DOI: 10.1002/masy.200750333

In-situ Crosslinked Polymer Electrolyte Membranes from Thermally Reactive Oligomers for Direct Methanol Fuel Cells

Sam Dae Park,[1] *Yoon Ju Chang,*[1] *Jin Chul Jung,*[1] *Wonmok Lee,*[2] *H. Chang,*[2] *Haekyoung Kim**[2]

Summary: Thermally reactive ally-terminated sulfonated oligosulfone was easily synthesized and made it possible to fabricate crosslinked membrane with high ionic group contents for direct methanol fuel cells. The crosslinked network structures of rigid rod sulfonated polyarylene sulfone showed high suppression of swelling with high sulfonation degree of 70%, which gave excellent properties for direct methanol fuel cell applications. The proposed membranes gave unprecedented reduction in methanol cross-over (less than 3% of Nafion 112) and high ionic conductivity (~80% of Nafion 112).

Keywords: allyl-terminated oligosulfone; crosslinking; direct methanol fuel cell; membrane; poly(ether sulfone)

Introduction

The direct methanol fuel cell (DMFC) is an attractive candidate for a mobile energy source because of its advantageous properties such as easy fuel storage, low operating temperature, and simple design applicability. Unfortunately, DMFC has not shown performance enough for application in small electronics. Low catalytic activity and methanol cross-over through the membrane have been substantial drawbacks for increasing the DMFC performance.[1] Critical requirements for a useful PEM include sufficiently high in proton conductivity, hydrolysis resistance, mechanical stability, and negligibly low in methanol cross-over. Even though Nafion is excellent in ionic conductivity and film quality, the Nafion-based DMFCs aroused a detrimental problem that even at low concentration and feed rate methanol rapidly transports over to cathode and then generates mixed potential and undesirable heat at cathode. This drawback leads to decrease not only in the fuel efficiency but also in the entire cell performance.[2] Many researches have been conducted to solve the methanol cross-over problem by enhancing activity of metallic oxidation catalyst,[3] optimization of electrodes,[4,5] carefully controlling fuel feed conditions,[6] and/or replacing Nafion with other PEM.[7–9] Among them, aromatic polymers have been suggested as new PEM materials because of their superiority in lowering methanol cross-over due to their inherently low compatibility with methanol and rigid backbone structures.[10–16] In particular, poly(ether sulfone)s (PES)s have been an ideal candidate because they are outstanding in film formation with mechanical strength for membranes as engineering polymers.[11,12,17–19] However, if the sulfonate group content of co-PESs was increased to higher than 50 mol %, their ionic character and water uptake tremendously increase to make them so brittle that no films exhibiting sufficient flexibility and toughness could be cast.

---

[1] Polymer Research Institute/Center for Advanced Functional Polymers, Department of Material Science and Engineering, Pohang University of Science and Technology (POSTECH)

[2] Energy and Materials Research Lab, Samsung Advanced Institute of Technology (SAIT), Yongin
E-mail: hkkim@sait.samsung.co.kr

Particularly the co-PES containing higher than 70 mol % of suflonate group unit was known to be completely soluble in water and no films could be obtained at all.[19]

In this work, we report synthesis of crosslinked sulfonated polysulfone-based PEMs with excellent methanol impermeability and good proton conductivity with high sulfonated contents of 70%. Using a simple but well-defined synthetic route illustrated in Scheme 1, allyl-terminated telechelic sulfonated sulfone oligomers were easily synthesized and transformed to membranes by thermal crosslinking.[20] Resulting films gave unprecedented reduction in methanol cross-over (less than 3% of Nafion-based PEMs) and high ionic conductivity (~80% of Nafion-based PEMs).

Experiments and Results

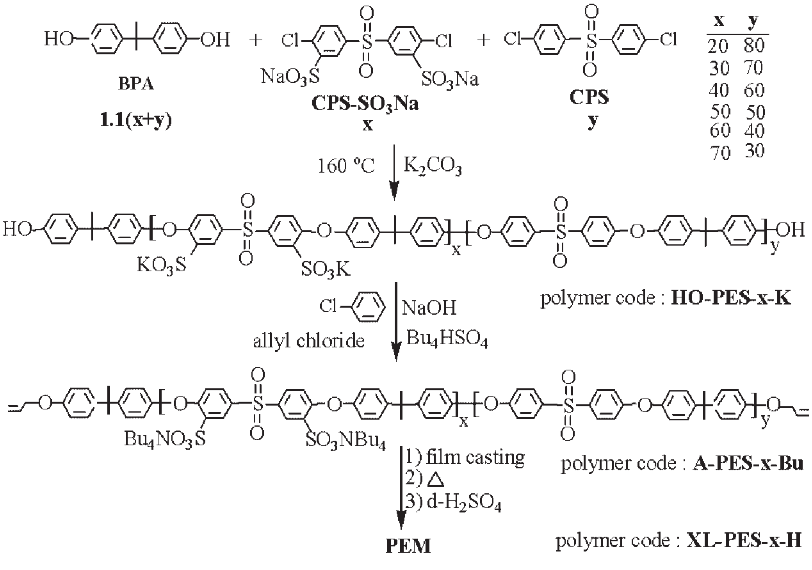
Materials

N,N-Dimethylacetamide (DMAc), dimethylsulfoxide (DMSO), N-methyl-2-pyrrolidone (NMP), toluene, and chlorobenzene were distilled after drying over P_2O_5. Potassuim carbonate, fuming sulfuric acid (30%), isopropanol, tetrabutylammonium hydrogen sulfate (TBAHS) and allyl chloride were purchased from Aldrich and used as received. Bisphenol A (BPA) and 4,4′-dichlorodiphenyl sulfone (CPS) were purified by recrystallization from toluene and methanol, respectively. Sodium CPS-3,3′-disulfonate (CPS-SO_3Na) used was prepared and purified in-house from CPS according to the literature,[12] kept over P_2O_5 and thoroughly dried before use. All the other solvents and chemicals were used without further purification unless otherwise described.

^{1}H-NMR spectra were obtained from a 300 MHz Bruker Fourier Transform DPX AM 300 spectrometer at room temperature. Thermal analyses of the polymers were conducted using DSC-7 and TGA-7 from Perkin-Elmer Seires under nitrogen at a scan rate of 10 °C/min.

Synthesis of Hydroxy-Terminated Cooligo-PESs (HO-PES-x-K)

Into a 250 mL round-bottomed flask equipped with a Dean-Stak trap, a magnetic stirrer, a nitrogen inlet and a reflux condenser were dissolved 5.016 g corresponding to 1.1(x+y) mmol BPA (For x and y see Scheme 1), 12.144 g corresponding to



Scheme 1.

Preparation of proton exchange membranes based on cross-linked sulfonated poly(ether sulfone)s.

4.4(x+y) mmol K_2CO_3, x mmol CPS-SO_3Na and y mmol CPS with 60 mL DMAc and 20 mL toluene under nitrogen flow at room temperature. The reactants were heated to 170 °C for 4 h for azeotropic removal of water followed by toluene and further stirred at 160 °C for 72 h under nitrogen atmosphere until no drop of water was detected in the Dean-Stark trap. During this time the reaction mixture turned to light brown color. At end of polymerization the flask contents were cooled to room temperature and poured into large excess of isopropanol. The precipitates formed were filtered and dried in vacuum at 70 °C for 3 h. The dried products were washed and filtered twice, dired in vacuum over 12 h. As a representative example of our seven samples, the results of HO-PES-50-K are summarized and its ^{1}H-NMR spectrum is reproduced in Figure 1. All these characterization data show that the chemical structure of HO-PES-50-K is well coincident with that expected.

In Table 1 it is seen that HO-PES-x-K's have all 8 to 10 degrees of polymerization. These values are only half the 21 degrees of polymerization to be theoretically calculated by the Carothers equation for polycondensation of a monomer in 10 mol % excess to 100% conversion. In this work the temperature of polymerization aiming at attaining about 10 degrees of polymerization was intentionally kept 30 to 40 °C lower (at 160 °C) than that known for polymerization (at 190 to 200 °C) to obtain high molecular weight PESs. Therefore, as shown in Table 1, our polymerizations for 72 h were ceased at the yields that were 10 to 20% lower than quantitative. In Table 1 it is also to see that the CPS-SO_3K contents in cooligomers are fairly well coincident with the CPS-SO_3Na concentration fed in comonomer mixture.

Synthesis of Allyl-Terminated Cooligo-PESs (A-PES-x-Bu)

In a 100 mL round-bottomed flask were dissolved in 50 mL chlorobenzene 5 g of a HO-PES-x-K, 2.2 equivalents of TBAH based on its SO_3K content and 10 equivalents allyl chloride based on its OH content, and then 5 mL 12.5 N NaOH were added and magnetically stirred for 48 h at room temperature. The reaction mixture was transferred to a separating funnel and the lower aqueous layer was separated and extracted twice with chlorobenzene and this extract was added to the upper organic layer. The product was obtained from large excess of hexane by dropping chlorobenzene solution. The precipitates were collected by filtration and dried in vacuum at

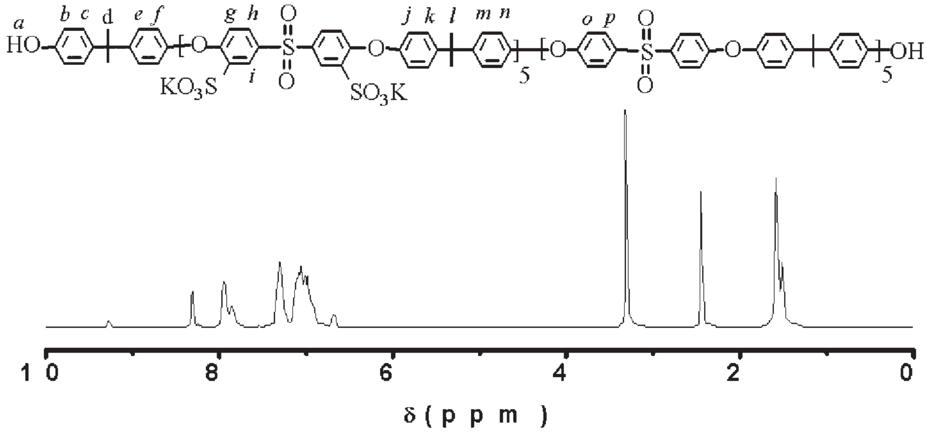


Figure 1.
^{1}H-NMR (DMSO-d_6, ppm) Spectrum of HO-PES-50-K : 1.58∼1.64(br m;d,l), 6.64(d;b;4H), 6.80∼7.10(br m;c,f,j,m,n,o), 7.10∼7.30(br m;e,g,k,m), 7.7∼8.0(br s;p,h), 8.29(s;i) 9.21(s;a).

Table 1.
Characterization of HO-PES-x-K's.

Polymer Code	x Fed mol %	Yield wt %	η_{inh}[a] dL/g	DP[b]	MW[c]	x-K[d] mol %
HO-PES-20-K	20	86	0.17	9.6	4,855	19
HO-PES-30-K	30	87	0.16	9.3	4,868	27
HO-PES-40-K	40	90	0.21	9.6	5,248	39
HO-PES-50-K	50	84	0.23	9.1	5,123	46
HO-PES-60-K	60	82	0.28	8.1	4,715	54
HO-PES-70-K	70	81	0.45	9.8	5,882	65

[a] Inherent viscosity measured from 0.5 g/dL NMP Solutions at 25 °C.
[b] Degree of polymerization.
[c] Molecular weight.
[d] CPS-SO_3K unit content in cooligomers.

50 °C. As a representative example of our seven samples, the results of A-PES-50-K are summarized and its ^{1}H-NMR spectrum is reproduced in Figure 2. In principle, if the analysis is accurate enough, the degrees of polymerization and SO_3NBu_4 group contents of A-PES-x-Bu's must be identical with those and SO_3K contents of HO-PES-x-K's, respectively, since the end-allylation and cation exchange reactions must be irrelevant to any change in their colligative values. When the ionic group contents are compared, they are very well coincident with each other. But when the degrees of polymerization are compared, those of A-PES-x-Bu's are roughly two degrees higher than those of HO-PES-x-K's. from the limitation of ^{1}H-NMR peak areas measurement.

The CPS-SO_3K unit contents were measured in mol % from $100 \times 2A_i/(2A_i + A_p)$ and the degrees of polymerization from $100 \times (A_d + A_l - 6)/6$, where A_i, A_p, A_d and A_l are areas of i, p, d and l peaks of Figure 1, respectively.

Membrane Fabrication and Characterization

The A-PES-x-Bu's were cast into films from 3 wt/v % solutions in DMSO onto the glass plates. In a vacuum oven, the plates were heated under nitrogen flow successively at

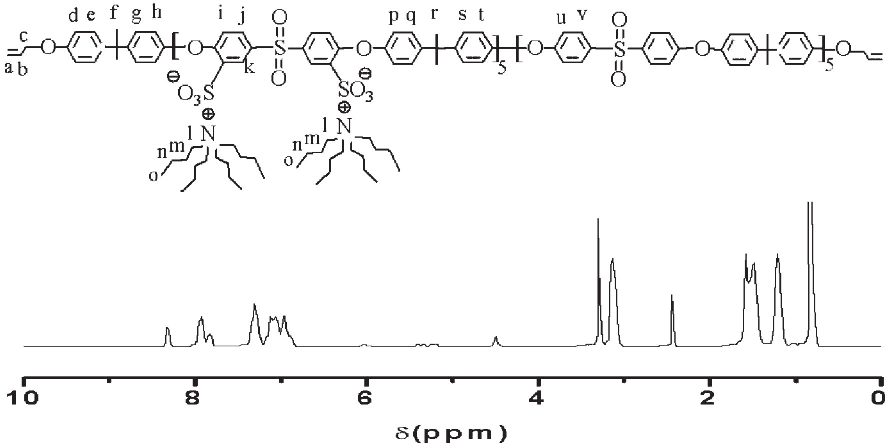


Figure 2.
^{1}H-NMR (DMSO-d_6, ppm) Spectrum of A-PES-50-Bu : 0.88∼0.93(t;o), 1.2∼1.32(m;n), 1.56∼1.62(br m;f,m,r), 3.13∼3.19(t;l), 4.50(br s;c), 5.19∼5.38(dd;a), 5.93∼6.06(br s;b), 6.83∼7.05(br m;d,h,p,t,u), 7.26(br s;e,g,i,q,s), 7.76∼7.88(br m;j,v), 8.28(br s;k).

80 °C for 12 h, at 120 °C for 2 h, at 160 °C for 2 h, and finally at 200 °C for 4 h. The PEMs containing SO_3H groups were fabricated by acidifying the thermally cured A-PES-x-Bu films with two methods; (a) 5 wt% sulfuric acid solution at 80 °C for 24 h, followed by thoroughly washing with distilled water and drying in vacuum at 100 °C for 12 h (b) 5 wt% H_2O_2 at 80 °C for 24 h, 5 wt% NaOH at 80 °C for 24 hr, 5 wt% sulfuric acid solution at 80 °C for 24 h followed by thoroughly washing with distilled water and drying in vacuum at 100 °C for 12 h.

To analyze if all the allyl end-groups were consumed by the thermal cross-linking, the films were investigated by solid-state NMR spectroscopy. In the NMR spectra, no allyl protons could be detected, but it should be mentioned that this might not be a safe evidence that all the allyl groups participated at the cross-linking because their absorptions were inherently very low and the spectra were very broad due to cross-linking. If the films are really cross-linked was also confirmed by sample weight decreases determined after soaking for 24 h in DMAc, NMP, DMSO, and 10% aqueous NaOH solutions at room temperature, 5% H_2O_2 and 5% H_2SO_4 solutions at 80 °C, respectively. All the samples were not soluble at all in the solvents and except in NaOH solution; the weight decreases were all less than 3%.

Properties as a Proton Exchange Membrane

Ionic conductivity of membranes was measured by four point probe method by using an ac impedance analyzer (Solartron 1260, UK) at room temperature with fully humidified condition.[21] Water uptake (W_{H_2O}) of the PEMs was determined in weight % by immersing them into pure water for 24 h at room temperature, rapidly wiping off the water present on the surface with porous paper, and weighing the swollen PEMs until weight of the PEMs do not change. $\%W_{H_2O}$ was calculated from 100(Ww-Wd)/Wd, where Ww is weight of wet PEM and Wd is that of dried PEM. Methanol cross-over of the PEMs was measured using a diffusion cell with 3M methanol and pure water by using a digital refractometer at room temperature.

Discussion

In our three step process, hydroxyl-terminated co-PESs (OH-PES-x-K) were first prepared by copolymerizing comonomer mixtures of x mol CPS-SO_3Na and y mol CPS with 1.1 (x+y) mol of BPA with varying x:y ratio from 20:80 to 70:30 at 160 °C in DMAc for 72 h in the presence of K_2CO_3. The low molecularity of HO-PES-x-K's adjusted by using Carothers equation enabled us quantitative determination of polymer chain length ($\sim$10 degrees of polymerization) and CPS-SO_3K unit contents using relative ^{1}H-NMR absorption peak areas (Table 1). The hydroxyl-terminated cooligomers were end-capped with allyl chloride under phase transfer-catalyzed reaction in the presence of 10 mol % excess of tetrabutylammonium hydrogen sulfate. This reaction was designed to allylate terminal hydroxyl groups and to replace simultaneously all inorganic SO_3K groups with organic SO_3NBu_4 for a purpose described in the later. The dilute allyl-terminated oligomers, A-PES-x-Bu's, solutions in DMSO were solvent-cast and thermally crosslinked, followed by exchange of SO_3NBu_4 groups in resulting films to SO_3H by acidification treatment. Final membranes were insoluble in organic solvents such as DMAc, DMSO and N-methyl-2-pyrrolidone, and no allyl protons were observed in NMR spectra, showing successful network structuring. In our approach, the transformation of strongly ionic alkali metal cation into organic NBu_4 cation reduced ionic character so drastically that any samples containing up to 70 mol% SO_3NBu_4 group produced tough films, otherwise too brittle or no films were obtained. Distinct glass transitions appeared over 150 °C after ion conversion via acidification of cured membranes and kept increasing with SO_3H contents up to 231 °C presumably by interchain hydrogen

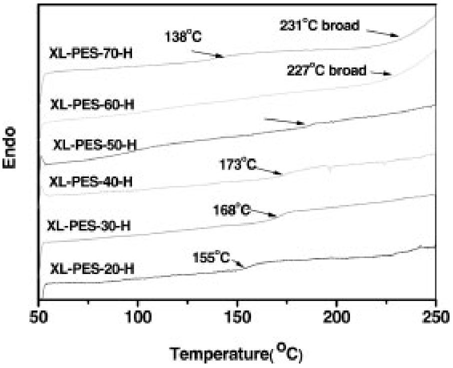


Figure 3.
DSC thermograms of XL-PES-x-H's.

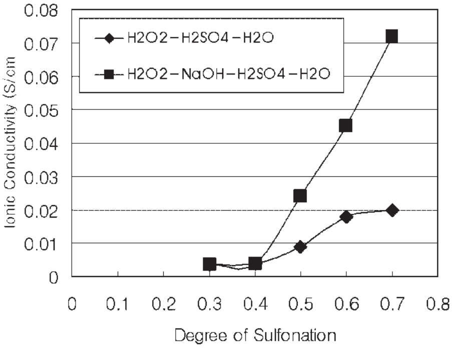


Figure 4.
Ionic conductivities with degree of sulfonation.

bondings. The membranes were also thermally stable up to 270 °C in nitrogen atmosphere as shown as in Figure 3.

Water content per ionic group calculated by measuring equilibrium water up-takes of membranes is a good indicator for the usefulness of the membranes as PEMs. It is interesting to see in Table 1 that water up-takes per ionic group of crosslinked membranes tremendously increase with sulfonic acid content while films before crosslinking and acidification remain practically constant. These results signify that the hydrophobic organic tetrabuylammonium groups make the films repel water molecules regardless of ionic group portion and enable us to cast good-quality films with over 60 mol% ionic groups.[11] As a result, membranes with high water content per ionic groups could be fabricated by acidification of crosslinked cast films.

Ionic conductivity of membranes increased with the degree of sulfonation as expected, but presented different values with varying acidification routes as shown in Figure 4. In the first pathway of successive treatments in 5 wt% H_2O_2, 5 wt% H_2SO_4, and deionized water, XL-PES-(50, 60, and 70)-Hs still showed low ionic conductivity even though their sulfonation degrees were over 50%. In contrast to this, the second route of 5 wt% H_2O_2, 5 wt% NaOH, 5 wt% H_2SO_4, and deionized water drastically increased the conductivity as high as 0.07 S/cm. These results suggest that ionic clusters in membranes were not thoroughly formed, so bulky tetrabutyl ammonium could not be readily converted to proton in the first way, and that the swelling of outer membrane by first converting tetrabutyl ammonium to sodium cation in the second path facilitated subsequent cation exchange deep into bulk film. These network structures of the rigid rod polymer has percolation threshold of 40~50% sulfonation degree in ionic conductivity. Many researchers have reported that percolation threshold for ionic conductivity or water swelling is shown around 35~50% of sulfonation in kinds of hydrocarbon based rigid rod polymers.[22] Higher glass transition temperature and lower acidity in aromatic sulfonic acids in XL-PES-x-H than perfluorinated PEM explains higher loading in IEC for comparable ionic conductivity.[23,24] Non-existence of ionic clusters during membrane preparation also means that sulfonate groups are evenly distributed over bulk membrane. Even after the ionic groups are exchanged to highly dissociable sulfonic acid form, crosslinked membrane structure does not allow bigger ionic cluster formation which could otherwise have happened by rearrangement of polymer chains.

Methanol permeabilities of XL-PES-50-H, XL-PES-60-H, and XL-PES-70-H membranes acidified via the second route were below 5×10^{-8} cm^2/sec; they were just 1.5, 2.9, and 2.6% of that of Nafion 112, respectively, and one order less than those reported for rigid rod polymer membranes.[11,22] The reason of extremely low methanol permeability of our membranes while maintaining high proton conductivity can also be attributed to the homogeneous distribution of sulfonic acid groups which will consequently minimize channel formation through which methanol is transported along with proton and water. The inherently properties of sulfonated poly(arylene sulfone) in lowering methanol cross-over were highly improved by in situ crosslinking with the thermally reactive ally terminated sulfonated oligosulfone. The proposed crosslinked PEM showed much lower methanol cross-over than reported PEMs with high sulfonation degree of 70%.

Conclusion

In conclusion, thermally reactive cooligomers were easily synthesized and fabricated for getting polymer electrolyte membrane followed by thermal cross-linking. Crosslinked membrane with 70% of sulfonation group showed 0.07 Scm^{-1} of ionic conductivity and $5.5 * 10^{(-8)}$ cm^2/s of methanol cross-over. Those values correspond to a methanol permeability over 95% lower than Nafion membrane while ionic conductivity is comparable (~80%) to that of Nafion membranes. Thermally reactive cooligomer with higher ionic groups made it possible that ionic groups were distributed homogeneously in PEM and insoluble despite of high IEC. It indicates that ionic conductivity was increased with sulfonation degree but methanol cross-over was not increased with high IEC. Crosslinked network structure of our membrane by thermal cross-linking of allyl oligomers is the most important technological feature which achieved high ionic conductivity and low methanol cross-over for DMFC applications.

[1] R. Dillon, S. Srinivasan, A. S. Arico, V. Antonucci, *J. Power Sources* **2004**, 111.

[2] K. Scott, W. M. Taama, P. Argyropoulos, K. Sundmacher, *J. Power Sources* **1999**, *83*, 204.

[3] W. Chrzanowski, A. Wieckowski, *Langmuir* **1998**, *14*, 1967.

[4] J. H. Kim, H. Y. Ha, I. H. Oh, S. A. Hong, H. I. Lee, *Journal of Power Sources* **2004**, *135*, 29–35.

[5] X. Ren, J. J. Becerra, R. S. Hirsch, S. Gottesfeld, F. W. Kovacs, K. J. Shufon, Direct Oxidation Fuel Cell Operating with Direct feed of Concentrated Fuel under passive water management, in: vol US2004/0209136A1, USA, **2004**.

[6] H. Kim, C. Lim, H. Chang, in: *Electrochemical Society*, Washington, DC, USA **2001**.

[7] E. Reddington, A. Sapienza, B. Gurau, R. Viswanathan, S. Sarangapani, E. S. Smotkin, T. E. Mallouk, *Science* **1998**, *280*, 1735.

[8] M. Watanabe, S. Saegusa, P. Stonehart, *J. Electroanal. Chem.* **1989**, *271*, 213.

[9] B. Smitha, S. Sridhar, A. A. Khan, *Macromolecules* **2004**, *37*, 2233–2239.

[10] M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* **2000**, *25*, 1463.

[11] M. A. Hickner, H. Ghassemi, Y. S. Kim, B. R. Einsla, J. E. McGrath, *Chem. Rev.* **2004**, *104*, 4587–4612.

[12] M. Ueda, H. Toyota, T. Ochi, J. Sugiyama, K. Yonetake, T. Masuko, T. Teramoto, *J. Polym. Sci., Polym. Chem. Ed.* **1993**, *31*, 853.

[13] C. Genies, M. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, *Polymer* **2001**, *42*, 359.

[14] B. Kruczek, T. Matsuura, *J. Membr. Sci.* **1998**, *148*, 263.

[15] G. Xiao, G. Sun, D. Yan, P. Zhu, P. Tao, *Polymer* **2002**, *43*, 5335.

[16] M. B. Gieselman, J. R. Reynolds, *Macromolecules* **1992**, *25*, 4832.

[17] R. B. Seymour, G. S. Kirshenbaum, *High Performance Polymers: Their Origin and Development*, Elsevier, 1989, p. 149.

[18] F. Wang, M. Hickner, Y. S. Kim, T. A. Zawodzinski, J. E. McGrath, *J. Mem. Sci.* **2002**, *197*, 231.

[19] W. L. Harrison, F. Wang, J. B. Mecham, V. Bhanu, M. Hill, Y. S. Kim, J. E. McGrath, *J. Polym. Sci., Polym. Chem. Ed.* **2003**, *41*, 2264.

[20] C. E. Schildknecht, *Allyl Compounds and Their Polymers*, Wiley-Interscience, **1973**.

[21] C. H. Rhee, H. Kim, H. Chang, J. S. Lee, *Chem. Mater.* **2005**, *17*, 1691–1697

[22] M. J. Summer, W. L. Harrison, R. M. Weyers, Y. S. Kim, J. E. McGrath, J. S. Riffle, A. Brink, M. H. Brink, *J. of Membrane Science* **2004**, *239*, 199–211.

[23] P. Xing, G. Robertson, M. D. Guiver, S. D. Mikhailenko, S. Kaliaguine, *J. Poly. Sci.: Part A.: Poly. Chem.* **2004**, *42*, 2866–2876.

[24] P. Xing, G. P. Robertson, M. D. Guiver, S. D. Mikhalilenko, S. Kaliaguine, *Macromolecules* **2004**, *37*, 7960–7967.