thermograms of ungrafted FEP (a) and FEP-g-PSA membranes with various degrees of grafting in the range of 6.5–40% [(b)–(e)] are presented in Figure 1. The melting temperature in membranes is marginally reduced as compared to the ungrafted
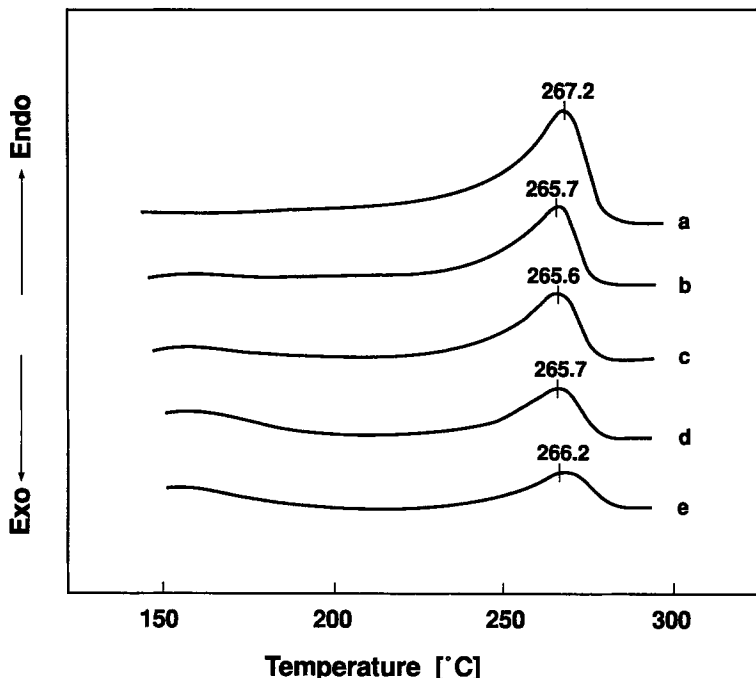
Figure 1   DSC thermograms of ungrafted FEP (a) and (FEP-g-PSA) membranes with various degrees of grafting: (b) 6.5%; (c) 15%; (d) 26%; (e) 40%.

FEP film. The shape of thermograms under the melting peak remains almost the same for all the membranes. However, the beginning of the thermograms in the membranes shows a different shape as compared to the ungrafted film (plot a). This is because of the changes in the specific heat associated with the sulfonated polystyrene moiety in the membranes. The size of thermograms decreases with in-creasing degree of grafting. Accordingly, the heat of fusion in membranes, $\Delta H_{f(mem)}$, as obtained from the area under the thermograms, also decreases and is presented as a function of $(1 - W_x)$ in the form of plot a in Figure 2. The results show that the heat of fusion does not follow a linear decrease. Instead, the decrease is faster for lower as compared to the higher $(1 - W_x)$ values.
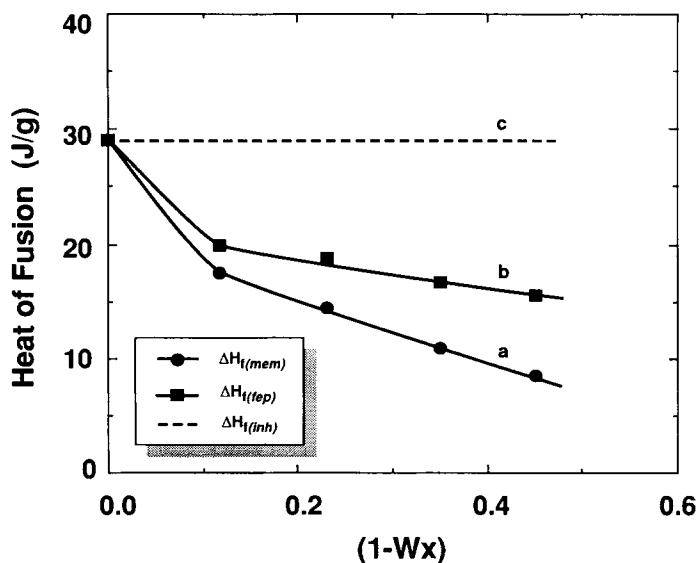

Figure 2   Variation of the heat of fusion of the membrane $\Delta H_{f(mem)}$, FEP component in the membrane $\Delta H_{f(fep)}$, and inherent value $\Delta H_{f(inh)}$ with $(1 - W_x)$ in the membranes.

Our earlier studies on FEP-g-polystyrene graft copolymer films showed that the heat of fusion is a function of the FEP fraction in grafted films.[27] It was found that the grafting takes place by the incorporation of amorphous polystyrene chains in the noncrystalline region of the FEP film. The grafted polystyrene chains, therefore, exerted simply a "dilution effect" on the crystallinity of the FEP film and no disruption of the inherent spherulitic crystallites for the whole range of degree of grafting was observed.

To evaluate the crystalline changes in the FEP component, it is necessary to correct the heat of fusion, $\Delta H_{f(\text{mem})}$, with the weight fraction of FEP in the corresponding membrane. The FEP fraction in the membranes decreases with increasing $(1 - W_x)$ according to eq. (2). The corrected heat of fusion, $\Delta H_{f(\text{fep})}$, values obtained from eq. (3) are presented as plot b in Figure 2. These values represent the true heat of fusion of the FEP component present in copolymer membranes. The dotted line represented by plot c, on the other hand, shows the experimentally determined inherent heat of fusion, $\Delta H_{f(\text{inh})}$, of the FEP component in the membranes. Considering that the grafted chains are amorphous in nature[27] and sulfonation of these polystyrene units further increases the amorphous content in a membrane, the heat of fusion values after correction should correspond to the inherent heat of fusion, $\Delta H_{f(\text{inh})}$, of 29.1 J/g, represented by plot c. The observed deviation of $\Delta H_{f(\text{fep})}$ from plot c suggests that a certain crystalline distortion occurs as a result of the sulfonation process of grafted films, which is responsible for the observed decrease in the heat of fusion. This loss in heat of fusion from plot c to b may, therefore, be attributed to the "crystal disruption." The decrease in the heat of fusion of the FEP component, $\Delta H_{f(\text{fep})}$, in membranes is, therefore, due to the cumulative influence of the "dilution effect" and "crystal disruption" in the FEP film.

The contribution of the "dilution effect" and the "crystal disruption" to the decrease in heat of fusion is presented in Figure 3. Both these factors show an increasing trend with the increase in $(1 - W_x)$. The influence of the "dilution effect" of grafted chains in reducing the heat of fusion increases smoothly as the grafting increases, which is quite obvious due to the amorphous nature of the incorporated polystyrene grafts. The trend in the "crystal disruption," on the other hand, suggests that the disruption is more pronounced for low levels of $(1 - W_x)$ and tends to slow down as the grafted content increases. This indicates that there is a faster crystal distortion for low levels of $(1 - W_x)$ in the membrane. Both
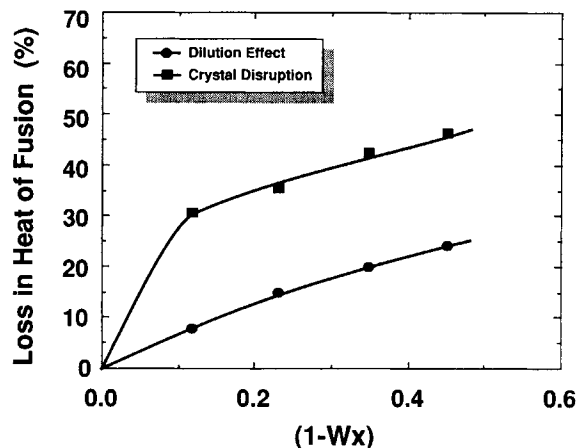
Figure 3 Relative contribution of dilution effect and crystal disruption to the loss of heat of fusion with $(1 - W_x)$.

these factors, "dilution effect" and "crystal disruption," therefore influence the heat of fusion simultaneously but in an independent manner.

The above observations may be understood from the fact that the distribution of free radicals in the FEP film is random in nature. The radicals are produced both in the crystalline and amorphous regions. Therefore, some of these grafted chains are attached to the lamellar surfaces in the crystalline region as well. This results in certain stresses developing at the lamella–graft interjuncture within the grafted zones. Once the grafted film is sulfonated, it becomes hydrophilic in nature and absorbs water, which leads to the swelling of the grafted domains. As a result, strong hydrophilic–hydrophobic stresses at the lamellar surface arise within the perfluorinated matrix. Due to the high mobility of grafted chains in a water-swollen medium, these stresses are subsequently released in the swollen state, leading to the distortion of crystallites, which is reflected in a decrease in the heat of fusion of membranes (from plot c to b in Fig. 3). The distortion of the crystalline region during sulfochlorination of a polyethylene film has also been reported by Zevin and Messalem and Konishi et al.[29,30]

Interestingly, these strains do not show up in nonsulfonated FEP-g-polystyrene graft copolymer films.[27] Grafted films also swell in the reaction medium, comprising styrene and benzene, during the grafting process, which may also introduce certain lamellar strains. It seems that in spite of the incompatibility between perfluorinated FEP and hydrocarbon polystyrene moieties in graft copolymer films, the lamellar strains are not pronounced enough due to the hydrophobic nature of both the

components.[27] Such a balance is no longer feasible when the grafted films are sulfonated and the polystyrene component is transformed into a hydrophilic one.

The observed trend of "*crystal disruption*" in Figure 3 may be understood from the fact that for low levels of grafting polystyrene chains are sparingly distributed within the surface layer of the FEP matrix. Our kinetic as well as our microprobe analyses showed that the initial grafting takes place at the film surface only.[24,31] This grafted layer swells in the grafting medium and the further grafting proceeds by the progressive diffusion of monomer through the grafted zones until it reaches the middle of the film. It was found that the grafting approached the middle of the film at a graft level of 6.5%, but a decreasing gradient in the graft distribution from the surface to the middle exists. Once sulfonated, the swelling of the membrane in water at low graft levels ($\sim$ 6.5%) takes place in such a way that it causes a high degree of inhomogeneity due to the presence of very few hydrophilic domains within the hydrophobic matrix. As a result of this imbalance, several of these chains might cleave off the crystal surface, leading to a higher disruption of crystallites in the membrane. At a higher degree of grafting, the distribution of grafted chains is more homogeneous.[24,31] This leads to a more uniform swelling of the membrane matrix. The crystal distortion due to the strong hydrophilic–hydrophobic interaction is lowered. As a result, the influence of the "*crystal disruption*" in reducing the crystallinity slows down. The melting temperature of membranes as seen in Figure 1 also decreases slightly as compared to the ungrafted film, which is a further indication of the crystal distortion arising in the membranes. It may be noted again that this behavior is not visible in the nonsulfonated graft copolymer films.[27] The distortion arises only when the grafted films are sulfonated. The contribution of hydrophilic–hydrophobic balance in the crystal distortion is further supported from our DSC studies on FEP-g-polyacrylic acid membranes, where the heat of fusion was observed to follow a similar trend with increasing $(1 - W_x)$.[32]

The variation of crystallinity of membranes with the degree of grafting is presented in Figure 4. All the membranes show a decrease in crystallinity depending on the degree of grafting. This is evident from the cumulative influence of the dilution of the inherent crystallinity by amorphous polystyrene grafts as well as the disruption of spherulitic crystallites of the FEP component, as discussed above. The extent of the influence of these two effects in
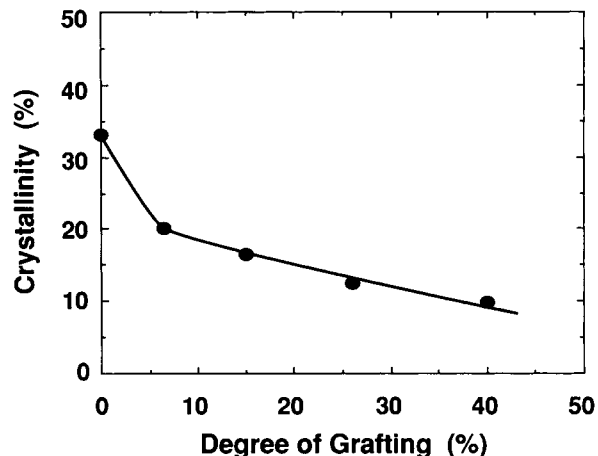

Figure 4   Variation of crystallinity with degree of grafting in the membranes.

this system is evident from the fact that the crystallinity of a membrane with a 40% degree of grafting decreases to nearly one-third of its original value. The decrease in the crystallinity of is further evident from the X-ray diffraction studies on the membranes.[18] The intensity of crystalline reflections of FEP film was observed to decrease considerably with the increase in the degree of grafting in the membranes.

Glass Transition Temperature in Membranes

The investigation was made to follow the variation in glass transition temperature of the sulfonated polystyrene component in the membranes. The DSC thermograms of a 26% grafted membrane, dried at different temperatures, in the glass transition region are presented in Figure 5(b)–(h). Plot a in Figure 5, on the other hand, shows a strong endothermic transition with a well-defined onset at 115°C in the undried membrane (preserved under ambient conditions for several weeks). In our earlier studies on FEP-g-polystyrene graft copolymer films (26% grafted), T_g for the polystyrene component was observed at 108°C.[27] However, this T_g cannot be traced in the undried membrane in the whole range of the thermogram, 40–180°C (plot a in Fig. 5). This membrane was found to have a water content of 5.5%.[25] Hence, the observed peak in plot a may be attributed to the loss of water from the membrane matrix. However, with the progressing drying of the membrane, T_g becomes more and more evident and shifts to higher temperatures as the drying temperature is further enhanced. This is evident from the increase in T_g from 61 to 151°C for an increase in
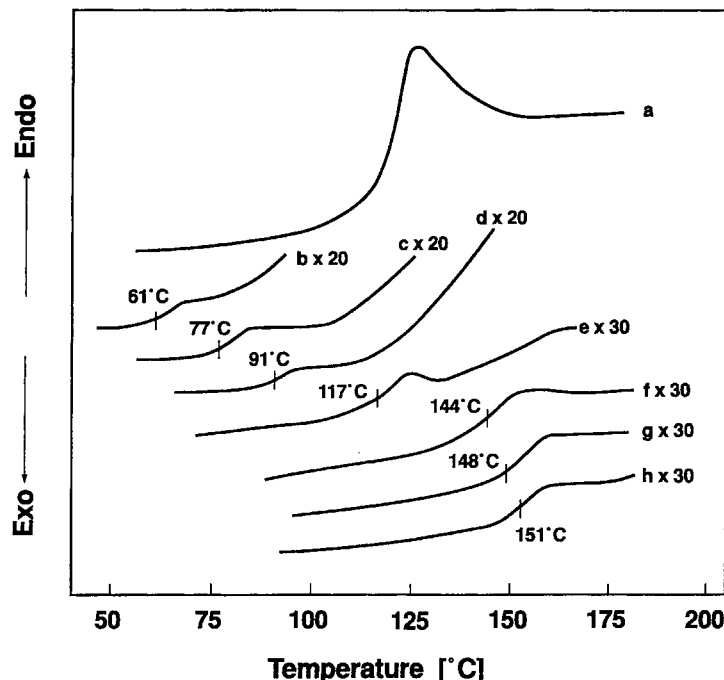
Figure 5   DSC thermograms in the glass transition temperature region for a membrane with 26% degree of grafting: (a) undried membrane and dried at (b) 40°C, (c) 60°C, (d) 80°C, (e) 100°C, (f) 120°C, (g) 130°C, and (h) 140°C. Drying time 24 h [from (b)-(h), membranes were dried at ∼ 1 Torr just before the DSC run).

the drying temperature from 40 to 140°C [plot (b) - (h)]. These results indicate that the T_g of an undried membrane is masked by the strong endothermic transition of water in this temperature range. T_g is visible only if the membrane is dry. The trend is similar to the observation made by Kyu and Eisenberg for the glass transition in the Nafion membrane.[33]

The variation of T_g with the drying temperature is presented in Figure 6. The trend in this figure shows that there is a sharp increase in T_g as the drying temperature is increased up to 120°C, beyond which the increase is very slow. The higher T_g of the polystyrene component in a membrane (e.g., 144°C at a drying temperature of 120°C) as compared to that in a grafted film (108°C) may be ascribed to the strong intermolecular ionic interaction among sulfonated polystyrene chains. A higher value of T_g in sulfonated polystyrene has been reported by Molnar and Eisenberg.[34] The authors found that Na and Li salts of sulfonated polystyrene have a glass transition temperature of 133°C in a sample dried at 80°C under vacuum for 2 days. However, in our system, the membrane is in the proton form and the drying time was 6 h, which may account for the lower value of 91°C dried at the same temperature.

The ionic interaction resembles a situation where a physical cross-linking within the ionic domain takes place. This necessarily hinders the mobility of molecular chains within the polystyrene domains. The membrane matrix becomes rigid and enhances the T_g of the polystyrene domain in a membrane to a higher temperature. Once the membrane absorbs water, these water molecules interact directly with the ionic sites. As a result, the interionic interaction among the grafted chains is considerably lowered. This situation corresponds to the solvation of ionic sites by water molecules. It is, therefore, the plasticizing effect of water that decreases the T_g of the polystyrene domain in the membrane to a considerable extent.[35,36]

To evaluate any possible influence of the drying process on structural changes occurring in the membrane during heating, and, hence, over T_g, the ionic content of all the six membranes was determined. It was found that the sulfonic acid groups remain intact up to a drying temperature of 120°C. The membrane lost 1.4 and 4.2% active sulfonic acid groups after 6 h drying at 130 and 140°C, respectively. Our earlier studies on these membranes showed that the loss of sulfonic acid groups proceeds via a cross-linking reaction between two sulfonic acid groups from the same or adjacent polystyrene
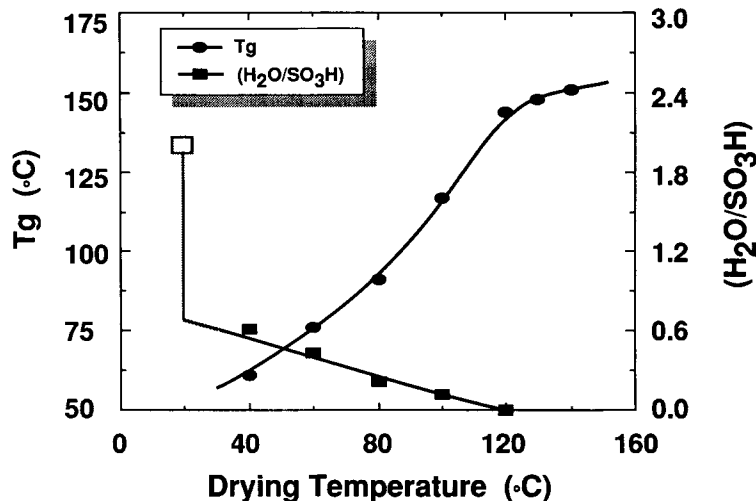
Figure 6 Variation of glass transition temperature and H_2O/SO_3H ratio with the drying temperature.

graft chains.[25,26] This cross-linking imparts rigidity in a polystyrene domain of the membrane matrix that enhances the T_g of the membrane.

From the above discussion, it is evident that the T_g of a membrane is directly related to its water content. Therefore, T_g would reach a maximum value once the membrane reaches a dry state. Considering that the desulfonation has its own impact over the T_g, it may be deduced that the membrane has reached the dry state at 120°C. A slight increase in T_g beyond a drying temperature of 120°C (Fig. 6) may not be because of the loss of water, but could be the result of the desulfonation-induced cross-linking reaction that decreases the mobility of polystyrene chains. Even if any water is left in the membrane at 120°C, it seems that it is not possible to remove it from the membrane matrix. Under such cases, drying of a membrane at 120°C may be taken as the reference for the amount of water at drying temperatures in the range of 40–140°C. The average number of water molecules per ionic site in a membrane is presented in Figure 6. The results show a good correlation between the T_g and the water/ionic site ratio in the membranes. The dotted square represents the value of the undried membrane. A sharp decrease in the water content is accompanied by a sharp increase in the T_g of the membrane as well. Even after drying at 100°C, the membrane still contains 0.12 molecules of water per ionic site. Therefore, the plasticizing effect of water still operates at such a high drying temperature.

The above studies indicate that an exact location of the T_g in water-swollen membranes is not possible by DSC measurements. A more fruitful approach toward determination of this transition would be to follow mechanical relaxation using dynamic mechanical analysis. A correlation between the crystalline changes occurring in the membrane matrix and some of the physical properties, such as the nature of water and its content, will be discussed in a subsequent publication.[37]

CONCLUSIONS

Proton-exchange membranes prepared by the simultaneous radiation grafting of styrene onto FEP films and subsequent sulfonation undergo considerable deterioration in the crystalline structure. The decrease in crystallinity of membranes is both in the form of a *dilution effect* of inherent crystallinity by the addition of amorphous polystyrene grafts in the noncrystalline region of the FEP matrix and of *crystal disruption*. No crystal disruption takes place after the grafting process. The disruption originates only after the sulfonation process due to the strong hydrophilic–hydrophobic stresses developing at the lamellar–graft interjuncture in a hydrophilic membrane matrix. These stresses are relieved when the membrane is swollen in water, leading to the disruption in the crystalline region. The glass transition temperature in membranes could only be ascertained in the dry state. In the presence of water, the transition may be considerably lowered, but cannot be detected due to the masking effect from the strong endothermic peak for water desorption. This transition is shifted to a higher temperature with the progressive drying of the membrane. Such a behavior

is due to the water molecules associated with ionic sites in the membrane at different drying temperatures. These water molecules exert a plasticizing effect on sulfonated polystyrene domains by interacting with the ionic sites. With the increasing drying temperature, the water/ionic site ratio decreases. As a result, the plasticizing effect of water diminishes, leading to the higher glass transition temperature.

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