

## A novel sulfonated dendritic polymer as the acidic component in proton conducting membranes

P. Gode<sup>a</sup>, A. Hult<sup>b</sup>, P. Jannasch<sup>c</sup>, M. Johansson<sup>b</sup>, L.E. Karlsson<sup>c</sup>,  
G. Lindbergh<sup>a,\*</sup>, E. Malmström<sup>b</sup>, D. Sandquist<sup>a</sup>

<sup>a</sup> Department of Chemical Engineering and Technology, Applied Electrochemistry, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

<sup>b</sup> KTH Fibre and Polymer Technology, Royal Institute of Technology, SE-100 44 Stockholm, Sweden

<sup>c</sup> Polymer Science and Engineering, Lund University, P.O. Box 124, SE-221 00 Lund, Sweden

Received 17 January 2005; received in revised form 12 December 2005; accepted 15 December 2005

### Abstract

The present study involves the synthesis of sulfonated poly(3-ethyl-3-(hydroxymethyl)oxetane), sPTMPO, by end-capping the hydroxy-groups in the PTMPO with 1,4-butane sultone. A series of the polymer with different degrees of substitution was investigated. Furthermore, the subsequent use of the sulfonated PTMPO as the acidic component in proton conducting membranes was explored. The membranes were prepared by either a) mixing the partly sulfonated PTMPO with hexamethoxymethyl melamine (HMMM) to form cross-links by ether formation between the methylol groups on HMMM and the remaining hydroxyl groups on the hyperbranched polyether or b) using the sulfonated polyether in conjunction with a pyridine functionalised polysulfone, PSU-pyridine, to produce acid–base blend membranes. Membrane properties such as proton conductivity, water uptake and mechanical properties are discussed.

© 2006 Elsevier B.V. All rights reserved.

**Keywords:** Polymer electrolyte membrane; PEM; Hyperbranched; Dendritic; Water uptake; Conductivity; Polysulfone; Blend membranes; PEFC; Fuel cell

### 1. Introduction

The search for alternative energy resources has spurred the development of new technologies such as solar cells and fuel cell technology. This has subsequently brought new demands on the materials used in these applications and the development of improved materials is often the key for success. One example is the membrane in polymer electrolyte fuel cells (PEFC), which has to function under harsh conditions not normally encountered by most synthetic polymers.

The PEFC-membrane is a proton conducting polymeric film. The film acts as a gas barrier and a proton conductor, sandwiched in between two electrodes. In the direct methanol fuel cell (DMFC), the membrane also acts as a methanol barrier. Beside gas permeability and proton conductivity, the long-term durability and mechanical stability are important parameters.

Perfluorinated polymers, such as Nafion™ (DuPont), have been successfully used because of their excellent stability and high proton conductivity at high water contents. However, the high cost, poor proton conductivity at elevated temperatures, high methanol cross-over, etc., have prompted an intensive research for new proton conducting membranes. To obtain less expensive materials, low methanol permeation, high-temperature conducting properties, proton conducting membranes based on polybenzimidazole (PBI), sulfonated polysulfones (sPSU), sulfonated poly(ether ether ketone) (sPEEK), and poly(vinylidene difluoride) (PVDF) based radiation grafted polystyrene sulfonic acid membranes (PVDF-g-PSSA) have been in the focus of research. Recent developments have been summarised in several reviews [1–9].

A membrane can, for example, be thermoplastic in nature, or covalently cross-linked in its structure, to produce the necessary mechanical stability. Due to the hydrophilic nature of the acidic functional groups, the water uptake and swelling strongly affect the mechanical properties. A too large water uptake will

\* Corresponding author. Tel.: +46 8 790 84 13.

E-mail address: [goeran.lindbergh@ket.kth.se](mailto:goeran.lindbergh@ket.kth.se) (G. Lindbergh).

drastically decrease the mechanical strength of the membrane [9]. On the other hand, membranes can be very flexible and mechanically strong when soaked in water, but very brittle when dried out. Swelling, water uptake and proton conductivity are strongly dependent on the molecular structure and the micro-phase separation in the membranes. For example, a general problem with direct sulfonated arylene main-chain membranes is the tremendously high water uptake and subsequent swelling, especially in hot water [4]. Kreuer has in detail investigated the water uptake and proton transport properties of sPEEK in comparison to Nafion [10,11]. The non-fluorinated polymer was shown to have low degree of interaction/phase separation between the hydrophilic sulfonic acid groups and could therefore incorporate water to a much higher extent than Nafion. In order to control the membrane swelling, cross-links can be introduced to improve the mechanical properties [12–15]. Co-polymerisation or microstructure modification by grafting are other examples carried out to reduce extensive hydration [8,16,17]. To overcome the problems related to swelling, Kerres et al. have developed membranes based on blends of various acidic and basic polymers. Examples of acidic polymers utilised are sulfonated polysulfone (SPSU), sPEEK and sulfonated poly(etherketones) (sPEK) [13,18]. Examples of basic polymers utilised are modified PSU Udel(R) containing N-basic side groups, poly(4-vinylpyridine), and polybenzimidazole [4,13,18–20]. In these acid/base blend membranes, physical cross-linking is introduced by strong ionic interactions between the acid and base functional groups. The physical cross-linking is much more flexible than the chemical, covalent, cross-linking and the blend membranes turned out to have better mechanical properties in the wet state [4]. Contrary to the mechanical strength, the proton conductivity in sulfonated membranes is favoured by increasing water content [21,22]. The self-diffusion coefficient of water and the proton diffusion coefficient are typically increasing as a function of water content. As a consequence, the higher water contents, i.e., access to mobile water in the membrane, the higher proton conductivity. The superior conductivity properties of Nafion compared to hydrocarbon polymers at dry conditions (<100 °C) is correlated to a better hydrophilic/hydrophobic separation [11].

Dendritic polymers [23], comprising of dendrimers and hyperbranched polymers, is a group of polymers that, during the last decades, has obtained an increased interest due to their special properties. Dendritic polymers are highly branched polymers based on AB<sub>x</sub>-monomers introducing potential branching points in every repeating unit. Dendrimers are perfectly layerwise built, monodisperse structures where all monomers are fully reacted, while hyperbranched polymers are polydisperse and contain linear segments, i.e., not fully reacted monomers, in the backbone. Hyperbranched polymers are easier to produce and less costly which is why they have been suggested to be an alternative for material-consuming applications where a certain degree of imperfection is acceptable. Dendritic polymers have been shown to exhibit unique properties, such as low viscosity and high solubility, compared to their linear analogues. The extensive branching results in few,

or no, entanglements, a globular shape, and properties greatly dependent on the nature of the numerous end-groups. The unique properties of dendritic polymers have resulted in several proposed applications ranging from medical devices [24] to photonic materials [25], coatings [26,27], barrier materials [28] and rheological additives [29]. The possibility to obtain tailored barrier properties, as well as the introduction of cross-linking points and other functional groups to a dendritic polymer by end-group modification, suggests that they have potential as polymer electrolyte fuel cell membrane components. Dendritic polymers have been investigated by several groups as possible electrolyte candidates in lithium-battery applications [30,31]. However, there are only a very few publications on dendritic polymers as proton conducting membranes in PEFC. Taylor et al. have studied the effect of sulfonated poly(propylene imine) dendrimers in Nafion on morphology and methanol cross-over [32–34]. Recently, Takeuchi et al. have demonstrated novel PEFC-membranes based on a hyperbranched poly(ethersulfone), HPES [35,36].

The present study deals with the synthesis of sulfonated poly(3-ethyl-3-(hydroxymethyl)oxetane), sPTMPO, by end-capping the hydroxy-groups in the poly-TMPO with 1,4-butane sultone. Furthermore, the subsequent use of the dendritic polymer as the acidic component in proton conducting membranes is explored. The sPTMPO was either chemically or physically cross-linked and membrane properties such as proton conductivity, water uptake and mechanical properties are discussed. The purpose of this study was to demonstrate the potential use of dendritic polymers as the acidic components in proton conducting membranes.

## 2. Experimental

### 2.1. Materials

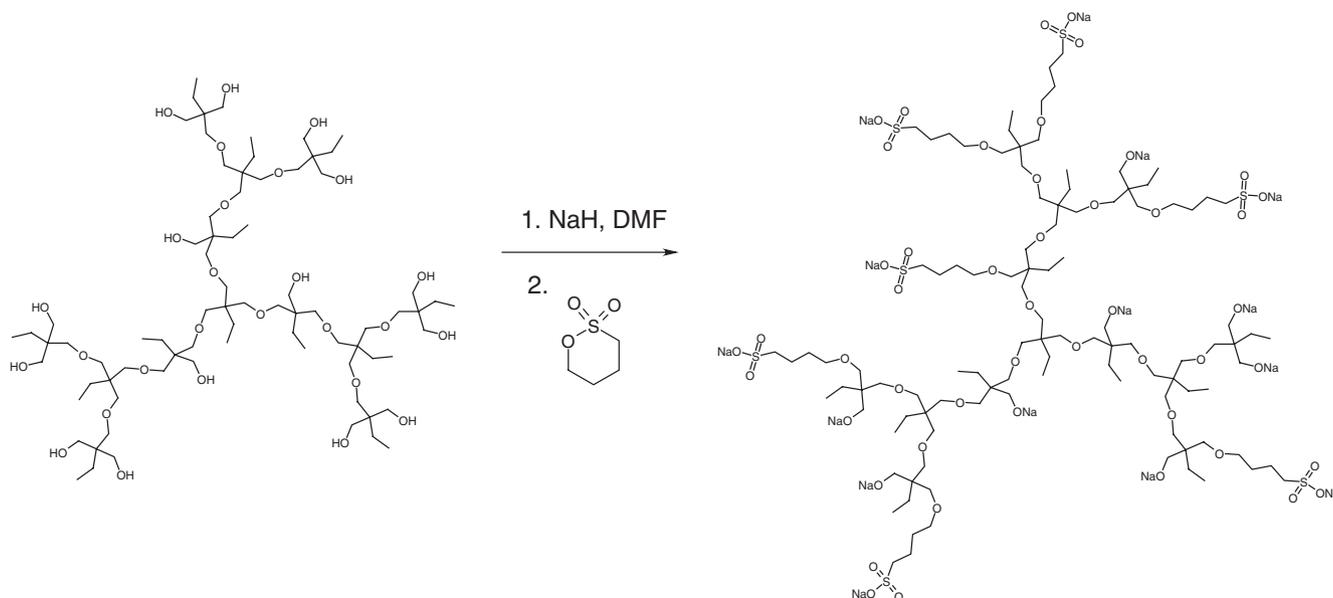
PTMPO was synthesised following the procedure according to Magnusson et al. [37]. Hexamethoxymethyl melamine (HMMM) was obtained from Perstorp AB, Sweden. All other chemicals were purchased from Aldrich or Acros and used as received.

### 2.2. Instrumentation

<sup>1</sup>H-NMR spectra were recorded on a Bruker AM 400 using DMSO-*d*<sub>6</sub>. The solvent signal was used as internal reference. Proton conductivity was measured using a Solatron 1255 Frequency Response Analyser and a Solatron 1287 Electrochemical Interface. The impedance equipment was interfaced by GPIB to a PC for electronic data acquisition using Zplot (Schriber Associates, Inc.) as software.

### 2.3. Sulfonic acid functionalisation of PTMPO

General description: PTMPO (5.0 g, 43 mmol-OH-groups) was dissolved in DMF (150 ml, pa) in a three necked round bottomed flask equipped with a drying tube. NaH, (1.29 g, 43 mmol, 80%) was then added to the solution and the reaction mixture was stirred for 16 h at room temperature.



Scheme 1. Sulfonation of PTMPO by end-capping with 1,4-butane sultone.

1,4-Butane sultone (5.9 g, 43 mmol, 99+%) was then added drop-wise to the solution and the reaction was left to react over night, stirred at room temperature, see Scheme 1.

When the desired degree of substitution (DS) was reached, as estimated from  $^1\text{H-NMR}$  spectroscopy, the end-capped PTMPO salt was precipitated in acetone (400 ml). The polymer was then dissolved in methanol and re-precipitated in acetone. This procedure was repeated 2–3 times to fully remove any remaining DMF. Finally, the product was dried in a vacuum oven at ambient temperature.

The PTMPO salt was dissolved in methanol (50 ml) and the acid form of the polymer was obtained by cation exchange (DOWEX 50 $\times$ 8). Next, the solution containing the acid functionalised PTMPO was rotovaped to dryness. The product was finally dried in a vacuum oven at room temperature. The general description mentioned above was used to produce a series of sPTMPO with different ion exchange capacities, Table 1. Yield: 55–75%.

#### 2.4. Synthesis of pyridine modified PSU

PSU-pyridine was synthesised using the method reported by Kerres et al. [19]. An amount of 5 g of dry polysulfone (PSU, 26 kg/mol) was dissolved in 300 mL tetrahydrofuran (THF, anhydrous, 99.9%) in a reactor fitted with a gas inlet/outlet, and a thermometer. The solution was cooled to  $-60\text{ }^\circ\text{C}$ , carefully degassed and left under a blanket of  $\text{N}_2$ . The reaction solution was then titrated with a solution of *n*-butyllithium (2.5 M *n*-BuLi in hexanes) until a reddish color persisted. Next, 4.5 ml *n*-BuLi

(11 mmol) was added in order to lithiate the PSU. After 30 min, a volume of 3.4 mL of ethyl isonicotinate, (22 mmol, 98%), was charged to the solution. After leaving the solution for 30 min, 5 mL of isopropanol (May and Baker Ltd., analytical reagent) was added to terminate the reaction. The polymer was then precipitated in 1 L of isopropanol, filtered, and finally thoroughly washed with fresh isopropanol. The dried product was characterized by  $^1\text{H-NMR}$  spectroscopy as previously described by Kerres et al. [19].

#### 2.5. Determination of ion exchange capacity (IEC) and degree of substitution (DS)

The ion exchange capacity (IEC, meq/g polymer) of the sulfonated PTMPO was determined by titration. The sPTMPO (0.1 g) was dissolved in Milli-Q water (25 ml). Using a standard graded titration burette and phenolphthalein as pH-indicator, a NaOH-solution (99 mM) was added drop-wise to the stirred solution until a colour change was recorded (clear to purple). The IEC was determined from the equivalent amount of NaOH consumed during the titration. In addition, the theoretical IEC was calculated from the degree of substitution (DS) obtained directly from  $^1\text{H-NMR}$  spectra (Eqs. (1)–(3)).

#### 2.6. Membrane preparation

Two different routes of membrane preparation were evaluated: a) chemical cross-linking by reacting the partly sulfonated PTMPO with hexamethoxymethyl melamine

Table 1

IEC, DS obtained from titration and theoretically calculated DS obtained from  $^1\text{H-NMR}$  spectroscopy for sulfonated PTMPO (S1–S3)

sPTMPO	$n_{\text{-OH/poly-TMPO}}/\text{mmol}$	$n_{1,4\text{-butane sultone}}/\text{mmol}$	$n_{\text{NaH}}/\text{mmol}$	IEC/meq $\text{g}^{-1}$	DS titration	DS $^1\text{H-NMR}$
S1	86	51	51	2.2	0.36	0.33
S2	43	39	39	2.3	0.39	0.33
S3	43	43	43	2.6	0.46	0.47

(HMMM) and b) physical cross-linking using the sPTMPO in conjunction with pyridine functionalised polysulfone, PSU-pyridine, to produce acid–base blend membranes.

### 2.6.1. Chemical cross-linking

Mixtures of the sPTMPO (0.5 g) and HMMM (10 wt.%), Table 2, were cast on a Teflon substrate and the solvent (NMP, 3–4 ml) was evaporated at a temperature of 85 °C for three hours. The films were then cross-linked during 15 min in an oven thermostated to 120 °C.

### 2.6.2. Physical cross-linking (blends)

Acid–base blend membranes were prepared by blending sPTMPO with PSU-pyridine, as presented in Table 2. The PSU-pyridine (0.15 g, 0.84 DS) was dissolved in NMP (3–4 ml). For each membrane prepared, the amount of sulfonated PTMPO, corresponding to the final IEC of the resulting membrane, was dissolved in NMP (1.5 ml). When both polymers had dissolved, the solutions were mixed and poured into a Teflon evaporation mold. To evaporate the NMP, the substrate was placed on a plate pre-heated to 120 °C. When the film had solidified, the plate was placed in a vacuum oven (110 °C) for 16 h. After cooling to room temperature, the mold was submerged in Milli-Q water, where it was left until the membrane detached from the substrate to form a free film.

### 2.7. Proton conductivity measurements

The proton conductivity of the HMMM cross-linked membranes was determined as a function of relative humidity (RH), in the range 43–95%, at a temperature of 25 °C. Proton conductivity measurements of the acid–base blend membranes were carried out in the fully wet state, i.e., immersed in water prior the measurements. A four-electrode cell of the same type used by Sone et al. [22] was modified to give the membrane sufficient mechanical support and to simplify conditioning of the membrane at various RHs. The electrode set-up consisted of four gold wires (250 μm) integrated in a Teflon-plate where the two inner wires were used as reference electrode and the two outer wires were used as counter and working electrode, respectively, Fig. 1. The membranes were placed in the cell holder between a Teflon-net attached to an aluminium block on one side, and the four electrodes on the other side. The aluminium block was supplied with gas inlet and outlet and the Teflon-net distributed the humidified gas onto the membrane

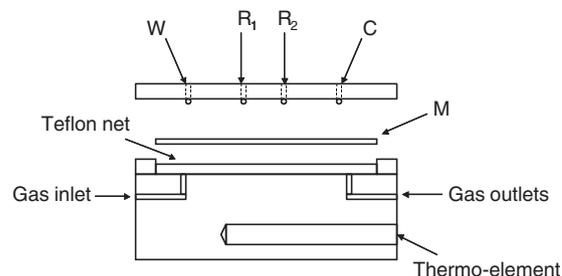


Fig. 1. Schematic representation of the four-electrode cell set-up, utilised for proton conductivity measurements; working electrode (W), reference electrodes ( $R_1$ ,  $R_2$ ), counter electrode (C) and membrane sample (M).

surface. Gas humidity was controlled by mixing dry and humidified nitrogen gas and the relative humidity was measured with a HMP42 probe (Vaisala) at the cell outlet.

## 3. Results and discussion

### 3.1. Sulfonic acid functionalisation of PTMPO

Sulfonated PTMPOs with different ion exchange capacities (S1–S3) were synthesised in accordance to Scheme 1. PTMPO has  $n+1$  end-groups where  $n$  is the number of repeating units [37]. To estimate the desired amount of 1,4-butane sultone to be added, the ratio of functional OH-groups in the PTMPO to the number of repeating units ( $n$ ) was assumed to be 1:1.

$^1\text{H-NMR}$  spectroscopy was found to be a versatile tool to characterise the sulfonated polymers. The peaks in the  $^1\text{H-NMR}$  spectrum of the 1,4-butane sultone arm has previously been assigned by Luna et al. [38]. Fig. 2 presents the  $^1\text{H-NMR}$  spectrum of S2 after purification by precipitation and subsequent ion-exchange. By comparing the integrals originating from the two middle methylene-groups (peaks g and h, Figs. 2 and 3) remaining from the 1,4-butane sultone with the integrals emanating from the ethyl-group in the repeating unit in PTMPO (peak a or b, Figs. 2 and 3) it was possible to assess the degree of substitution. After following the substitution reaction in more detail, Fig. 3, it was possible to conclude that the functionalisation reaction reached the maximum yield after ca. 5 h.

#### 3.1.1. Influence of reaction condition

The sulfonic acid was introduced by reacting the primary hydroxyl groups with 1,4-butane sultone after deprotonation with NaH. The first sulfonation reaction was conducted in THF, a good solvent for the PTMPO. However, the partly end-capped PTMPO precipitated from the reaction mixture during the reaction and the formation of a low molecular weight by-product was observed by  $^1\text{H-NMR}$  spectroscopy. The by-product was easily removed by repetitive precipitations from methanol into acetone. However, in an attempt to increase the degree of substitution, THF was replaced with DMF since it is a solvent known to more effectively solubilise highly polar/ionic components. DMF performed better as a solvent, preventing precipitation, but was also found to induce a second side-reaction if running the reaction at elevated temperature (85 °C),

Table 2  
Composition, thickness and calculated IEC of chemical cross-linked membranes (M1–M2) and acid/base blend membranes (M3–M5) based on sPTMPO with different degrees of substitution (S1–S3)

Membrane	sPTMPO	Cross-linker	$x_{\text{cross-linker}}/\text{wt.}\%$	$l/\mu\text{m}$	$\text{IEC}_{\text{calc}}/\text{meq g}^{-1}$
M1	S1	HMMM	10	160	2.0
M2	S3	HMMM	10	100	2.3
M3	S2	PSU-pyridine	33	240	1.0
M4	S2	PSU-pyridine	24	130	1.3
M5	S2	PSU-pyridine	19	150	1.6

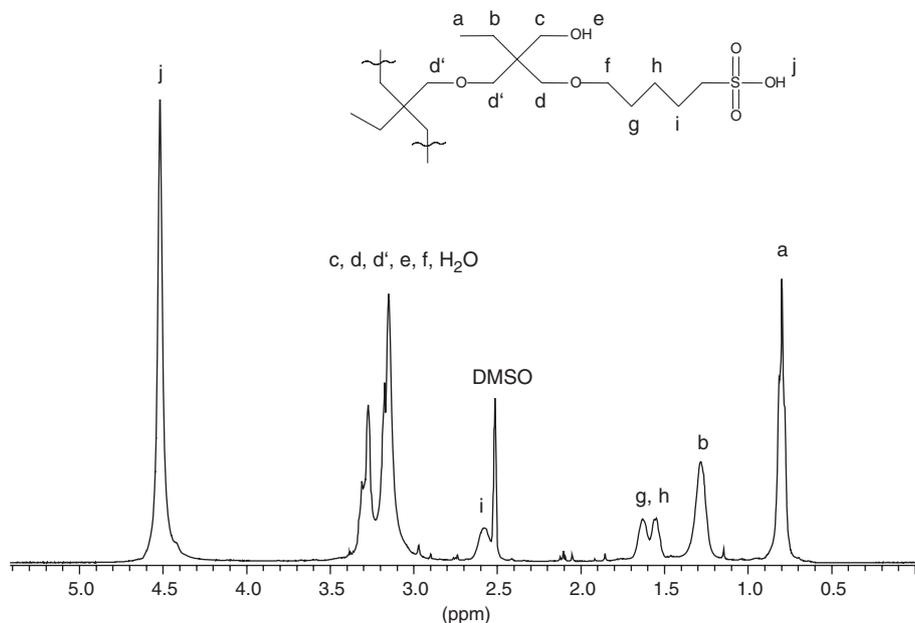


Fig. 2.  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) spectrum of sPTMPO (S2).

resulting in a by-product impossible to remove by precipitation. Following these results, all sulfonation reactions were carried out in DMF at room temperature and no further effort was directed towards the optimisation of the sulfonation-reaction.

### 3.1.2. Determination of ion exchange capacity (IEC) and degree of substitution (DS)

The DS can be calculated directly from the  $^1\text{H-NMR}$  spectroscopy by comparing the integrals emanating from the “g–h”-peaks and peak “a” or “b”, seen in Fig. 3. Since the number of repeating units ( $n$ ) in PTMPO and the number of functional groups ( $n+1$ ) were assumed to be equal, the equivalent weight,  $E_w$  (g/mol,  $\text{R-SO}_3\text{H}$ ), was determined as:

$$E_w = \frac{n \cdot M_{w, \text{ repeating unit poly-TMPO}} + n \cdot \text{DS} \cdot M_{w, 1,4\text{-butane sulfone}}}{n \cdot \text{DS}} \quad (1)$$

$$E_w = \frac{1}{\text{IEC} \cdot 10^{-3}} \quad (2)$$

By combining Eqs. (1),(2), the IEC of the sulfonated PTMPO can be expressed as:

$$\text{IEC} = \frac{\text{DS} \cdot 10^3}{(M_{w, \text{ repeating unit poly-TMPO}}) + \text{DS} \cdot M_{w, 1,4\text{-butane sulfone}}} \quad (3)$$

As a comparison, the degree of substitution determined from  $^1\text{H-NMR}$ -spectra and from titration is presented in Table 1. A good agreement between the outcome of these two methods was obtained. However, due to experimental errors in the  $^1\text{H-NMR}$  integration and the assumption that  $n \approx n+1$ , the IEC-data acquired from the titrations were utilised for the membrane preparation.

### 3.2. Membrane preparation and characterisation

The proton conductivity in sulfonated membranes is favoured by a high concentration of sulfonic acid groups and increasing water contents. A high IEC will increase the conductivity, but at the same time the mechanical strength is reduced due to high water uptake and swelling. According to Kreuer [10,11], the molecular structure of the polymer backbone and phase separation due to hydrophobic and hydrophilic groups strongly affect the water uptake and the proton conductivity. In dendritic polymers, the water uptake has

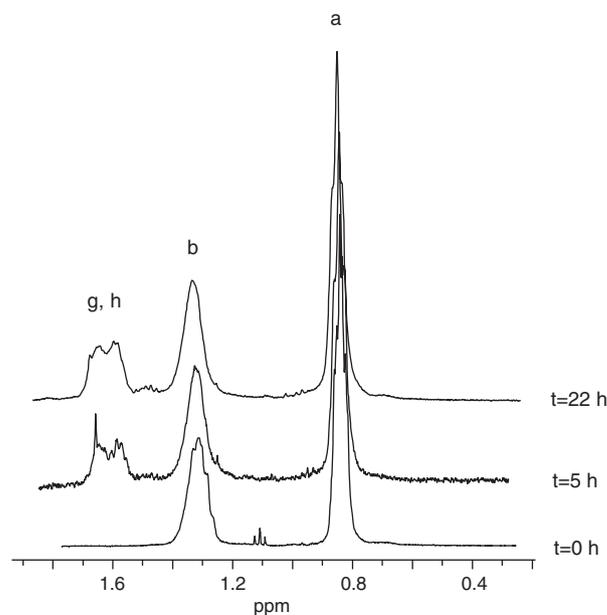
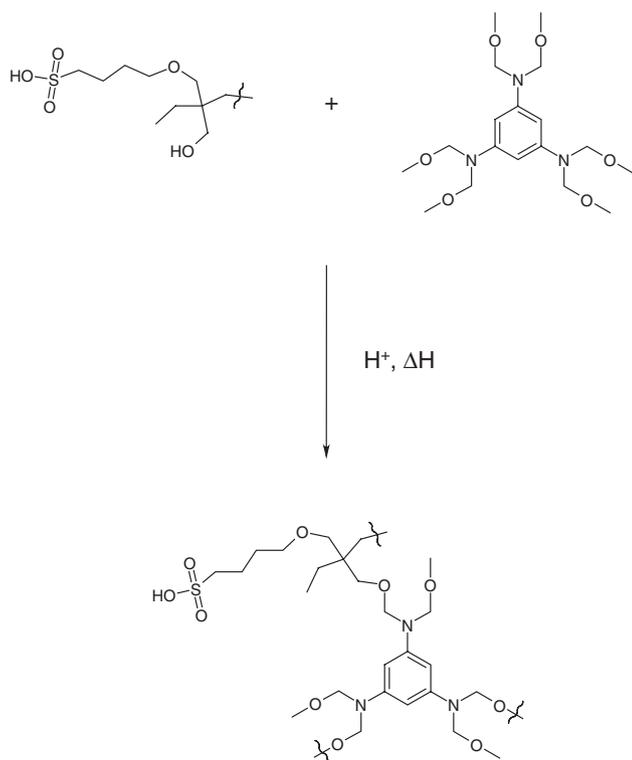


Fig. 3.  $^1\text{H-NMR}$  ( $\text{DMSO-}d_6$ ) spectrum representing the sulfonation reaction as a function of time.

to be controlled by cross-linking or by introduction of grafts by end-group modification due to the globular shape and lack of entanglements. The material properties are greatly dependent on the nature of the numerous end-groups. The sulfonated PTMPOs were highly water soluble, which complicated the membrane preparation. To investigate whether or not it was possible to prepare membranes with sufficient mechanical properties, two different approaches were explored — chemical and physical cross-linking.

### 3.2.1. Chemical cross-linking

Membranes consisting of sPTMPO (S1 and S3) and HMMM as cross-linking agent were prepared, Table 2. The cross-linking reaction is outlined in Scheme 2. The two components were mixed in NMP and the slow evaporation at 85 °C allowed the formation of defect free homogeneous films prior to the final cure at 120 °C. No catalyst was needed since the sulfonic acid groups on the hyperbranched polyether provided enough acidity to catalyse the ether formation between the methylol groups on HMMM and the hydroxyl groups on the hyperbranched polyether. The amount of methylol groups on HMMM was significantly lower than the number of hydroxyl groups on the polyether to allow complete conversion of HMMM. Over all, the HMMM cross-linked membranes exhibited poor mechanical properties, to some extent, in the humidified state and became brittle when dried. It was difficult to find a polymer/cross-linker ratio giving a membrane with sufficient mechanical properties in both wet and dry state. A concentration of 10 wt.% HMMM was found to give acceptable mechanical properties while still retaining a high concentration of proton conducting



Scheme 2. Cross-linking reaction of sPTMPO with HMMM.

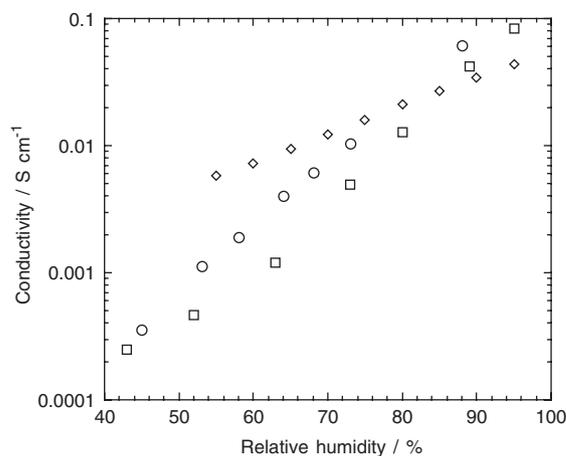


Fig. 4. Proton conductivity as a function of relative humidity (RH): (◇) Nafion 117 at 20 °C, [22], (O) sPTMPO cross-linked with HMMM, (M2, IEC=2.3 meq/g), (□) sPTMPO cross-linked with HMMM, (M1, IEC=2.0 meq/g).

sulfonic acid groups in the membrane. Perhaps, another choice of cross-linker may improve the mechanical properties. Takeuchi et al. [36] have used an epoxy resin and a hyperbranched polyamide as cross-linking agent to prepare membranes from a water-soluble hyperbranched poly(ethersulfone), HPES, having an IEC of 2.3 meq/g with promising results.

The proton conductivity of the chemically cross-linked membranes (M1–M2) is presented in Fig. 4 as a function of relative humidity. As a reference, the conductivity of Nafion 117 at 20 °C is included using a polynomial equation fitted to experimental data (Nafion hot-pressed at 80 °C) presented by Sone et al. [22]. The proton conductivity was, as expected, found to be proportional to the IEC and strongly dependent on relative humidity. At a relative humidity of 80%, the conductivity for both membranes (M1–M2) was comparable to that of Nafion. At higher RHs, the conductivity exceeded the conductivity of Nafion. At relative humidities below 80%, Nafion exhibited superior conductivity properties. The results are in line with what has been observed for other kinds of alternative membranes, e.g., sPEEK and PVDF-*g*-PSSA [11,21]. Kreuer has related this phenomenon to a higher self-diffusion coefficient of water and proton mobility due to the better hydrophobic/hydrophilic separation in Nafion [11].

### 3.2.2. Physical cross-linking (blends)

Acid/base blend membranes were prepared aiming at ion exchange capacities (IEC) in a range from 1.0 to 1.6 meq/g, Table 2. The ion exchange capacity of the acidic and basic components was 2.3 meq/g (S2) and 1.6 meq/g (PSU-pyridine), respectively. The blends of the PSU-pyridine and the water-soluble acidic polymer resulted in water-insoluble proton conducting membranes due to strong interactions between the basic and the acidic compounds, Fig. 5. Water uptake and proton conductivity as function of IEC at a temperature of 25 °C are presented in Fig. 5. The water uptake in these membranes ranged from  $\lambda=45\text{--}177$  nH<sub>2</sub>O/SO<sub>3</sub>H. This is far too high even for the 1.0 meq/g membrane (M3) and further development for

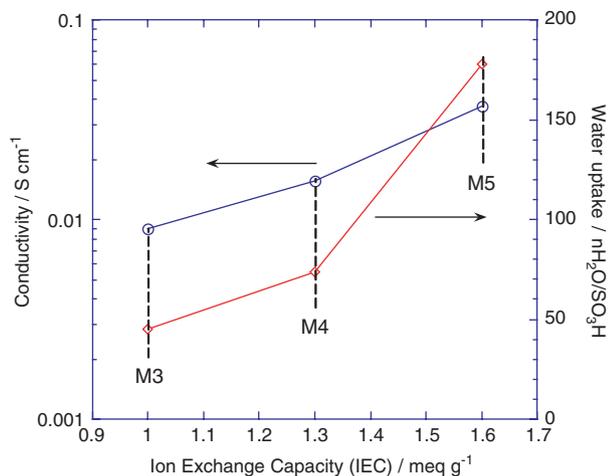


Fig. 5. Proton conductivity and water uptake of acid/base blend membranes based on sPTMPO and PSU-pyridine (M3–M5) as a function of IEC.

reduced swelling is necessary, e.g., by reducing the degree of substitution. The dependence on hydration number of non-cross linked and cross-linked sPSUs on IEC, presented in [4,12,39,40], have been gathered by Rozière and Jones [8]. At high IEC's high water uptake up to  $\lambda \approx 70\text{--}140$  nH<sub>2</sub>O/SO<sub>3</sub>H at 80 °C was reported even for the cross-linked membranes [12]. Besides reducing the sulfonic acid concentration a combination of chemical and physical cross-linking may be one way to restrict the water uptake. Kerres et al. suggested a combination of physical and chemical cross-linking to optimise the mechanical properties regarding reduced swelling, flexibility and mechanical strength [13,14]. In general, it is preferable to keep the water uptake as low as possible ( $\lambda < 25$ ) but still maintaining a high proton conductivity ( $\lambda_{\text{Nafion}} \approx 22$  nH<sub>2</sub>O/SO<sub>3</sub>H, immersed in water [41]). In spite of the high water uptake, the membranes showed good mechanical properties in the wet state up to 1.3 meq/g (M4). However, when reaching IEC's of 1.6 meq/g for the membrane (M5), the high water uptake and swelling of the membrane strongly reduced the mechanical strength of the membrane. All membranes were found to be brittle when dry, especially at low IEC. The brittleness can be explained by the strong physical cross-linking introduced by the interactions between the acid and base functional groups. The brittleness decreased noticeably when the amount of sulfonated PTMPO was increased. Membrane M4 (IEC<sub>calc</sub> = 1.3 meq/g) was found to have a good balance between the amount of sPTMPO and PSU-pyridine and showed the best mechanical stability of the investigated membranes both in the dry state and when soaked in water. The proton conductivity was in the range between 0.01 and 0.04 S cm<sup>-1</sup> for the membranes M3–M5. To improve on these acid/base blend membranes, it is important to maintain the high proton conductivity and reduce the water uptake and brittleness.

### 3.3. General discussion

All membranes showed high proton conductivity, especially at humidified conditions. The main challenge was to obtain good mechanical properties in both the dry and wet state. As

mentioned above, the brittleness of the blend membranes was probably due to the physical cross-linking introduced by strong interactions between the acid and base functional groups. Nevertheless, the acid/base blend membranes were found to be more flexible and have better mechanical properties than the chemically cross-linked membranes. On the other hand, the IEC values of the blend membranes (M3–M5) investigated in this study were much lower than the IEC of membrane M1–M2, which complicates a direct comparison.

The durability of PTMPO-based membranes is still an open question but most probably an increased chemical stability is needed to obtain a long-term durability in PEFC applications. The PTMPO-backbone consists of secondary  $\alpha$ -hydrogens, which are relatively sensitive to hydrolysis and hydroxy-radicals produced in the fuel cell environment. The investigated membranes in this study are therefore addressed as model materials. On the other hand, PVDF-g-PSSA membranes, known to have poor chemical stability due to the tertiary  $\alpha$ -hydrogens in the polystyrene grafts, have received attention from several research groups and has been demonstrated to last thousands of hours of operation in fuel cells at elevated temperatures [42–44]. In order to increase the long-term durability, there are several hyperbranched polymers having perfluorinated or other thermally stable backbones that can be utilised. The hyperbranched poly(ethersulfone), HPES, presented by Takeuchi et al. [35,36] is one example of such a promising structure.

In a future work, the reduction of water uptake and swelling should be in focus. One approach could be to increase the amount of PTMPO in the membrane, to tune the IEC of the membrane. This can be accomplished by using a sPTMPO with a lower degree of substitution. Using this approach, the brittleness of the acid/base blend membranes at dry conditions may also be reduced. The effect of the cross-linking level, the nature of the cross-linkers and the composition of the blend membranes are also of crucial importance. Furthermore, the architecture of sulfonated dendritic polymers having extensive branching and numerous end-groups, i.e., is interesting from a morphological perspective. The surface location of sulfonic acid groups will affect the formation and shape of hydrophilic regions/clusters in the membrane. Therefore, morphological studies of nano-scale phase separation and percolation in these materials are of great interest.

## 4. Conclusions

The use of a sulfonated dendritic polymer as the acidic component in proton conducting membranes was demonstrated. A series of the sulfonic acid functionalised polymers having different degrees of substitution, was successfully synthesised by end-capping the hydroxy-groups of poly(3-ethyl-3-(hydroxymethyl)oxetane), PTMPO, with 1,4-butane sultone. A good correlation between ion exchange capacity data determined from <sup>1</sup>H-NMR spectroscopy and titration was obtained.

Proton conducting membranes were prepared by either a) mixing the partly sulfonated PTMPO with HMMM and cross-linking by ether formation between the methylol groups

on HMMM and the hydroxyl groups on the hyperbranched polyether or b) using the sulfonated PTMPO in conjunction with PSU-pyridine to produce acid–base blend membranes.

All membranes showed reasonably high proton conductivity, comparable to Nafion at humidified conditions. The main challenge was to obtain good mechanical properties in both the dry and wet state. The membranes exhibited poor mechanical properties in the humidified state and became brittle when dried. The acid/base blend membranes were found to be more flexible and had better mechanical properties than the chemically cross-linked membranes.

In general, it was shown that dendritic polymers could be used as the acidic component in proton conducting membranes. The molecular architecture makes it possible to introduce various amounts of functional groups and cross-linking points by end-group modification and, as a consequence, to control the properties of the membrane. Dendritic polymers could be useful in various membrane approaches such as chemical and physical cross-linked membranes, or in a combination of these two. To maintain the high proton conductivity and reduce the water uptake, the membranes presented in this study have to be further optimised.

### Acknowledgement

The financial support of the Swedish Foundation for Strategic Environmental Research, MISTRA, is gratefully acknowledged. The work was done within the framework of the Jungner Center. Eva Malmström gratefully acknowledge the Swedish Foundation for Strategic Research for financial support.

### References

- [1] G. Inzelt, M. Pineri, J.W. Schultze, M.A. Vorotyntsev, *Electrochim. Acta* 45 (2000) 2403.
- [2] P. Jannasch, *Curr. Opin. Colloid Interface Sci.* 8 (2003) 96.
- [3] D.J. Jones, J. Roziere, *J. Membr. Sci.* 185 (2001) 41.
- [4] J.A. Kerres, *J. Membr. Sci.* 185 (2001) 3.
- [5] K.D. Kreuer, *Solid State Ionics* 97 (1997) 1.
- [6] Q.F. Li, R.H. He, J.O. Jensen, N.J. Bjerrum, *Chem. Mater.* 15 (2003) 4896.
- [7] M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* 25 (2000) 1463.
- [8] J. Roziere, D.J. Jones, *Annu. Rev. Mater. Res.* 33 (2003) 503.
- [9] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chem. Rev.* 104 (2004) 4587.
- [10] K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29.
- [11] K.D. Kreuer, *Solid State Ionics* 136 (2000) 149.
- [12] J. Kerres, W. Cui, R. Disson, W. Neubrand, *J. Membr. Sci.* 139 (1998) 211.
- [13] J. Kerres, W. Zhang, L. Jorissen, V. Gogel, *J. New Mat. Electrochem. Syst.* 5 (2002) 97.
- [14] J. Kerres, M. Hein, W. Zhang, S. Graf, N. Nicoloso, *J. New Mat. Electrochem. Syst.* 6 (2003) 223.
- [15] W. Zhang, G. Dai, J. Kerres, *Acta Polym. Sin.* (1998) 608.
- [16] Y. Yang, S. Holdcroft, *Fuel Cells* 5 (2005) 171.
- [17] P. Jannasch, *Fuel Cells* 5 (2005) 248.
- [18] J. Kerres, A. Ullrich, T. Haring, M. Baldauf, U. Gebhardt, W. Preidel, *J. New Mat. Electrochem. Syst.* 3 (2000) 229.
- [19] J. Kerres, A. Ullrich, M. Hein, *J. Polym. Sci. Polym. Chem.* 39 (2001) 2874.
- [20] J. Kerres, A. Ullrich, *Sep. Purif. Technol.* 22-3 (2001) 1.
- [21] T. Kallio, M. Lundström, G. Sundholm, N. Walsby, F. Sundholm, *J. Appl. Electrochem.* 32 (2002) 11.
- [22] Y. Sone, P. Ekdunge, D. Simonsson, *J. Electrochem. Soc.* 143 (1996) 1254.
- [23] J.M.J. Fréchet, D.A. Tomalia, *Dendrimers and Other Dendritic Polymers*, John Wiley and Sons Ltd., Chichester, UK, 2001.
- [24] U. Boas, P.M.H. Heegard, *Chem. Soc. Rev.* 33 (2004) 43.
- [25] H. Ma, A.K.Y. Jen, *Adv. Mater.* 13 (2001) 1201.
- [26] M. Johansson, T. Glauser, A. Jansson, A. Hult, E. Malmstrom, H. Claesson, *Prog. Org. Coat.* 48 (2003) 194.
- [27] R.A.T.M. van Benthem, *Prog. Org. Coat.* 40 (2000) 2003.
- [28] J. Lange, E. Stenroos, M. Johansson, E. Malmstrom, *Polymer* 42 (2001) 7403.
- [29] Y. Hong, J.J. Cooper-White, M.E. Mackay, C.J. Hawker, E. Malmstrom, N. Rehnberg, *J. Rheol.* 43 (1999) 781.
- [30] C.J. Hawker, F.K. Chu, P.J. Pomery, D.J.T. Hill, *Macromolecules* 29 (1996) 3831.
- [31] Z.Y. Wen, T. Itoh, M. Ikeda, N. Hirata, M. Kubo, O. Yamamoto, *J. Power Sources* 90 (2000) 20.
- [32] E.P. Taylor, R.B. Moore, *Abstr. Pap. - Am. Chem. Soc.* 215 (1998) U380.
- [33] E.P. Taylor, R.B. Moore, *Abstr. Pap. - Am. Chem. Soc.* 218 (1999) U440.
- [34] E.P. Taylor, R.B. Moore, *Abstr. Pap. - Am. Chem. Soc.* 220 (2000) U256.
- [35] M. Takeuchi, M. Jikei, M.A. Kakimoto, *Chem. Lett.* 32 (2003) 242.
- [36] M. Takeuchi, M. Jikei, M.A. Kakimoto, *High Perform. Polym.* 15 (2003) 219.
- [37] H. Magnusson, E. Malmström, A. Hult, *Macromol. Rapid Commun.* 20 (1999) 453.
- [38] E.A. Luna, D.G. VanderVelde, R.J. Tait, D.O. Thompson, R.A. Rajewski, V.J. Stella, *Carbohydr. Res.* 299 (1997) 111.
- [39] F. Lufrano, G. Squadrito, A. Patti, E. Passalacqua, *J. Appl. Polym. Sci.* 77 (2000) 1250.
- [40] P. Genova-Dimitrova, B. Baradie, D. Foscallo, C. Poinsignon, J.Y. Sanchez, *J. Membr. Sci.* 185 (2001) 59.
- [41] T.A. Zawodzinski, C. Derouin, S. Radzinski, R.J. Sherman, V.T. Smith, T.E. Springer, S. Gottesfeld, *J. Electrochem. Soc.* 140 (1993) 1041.
- [42] F.N. Buchi, B. Gupta, O. Haas, G.G. Scherer, *J. Electrochem. Soc.* 142 (1995) 3044.
- [43] N. Buchi, B. Gupta, O. Haas, G.G. Scherer, *Electrochim. Acta* 40 (1995) 345.
- [44] J. Huslage, T. Rager, B. Schnyder, A. Tsukada, *Electrochim. Acta* 48 (2002) 247.