The influence of crosslinker on the properties of radiation-grafted films and membranes based on ETFE

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Abstract

Crosslinked proton-exchange membranes were prepared by radiation-induced grafting of styrene into poly(ethylene-alt-tetrafluoroethylene) (ETFE) and subsequent sulfonation. The influence of the crosslinker, divinylbenzene (DVB), on various film and membrane properties was investigated in detail. A series of grafted films and membranes were prepared at varying DVB concentrations at a fixed graft level (∼25%) for this purpose. Grafting kinetics and kinetic parameters, including initial polymerization rate (rpo), radical recombination rate (γ) and delay time (t0) at different DVB concentrations were evaluated. Moreover, resultant grafted films and membranes have been characterized with respect to their dimensional stability, chemical composition, thermal stability, crystallinity and fuel cell relevant properties. The concentration of crosslinker in the initial grafting solution was found to influence crucially the grafting reaction and graft levels. Dimensional increase, considerably especially after sulfonation, can be controlled by the introduction of DVB. Furthermore, the FTIR-ATR measurements exhibited that the grafted films were highly crosslinked within the surface near as compared to the entire bulk region. The influence of DVB on the crystallinity and thermal stability was not significant. On the contrary, the water uptake and proton conductivity of the membranes decreased substantially, while the IEC decreased slightly with increasing DVB concentration.

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1. Introduction

The proton-exchange membrane is a key component in low temperature fuel cells. Such a membrane should fulfill certain requirements, including being impermeable to gases, non-electronically conducting and mechanically and chemically stable, to be used in polymer electrolyte fuel cells [1]. One of the main challenges to the commercialization of fuel cell technology is the reduction of the material costs (the metal catalyst, proton-exchange membrane, separators, etc.). The radiation-induced grafting method [2–4] offers an alternative option to achieve the ultimate goal and to substitute the state-of-the-art in membranes, such as Nafion® (trademark of DuPont), Aciplex® (trademark of Asahi Kasei Corp.) and Flemion® (trademark of Asahi Glass Co. Ltd.) [5]. Further advantages of the technique are the versatility and the possibility to use a variety of base films and monomers to yield the desired materials with low costs.

The need for alternative cost-effective materials induces the development of novel membranes based on different commercially available base polymers, either perfluorinated such as poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) [6,7], poly(tetrafluoroethylene-co-perfluorovinyl ether) (PFA) [8], polytetrafluoroethylene (PTFE) [9] or partially fluorinated such as poly(ethylene-alt-tetrafluoroethylene (ETFE) [10,11] and poly(vinylidene fluoride) (PVDF)) [12]. Our laboratory has been developing radiation-grafted membranes for low temperature fuel cells since 1992. Membranes prepared by styrene grafting into FEP using divinylbenzene (DVB), have been demonstrated to exhibit comparable fuel cell performance with Nafion®112 and durability of several thousands hours has been reported [4,13].

Recently, our laboratory has been revisited the development of ETFE-based membranes since ETFE has a higher radiation stability and exhibits superior mechanical properties as compared to FEP. Previously, we reported on radiation-initiated
grafting of styrene into ETFE in the presence of DVB as the crosslinker, and the characterization of fuel cell relevant properties and cell performance of the resultant membranes [10]. These results revealed the potential of ETFE as a base material for the preparation of fuel cell membranes due to encouraging fuel cell performance and durability of the ETFE-based membranes. Moreover, Chen et al. reported on quite good resistance to irradiation and reasonable mechanical properties (relatively higher elongation at break and tensile strength compared to other base polymers such as PFA, FEP, etc.) for pristine ETFE base film for fuel cell applications [14].

Crosslinkers are monomers, with two or more vinyl groups, can be used to modify various membrane properties. In the earlier investigations of our group, it was reported that crosslinking using DVB resulted in substantial changes, not only in the \textit{ex situ} properties of FEP based membranes (styrene as the monomer), such as water uptake, proton conductivity, surface energy, thermal stability but also gas crossover, polarization performance and lifetime in fuel cells [7,15–18]. On the other hand, the concentration of DVB in the initial grafting solution was found to be important since higher concentrations of DVB led to adverse effects on numerous membrane properties [7,19]. Previously, the influence of the concentration of DVB on the \textit{ex situ} properties and the single fuel cell performance of FEP based membranes were evaluated and an optimum crosslinker concentration was defined for this system [20].

A detailed study of the influence of the crosslinking on grafting kinetics or \textit{ex situ} membrane properties for ETFE/styrene combination has not been performed. Recently, Chen et al. investigated the influence of different crosslinkers on radiation grafting of \textit{p}-methyl styrene into ETFE [21]. However, not only the monomer used but also grafting and membrane preparation steps are very different from our current process.

Very recently, we investigated in detail the influence of the grafting parameters on the extent and rate of grafting for the styrene grafting into ETFE-based films without a crosslinker [22]. This approach is very valuable to figure out the grafting process in terms of the influence of significant reaction parameters without a crosslinker. Since the crosslinker brings about a complexity in the grafting process. For instance, the restricted diffusion of monomers due to the formation of crosslinked network structure is expected in the presence of crosslinker.

As mentioned previously, we performed a detailed study on \textit{ex situ} properties (IEC, water uptake, conductivity) and fuel cell performance of ETFE-based membranes at fixed crosslinker concentration (10% DVB, which was found as the optimum concentration for styrene/FEP system). However, we are currently using a different membrane preparation procedure in terms of composition of grafting solution, reaction temperature, etc. Moreover, we know that the concentration of the crosslinker used during membrane preparation has to be carefully considered to prepare fuel cell membranes with desired properties. Therefore, it is of interest to investigate the influence of DVB concentration for styrene/ETFE combination. Furthermore, we currently perform the characterization of ETFE-based membranes (with varying crosslinker content) in fuel cells and we found that the performance and the lifetime of these membranes are very promising [23,24].

In this study, we investigate the influence the crosslinker content on various film and membrane properties including grafting kinetics, the dimensional increase, chemical composition, crystallinity, thermal stability and fuel cell relevant properties. Selected grafted films and membranes, obtained under the same synthesis conditions (irradiation dose, temperature, solvent composition, total monomer concentration) and graft level but with varying DVB concentration in the initial grafting solution were characterized for this purpose. The aim is not only to correlate the \textit{ex situ} properties as function of the crosslinker concentration but also to pre-evaluate the optimum concentration of crosslinker, which is expected to yield the desired performance and stability in the fuel cell.

2. Experimental

2.1. Materials

ETFE (Tefzel® 100LZ) films with 25 µm thickness, purchased from DuPont (Cirleville, USA), were used as the base polymer. The reagents used during membrane preparation were styrene (purum grade; Fluka) and divinylbenzene tech. (∼80%, mixture with isomers 3- and 4-ethylvinylbenzene; Fluka), isopropanol (analytical grade; Fisher Scientific), dichloromethane (Fluka), chlorosulfonic acid (Fluka).

2.2. Preparation of grafted films and membranes

ETFE films were electron beam irradiated with a dose of 1.5 kGy at Studer AG, Däniken, Switzerland, at conditions described elsewhere [22]. Subsequently, the films were stored at −80 °C until the grafting reaction was performed.

Grafting reactions were carried out in a stainless steel reactor except for the kinetic studies (results are shown in Fig. 1(a)), which were performed in cylindrical glass reactors under a nitrogen atmosphere. The grafting solution consisted of 20% (v/v) monomer (mixture of styrene and divinylbenzene (DVB)), 65% (v/v) isopropanol and 15% (v/v) water as described previously [22]. The DVB concentration, given as the volume ratio of DVB with respect to the total of monomer (DVB + styrene) in the initial grafting solution, was varied from 0%, 5%, 8%, 10%, 15%, 20%. The grafting reaction was initiated by placing the reactor in a thermostatic bath at 60 °C and performed for varying reaction times. The grafted films were extracted with toluene, then dried at 80 °C, and reweighed in order to determine the graft level, which is the weight increase of the film after grafting process.

Radiation-grafted membranes were prepared by sulfonation of the grafted films with chlorosulfonic acid in dichloromethane (2% (v/v)) at room temperature for 5 h, followed by hydrolysis in 0.1 M NaOH solution and re-protonation in 2 M H2SO4 solution. Finally, the resultant membranes were swollen in deionized water at 80 °C for 5 h.
2.3. Grafting kinetics and dimensional changes

Grafting reactions were performed for different DVB concentrations (0%, 5%, 8%, 10%, 15%, 20%) in the initial grafting solution for various reaction times (1–24 h) to investigate the reaction kinetics. The influence of the DVB content on important kinetic parameters, such as the apparent initial polymerization rate ($r_{po}$), the characteristics radical recombination rate ($\gamma$) and the delay time ($t_0$) (resulted by the slow progression of the grafting front to the center of the polymer film), was then studied. A mathematical model, which neglects the local differences in monomer concentration or reactivity and also volume changes during grafting, was employed for this purpose [19,22,25].

The dimensional increase in machining direction (where the extrusion of pristine polymer films was employed), transverse direction (perpendicular to extrusion) and thickness of the grafted films and membranes was calculated from

$$\text{Dimensional increase} = \frac{D_1 - D_0}{D_0} \times 100\%$$

where $D_0$ is the initial dimension of the pristine ETFE film and $D_1$ is the final dimension of the film after grafting or sulfonation processes. The thickness of the grafted films and the membranes (in wet state) were measured using a digital thickness gauge (MT12B Heidenhain, Germany).

2.4. Fourier transform infrared spectroscopy (FTIR)

The FTIR measurements of ETFE-based grafted films were performed with a PerkinElmer FTIR System 2000 spectrometer. The curve-fitting was carried out using GRAMS/386 software (version 3.02) from Galactic Industries. In addition, attenuated total reflectance (ATR) measurements were performed using a 45° ZnSe crystal (Graseby Specac) to probe the surface of the grafted films.

In order to define the molar ratio of DVB versus styrene in the grafted films, the empirical equations found in an earlier study in our group were used [26].

2.5. Thermal properties

Thermal stability and degradation behaviour of both ETFE-based grafted films and their respective membranes were studied by TGA. These measurements were carried out on a PerkinElmer TGA7 instrument at a constant heating rate of 20 °C/min over a range of 50–650 °C under nitrogen atmosphere. ETFE-based membranes were pre-heated up to 100 °C in the TGA and then hold at this temperature for 10 min to reduce the influence of excess water, and finally heated at a constant heating rate of 20 °C/min over the range between 100 and 650 °C under nitrogen atmosphere. The initial decomposition temperature (IDT), the maximum rate decomposition temperature (MRDT), the specific weight loss, and the residue of decomposition were extracted from the thermograms [27].

DSC measurements were performed by a PerkinElmer DSC7 for a temperature range of 30–300 °C under nitrogen atmosphere at constant heating rate of 20 °C/min, and the crystallinity and melting temperature were determined from the heating curves [27,28]. Prior to DSC experiments, the membranes were converted to the potassium salts and then dried to reduce the water interference.

2.6. Ion exchange capacity, proton conductivity, water uptake and hydration number

The bulk membrane properties of the ion-exchange capacity, proton conductivity, water uptake and hydration number at room temperature of ETFE-based membranes with varying DVB content were examined, using our standard procedures, which can be found elsewhere [10].

3. Results and discussion

3.1. Grafting kinetics and dimensional changes

Styrene grafting into ETFE films was carried out at different DVB concentrations in the initial grafting solution. We determined that the concentration of the crosslinker in the initial grafting solution affects significantly the grafting behaviour and reaction kinetics. The variation of graft level as a function...
of reaction time at several DVB concentrations (in the initial grafting solution) for styrene grafting into ETFE base film is presented in Fig. 1(a). The highest graft level is achieved for 0% DVB at very early phases of reaction (<8 h) and the graft level decreases as the DVB concentration increases. This behaviour can be attributed to the formation of a crosslinked structure, which serves a barrier for monomer diffusion.

On the other hand, for the longer reaction times (8, 16, 24 h), the introduction of DVB at a low concentration (5% DVB) yields the highest graft level. Beyond 5% DVB, the graft level is found to be reduced with DVB concentration. That is to say, at a low crosslinker concentration, in the presence of water in the grafting solution, a higher graft level than with 0% DVB in solution is observed. The increase of the graft level with the introduction of a small amount of DVB can be explained by the immobilization of growing chains and their reduced mobility, which results in the decreased chain recombination. As a consequence, the polymer chains can reach higher length and the graft level increases. Moreover, the high reactivity of the double bonds of DVB induces higher graft levels. A similar behaviour was reported previously for styrene/FEP [19], and p-methylstyrene/ETFE combinations [21].

The kinetic parameters were determined by fitting the kinetic data in Fig. 1(a) using the equations given in experimental section. Fig. 1(b) shows that, both the initial polymerization rate ($r_{p0}$) and radical recombination rate ($\gamma$) decrease with increasing the DVB concentration. Owing to the reduction of the polymer phase swelling in the grafting front and the creation of a three-dimensional network, which reduce the diffusion of the monomer, a slow down of the polymerization reaction and an increase in the radical lifetime are observed as DVB concentration increases.

Moreover, the delay time of the polymerization front is increasing up to 5% DVB which can be again caused by the restricted diffusion of monomer as DVB concentration increases. However, delay time decreases up to 10% DVB and then levels off which is somewhat unexpected. In fact, this mathematical model does not perfectly fit to our system since model has several assumptions as mentioned in Section 2.3. One of the assumptions is that there are no local differences in the monomer concentration; however, we believe that during kinetic investigations, since the films are rolled there are differences in different regions of the film in terms of monomer concentrations. As a result, the deviations and unexpected results are observed in some cases.

A series of grafted films and membranes with varying DVB concentrations at a fixed graft level (25%) were prepared, according to the data shown in the kinetic curves (Fig. 1(a)) for further ex situ characterization, which will be described in the next sections. The preparation conditions are displayed in Table 1. It is clear that longer reaction times are required to achieve a certain graft level at higher crosslinker concentration.

The increase in all three-dimensions of the grafted films and membranes as a function of DVB concentration is presented in Fig. 2. All the films and membrane samples were examined for their machining direction, transverse direction and thickness. Concerning the grafted films, an increase of 15.3–20.7% in thickness; however, an increase of 12.3–16.5% and of 9.8–13.6% in machining and transverse direction is determined, respectively (Fig. 2(a)). After sulfonation, the dimensional increase becomes more substantial. That is to say, an increase of the thickness of 28.1–35.2%, an increase of 17.7–29.4% in machining direction, and of 18.4–28.2% in transverse direction are observed (Fig. 2(b)). Apparently, the highly affected dimension is the thickness in comparison with the two other dimensions. In addition, only a slight difference between the machining and the transverse direction are observed after grafting reaction and sulfonation.

It is clear that the dimensional increase is found to be almost independent of crosslinker concentration for the case of grafted...
films. However, concerning the membranes, the dimensional increase becomes lower with an increase of the DVB concentration. This can be a result coming from the restricted free volume and the decreased swelling owing to the presence of a crosslinker.

3.2. FTIR-ATR measurements

It is of interest to determine the crosslinker content in the 
grafted films and the membranes to understand and to compare the differently crosslinked materials for their ex situ and relevant fuel cell properties. In fact, several studies were performed to evaluate the reactivity of the isomers in the styrene/DVB copolymers and their influences on the distribution of monomers and the mechanical properties [6,29,30]. The main obstacles for a direct quantification of the DVB content in the grafted films is due to the high absorbance of the ETFE base film and the quite low graft levels obtained with pure DVB. Furthermore, in this study technical grade DVB, a mixture of several isomers including p-divinylbenzene, m-divinylbenzene, p-ethylvinylbenzene and m-ethylvinylbenzene, is employed. Although, the para and meta species can be distinguished by distinct positions of some of their respective absorption peaks. Indeed, the styrene and the DVB isomers have different absorption bands at 1486 cm\(^{-1}\) (for m-disubstituted benzene), 1493 cm\(^{-1}\) (mono-substituted benzene) and 1510 cm\(^{-1}\) (p-disubstituted benzene). To overcome these difficulties, a quantification method, based on the use of homopolymers with well-known compositions as the standards, was developed [26].

The absorption spectra in transmission and ATR mode of ETFE-based grafted films were investigated, and the bands were fitted to determine the molar ratio of DVB/styrene and to resolve the overlapping of the peaks of the mono-substituted benzene and meta-disubstituted benzene. Then, the molar ratios of DVB/styrene were plotted against the DVB concentrations in the initial grafting solution (Fig. 3). The following relationships were obtained by means of regression analysis:

\[
\begin{align*}
(D\text{VB}/\text{styrene})_{\text{surface}} > (D\text{VB}/\text{styrene})_{\text{initial solution}} > (D\text{VB}/\text{styrene})_{\text{bulk}}
\end{align*}
\]

This observation confirms the dependency of the grafting reaction on both, the high reactivity of DVB and the diffusion of the monomer into the grafting. Indeed, the more DVB is reacting on the surface, the denser will be the created three-dimensional network. Consequently, the diffusion of monomer(s) is restricted and a longer reaction time is required to accomplish the desired graft level.

Brack et al. investigated grafted films, mainly based on styrene and FEP, by FTIR spectroscopy, using both the transmission mode and the surface sensitive ATR mode [26]. Results from both methods showed that a higher crosslinker content was found at the surface, expressed as the ratio of styrene to double substituted benzenes.

3.3. Thermal properties

The ETFE-based grafted films and membranes with varying crosslinker concentration were characterized for their thermal properties by TGA and DSC. The pristine ETFE film exhibits a single step degradation, as we reported earlier [27]. The presence of polystyrene grafts does not alter the decomposition temperature of the ETFE base polymer and the grafted film shows an additional degradation step starting at \(\sim 380^\circ\text{C}\). Several steps in the degradation pattern for the membranes, due to dehydration, desulfonation, de aromatization and finally backbone degradation, are detected [31].

Similar degradation profiles are observed for the ETFE-based grafted films with different DVB concentrations. The initial decomposition temperature (IDT), the maximum rate decomposition temperature (MRDT), the specific weight loss, and the % residue of decomposition were determined for both grafted films (Table 2) and membranes (Table 3). As far as the grafted films are concerned, the IDT and the MRDT of the uncrosslinked film (0% DVB) are slightly higher than those of the crosslinked ones, whereas the values are very similar for the different DVB concentrations (Table 2). This can be explained by the substantial difference in decomposition behaviour of the linear polystyrene
chains and three-dimensional networks created in the presence of a crosslinker. In fact, the number of the chain ends is higher for the crosslinked films and consequently, the probability to form polymers with lower molecular weight is higher, which are known to degrade more readily. The weight loss values of the grafted styrene and DVB components are more or less constant and are in agreement with the fixed graft level of these samples.

ETFE-based membranes with varying DVB exhibit very similar degradation pattern as well. Moreover, similar IDT and MRDT values are obtained for the uncrosslinked (0% DVB) and the crosslinked membranes. Besides, the IDT and the MRDT are not influenced by the increasing DVB concentration and there is no clear trend (Table 3). As a consequence, the concentration of DVB in the initial grafting solution does not have a significant contribution of the thermal stability of the membranes.

The amount of residue obtained for the membranes increases with DVB concentration (Table 3). It was also reported previously that the amount of residue obtained is higher for the crosslinked membranes as compared to their uncrosslinked counterparts [27].

The crystallization and melting behavior of ETFE-based grafted films and membranes, with various crosslinker concentrations, were determined by the integration of the melting endotherms from DSC, as described previously [27]. The variation of crystallinity and the melting temperature for both, the grafted polystyrene and DVB components are more or less constant and are in agreement with the fixed graft level of these samples.

Fig. 4. (a) Crystallinity of ETFE-based grafted films and membranes at various DVB concentrations in the initial grafting solution and (b) melting temperature ($T_m$) of ETFE-based grafted films and membranes at various DVB concentrations in the initial grafting solution.

The proton conductivity shows a clear dependency on DVB concentration. That is to say, it decreases considerably with the increasing DVB concentration for the membranes of similar of the membranes are comparably lower than those of grafted films, because of the dilution effect and crystal disruption as we explained in detail previously [27].

A single melting peak was observed for the differently crosslinked films and membranes. Melting temperature remains almost unaltered as DVB concentration increases. It is important to notice here that the melting point of the base material is not significantly influenced, neither by crosslinking nor sulfonation (Fig. 4(b)).

### 3.4. Ion-exchange capacity, water uptake and ionic conductivity

Fuel cell relevant properties, including ion-exchange capacity (IEC), ex situ conductivity, water uptake, hydration number of ETFE-based membranes as a function of crosslinker concentration were studied.

The degree of sulfonation, the ratio of sulfonic acid groups to grafted polystyrene, is found to be 98–100% for lower DVB concentrations, while 90–95% for higher DVB concentrations. We determined that the mono-substituted benzene (styrene) can be sulfonated readily; however, sulfonation becomes difficult in the presence of the double substituted benzene rings in the case of DVB and its isomers, especially at higher concentrations.

Both, the ion exchange capacity (IEC) per unit weight and the proton conductivity at various DVB concentrations are depicted in Fig. 5. The IEC, the measure of the total number of sulfonic acid groups, seems to be unaffected in the range of lower DVB concentrations (5%, 8%, 10% DVB) and decreases considerably with higher DVB content. This means that the introduced ionic sites are equally accessible through the hydrophilic domains in crosslinked membranes, regardless of the more constrained polymer structure, at least up to 10% DVB. Beyond that concentration, the number of exchange sites decreases, as deduced from the lower degree of sulfonation.

Table 2

<table>
<thead>
<tr>
<th>Graft level (%)</th>
<th>DVB (vol%)</th>
<th>IDT (°C)</th>
<th>MRDT (°C)</th>
<th>Weight loss (%)</th>
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<tbody>
<tr>
<td>26</td>
<td>0</td>
<td>289</td>
<td>338</td>
<td>2.3</td>
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<tr>
<td>26</td>
<td>5</td>
<td>287</td>
<td>337</td>
<td>6.9</td>
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<tr>
<td>26</td>
<td>8</td>
<td>293</td>
<td>341</td>
<td>2.8</td>
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<tr>
<td>25</td>
<td>10</td>
<td>281</td>
<td>333</td>
<td>12.5</td>
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<tr>
<td>27</td>
<td>15</td>
<td>280</td>
<td>345</td>
<td>11.2</td>
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<tr>
<td>25</td>
<td>20</td>
<td>289</td>
<td>346</td>
<td>13.8</td>
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Table 3

<table>
<thead>
<tr>
<th>Graft level (%)</th>
<th>DVB (vol%)</th>
<th>IDT (°C)</th>
<th>MRDT (°C)</th>
<th>Residue (%)</th>
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<tr>
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The specific conductivity shows values of around 100 mS/cm for the uncrosslinked membrane and significantly lower values, such as 18 mS/cm for the membrane prepared with 20% DVB. This can be attributed to the reduced mobility of protons in the membrane with increasing DVB concentrations, due to decreasing water uptake.

The water uptake and the hydration number of the membranes are plotted versus the DVB concentration in the initial grafting solution (Fig. 6). The water uptake is substantially reduced upon crosslinking, due to a compact crosslinked network structure. Consequently, the average number of water molecules per ion exchange site, known as hydration number, decreases substantially with the increase in DVB concentration. This number decreases almost fourfold for an increase in DVB concentration from 0% to 20%. The highest hydration number is found as 11 for 0% DVB, which is considerably lower than 18, which is the value reported for the Nafion®112 membrane [10]. Furthermore, the water uptake of FEP based membranes is also influenced by the DVB concentration.

These observations can be related and supported by FTIR, the dimensional increase, and the crystallinity results. FTIR reveals the increased effective crosslinker content as the DVB concentration increases in the initial grafting solution. The rise of the incorporation of crosslinker induces a reduction of the number of ion-exchange sites, rendering the material less hydrophilic. Furthermore, the creation of a three-dimensional network reduces the free volume available and then hinders the flexibility of the chains. As a consequence, water uptake and conductivity decreases. Besides, lower values of the dimensional increase with increasing DVB concentration relate to a decreased water uptake. Moreover, the decrease in crystallinity is not pronounced, as the DVB concentration increases. In fact, the greater stress due to the crosslinker is expected to cause a substantial decrease of crystallinity, while the reduced water uptake balances that stress.

4. Conclusions

Radiation-grafted films and membranes based on styrene and ETFE were prepared in the presence of varying concentrations of DVB as crosslinker. The results indicate that the concentration of DVB (with respect to total monomer volume) in the initial grafting solution have significant influences, not only on the grafting reaction itself, but also the characteristics of the resultant films and membranes. First of all, the addition of DVB at low concentration enhances the grafting, while higher concentrations of DVB induce lower graft levels. In addition, the initial polymerization rate and the radical lifetime exhibit a decrease with increasing crosslinker content. These kinetics variations were apparently accompanied by several morphological and structural changes, caused by the location and inhomogeneous distribution of crosslinker in the surface and the bulk of the ETFE-based grafted film. Obviously, the increase of crosslinker affects strongly the conductivity and water uptake, which were reduced substantially as the crosslinker concentration is increased. However, neither the thermal stability nor the crystallinity of the films and membranes were significantly influenced by the DVB concentration.

References


