Proton Exchange Membranes by Radiation Grafting of Styrene onto FEP Films. IV. Evaluation of the States of Water

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SYNOPSIS

The nature of water in proton exchange membranes, obtained by radiation grafting of styrene onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films and subsequent sulfonation, was investigated by differential scanning calorimetry. It was found that the membranes contained three different types of water, which were categorized as freezing-free, freezing-bound, and nonfreezing water. The degree of grafting had a considerable influence on the relative ratios of these three types of water molecules. The nonfreezing water per ion-exchange site ratio was found to be independent of the degree of grafting. However, freezing-free and freezing-bound water per ionic site ratios increased with increasing graft levels. A correlation between the water uptake and the structural changes occurring in the membrane as a function of the degree of grafting was established. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

The state of water in proton exchange membranes plays an important role in determining the transport behavior of protons. Several studies have been devoted to investigate the nature of water in different radiation-grafted membranes.[1-3] The water directly associated with ionic sites in a membrane may behave in a way different from the normal water due to its strong association in the form of hydrogen bonding and polar interaction. This type of water shows no phase transition, such as crystallization or melting in the temperature range of 273–200 K, and is referred to as the nonfreezing water. However, water with well-defined transitions, such as bulk water, is defined as the freezing water.

The evaluation of the states of water sorbed in membranes has been carried out by different methods including nuclear magnetic spectroscopy,[4-6] sorption–desorption isotherm,[7] dielectric measurements,[8] infrared spectroscopy,[9,10] and differential scanning calorimetry (DSC).[11-15] DSC offers an useful method in terms of quick evaluation of the

phase transition of water as well as small size of the sample. Both the melting and crystallization transitions have been followed in studies on water using DSC. In these measurements, a sample is cooled down to below 0°C, at which temperature the free water freezes leaving behind nonfreezing water associated with ionic sites. The monitoring of the melting of the frozen water by DSC, therefore, leads to information about freezable water in a membrane.

Membrane preparation by radiation grafting of vinyl and acrylic monomers onto poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) films has been carried out by several workers, and the relation between physicochemical properties and the degree of grafting has been established.[16-31] However, these membranes have not been investigated with respect to the nature of the sorbed water. In a graft copolymer membrane, the grafted chains remain dispersed within another polymeric matrix of different physico-chemical nature. Therefore, it is the nature and distribution of the ionic component in the matrix which determines the swelling and, hence, the fractional ratio of different types of water molecules.[15] Any kind of physical or chemical variation in the membrane structure that alters the total water uptake would also influence the relative content of the different states of water. As a result, the

diffusivity of a species would also be considerably influenced.[32,33] It becomes, therefore, interesting to study the nature as well as the fractional variation of different types of water in radiation-grafted membranes as a function of the degree of grafting. We have reported membrane preparation by simultaneous radiation grafting of styrene onto FEP films and subsequent sulfonation.[25] These membranes were investigated with respect to their thermal behavior and crystallinity changes.[27-30] In the present study, the investigation of the states of water and its fractional variation in FEP-g-polystyrene sulfonic acid (FEP-g-PSA) membranes containing different degrees of grafting is carried out. A correlation between structural changes and the water content is established.

EXPERIMENTAL

Materials and Grafting Procedure

Membranes were prepared by simultaneous radiation grafting of styrene onto FEP films of 50 μm thickness (supplied by DuPont) and subsequent sulfonation, as reported earlier.[25] The reaction tubes containing styrene were evacuated by freeze–thaw cycles at 10^{-3} torr. The grafting was carried out by placing reaction tubes in a thermostated water bath maintained at 60°C and subsequent irradiation from a Co-60 source operating at a dose rate of 0.5 Gy/min. The degree of grafting refers to the percent increase in the weight of the FEP film after the grafting reaction:

$$\text{Degree of grafting (\%)} = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

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

The grafted films were sulfonated using a chlorosulfonic acid/1,1,2,2-tetrachloroethane mixture at 90°C for 5 h.[25] The degree of sulfonation in membranes was found to be ca. 95%. Membranes containing degrees of grafting in the range of 15–40% were evaluated as to the nature of the sorbed water.

Differential Scanning Calorimetry (DSC)

The equilibrium swelling of membranes with different degrees of grafting was achieved by placing them in boiling water for 6 h. High-purity water (Seralpur 90 CN, 18 MΩ) was used for all experiments. Before DSC measurements, the water-swollen membrane samples were blotted with an adsorbent paper to remove water adhering to the surface and kept in the microbalance at room temperature for different periods of time to obtain membranes with different water uptakes. Each membrane sample was weighed before the DSC run in a Perkin-Elmer DSC-7 system, calibrated according to Perkin-Elmer Standards, and a typical run was made using 2–3 mg of the sample. The thermogram was studied in the temperature range of −50–5°C. The sample was cooled down to −50°C and the melting thermogram was obtained at a constant heating rate of 5 K/min under nitrogen atmosphere. After the run, the Al pan was evacuated at 120°C under vacuum (~1 torr) and the weight of the sample was determined. The water uptake of membranes was represented as the amount of water per gram of the dry membrane:

$$\text{Water uptake } (W_t) = \frac{W_s - W_d}{W_d} \quad (2)$$

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

The amount of water from DSC was calculated from the heat of melting value as obtained from the area under the thermogram. The heat of melting of ice was used as 334 J/g.[34]

The crystallinity of membranes was obtained from DSC thermograms of samples as reported in a previous communication.[30]

Apparent Proton Mobility

The membrane conductivity was determined at ambient temperature (20 ± 1°C) by ac impedance measurements using a frequency response analyzer (Solartron 1250) in combination with an electrochemical interface (Solartron 1186).[23,35] An *apparent proton mobility* (μ) was calculated from the following relationship:

$$\mu = \sigma e_0 n \quad (3)$$

where σ is the specific conductivity of the membrane, e_0 is the elementary charge, and n is the number of charge carriers per cubic centimeter. In order to determine n, a defined size of the wet membrane was taken and exchanged with 0.5M KCl solution. The protons released into the medium were titrated with 0.05M KOH and were calculated as meq/cm^3 of the wet membrane. The value of n was obtained by multiplying the meq/cm^3 value with Avogadro's number.

RESULTS AND DISCUSSION

DSC thermograms for a FEP-g-PSA membrane with degree of grafting of 40% containing different water uptakes are presented in Figure 1. Since, these membranes were found to undergo no transitions between -50 and $-35°C$, for simplicity, thermograms are presented in the temperature range of $-35–5°C$. The broken line in Figure 1 shows the thermogram of bulk water with a sharp melting at $-0.5°C$. However, the membrane with a maximum water uptake (0.962 g/g) shows two well-defined peaks in the thermogram. One of the peaks (peak I) is quite close to that of bulk water, while the other one (peak II) shows melting at a lower temperature. This indicates that the membrane contains at least two types of water molecules. One of them behaves as free water and the other one, showing phase transition at lower temperature, exhibits weak interaction with the ionic network in the membrane. From Figure 1, the total amount of water obtained from the area under the thermogram for the membrane with maximum water uptake showed it to be 0.666 g/g. However, the water uptake from gravimetry, as per eq. (2) was found to be 0.962 g/g. These observations suggest that there is another type of water in the membrane which does not crystallize during the cooling process down to $-50°C$ and is not visible in the melting thermogram. This water may, therefore, be termed as the nonfreezing water.

Based on the above observations, it may be stated that there are three types of water molecules in a graft copolymer membrane, i.e., freezing-free water (W_{ff}), freezing-bound water (W_{fb}), and nonfreezing water (W_{nf}). The most interesting observation from Figure 1 is that with the decrease in the water uptake, it is the peak for the free water (peak I) which preferentially diminishes, followed by a decrease in the freezing-bound water (peak II). Moreover, at lower water uptake, peak II becomes broader and shifts to lower temperature. The area under the melting thermogram decreases as the water uptake in the membrane is lowered (Fig. 1). No melting transition could be detected for the membrane containing 0.051 g/g of water. This indicates that the membrane does not have any freezing-free or freezing-bound water in its matrix, but the nonfreezing water is still present.

Different observations have been made by authors in various systems. Boake and Yeager[36] investigated the nature of sorbed water in Dow perfluorosulfonic acid membranes by Fourier transform infrared (FTIR). Authors could distinguish spectroscopically among three distinct waters. On the other hand,
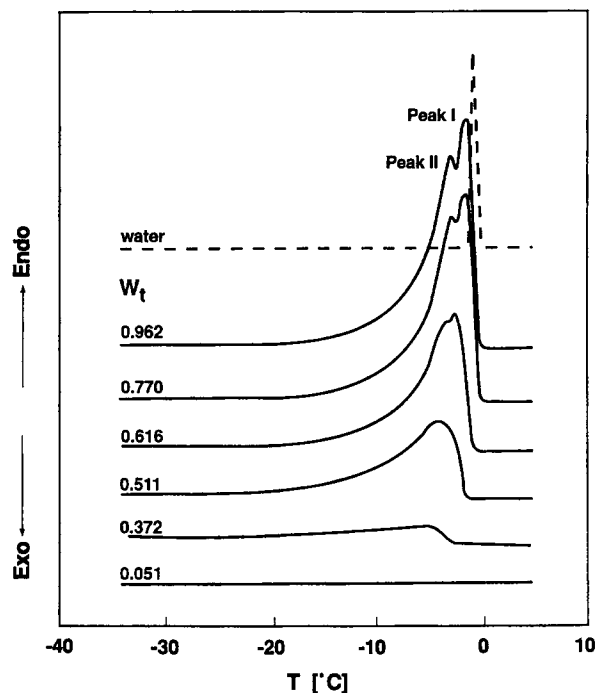

Figure 1 DSC thermograms of water and FEP-g-PSA membrane with different water uptakes. Degree of grafting, 40%.

Takigami et al.[15] found by DSC that acrylic-acid-grafted membranes show three distinct types of water molecules as discussed above, while nylon-g-polystyrene sulfonic acid (SS-GN) membranes contain two types of water, i.e., the nonfreezing water and the freezing water. The membrane showed only one melting peak temperature and no differentiation of freezing water into freezing-bound and freezing-free water was observed. The discrepancy between the two types of membranes, i.e., FEP-g-PSA and SS-GN, appears because of the difference in the heating rate in these two systems. We have used a heating rate of 5 K/min instead of 10 K/min being used by Takigami et al.[15] for SS-GN membranes. We have observed that at low heating rates of 1–5 K/min, membrane showed two melting peaks for the freezing-free and freezing-bound water. As the heating rate was increased to 10–20 K/min, two peaks merge together and only one broad melting peak was observed. It may, therefore, be assumed that in the studies of Takigami et al.[15] it is the relatively higher heating rate of 10 K/min which is responsible for the origin of one single peak in the melting thermogram.

The relation between freezing water W_f (cumulative weight fraction of W_{ff} + W_{fb}) and total water uptake W_t was determined according to the following expression.[1]

$$W_f = W_{ff} + W_{fb} = W_t - W_{nf} \qquad (4)$$

where W_t is the total water content, W_{ff} is the freezing-free water, W_{fb} is the freezing-bound, and W_{nf} is the nonfreezing water content.

This relation as presented in Figure 2 for a 40% grafted membrane shows a linear increase in freezing water ($W_{ff} + W_{fb}$) with increasing total water uptake. Extrapolating the plot to the X axis gives a value of 0.27, which represents the nonfreezing water (W_{nf}) strongly associated with ionic sites. The nonfreezing water as obtained from eq. (4) increases initially with increasing water uptake and reaches a saturation value. A similar trend has been observed in acrylic acid and methacrylic acid/hydroxyethylacrylate grafted polypropylene membranes as well.[1] From the results in Figure 2, it may be stated that the very first water molecules are incorporated into the membrane as the nonfreezing water. These water molecules disrupt the interionic hydrogen bonding and get associated at the core level.[7] As soon as all the ionic sites are saturated, the very next molecule is introduced as the freezing water, and this transition takes place at a total water uptake of 0.27 g/g. This value corresponds to 7.8 water molecules per ionic site as discussed later. From the results in Figures 1 and 2, it may be stated that it is the freezing water fraction which preferentially changes and makes a considerable contribution to the water uptake of the membrane. The freezing water in a membrane with 96% water uptake constitutes to

72%, which decreases to 0% in the same membrane with lower water uptake of 5%.

The degree of grafting has considerable influence over the variation and the nature of water in membranes (Fig. 3). In the following, results for three membranes with degrees of grafting of 15, 26, and 40% are presented. Both the DSC-detectable and total water content show considerable reduction with the decreasing degree of grafting. The extrapolated values on the X axis also show a decreasing trend. This can be attributed to the decrease in the number of ionic sites at lower levels of grafting in the membrane. These extrapolated values are, therefore, referred to as the *critical water content* (W_{cr}), which is needed to achieve the nonfreezing/freezing water transition in a membrane and depends on the degree of grafting. It is important to note that the critical number of water molecules per ion-exchange site as calculated from eq. (4) remains nearly the same for all three membranes. The results are presented in Figure 4. The total number of water molecules per ionic site increases with increasing degree of grafting. This is evident from the increase from 12 for 15% to 25 for 40% degree of grafting. However, it is the free or freezing-bound water which varies with the change in the degree of grafting. The nonfreezing water (which corresponds to the W_{cr}) per ionic site remains nearly constant, i.e., 6–8 water molecules per ionic site in membranes with degree of grafting in the range of 15–40%. These observations in grafted membranes are well in agreement with the
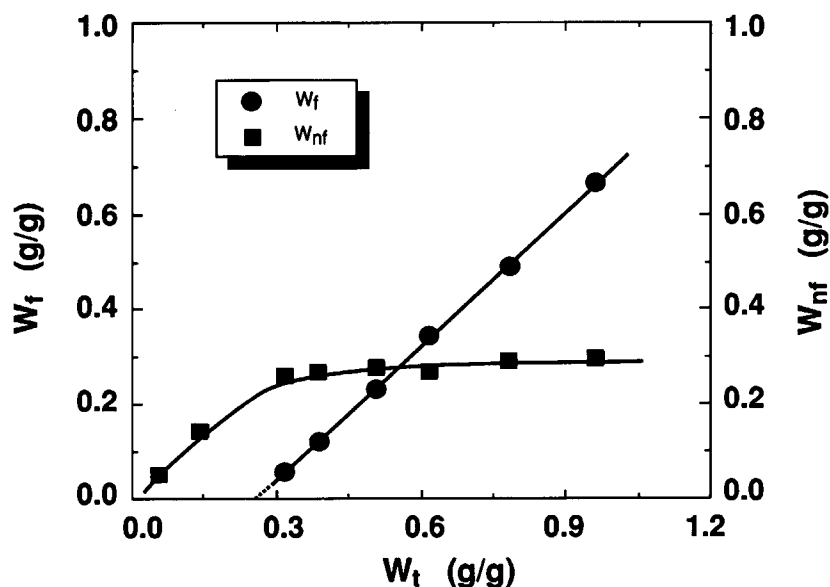

Figure 2 Variation of freezing and nonfreezing water with water uptake in FEP-g-PSA membrane. Degree of grafting, 40%.
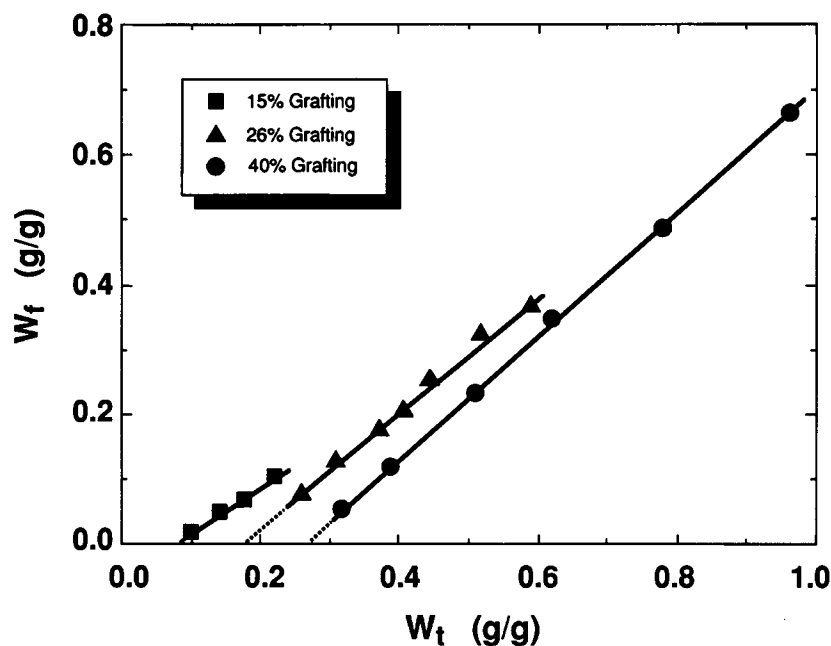
Figure 3 Variation of freezing water with water uptake in FEP-g-PSA membranes with different degrees of grafting.

studies of Escoubes and Pineri[37] on Nafion perfluo-rosulfonic acid membranes as well as Hatakeyama et al.[13] on the water uptake in sodium polystyrene sulfonate polymers by DSC. Authors found that the nonfreezing water in such polymers was 5–7 H_2O/ ionic site.

As evident from Figure 4, an increase in the number of water molecules per ionic site can be attributed to both the physical as well as chemical changes occurring in membranes due to the grafting and subsequent sulfonation. These changes are in the form of an increase in the hydrophilicity and a decrease in the crystallinity of the membrane with increasing degree of grafting, as discussed in the subsequent section.

Based on our earlier studies,[27,30] a three-phase model may be proposed for the FEP-g-PSA system where PSA chains remain grafted into the hydrophobic amorphous region of the FEP matrix. The PSA chains are amorphous in nature and remain dispersed in the FEP matrix. The membranes, therefore, contain hydrophilic (PSA-grafted) amorphous regions, hydrophobic (ungrafted) amorphous FEP chains, and highly ordered crystalline FEP zones. Since grafted chains are hydrophilic in nature, this introduces hydrophilicity in the hydrophobic amorphous region of the FEP film. Based on this model, the fractional hydrophilicity (by weight) of the amorphous region in a membrane may be obtained from the following equation:

$$f_{\text{hydrophilicity}} = \frac{W_{\text{PSA}}}{W_{\text{PSA}} + W_{\text{FEPam}}} \quad (5)$$

where W_{PSA} and W_{FEPam} are the weight fraction of sulfonated polystyrene grafts and amorphous FEP in a membrane, respectively.

The variation in the fractional hydrophilicity of the amorphous region of copolymer membranes versus degree of grafting is presented in Figure 5. This indicates how the membrane matrix is gradually transformed into a more and more hydrophilic structure with increasing degree of grafting. At low graft level, the number of PSA chains is low, and they remain distributed sparingly within the perfluorinated matrix. The water associated with these ionic chains, therefore, remain isolated from each other. As the degree of grafting increases, the number of PSA chains also increases and the ionic domains lie much closer to each other. At the same time, the hydrophilicity of the amorphous region in a membrane increases (as visible in Fig. 5). Under such circumstances, the three-dimensional network formation among water domains within the hydrophilic matrix is facilitated. The water uptake, as a result, increases to such an extent that the number of water molecules per ion-exchange site rises from 12 to 25% for an increase in the grafting from 15 to 40%.

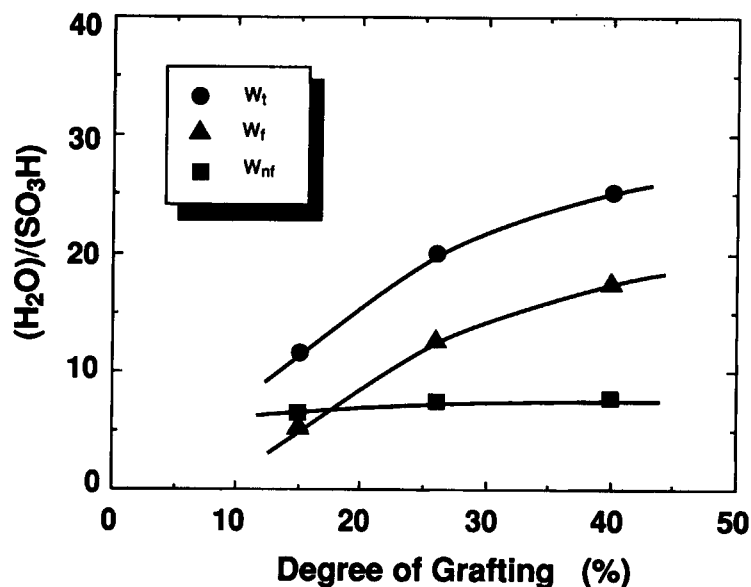The crystalline-amorphous changes in membranes are another important factor in influencing

Figure 4   Variation of water/ionic site ratio with degree of grafting in FEP-g-PSA membranes.

the water uptake. There is a decrease in the crystallinity of membranes due to its dilution by the incorporation of amorphous PSA chains and partial disruption of inherent crystallites of the FEP component.[30] With the decrease in crystallinity of the membrane, water molecules can easily approach sites in the noncrystalline region. The water uptake, as a result, increases with an increase in the graft levels. The contribution of the decrease in crystallinity of the membrane in regulating the water penetration is in addition to the increase in the hydrophilicity of the amorphous region.

The variation in the apparent proton mobility in membranes with different degrees of grafting is presented in Figure 6. As discussed in an earlier publication,[25] the proton concentration per unit volume remains nearly constant for all the membranes. This explains the contribution of higher hydration states of ionic sites to the increase in the apparent proton mobility. However, the results may best be under-
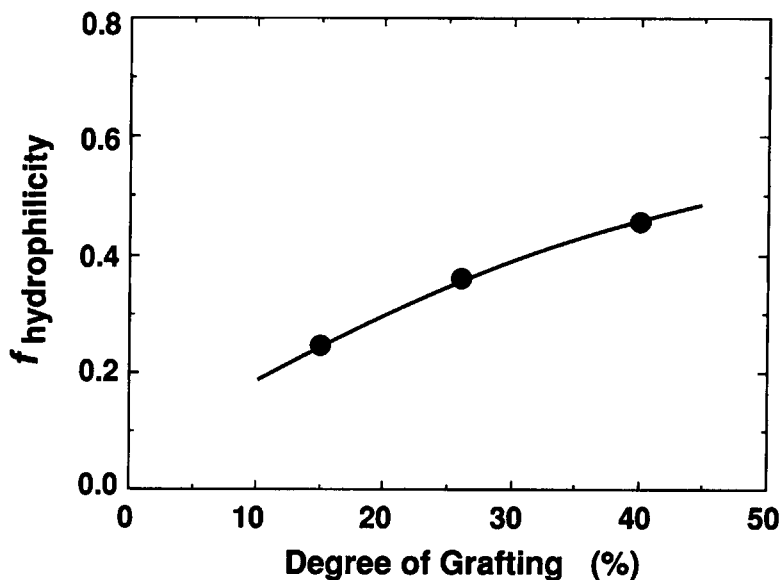

Figure 5   Variation of fractional hydrophilicity with degree of grafting in FEP-g-PSA membranes.
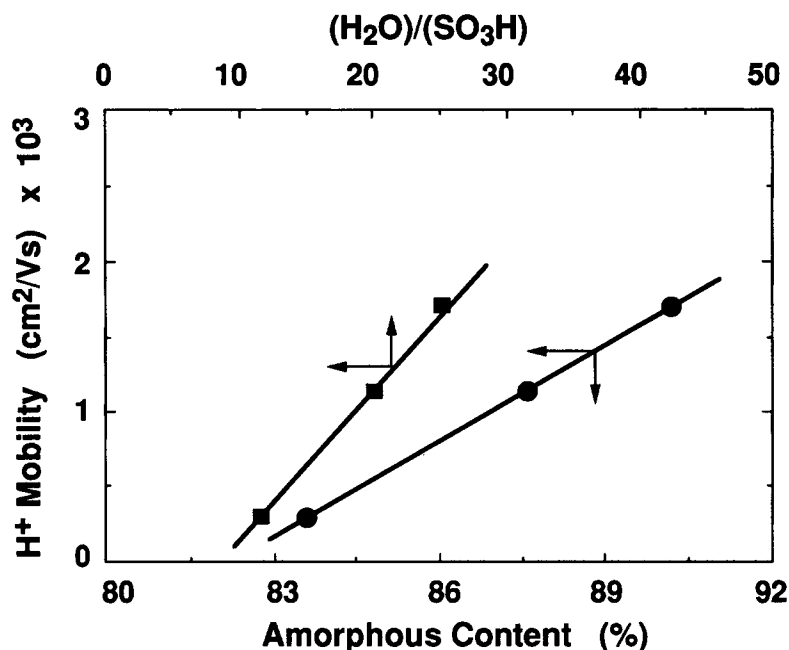
$$(H_2O)/(SO_3H)$$

Figure 6   Variation of proton mobility with amorphous content and water/ionic site ratio in FEP-g-PSA membranes.

stood on the basis of the cumulative effect of the hydration number and increase in the amorphous fraction in the membrane. Moreover, the crystalline regions act as crosslinks in a polymer.[38] These impermeable crystalline regions increase the path length of species by impeding the motion across them. With the decrease in the crystallinity, proton movement in the three-dimensional network involving water domains within the amorphous region is facilitated. The decrease in crystallinity, therefore, not only increases hydration states of the ionic sites but also enhances the apparent proton mobility.

CONCLUSION

Proton exchange membranes obtained by radiation grafting of styrene onto FEP films and subsequent sulfonation contain three different types of water molecules, which may be referred to as the freezing-free, freezing-bound, and nonfreezing water. The relative ratio of these different types of water molecules depends on the degree of grafting. The nonfreezing water per ionic site remains independent of the degree of grafting. It is the freezing-free and freezing-bound water per ionic site which increases with increasing graft levels. The apparent proton mobility increases with an increase in the degree of grafting. This is due to the changes in the physicochemical structure of the membrane. The most im-

portant changes are in the form of crystalline/amorphous ratio and hydrophilicity of the amorphous fraction in the membrane, both of which make the membrane structure more amenable to water and facilitate the proton transport.

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