Macromolecules **2004,** *37,* 9909−9915

Versatile Synthetic Route to Tailor-Made Proton Exchange Membranes for Fuel Cell Applications by Combination of Radiation Chemistry of Polymers with Nitroxide-Mediated Living Free Radical Graft Polymerization

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Received September 12, 2003; Revised Manuscript Received September 27, 2004

ABSTRACT: A versatile method for the preparation of proton exchange membranes (PEMs) by the combination of radiation chemistry of polymers with nitroxide-mediated living free radical graft polymerization with subsequent sulfonation is presented. Thus, poly(vinylidene fluoride) (PVDF) membranes were first irradiated with electron beam and then the free radicals formed were immediately quenched with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TEMPO). In the second step, the produced TEMPO-capped macroinitiator sites were utilized in nitroxide-mediated living free radical graft polymerization of styrene or for the controlled graft copolymerization of styrene and *N*-phenylmaleimide onto the PVDF membrane. In the final step, the membranes were either directly sulfonated, or in the former case, alternatively the alkoxyamine moieties at the polymer chain ends were substituted by a maleimide derivative prior to sulfonation. The introduction of the *N*-phenyl maleimide moieties into the grafted chains significantly increased the thermo-oxidative stability of the PEMs as determined by thermogravimetric analysis (TGA). In this work, also a comparison between these membranes prepared by the controlled nitroxide-mediated graft polymerization and those membranes prepared by the conventional preirradiation grafting method in terms of grafting yields, thermo-oxidative stability, water uptake, and ion exchange capacity, proton conductivity, etc. is presented. Noteworthy is the fact that the membranes using the controlled grafting technique are grafted through the membrane already at a degree of grafting of 14%, whereas the penetration limit for the membranes prepared by conventional radiation-induced grafting is approximately 30% as determined by SEM-EDX analysis. Furthermore, preliminary H_2/O_2 fuel cell tests showed promise for the development of this type of PEMs prepared by means of a nitroxide-mediated living free radical grafting process. Thus, already the PVDF membrane that had been grafted with styrene by means of controlled radical polymerization could after sulfonation be used in a fuel cell for 930 h at 70 °C without any drop in current density. In contrast, according to our previous studies, PVDF membranes prepared by conventional preirradiation grafting of styrene fail within 150 to 200 h under similar conditions.

Introduction

At present, there is a major concern that in the future the limited availability of nonrenewable energy resources such as oil and coal will pose serious problems for our societies. Furthermore, the environmental problems caused by the high emissions produced by the internal combustion engine have called for the development of low emission vehicles.[1] Fuel cells and in particular polymer based proton exchange membrane (PEM) fuel cells, which generate electric energy by electrocatalytic oxidation of hydrogen or methanol, are seen as the most promising energy supplies for such environmentally friendly vehicles and also for portable electronic devices. The PEM is used in the form of a thin film (20−100 μm) and must serve several functions.[2] In particular, it must promote high electrocatalytic activity at solvent-free polymer−catalyst interfaces to give high efficiency and enable high-power operation. In addition, it must allow the transport of protons from the anode to the cathode of the fuel cell but at the same time prevent the transport of reactants (oxygen and hydrogen or methanol) across the membrane. It must in addition possess high mechanical as well as chemical and thermal stability to withstand the demanding operating conditions of a fuel cell. Finally, the membrane should fulfill the commercial requirements of the fuel cell market in terms of cost and be acceptable from an ecological point of view in terms of safe disposal and recyclability.

Over the past few years, several efforts to replace the most widely used perfluorinated Nafion as proton conducting membrane in polymer electrolyte fuel cells by cheaper and ecologically more acceptable materials have been undertaken by various academic and industrial groups.[3] So far, the work done has been only partially successful. The cost of the perfluorinated ionomer membranes, ca. \$600/m^2, is at least 1 order of magnitude too high. There is also interest in running the fuel cell at temperatures above 100 °C, to reduce catalyst poisoning and increase the efficiency of the cell. If methanol is to be used directly as fuel, the Nafion

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10.1021/ma0353641 CCC: \$27.50

and other similar membranes have high methanol crossover, which makes them less attractive. These fluorinated polymers are also less environmentally friendly than protonated ones.

The approaches of optimization and development of PEMs has mainly involved the synthesis of new hydrocarbon based aromatic polymer membranes such as polybenzimidazole (PBI),[4] sulfonated polyethersulfone (PSU),[5] polyether(ether)ketone (PEEK),[6] and polyethylene polystyrenesulfonic acid polymers (PE/SPS).[7] In addition, the production of ion-exchange membranes by radiation-induced grafting of styrene onto various commercially available fluorinated matrix polymers followed by sulfonation of the styrene moieties has generated considerable interest over the past decades.[8] This grafting technique offers the advantages of low preparation costs and the possibility to use preprocessed films. However, a serious shortcoming of this conventional radiation-induced grafting technique is that it offers little or no control over the macromolecular graft structure. Therefore, we wanted to develop the conventional radiation-induced technique into a more versatile and chemically controlled grafting method that would permit the production of well-defined graft homopolymers, block copolymers, or polymers containing functional groups at specific loci either at chain ends or along the grafted backbone itself. Thus, we started to explore the possibility of grafting styrene onto a poly(vinylidene fluoride) (PVDF) membrane by combining the pre-irradiation method with living radical polymerization techniques. In general, controlled or living radical polymerization can be achieved by atom transfer radical polymerization (ATRP),[9] by nitroxide stable free radical polymerization (SFRP),[10] or by reversible addition−fragmentation chain-transfer (RAFT) polymerization.[11]

In our previous paper, we described the utilization of ATRP in the production of PEMs,[12] whereas in this article we present our preliminary results on the production of PEMs using the SFRP process. In the literature, the subject of controlled grafting has received attention recently.[13] The principle of nitroxide-mediated polymerization is based on the concept of a dormant-active species equilibrium that allows the polymerization to be controlled, thereby facilitating the smart construction of well-defined macromolecular architectures. The SFRP is usually mediated by various nitroxides as outlined by Georges and co-workers[10a] as well as by Hawker et al.[10b] By utilizing the SFRP process in membrane modification, we introduced the necessary proton conductivity into the membrane without influencing other important characteristics of the matrix polymer, such as its thermal, mechanical, or chemical stability. Furthermore, we were intrigued by the fact that the dormant alkoxyamine chain end could be useful in cross-linking reactions or in the production of tailor-made block copolymers. And above all, the alkoxyamine chain end moiety could be replaced by other functional groups such as various maleic anhydride or maleimide derivatives, which at least in theory would enhance the thermo-oxidative stability of the membrane.[14] In general, the present paper explores the potential of a novel, versatile, and chemically controlled method for obtaining low cost, mechanically strong, and highly conductive solid polymer membranes.

Experimental Procedures

Materials. The matrix PVDF film of 80 μm thickness was purchased from Goodfellow. 2,2,6,6-Tetramethylpiperidinyl-1-oxy (Acros), styrene (Acros), camphorsulfonic acid (Aldrich), benzoic anhydride (Acros), toluene (LabScan) *N*-phenylmaleimide (Aldrich), 1,2-dichloroethane (Merck), and cumene (Acros) were all of reagent grade and used as received.

Attaching of TEMPO onto PVDF. Irradiation was carried out using an Electrocurtain electron accelerator (Energy Sciences Inc.) under nitrogen atmosphere (<200 ppm O_2) at an acceleration voltage of 175 kV. The irradiated (100 kGy) films were immediately immersed in a 0.32 M solution of TEMPO in toluene. The reaction was carried out in nitrogen atmosphere at 70 °C for 24 h. The membranes were Soxhlet extracted with chloroform.

TEMPO Mediated Grafting of Styrene to PVDF. The membranes (size 50 × 50 mm, thickness 80 μm, and weight 250 mg) with the attached TEMPO radical were immersed in the monomer solution typically containing 80 mL of styrene and 0.05 g of camphorsulfonic acid (or styrene and *N*-phenylmaleimide without adding camphorsulfonic acid; in the direct graft copolymerization of styrene and *N*-phenylmaleimide, the initial molar ratio between styrene and *N*-phenylmaleimide was 500:1). The camphorsulfonic acid was used to reduce the formation of styrene homopolymer. In addition, cumene was used as a solvent in some reactions to reduce the viscosity of the graft solution at long grafting times. The reaction was performed at 125 °C. The monomer solution was purged with nitrogen for 30 min prior to grafting, and an inert atmosphere was maintained throughout the reactions. The grafted membranes were then Soxhlet extracted with chloroform. The degree of grafting (d.o.g.) was determined gravimetrically, d.o.g. $= (m_2 - m_1)/m_1 \times 100\%$, where m_1 is the mass of the original membrane and m_2 is the mass of the membrane after polystyrene grafting.

Endcapping. The polystyrene grafts were end-capped by treatment with *N*-phenylmaleimide at 125 °C for 24 h in a solution typically containing 50 mmol of *N*-phenylmaleimide and 20 mL of cumene. The reaction was performed in a nitrogen atmosphere, and after the reaction the membranes were Soxhlet extracted with chloroform.

Nitrogen Content. The amount of bound TEMPO and phenylmaleimide was determined by elemental analysis after extraction of the membranes with chloroform. Mikro Kemi AB, Sweden, performed the elemental analysis.

Sulfonation. The membranes were immersed in 0.5 M chlorosulfonic acid in 1,2-dichloroethane at ambient temperature for 24 h. The sulfonated membranes were washed thoroughly with tetrahydrofuran and distilled water.

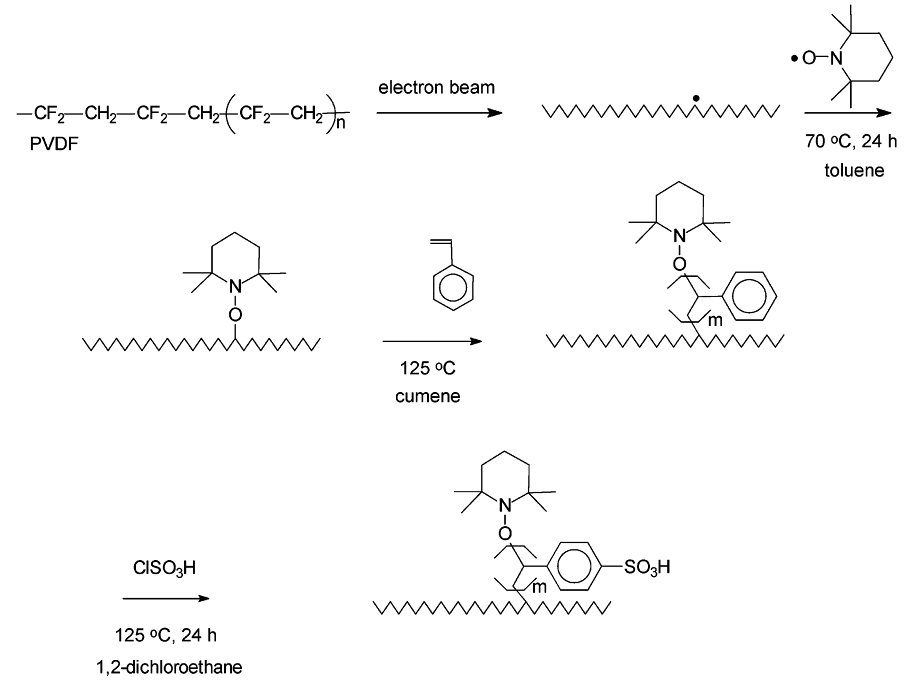
X-ray Diffraction Analysis. The graft penetration at different degrees of grafting of the sulfonated membranes was studied with energy-dispersive X-ray analysis of the sulfur and fluorine distribution in the transverse plane of the membranes. The instrument used was an IMIX analyzer by Princeton Gammatech, which was connected to a scanning electron microscope, Leica Cambridge S 360.

Thermal Analysis. Differential scanning calorimetry, DSC, was used to determine the crystallinity of the membranes using a Perkin-Elmer DSC-7 under nitrogen atmosphere in the range of 100−220 °C at 10 °C/min. The overall crystallinity of the membranes was determined from the DSC curves using the value 104.7 J/g for the heat of fusion of PVDF crystals. In addition, the crystallinity of the PVDF part of the membrane was calculated from the following: crystallinity of the PVDF part = overall crystallinity/$[1/(1 + g)]$, where overall crystallinity is the crystallinity for the whole membrane determined above and g is the degree of grafting for the membrane divided by 100.

A TGA/DTA TA Instrument SDT 2960 or a Netzsch Thermo Microbalance, TG 209, was used for thermogravimetric analysis. The measurements were carried out under air in the temperature range 20−470 °C using a heating rate of 10 °C/min.

Water Uptake and Ion Exchange Capacity. The dry weight of the samples was determined after drying in a desiccator over P_2O_5 to constant mass. Then, the samples were boiled in water for at least 1 h and left to equilibrate at room temperature. After the excess water was removed by blotting

Scheme 1. Preparation of Proton Conducting Membrane Using TEMPO Mediated Polymerization



the surface, the samples were immediately weighed, and the water uptake was calculated.

The ion exchange capacity was determined by back-titration. A known amount of NaOH was added to the samples, and after equilibration for 1 day, the excess of NaOH was titrated with a standard HCl solution.

Proton Conductivity. Prior to the conductivity measurements, the membranes were equilibrated with water vapor for a minimum of 3 days, and the measurements were carried out at a temperature of 20 °C under humidified nitrogen atmosphere. Conductivities were determined from impedance spectra using data gathered in the frequency range 5–85 kHz. The measurements were done with an Autolab PGSTAT 20 instrument (EcoChemie B. V.) supplied with FRA 2.4 software connected to a two-electrode cell with 0.071 cm^2 platinum electrodes. Membrane resistance was determined by extrapolating the linear part of the Nyquist plot to the real axis of the complex impedance spectrum. The conductivity was calculated from the resistance using the electrode area and membrane thickness, the latter measured with a micrometer.

Fuel Cell Measurements. The performance and long-term stability of the membranes were tested in a 5 cm^2 fuel cell (GlobeTech, Inc.) under atmospheric pressure at a temperature of 70 °C. The fuel cell was operated with pure hydrogen and oxygen with flow rates of 1 mL s^{-1}. The hydrogen was humidified at the cell temperature and the oxygen at 40 °C. The membranes were clamped with a standard torque of 3.0 Nm between Nafion coated (0.5–0.8 mg cm^{-2}) commercial gas diffusion electrodes with 0.4 mg cm^{-2} Pt loading (E-TEK, ELAT/Std/SS/V2).

Results and Discussion

Preparation of PEMs using TEMPO mediated controlled radical graft polymerization of styrene onto PVDF. The PVDF matrix film is in the first step exposed to electron beam irradiation, which leads to the formation of radicals on the macromolecular chain.[8e] The radiation is carried out under inert atmosphere. In the second step, the formed macroradicals are reacted with TEMPO to give living free radical macroinitiators. These TEMPO macroinitiators are used for incorporation of polystyrene grafts into the PVDF. In the third step, the membranes were sulfonated with chlorosulfonic acid as depicted in Scheme 1. The degree of grafting versus the graft polymerization time is shown in Figure 1 for both the nitroxide-mediated controlled grafting process and conventional radiation-induced grafting of styrene. (To suppress the autopolymerization of styrene and enhance the controlled polymerization rate of styrene, a small amount of camphor sulfonic acid (CSA) was added.[15]) The results indicate that the grafting kinetics is significantly different in the previous two cases. Thus, the rate of grafting is many times faster in the case of conventional radiation grafting as compared to the controlled grafting process. This may be attributed to the fact that SFRP in general proceeds slower than conventional radical polymerization of styrene. In the SFRP process, the degree of grafting increases linearly with grafting time up to 20% d.o.g., after which the grafting proceeds much more slowly. However, if the membrane is removed and Soxhlet extracted with chloroform, the grafting can be continued by adding fresh styrene. After the extraction step, we can again graft about 20% of styrene onto the PVDF membrane within 8 h, to produce a PVDF membrane with a total of 40% d.o.g. This fact indicates that the macromolecular initiator can be used several times.

Characterization of the Prepared Membranes. The graft penetration limit of the membranes was

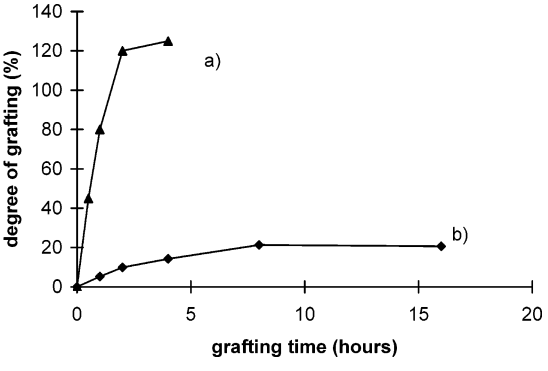


Figure 1. Degree of grafting of polystyrene onto PVDF membranes vs polymerization time at 125 °C: (a) conventional and (b) nitroxide mediated grafting.

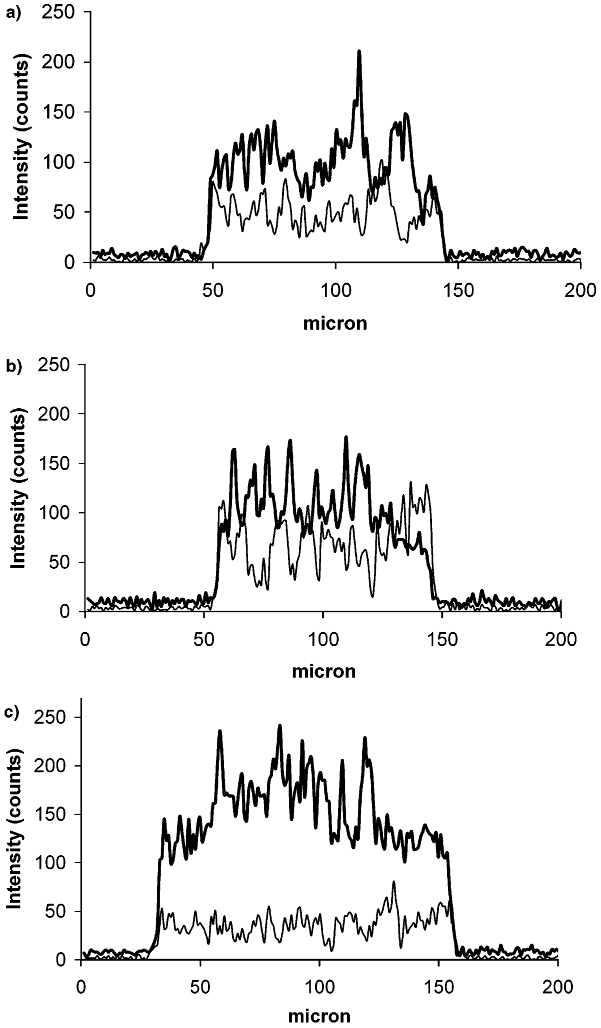


Figure 2. SEM-EDX analysis of the transverse plane of the PVDF-*TEMPOgraft*-PSSA membranes. The thinner line denotes fluorine and the darker line sulfur. (a) d.o.g. 14%, (b) d.o.g. 18%, and (c) d.o.g. 28%.

Table 1. Thickness, Proton Conductivity, Theoretical and Measured Ion Exchange Capacities, and Water Uptake for Differently Grafted and the Sulfonated Membranes with Different d.o.g

PS d.o.g. (%)	conductivity (mS/cm)	IEC_{theor} (meq/g)	IEC_{meas} (meq/g)	water uptake (g/g)	water uptake $N(H_2O/N(SO_3H)$
14[a]	13	1.08	0.96	0.21	12
18[a]	33	1.31	1.11	0.27	14
20[a]	n.d.[b]	1.42	1.28	0.29	13
28[a]	40	1.80	1.67	0.40	14
40[a]	80	2.22	1.73	0.55	18
15[c]	0[d]	1.14	0.19[e]	0.09[e]	26
34[c]	1[d]	2.04	0.62[e]	0.23[e]	21
53[c]	n.d.[b]	2.63	1.63[e]	0.95[e]	32
60[c]	102[d]	2.80	2.08[e]	1.16[e]	31
Nafion 105	56[f]		1.00[f]	0.51[f]	28[f]
Nafion 117	51[f]		0.89[f]	0.37[f]	23[f]

[a] Commercial Nafion 105 and 117 included for comparison.; TEMPO-grafting. [b] Not determined. [c] Conventional EB-grafting. [d] Ref 16. [e] Ref 8e. [f] Ref 17.

Table 2. Crystallinities for the Membranes in Different Stages of Preparation

membrane	overall crystallinity (%)	crystallinity of the PVDF part (%)
PVDF	36	36
PS 10%[a]	28	36
PS 15%[a]	26	32
PS 22%[a]	25	31
PS 28%[a]	24	30
Sulf PS 10%[a]	27	35
Sulf PS 15%[a]	23	28
Sulf PS 22%[a]	22	27
Sulf PS 28%[a]	20	24
PS 15%[b]	28	32
PS 23%[b]	27	33
PS 34%[b]	25	32
Sulf PS 15%[b]	25	32
Sulf PS 23%[b]	20	28
Sulf PS 34%[b]	15	24

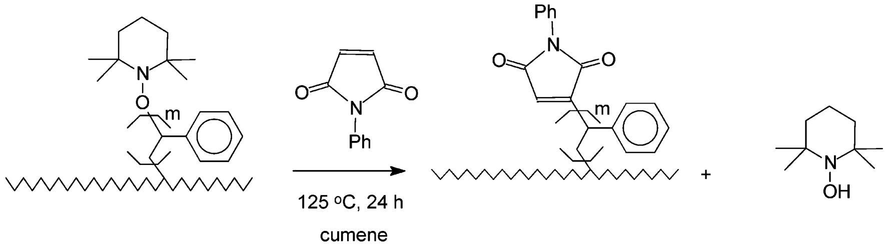
[a] TEMPO-grafting. [b] Conventional EB-grafting, ref 16.

determined by energy-dispersive X-ray measurements of the fluorine and sulfur distribution in the transverse plane of the grafted and sulfonated membranes. Noteworthy is the fact that according to this SEM-EDX analysis, the membranes prepared by the controlled grafting technique are grafted through the membrane already at 14% d.o.g. (see Figure 2), whereas the penetration limit for the membranes prepared by conventional radiation-induced grafting is approximately 30% d.o.g. for this relatively thick PVDF film (80 μm). As a consequence of this, the membranes prepared by the TEMPO mediated grafting technique become proton conducting at much lower d.o.g. than those prepared by conventional radiation-induced grafting. The proton conductivity increased from 10 mS/cm at 14% d.o.g. to 80 mS/cm at 40% d.o.g. as shown in Table 1. In addition, it was found that for the SFRP grafted membranes the measured and theoretical values of ion exchange capacity were in good agreement even at very low d.o.g. This means that sulfonation of the polystyrene grafts has been almost complete and that the sulfonic acid groups necessary for ion transport are highly accessible. The aforementioned observations are very much in line with the recent studies by Dargeville et al. on nitroxide-mediated preirradiation grafting of styrene onto PFA.[13d] Thus, they have established by microprobe Raman spectroscopy that in the presence of a nitroxide a uniform concentration of styrene graft has been obtained across the entire depth of the PFA membrane, and only very little graft has been formed at the PFA surface.

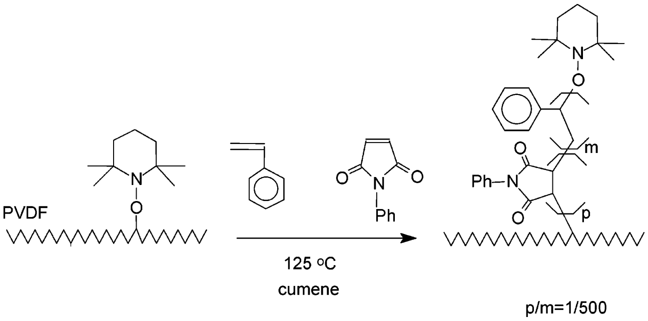
The water uptake from liquid water of the SFRP grafted membranes, defined as the ratio of mass of the hydrated membrane to that of the dry membrane, was determined by equilibrating the membranes in water. The water uptake for these membranes increased from 0.21 to 0.55 g/g when the d.o.g. increased from 14 to 40%. This in turn means that within this range of d.o.g. there are from 12 to 18 molecules of water per sulfonic acid group. The measured values for water uptake of the SFRP grafted membranes are lower than those normally measured for conventionally styrene grafted membranes (>20 molecules of water per sulfonic acid group) and also for Nafion membranes (see Table 1). This lower water uptake should make these membranes even more suitable for use in the PEMFC than those produced by conventional grafting.[16]

Thermal Analysis. According to DSC measurements, the overall crystallinity of the membranes decreased from 36 to 24% as the degree of grafting increased from 0 to 28%. In addition, the sulfonation of the membranes further decreased the crystallinity as anticipated, as shown in Table 2. These trends are quite

Scheme 2. Schematic Description of Endcapping of TEMPO Terminated Polystyrene Graft Chains



Scheme 3. Schematic Description of TEMPO Mediated Poly(styrene-*co*-*N*-phenylmaleimide) Grafting of PVDF Membrane



similar to those observed in our previous studies with conventionally grafted PVDF membranes.[8d,17] The decrease in overall crystallinity is attributed to both the dilution of inherent crystallinity by the incorporation of amorphous polystyrene grafts in the PVDF matrix as well as to the partial disruption of inherent crystallites.

Recently, Hawker and Waymouth et al.[14] reported an interesting method of improving the thermo-oxidative stability of SFRP produced polystyrene grades by controlled monoaddition of maleic anhydride or maleimide derivatives to alkoxyamine chains followed by elimination of the mediating nitroxide radical. Since high thermo-oxidative stability is essential for PEMs in terms of acceptable lifetime and it normally constitutes a serious problem for conventionally styrene grafted PVDF membranes, we wanted to explore whether the selectivity end functionalization of the alkoxyamine chains by maleimide could improve the thermal stability of the manufactured membranes. To test this hypothesis, the membranes were reacted with *N*-phenylmaleimide as shown in Scheme 2. In addition, we wanted to explore whether the thermo-oxidative membrane stability could be even further improved by preparing membranes via direct controlled radical copolymerization of styrene with phenylmaleimide onto the TEMPO functionalized membrane as shown in Scheme 3 (using an initial molar ratio of 500:1 between styrene and *N*-phenylmaleimide). To evaluate the thermal stability of these materials, thermogravimetric analysis of the following membranes were conducted: (1) matrix PVDF film, (2) PVDF-*TEMPOgraft*-poly(styrene-*co*-phenylmaleimide) membrane (containing 0.23 wt-% of phenylmaleimide units according to elemental analysis), (3) the membrane after exchange of the nitroxide end group with *N*-phenylmaleimide (containing 0.15 wt-% phenylmaleimide units), (4) the membrane prepared by the SFRP process, and (5) the membrane prepared by conventional radiation induced grafting. All of the membranes, except for the virgin PVDF matrix, had been sulfonated prior to thermogravimetric analysis. According to literature, three different stages of degradative processes, namely, dehydration, desulfonation, and graft chain as well as main chain degradation can normally be distinguished in these types of TGA curves.[2b] Thus, in general, membranes undergo dehydration within a broad range of temperature up to 150 °C, desulfonation proceeds to approximately 250 °C, and in the final stage the graft and the main chain undergoes degradation. As can be seen from Figure 3, the virgin PVDF film exhibits the highest thermo-oxidative stability, and both the PVDF-*TEMPOgraft*-poly(styrene-*co*-phenylmaleimide) membrane and the maleimide terminated membrane are significantly more stable than the corresponding alkoxyamine terminated membrane or the membrane prepared by conventional preirradiation technique, respectively. Consequently, the thermo-oxidative stability of the membranes can be further improved by substitution or via direct copolymerization with *N*-phenylmaleimide. Worth mentioning is also the fact that as anticipated the conventionally grafted PVDF membrane clearly has the lowest stability among all the measured membranes in this study. The preliminary results obtained from thermogravimetric analysis clearly suggest that the PVDF-*TEMPOgraft*-poly(styrene-*co*-*N*-phenylmaleimide) membrane is more stable than the other grafted membranes. Thus, by direct copolymerization of styrene with *N*-phenylmaleimide, membranes with excellent thermal stability, closer to that of the virgin PVDF film, can be obtained.

Fuel Cell Tests. The steady-state polarization curve for the styrene grafted membrane prepared by the SFRP is compared to that of Nafion 105 in Figure 4. The durability of this membrane was further investigated by a constant voltage test (0.4V) by following the changes in current density with time, as shown in Figure 5. To avoid excess water in the cell, the experiment was started with low water content in the gases. This was then gradually increased during the first 300

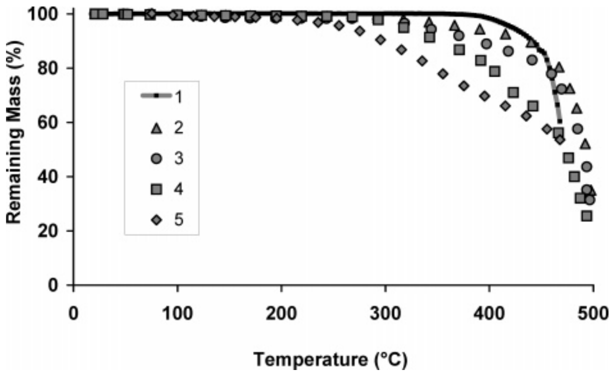


Figure 3. TGA analysis measurements of sulfonated PVDF-*graft*-PS membranes manufactured with different methods: (1) pure PVDF; (2) PVDF-*TEMPOgraft*-PSSA-*co*-PMI, d.o.g. 32 wt-%; (3) PVDF-*TEMPOgraft*-PSSA endcapped with PMI, d.o.g. 33%; (4) PVDF-*TEMPOgraft*-PSSA, d.o.g. 29%; and (5) PVDF-*graft*-PSSA, electron-beam grafted, d.o.g. 28%.

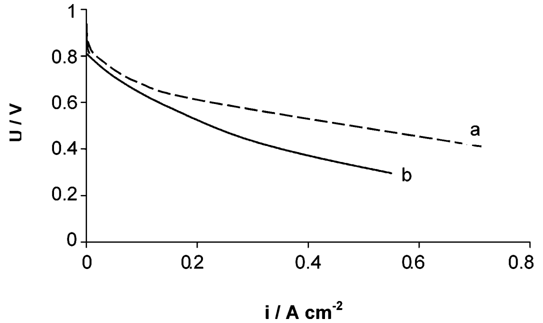


Figure 4. Polarization curves measured in a H_2/O_2 fuel cell at 70 °C (a) for a Nafion 105 membrane and (b) for a PVDF-*TEMPOgraft*-PSSA membrane with 28% d.o.g. (not corrected for IR-drop).

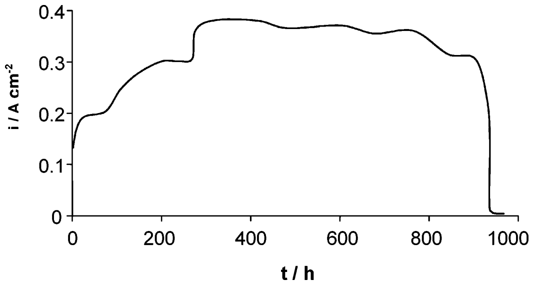


Figure 5. Current density vs time under 0.4 V constant load for a PVDF-*TEMPOgraft*-PSSA membrane with 28% d.o.g. in a H_2/O_2 fuel cell (70 °C, atmospheric pressure).

h of operation, which explains the corresponding increase in current density during the first part of the experiment. The results show that the current density did not drop during 930 h, which indicates that the PVDF-*TEMPOgraft*-PSSA membrane has a promising durability. In contrast, normally the PVDF membranes prepared by conventional preirradiation grafting of styrene fail within 150 to 200 h under similar conditions in our fuel cell.[16] In our previous work, we have used slightly different fuel cell conditions (i.e., the operating temperature was 60 not 70 °C as in this work). The fuel cell in this work was, however, clamped together with a lower standard torque than used previously because this was found to give improved performance. Thus, these fuel cell results are not directly comparable. However, these preliminary measurements indicate that the membrane prepared by the nitroxide mediated living free radical graft polymerization process gives better performance than those membranes prepared by conventional radiation-induced grafting techniques.

On the basis of the encouraging thermogravimetric analysis results, we expect that the maleimide functionalized membranes will exhibit even a significantly higher durability than 930 h under similar fuel cell conditions. This is a subject for further studies.

Conclusion

This work has demonstrated that irradiation of polymers films in combination with nitroxide mediated living free radical graft polymerization can be a very useful tool in the production of proton exchange membranes for fuel cell applications. Furthermore, we are currently investigating the possibility of using this radiation/alkoxyamine concept with a set of different matrix polymers including fluorine-free films, biopolymers, natural polymers, etc. In addition, we do envision that this approach could also be feasible for the immobilization of chiral ligands on polymer fibers.[19]

Acknowledgment. The authors gratefully acknowledge funding from the Academy of Finland (EMMA-program).

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MA0353641