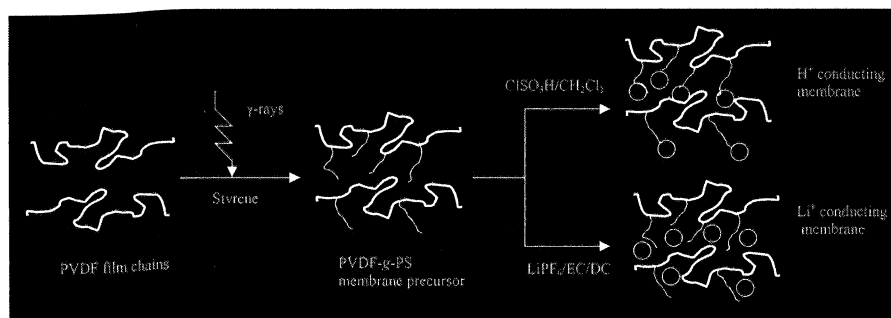


Summary: Two distinct types of polymer electrolyte membranes for conducting protons and lithium ions have been prepared by a radiation-induced grafting method. The polymer electrolyte precursor (PVDF-*g*-PS) is obtained by the simultaneous grafting of styrene onto poly(vinylidene fluoride) (PVDF) followed by one of two specific treatments. This includes sulfonation with a chlorosulfonic acid/dichloromethane mixture to obtain proton (H^+)-conducting membranes, or activation with $LiPF_6/EC/DC$ liquid electrolyte to obtain lithium ion (Li^+)-conducting membranes. The chemical structure of the obtained electrolyte membranes is verified by

FT-IR spectroscopy. Differential scanning calorimetry is used to examine the changes in the crystallinity and the thermal properties of both electrolyte membranes during the preparation process. The thermal stability of both electrolyte membranes is also evaluated using thermal gravimetric analysis. The obtained polymer electrolyte membranes achieve superior conductivity values: $1.61 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ for Li^+ and $5.95 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ for H^+ at room temperature at a polystyrene content of 50%. The results of this work suggest that high quality H^+ - and Li^+ -conducting membranes can be obtained using a single radiation-induced grafting method.



Schematic representation of the single route for preparation of Li^+ - and H^+ -conducting membranes started by radiation-induced grafting of styrene onto a PVDF film followed by chemical treatment.

Single Radiation-Induced Grafting Method for the Preparation of Two Proton- and Lithium Ion-Conducting Membranes

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Introduction

Polymer electrolyte membranes are a class of materials that is attracting ever-increasing attention in the field of material science and engineering. This is a result of their wide-spread application in a variety of solid-state and electrochemical devices, which include batteries, fuel cells, super capacitors, and chemical sensors.^[1,2] The replacement of the conven-

tional liquid electrolytes with polymer electrolyte membranes has driven the technology towards the development of new generations of modular, safer, and robust devices.^[3]

Among polymer electrolytes, proton (H^+)-conducting and lithium ion (Li^+)-conducting membranes are undergoing extensive investigations to make commercially attractive polymer electrolyte membrane (PEM) fuel cells and lithium polymer batteries, respectively. The research on

H⁺-conducting materials has been pursued because the most widely tested commercial membranes for PEM fuel cells such as Nafion (du Pont) and other structurally analogous materials (Aciplex, XUS Dow, Flemion) are considered to be very expensive and have limitations at high-temperature operations.^[4] Whereas, research on Li⁺-conducting membranes has been prompted by the need to enhance the low ionic conductivity of Li⁺ in most of the all-solid-state polymer electrolytes (less than 10⁻⁵ S · cm⁻¹ at room temperature), which is far from the adequate level for practical room temperature applications of lithium batteries.^[5]

To reduce the cost of H⁺-conducting polymer membranes and enhance their performance, various methods have been introduced to prepare alternative materials. This includes micro-reinforcement using very thin and porous poly(tetrafluoroethylene) (PTFE) films impregnated with liquid Nafion (Gore-selectTM perfluorinated ionomer composite membranes),^[6] and sulfonation of polyarylene polymers such as polystyrene,^[7] polyphosphazene,^[8] polyphenylene oxide,^[9] polyether sulfone,^[10] polyether ether ketone,^[11] and polyimides.^[12] Acid-base blending has also been proposed and reports on H⁺-conducting blends such as sulfonated polyether sulfone/polybenzimidazole can be found in the literature.^[13] The current state-of-the-art of alternative membranes for PEM fuel cells can be found in the reviews by Savadogo^[4] and Kerres.^[14]

Among alternative methods to prepare H⁺-conducting membranes, radiation-induced grafting of styrenic monomers onto polymer films followed by sulfonation has been reported to be very appealing.^[15-22] This method has the advantage of using radiation (gamma rays or electron beam) to initiate grafting reactions under controlled conditions in a way that allows a desired manipulation over the composition and properties of the obtained membranes. Moreover, the grafting reaction can be achieved on pre-formed polymer films, which overcomes the problem of processing the activated polymers into membrane form.

For applications requiring high chemical stability such as fuel cells, fluorinated polymers are mostly used as starting matrices because of their chemical resistance, thermal stability, and mechanical integrity. Among fluorinated polymers, poly(vinylidene fluoride) (PVDF) is known for its electrical properties, resistance to radiation, durability, biocompatibility, and processibility. The preparation of H⁺-conducting membranes by radiation-induced grafting of styrene onto PVDF films using a pre-irradiation method followed by sulfonation has been studied.^[23,24] However, the use of a simultaneous irradiation method to prepare these membranes has not been exploited, as indicated by the scarce number of reports in the literature.

On the other hand, to improve the Li⁺-conductivity of polymer electrolytes, gel-type polymer electrolytes having ionic conductivities of the order of 10⁻³ S · cm⁻¹ at room temperature have been developed by hosting a liquid solution of a lithium salt containing aprotic polar solvents

such as ethylene carbonate (EC) and diethyl carbonate (DEC) in a polymer matrix.^[25,26] PVDF is often used as a matrix for such electrolyte membranes after being modified by copolymerization with monomers such as hexafluoropropylene (HFP), chlorotrifluoroethylene (CTFE), or styrene to reduce the crystallinity and help generate electrolyte-hosting amorphous domains in an otherwise predominantly crystalline PVDF structure.^[27,28] However, most PVDF-based modifications carried out thus far have been performed using blending technology, in which the miscibility between different polymers is limited to the macroscopic level.

Very recently, an attempt to use radiation-induced grafting to modify pre-formed PVDF films by the incorporation of polystyrene grafts to obtain precursors that could be converted into gel polymer electrolytes by chemical activation with lithium liquid electrolyte has been made.^[29] To extend the utilization of the radiation-induced grafting method, the same grafting conditions have been applied to obtain one precursor that can be converted into two types of interesting polymer electrolyte, i.e., H⁺- and Li⁺-conducting membranes. The properties of the two polymer electrolyte membranes are investigated in correlation with the preparation procedures using a comparative approach.

Experimental Part

Materials

A PVDF film of 80 µm thickness and density of 1.76 cm³ · g⁻¹ (Goodfellow, UK) was used as a polymer matrix. Styrene of purity ≥99% (Fluka, Switzerland) was used without any further purification. A ready-made electrolyte solution composed of a 1.0 M solution of LiPF₆ in a 1:1 v/v EC/DEC mixture, was obtained from Merck. All the solvents and other chemicals were of reagent grade and used as received.

Preparation of the Polymer Electrolyte Membranes

The preparation of the two electrolyte membranes was carried out using a two-step procedure schematized in Figure 1. Firstly, styrene was grafted onto PVDF films under controlled conditions to obtain electrolyte precursors. Secondly, the precursors were activated with either one of two different post-grafting chemical treatments to confer the desired ionic characters.

Preparation of the Grafted Films (Electrolyte Precursors)

Simultaneous irradiation polymerization/irradiation grafting was used to prepare polystyrene grafted PVDF (PVDF-*g*-PS) precursor films. A PVDF film of known weight and dimension was immersed in styrene of a defined concentration diluted with dichloromethane in a glass ampoule. The mixture was flushed with purified N₂ to remove air and the ampoule was tightly sealed and irradiated using γ-rays from a ⁶⁰Co source at

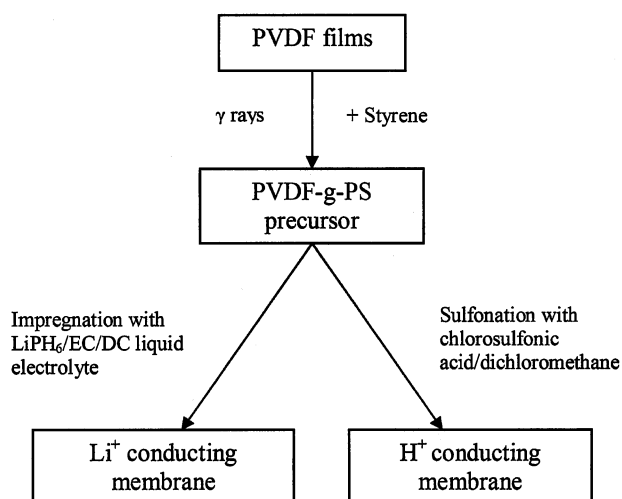


Figure 1. Schematic representation of the preparation procedure for H^+ - and Li^+ -conducting membranes by radiation-induced grafting.

a dose rate of $0.37 \text{ Gy} \cdot \text{s}^{-1}$ at room temperature. After the prescribed time, the grafted film was removed, washed thoroughly with toluene several times and soaked therein for 24 h to completely eliminate the homopolymer and the unreacted monomer occluded to the surface of the film. The clean PVDF-g-PS film was finally dried under vacuum, weighed, and its dimensions were measured. The grafting yield representing the content of incorporated polystyrene ($Y\%$) was calculated using the following equation:

$$Y\% = \frac{W_g - W_0}{W_0} \times 100 \quad (1)$$

where W_g and W_0 are the weights of PVDF-g-PS and the original PVDF films, respectively.

Conversion of the Precursor to Proton-Conducting Membranes

The PVDF-g-PS films were converted into H^+ -conducting membranes by sulfonation reaction under controlled conditions. The reaction was performed in a glass reactor using 0.5 M chlorosulfonic acid in dichloromethane at room temperature for 24 h as described in ref. [30]. The sulfonated membranes were washed with ion-free water a few times and then hydrolyzed with 0.5 M KOH solution overnight and regenerated into acid form by boiling with 1 M HCl for 2 h. The samples were then washed free of excess HCl with ion-free water a few times and stored under water in the dark.

Conversion of the Precursor to Lithium-Conducting Membranes

The PVDF-g-PS films were converted into Li^+ -conducting membranes by loading with the Li^+ liquid electrolyte mixture. To enhance the electrolyte uptake, the PVDF-g-PS films were initially swollen in aprotic solvent (dimethylformamide, DMF) for several hours and then the solvent was evaporated by drying in a vacuum oven at 60°C for 24 h. The grafted films were

transferred to a M-Braun re-circulating Ar glove box where both moisture and oxygen levels were kept below 1 ppm each at 70°C . The grafted films were immersed in 1 M LiPF_6 in a 1:1 (v/v) mixture of EC and DEC until the equilibrium weight was achieved. The electrolyte-loaded membranes were then stored in a tightly sealed vial in the glove box.

Thickness and Geometrical Changes

The thicknesses of the PVDF-g-PS films and their corresponding Li^+ - and H^+ -conducting membranes were measured with a digital micrometer (Mitutoyo, Japan). The width and the length of the samples were measured using a digital caliper (Mitutoyo, Japan).

FT-IR Analysis

FT-IR measurements were carried out using a Nicolet (Magna-IR 560) spectrometer equipped with attenuated total reflectance (ATR) (Thunder dome-HATR) having a Ge spherical crystal. The spectra were measured in transmittance mode over a wavenumber range of $4000\text{--}600 \text{ cm}^{-1}$.

Ion Exchange Capacity

The ion exchange capacity (IEC) of the H^+ -conducting membranes was determined by back titration. Membrane samples in acid form were immersed in a 0.5 M KCl solution overnight at room temperature. The H^+ released into the solution was titrated against standardized 0.05 M KOH solution by an automatic titrator (Metrohm, Switzerland) until pH 7 was reached. The IEC per unit mass of the dry membrane ($\text{mequiv} \cdot \text{g}^{-1}$) was calculated from the volume of the KOH solution consumed during the titration after taking the weight of the dry membrane into account.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) thermograms of the polymer electrolyte membranes were obtained by a Perkin-Elmer DSC-7 (Pyris 1) calorimeter under N_2 atmosphere. The Li^+ -conducting samples were sealed into aluminum pans prior to DSC runs in a glove box. The H^+ -conducting sample was dried for 7 d at a temperature of 80°C in a vacuum oven and stored over silica gel in an evacuated desiccator prior to DSC runs. Heating runs for both electrolyte membranes were obtained over a temperature range of $50\text{--}400^\circ\text{C}$ at a heating rate of $20^\circ\text{C} \cdot \text{min}^{-1}$. The sample was held for 5 min before cooling to 50°C at a rate of $20^\circ\text{C} \cdot \text{min}^{-1}$. The degree of crystallinity (X_c) in the original PVDF film was directly calculated using Equation (2).

$$X_c = (\Delta H_m / \Delta H_{m100}) \times 100 \quad (2)$$

where ΔH_m is the heat of melting of the PVDF film obtained from the peak area and ΔH_{m100} is the heat of melting of a 100% crystalline PVDF polymer, which equals $104.7 \text{ J} \cdot \text{g}^{-1}$. [27]

The X_c in the grafted PVDF film, and the Li^+ - and H^+ -conducting membranes were calculated by correcting their recorded ΔH_m by dividing over the weight fraction of PVDF in the investigated membrane as reported earlier. [29]

Thermal Gravimetric Analysis

Thermal gravimetric analysis (TGA) was performed on Li^+ - and H^+ -conducting membranes using a Perkin-Elmer TGA-7. All the heating runs were made over a temperature range of 50–700 °C at a constant heating rate of 20 °C · min⁻¹ and under an N_2 atmosphere.

Swelling Behavior

The swelling of the H^+ -conducting membranes was determined by equilibrating dry membrane samples in their acid form in ion-free water. The samples were removed, the excess water adhered to the surface was quickly blotted by absorbent paper, and the samples were weighed. The membrane water uptake was calculated as the weight increase in the dry membrane after swelling. Similarly, the electrolyte uptake and the porosity of the Li^+ -conducting membranes were determined from the difference in the weights of the liquid-electrolyte-equilibrated PVDF-*g*-PS and its dry counterpart as reported earlier.^[29]

Ionic Conductivity

The ionic conductivity of both polymer electrolyte membranes was measured at room temperature by complex AC impedance spectroscopy. Measurements were performed using a frequency response analyzer (Autolab PGSTAT 30) over frequency range of 0.01–100 kHz as reported in refs. [22,29]. Analysis was conducted on fully electrolyte loaded Li^+ -conducting membranes and H^+ -conducting membranes equilibrated in ion-free water for 24 h. Circular samples were sandwiched between two stainless steel electrodes having round-end discs (20 mm diameter) hosted in a self-made Teflon cell. The two halves of the cell were clamped in a way that prevented the samples from being squeezed between the two discs of the electrodes when the cell was assembled. The ionic conductivity of the polymer electrolyte membranes was calculated by taking the resistance obtained from the intercept on the real axis at the high frequency end of the Nyquist plot of complex impedance into consideration.

Results and Discussion

Grafting Reaction

The preparation of a PVDF-*g*-PS precursor has been carried out under controlled conditions. Samples with degrees of grafting in the range of 5–50% are obtained by varying the reaction time in the range of 3.72–22.56 h while keeping other parameters such as monomer concentration, dose rate, and solvent constant. Figure 2 shows the time course for the grafting reaction of styrene onto PVDF films. The grafting yield (*Y*%) is found to increase gradually with the increase in the irradiation time. This behavior can be explained on the basis of the fact that the increase in the irradiation time leads to an increase in the total dose absorbed, which concurrently increases the number of radicals formed in the

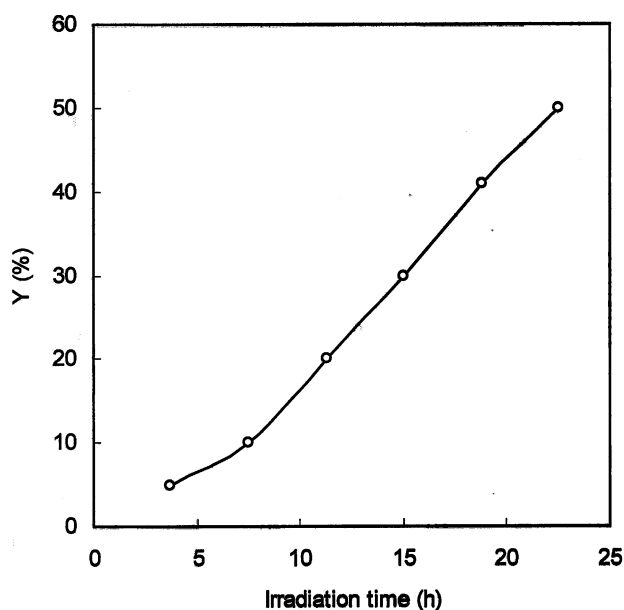


Figure 2. Time course for the grafting of styrene onto PVDF films. Reaction conditions are: 60 vol.-% monomer concentration, 0.37 G · s⁻¹ dose rate, dichloromethane diluent, and room temperature.

grafting system. Subsequently, more radicals on the PVDF films capture styrene molecules, which leads to a greater grafting yield with prolonged time.

Evidence of Grafting and Chemical Activation

Physical Changes

The grafting of styrene and the subsequent two chemical treatments have also been found to introduce changes in the geometry of the obtained precursor films and the electrolyte membranes compared to the original PVDF film. Such changes are found to have a greater influence on the thickness of the films than on the width and the length. Figure 3 shows the relationship between *Y*% and the thickness of the PVDF-*g*-PS film, the swollen activated lithium electrolyte membrane, and swollen sulfonated membranes. Both the grafting of styrene and the two subsequent chemical treatments are found to increase the thickness of the original and PVDF-*g*-PS films depending on *Y*%. However, the increase in the thickness of lithium-electrolyte-activated PVDF-*g*-PS films is higher than that caused by sulfonation. On the other hand, the sulfonated membranes have shown noticeable expansion in their length and width compared to the lithium-activated membranes, which are only marginally affected. These observations provide proof for the successful grafting and activation of PVDF films and reflect a discrepancy in the way by which the swelling affects the geometry of both electrolyte membranes. This is most likely a result of the difference in the chemical nature of each membrane after being activated. The Li^+ -conducting

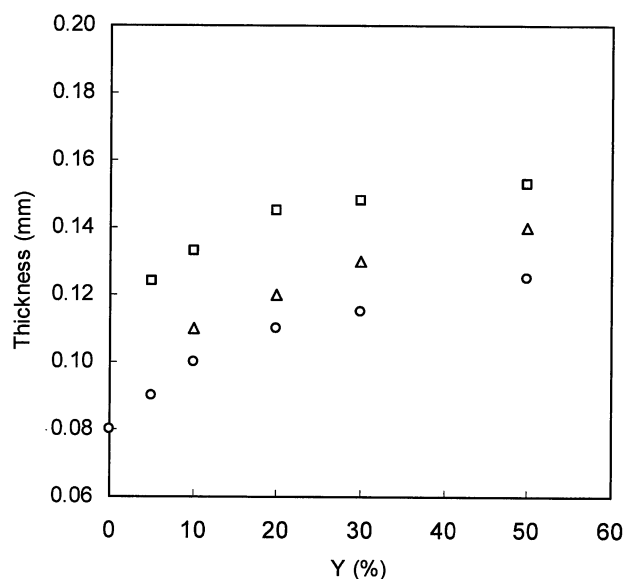


Figure 3. The relationship between $Y\%$ and the thickness of: (O) the grafted PVDF film, (□) swollen activated lithium electrolyte membranes, and (△) swollen sulfonated membranes.

membrane is a matrix that hosts a swollen gel electrolyte in the amorphous phase, whereas the H^+ -conducting membranes possess chemically bonded ionic sites that form hydrated amorphous polystyrene domains across the matrix.

Chemical Changes

Figure 4 shows typical FTIR-ATR spectra of H^+ - and Li^+ -conducting membranes both of which have a Y of 50% compared to pre-grafted PVDF and a PVDF- g -PS film ($Y = 50\%$). As can be seen, additional characteristic peaks that represent polystyrene are observed in the spectrum of the PVDF- g -PS film (Figure 5B). This includes the benzene ring features: C-H aromatic symmetric stretching vibrations at 3080 and 3015 cm^{-1} and skeletal C=C in-plane stretching vibrations at 1493 and 1602 cm^{-1} , respectively. The spectrum of a PVDF- g -PS film activated with $LiPF_6/EC/DEC$ (Figure 5C) shows characteristic bands of carbonyl groups at 1750–1800 cm^{-1} , which can be attributed to the fragmented and polymerized solvents (EC and DEC), respectively.^[31] The weak band at 3320 cm^{-1} can be assigned to $LiPF_6$.^[32] The spectrum of the sulfonated PVDF- g -PS film (Figure 5D) recorded a few additional absorption bands at 1123 and 1003 cm^{-1} , which represent SO_3^- groups. The two

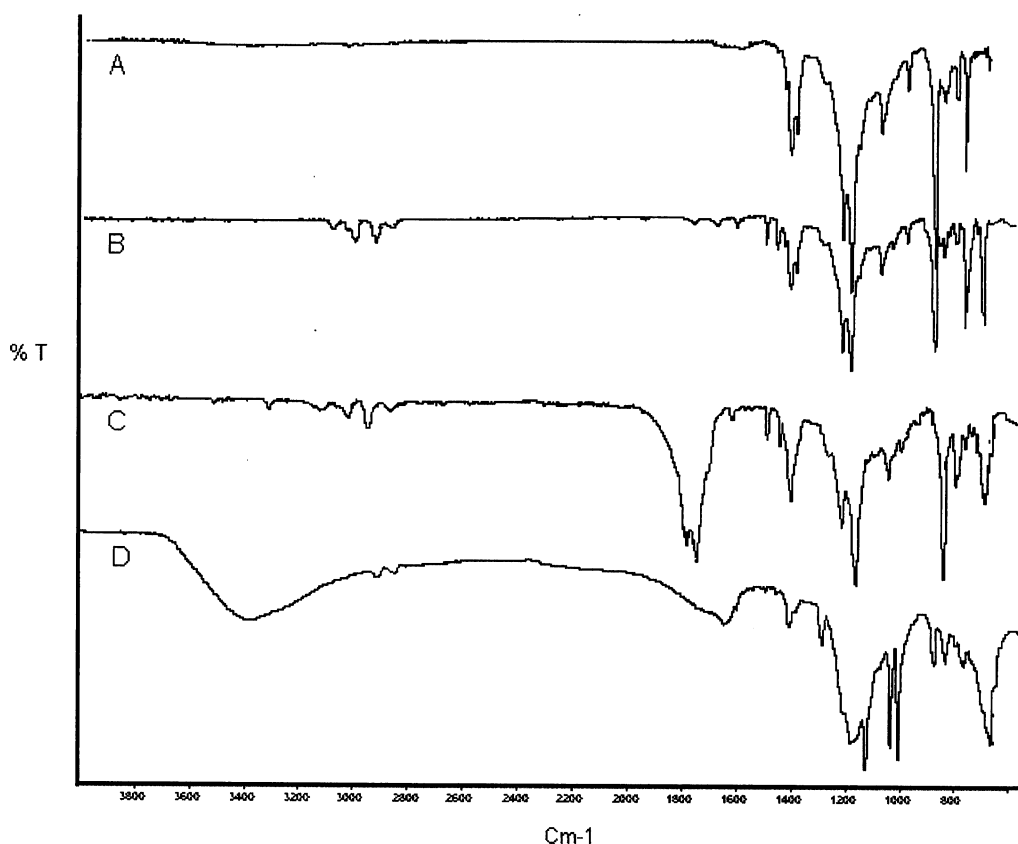


Figure 4. Typical FT-IR spectra of: A) original PVDF film, B) PVDF- g -PS film ($Y = 50\%$), C) Li^+ -conducting membrane ($Y = 50\%$), and D) H^+ -conducting membrane ($Y = 50\%$).

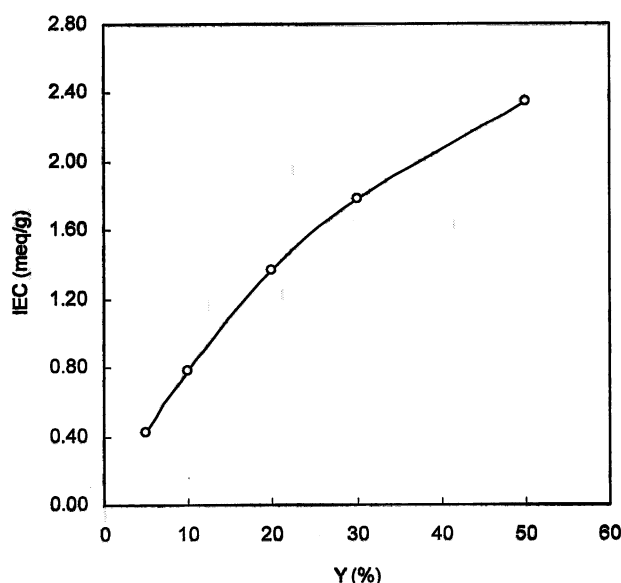


Figure 5. The relationship between IEC and Y% in H⁺-conducting membranes.

sharp peaks detected at 1 300 and 1 160 cm⁻¹ are assigned to S=O groups. The broad band at 3 100–3 700 cm⁻¹ is a result of the OH groups of water molecules strongly bound to SO₃⁻ groups by hydrogen bonding. The absorption bands of the aromatic groups are obscured because of the strong intensity of the sulfonic groups and their hydration spheres. These results further confirm the successful grafting and activation of the two types of polymer electrolyte membranes.

IEC of Proton Conducting Membranes

Figure 5 shows the relationship between the IEC and the grafted polystyrene content (Y%) in the H⁺-conducting membranes. The IEC is found to increase gradually with the increase in Y%. This is because of the increase in the number of sulfonic acid groups incorporated with the availability of more polystyrene in the grafted films at higher grafting levels. Similar results have been reported for polystyrene sulfonic acid membranes based on PVDF prepared by a pre-irradiation method.^[30,33]

Structure and Thermal Properties of the Polymer Electrolyte Membranes

The structure and the thermal properties of the H⁺- and Li⁺-conducting membranes have been investigated by DSC. Samples of both membranes having Y of 50% have been analyzed and the obtained DSC heating and cooling thermograms are presented in Figure 6 (a and b) whereas the corresponding data is summarized in Table 1.

Figure 6a shows typical DSC thermograms of Li⁺- and H⁺-conducting membranes with Y = 50%. Samples of an original PVDF film and PVDF-g-PS (Y = 50%) have

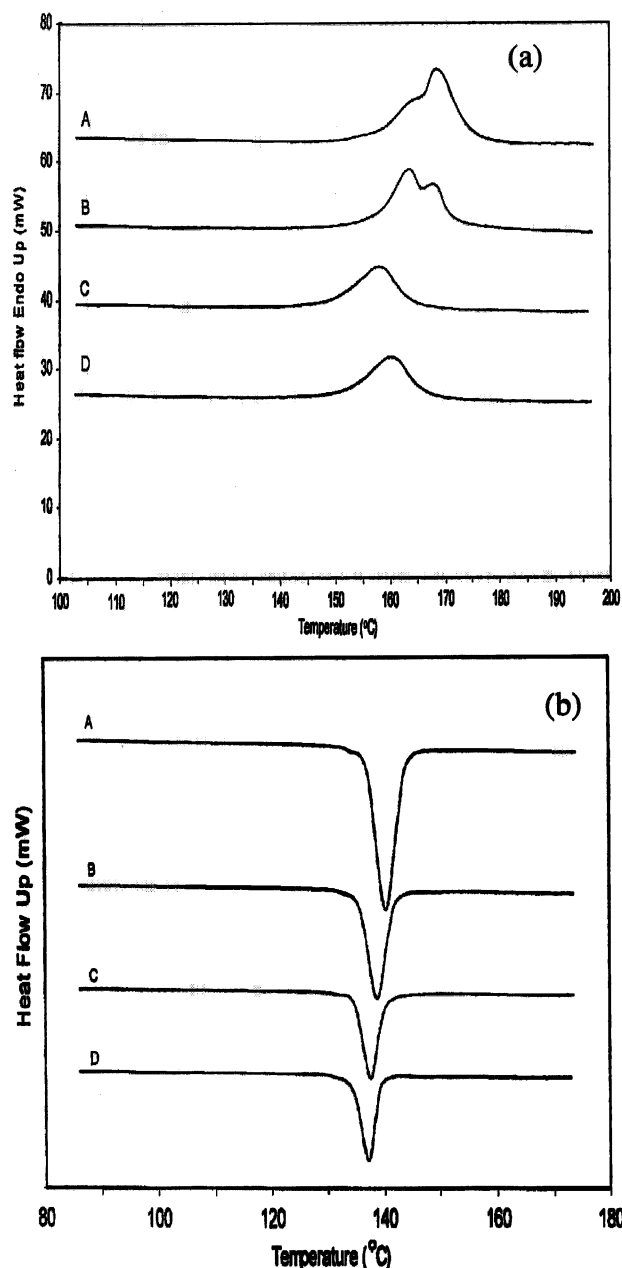


Figure 6. Typical DSC melting (a) and cooling (b) thermograms of various samples: A) original PVDF film, B) PVDF-g-PS film (Y = 50%), C) Li⁺-conducting membrane (Y = 50%), and D) H⁺-conducting membrane (Y = 50%).

Table 1. Summary of the data obtained from DSC thermal analysis.

Samples	$T_m^a)$	T_c	X_c
	°C	°C	
Original PVDF film	167.9*	139.8	39.2
PVDF-g-PS film	167.7*	138.9	26.6
H ⁺ -conducting membrane	160.4	137.8	20.8
Li ⁺ -conducting membrane	157.4	137.0	21.5

a) '*' refers to the main melting peak.

also been analyzed for reference. The original PVDF film reveals a bimodal melting endotherm with two melting temperatures at 162.6 and 167.9 °C, respectively, as a result of the presence of two lamellae of different thicknesses. The grafting of polystyrene is found to alter the shape of the melting peak so that the area under the lower melting peak increases while that under the high melting peak decreases, which indicates that the lamellar growth is inhibited by the formation of polystyrene grafts. The total area under the two peaks is reduced despite the absence of any significant change in the two melting temperatures of PVDF, and the degree of crystallinity (X_c) decreases from 39.2 to 26.6 upon grafting 50% polystyrene. These observations suggest that styrene does not cause swelling in the crystallites during grafting and the formed polystyrene grafts do not penetrate the crystallites of the lamellae despite the formation of radicals on their surfaces. It can be concluded that the grafting of polystyrene takes place over the entire amorphous region of the PVDF film and possibly at the surface of the crystallites present at the surface of the lamellae. Moreover, the decrease in X_c is caused by the dilution of the crystalline structure of the PVDF film with amorphous polystyrene.

Activation of PVDF-g-PS films with the liquid electrolyte after solvent treatment (plasticization) is found to drastically affect the melting behavior of the original PVDF film. For instance, the bimodal peak present in the original and the grafted PVDF films vanishes to leave a single peak with smaller area and lower melting temperature (157.4 °C). The X_c is lowered by introducing the liquid electrolyte and reaches a value of 21.5%. These observations suggest that liquid electrolyte impregnation induces a crystal disorder in a way that leads to a partial distortion in the crystalline structure of the PVDF-g-PS film. This is possibly a result of the strong interaction of the polymer chains with the diluting solvent and lithium salts, which results in a gel polymer electrolyte of reduced crystallinity. Similar results have been reported for a PVDF-based gel polymer electrolyte prepared by solvent casting a mixture of PVDF with LiBF_4 in EC/PC^[35] and another polymer electrolyte prepared by the complexation of PVDF mixed with LiPH_6 in EC/PC.^[36]

The sulfonation of PVDF-g-PS films to introduce sulfonic acid groups has also been found to cause substantial structural changes, which have been found to be in the form of a shift in the melting temperature to a lower value (160.4 °C) and a reduction in X_c to a value of 20.8%. This trend reflects the existence of not only an additional dilution effect but also a partial disruption in the crystallites of the PVDF matrix. The additional dilution is believed to be a result of the increase in the amorphous fraction by the incorporation of sulfonic acid groups. The partial disruption may be attributed to the penetration of the crystallites by some grafts under the influence of the aggressiveness of the sulfonation reaction and the hydrophilic/hydrophobic stress at the grafts/lamellae interface in the swollen membranes.

The latter is a result of the strongly hydrophilic nature of sulfonic acid groups, which is prompted at the surface of the lamellae to cause scission in some of polystyrene grafts. It can be concluded that the combined effects of the dilution of the crystalline structure with the amorphous polystyrene, and the partial crystal disruption caused by the possible penetration of some grafts during sulfonation, and the rupture of crystallites during the hydration, are accounted for by the changes in the X_c of the H^+ -conducting membrane. These results agree with the finding of Hietala et al.^[34] who have reported similar DSC investigations on polystyrene-sulfonic-based PVDF membranes prepared by a pre-irradiation method.

Figure 6b shows typical DSC cooling thermograms for the Li^+ - and H^+ -conducting counterparts having a Y of 50% in comparison with the original PVDF and 50% grafted PVDF films. The crystallization temperature (T_c) of the PVDF film is slightly lowered by polystyrene grafting and subsequent activation with liquid electrolyte as well as the sulfonation reaction as indicated in thermograms A, B, C, and D, respectively. The order of the decrease follows in sequence of PVDF > grafted PVDF > H^+ -conducting membrane > Li^+ -conducting membrane. Similarly, the area under the crystallization peak is found to be reduced. These observations suggest the presence of some interference of the amorphous polystyrene with the chains of the PVDF film, which might be caused by penetration of some of the grafted chains into the surface of the crystals. However, phase separation is most likely to occur in the grafted film because of the difference in chemical nature. Activation of the grafted film with the liquid electrolyte causes the highest disruption in the crystalline structure followed by the sulfonation reaction, as indicated by the continuous decrease in T_c . These results are in a complete agreement with DSC melting endothermic behavior.

Thermal Stability of the Membranes

Figure 7 shows the TGA thermogram of H^+ - and Li^+ -conducting membranes. Samples of original PVDF and PVDF-g-PS ($Y = 50\%$) films are used as control samples. All the degradation temperatures are measured at onset. For the original PVDF film (Figure 7A), the weight loss is confined to a single-step degradation pattern, which occurs around 440 °C and corresponds to the decomposition of the PVDF main chains by random scission. For the PVDF-g-PS film (Figure 7B), a two-step degradation pattern is observed. The primary weight loss is caused by polystyrene degradation followed by the decomposition of the PVDF matrix at 390 and 440 °C, respectively. The presence of these two characteristic weight losses provides obvious evidence for the formation of two phase-separated microdomains despite the interference of some of the amorphous polystyrene grafted with the PVDF crystalline structure as revealed from DSC cooling exotherms. This is because of

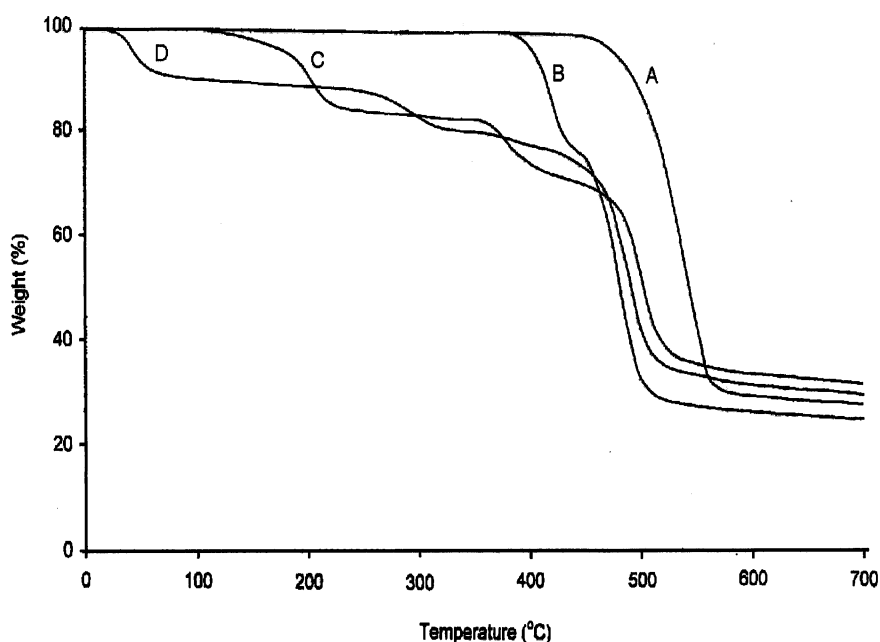


Figure 7. Typical TGA thermograms of: A) original PVDF film, B) PVDF-*g*-PS film ($Y = 50\%$), C) Li^+ -conducting membrane ($Y = 50\%$), and D) H^+ -conducting membrane ($Y = 50\%$).

the incompatibility of the grafted film components, i.e., polystyrene is of a hydrocarbon nature and PVDF is of a fluorocarbon nature. Similar results for the thermal decomposition of polystyrene-grafted PVDF films have been reported in the literature.^[37]

In Li^+ -conducting membranes (Figure 7C), a three-step degradation pattern is observed. The first step begins at 120°C and continues up to 150°C and is attributed to the loss of the solvents that dilute the liquid electrolyte. The second step at 370°C is a result of the decomposition of the grafted polystyrene. The third loss is related to the decomposition of the PVDF matrix, which starts at 425°C . It is noticed that the decomposition of both polystyrene and the PVDF matrix is lowered by approximately 20 and 15°C , respectively. These results suggest that activation of the PVDF-*g*-PS film with the liquid lithium electrolyte makes its components more vulnerable to thermal decomposition. However, the Li^+ electrolyte membrane remains stable up to 120°C . Since lithium battery applications are often operated over a temperature range of $30\text{--}70^\circ\text{C}$, it is suggested that these membranes are suitable for such an application. Similar thermal stability behavior has been reported for porous PVDF-HFP with a polyethylene glycol (PEG) hybrid polymer electrolyte that contains $\text{LiBF}_4/\text{EC/PC}$ prepared by extracting PEG during the casting process.^[38]

The H^+ -conducting membrane (Figure 8D) demonstrates multistep degradation transitions. The initial weight loss up to 200°C is attributed to the loss of water strongly bound to the sulfonic acid groups by hydrogen bonding. The

weight loss in the second step ($\approx 270^\circ\text{C}$) is a result of the elimination of sulfonic acid groups. This is followed by another two un-distinct transitions attributable to the decomposition of polystyrene and PVDF components at 390 and 440°C , respectively. From these results, it may be stated that the membranes are thermally stable up to $\approx 270^\circ\text{C}$ under nitrogen atmosphere. Similar conclusions were made by Hietala et al.^[37] for the degradation of similar membranes prepared by pre-irradiation using an electron

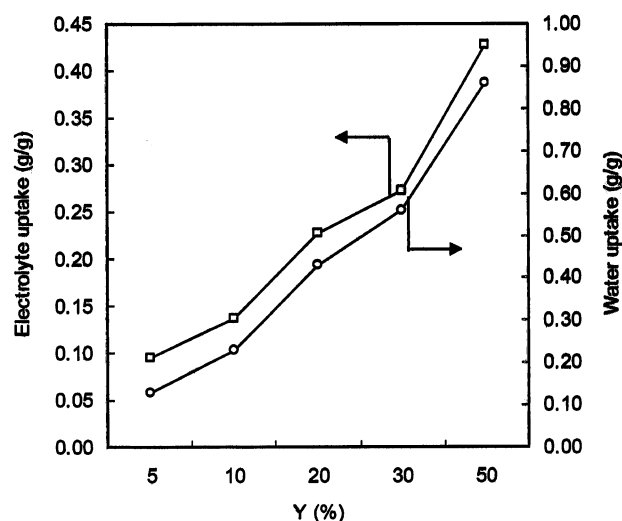


Figure 8. Variation of water uptake (○) and electrolyte uptake (□) in H^+ -conducting membranes and in their corresponding Li^+ -conducting membranes with $Y\%$.

beam. Other polystyrene sulfonic acid membranes based on PTFE, poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP), and poly[tetrafluoroethylene-co-(perfluorovinyl ether)] (PFA) behave in a similar manner.^[39–41]

It is worth mentioning that not all samples undergo complete degradation as indicated by the weight left (residues) at the end of their thermograms. However, the residues left behind for the H⁺-conducting (22%) and Li⁺-conducting membranes (25%) are higher compared to the original and the grafted PVDF films (20%), which suggests the formation of inorganic residues in a form of PF₆ anions and sulfur-rich ashes in the Li⁺-conducting and H⁺-conducting membranes, respectively. Similar observations have been made for a polymer electrolyte formed by dispersing nanoparticles of TiO₂ into PVDF complexes with LiPF₆.^[42]

Swelling Behavior

Figure 8 shows the water uptake and the liquid electrolyte uptake in H⁺-conducting membranes and their corresponding Li⁺-conducting membranes versus Y%. As can be seen, both water uptake and liquid electrolyte uptake increase with the increase in Y%. This behavior can be attributed to the increase in the hydrophilicity imparted to the membranes by the incorporation of more sulfonic acid groups, which absorb more water molecules. The increase in the liquid uptake with Y% in Li⁺-conducting membranes can be ascribed not only to the increase in the amorphous fraction of the film but also to the reduction in X_c when Y% increases, as revealed by DSC results presented in a previous study.^[29]

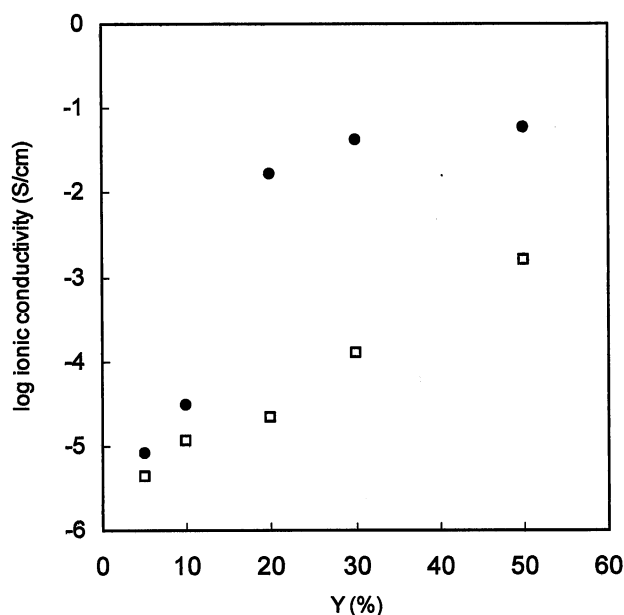


Figure 9. The relationship between the ionic conductivity of: (●) H⁺-conducting membranes and (□) Li⁺-conducting counterparts and Y%.

Ionic Conductivity of the Polymer Electrolyte Membranes

The relationships between the log ionic conductivity of the H⁺-conducting membranes and that of the Li⁺-conducting counterparts and Y% at room temperature is shown in Figure 9. The ionic conductivity in both electrolyte membranes is found to increase with the increase in Y%. Both membranes have superior conductivity values of $1.61 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$ for Li⁺ and $5.95 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$ for H⁺ at a Y of 50%. The former value is substantially higher than that of the PVDF-HFP- and PVDF-HFP/PS-based polymer electrolytes, which equal 0.2×10^{-3} and $0.162 \times 10^{-3} \text{ S} \cdot \text{cm}^{-1}$, respectively.^[43,44] Whereas, the latter conductivity value is higher than that of a Nafion membrane ($5.30 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$) obtained under similar testing conditions.^[45] A similar polystyrene sulfonic acid PVDF membrane (Y = 54%) prepared by pre-irradiation using an electron beam is reported to have a proton conductivity of $6.58 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}$.^[30]

However, the conductivity increase follows two different trends in both electrolyte membranes. For instance, the Li⁺-conducting membranes show a progressive non-linear increase with the increase in Y, whereas the H⁺-conducting membranes show a rapid increase at Y values below 20%, beyond which it tends to attain a more constant order of magnitude of $10^{-2} \text{ S} \cdot \text{cm}^{-1}$ despite the increasing values of Y%.

The behavior of Li⁺-conducting membranes can be generally attributed to the increase in the amorphous content, which entraps more liquid electrolyte with the increase in Y% as revealed by the dependence of the ionic conductivity on the electrolyte uptake shown in Figure 10. However, one should obtain a linear relationship if only the amorphous phase swells. Thus, one would expect the structural and the morphological changes induced during the preparation steps to influence the conductivity as reported earlier.^[29] The structure change is mainly in a form of a reduction in the crystallinity, which has been reported to be a function of Y%. On the other hand, the morphological change represents the distribution of electrolyte-swollen polystyrene domains across the electrolyte membrane and seems to be improving gradually as Y% increases. This allows the segregated polystyrene domains to be homogeneously distributed across the whole membrane and possibly form a network structure that enhances the Li⁺ mobility to a great extent. However, there is another factor that might be affecting the Li⁺-conductivity behavior: that is the possible formation of tiny electrolyte-filled pockets that result from the plasticization of PVDF-g-PS films with an aprotic solvent prior to the loading of the liquid electrolyte. This remark is supported by the increase in the porosity and the thickness determined for Li⁺-conducting membranes with the increase of Y% as shown in Figure 11. Therefore, it is suggested that the ionic conductivity is

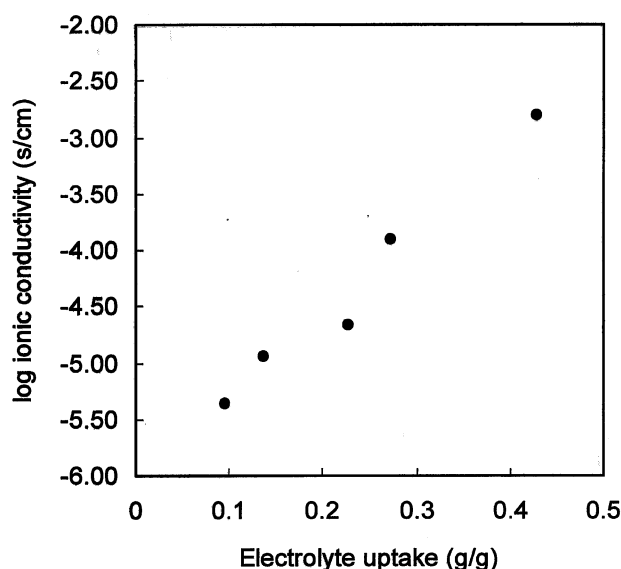


Figure 10. The dependence of the conductivity of Li^+ -conducting membranes on the liquid electrolyte uptake.

controlled by four combined factors: the swelling of the amorphous phase in the membrane matrix, the reduction in crystallinity, the filling of formed pockets, and the level of distribution of polystyrene grafts across the membranes. The effect of these parameters is collective but their relative contribution depends on the content of grafted polystyrene.

In the H^+ -conducting membranes, the increase in the conductivity with $Y\%$ is coupled with similar increasing trends in water uptake and IEC for the same membranes as shown in Figure 12 (a and b), respectively. This indicates that the introduction of more sulfonic acid groups leads to the incorporation of additional water, which enhances the proton conductivity. Therefore, it can be stated that the ionic conductivity of the membranes is a function of the content

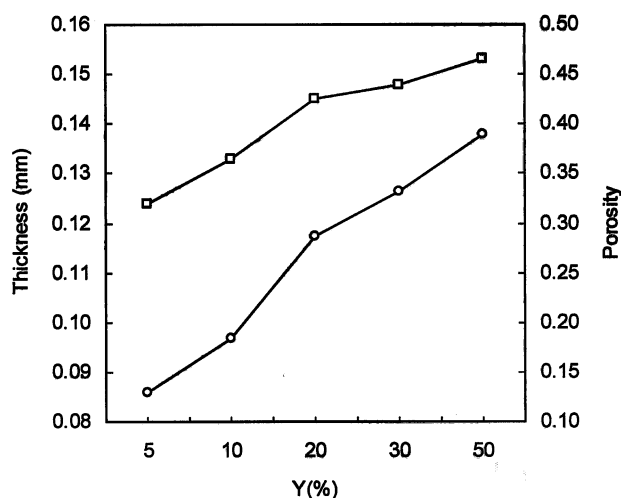


Figure 11. Variation of the porosity and the thickness of Li^+ -conducting membranes with $Y\%$.

of sulfonic acid groups when it is fully hydrated. Because the number of water molecules per sulfonic acid groups is expected to be the same in all membranes, a linear relationship should be obtained. Thus, the H^+ -conductivity of these membranes is most likely affected by other factors that arise during the membrane preparation procedure, such as a reduction in the crystallinity and the distribution of polystyrene grafts across the membranes. The latter plays a vital role in conducting protons. For instance, at low $Y\%$ in the membrane, polystyrene sulfonic acid grafts with their water domains are only located near the surface of the membrane

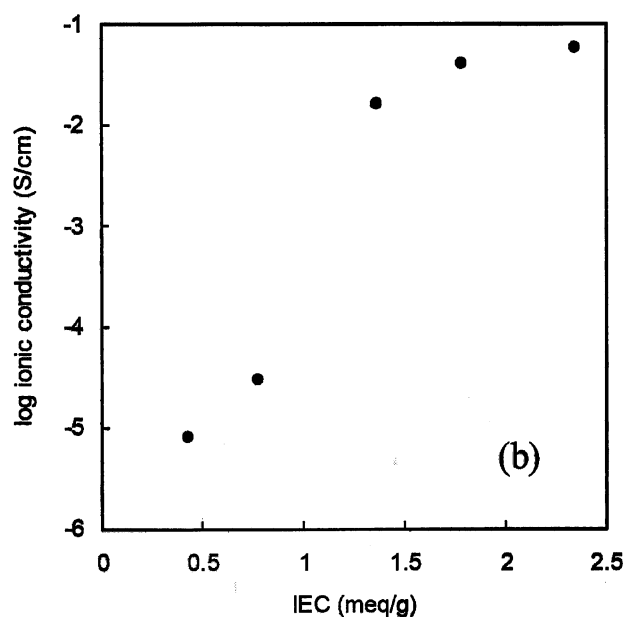
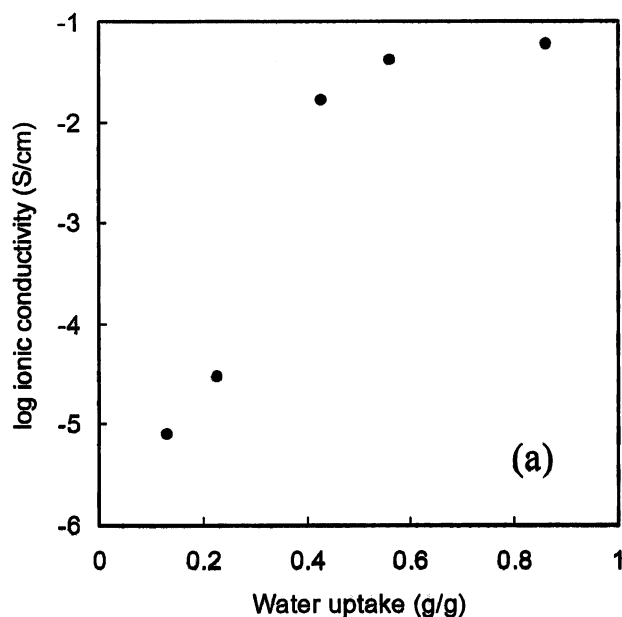


Figure 12. The dependence of the ionic conductivity of Li^+ -membranes on: a) the water uptake and b) IEC.

while its bulk remains ungrafted and exerts a high water resistance. Therefore, the mobility of H^+ is hindered and the conductivity is compromised. As $Y\%$ increases and approaches a sufficient level that achieves homogeneity, the ungrafted hydrophobic fraction diminishes to allow the water-swollen sulfonated polystyrene domains to form a network structure. This enhances the mobility of H^+ and allows the conductivity to reach high values so that any further increase in $Y\%$ no longer brings significant changes to it. Therefore, it can be concluded that the H^+ conductivity in these membranes is controlled by four parameters: concentration of sulfonic acid groups, water content, reduction in the crystallinity, and homogenous distribution of the polystyrene sulfonic acid grafts across the membranes. The effect of these parameters is collective but their relative contribution depends on polystyrene content. Similar behavior has been reported for various types of radiation-grafted polystyrene sulfonic membranes based on PTFE, FEP, and PFA films^[45–47] in addition to those prepared based on PVDF films using a pre-irradiation method.^[30]

Conclusion

Two polymer electrolyte membranes that conduct H^+ and Li^+ have been successfully prepared using a single method started by the radiation-induced grafting of styrene onto a PVDF film followed by activation with $LiPH_6/EC/DEC$ or chlorosulfonic acid, respectively.

DSC analysis reveals that the structure of the semi-crystalline PVDF films is affected by the procedure applied to prepare the polymer electrolyte membranes, i.e., grafting and activation. While styrene grafting is found to dilute the crystalline structure with amorphous polystyrene, activation of the grafted films with $LiPH_6/EC/DEC$ or chlorosulfonic acid causes a reduction in the crystallinity mainly because of the dilution of the crystallites and the partial crystalline disruption, which depends on the content of polystyrene. However both polymer electrolyte membranes retain a sufficient level of crystallinity.

TGA analysis reveals that Li^+ -conducting membranes have a thermal stability up to 120 °C, beyond which the solvents that dilute the electrolyte evaporate. Whereas H^+ -conducting membranes have a thermal stability up to ≈ 270 °C, after which the degradation starts by desulfonation reactions.

The conductivity of lithium-electrolyte-activated membranes is determined by four combined factors: the swelling of the amorphous phase of the membrane matrix, the reduction in the crystallinity, the filling of the tiny pockets formed in the matrix upon plasticization with solvent and, importantly, the level of distribution of polystyrene grafts across the membranes. Whereas, the conductivity of sulfonic acid membranes is dictated by the number of ionic sites, the water content, the reduction in the crystallinity, and the distribution of polystyrene domains.

The obtained polymer electrolyte membranes have achieved superior conductivity values of $1.61 \times 10^{-3} S \cdot cm^{-1}$ for Li^+ and $5.95 \times 10^{-2} S \cdot cm^{-1}$ for H^+ with a polystyrene content of 50%.

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