



Short communication

Preparation of new proton exchange membrane based on self-assembly of Poly(styrene-co-styrene sulfonic acid)-*b*-poly(methyl methacrylate)/Poly(vinylidene fluoride) blend

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ABSTRACT

Amphiphilic block copolymers are synthesized by sulfonation of poly(styrene-*b*-methyl methacrylate) (PS-*b*-PMMA) using acetyl sulfate, and are blended with poly(vinylidene fluoride) (PVDF) to prepare a new proton exchange membrane, in which PMMA is miscible with PVDF. The morphology and the transport properties of the membranes are investigated as functions of the degree of sulfonation as well as the blend ratio. Notable transition of phase-separated morphology is observed as the PVDF content of the blend is increased. Both the proton conductivity and the ion-exchange capacity (IEC) of the membrane increase with increasing the degree of sulfonation of PS-*b*-PMMA, and they are also enhanced as the phase-separated domains of blend membrane are well-ordered. Unlike the Nafion membrane, the proton conductivity of the blend membrane increases up to 90 °C, indicating the blend membrane shows better thermal stability than the Nafion membrane.

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1. Introduction

The proton exchange membrane fuel cell (PEMFC) has a lower operating temperature and a higher power density than other types of fuel cell [1]. The proton exchange membrane (PEM), is one of the critical components determining the efficiency of PEMFC. The primary requirements for proton exchange membranes are a high proton conductivity, a high chemical, mechanical and thermal stability, and low fuel and oxygen permeability [2].

Perfluorinated ionomer membranes such as Nafion® (Dupont) have been widely used as polymer electrolyte membranes of PEMFCs, because of their high proton conductivities due to the microphase-separated morphology [3]. These membranes are very expensive to produce, however and limited in the temperature range at which PEMFCs are operated. Various researchers have investigated the development of alternative proton exchange membranes such as sulfonated poly(ether ether ketone) [4], sulfonated poly(arylene ether sulfone) [5,6] and others [7,8]. These membranes have relatively low proton conductivity, however, due to imperfect microphase-separated morphology [9].

Recently, block copolymers have attracted much attention. They are microphase-separated on a nanometer scale due to

the thermodynamic incompatibility among chemically dissimilar blocks and thus form a variety of self-assembled nanostructures such as lamellar, spheres, cylinders and bicontinuous gyroids [10]. Block copolymer ionomers containing sulfonated polystyrene blocks have been prepared and used for PEMs, including sulfonated poly(styrene-*b*-[ethylene-co-butylene]-*b*-styrene) [11–17], sulfonated poly(styrene-*b*-isobutylene-*b*-styrene) [18,19], and sulfonated poly([vinylidene fluoride-co-hexafluoropropylene]-*b*-styrene) [20]. Several reports on sulfonated multiblock copolymers such as sulfonated poly(arylene ether sulfone-*b*-vinylidene fluoride) and sulfonated poly(arylene ether sulfone-*b*-butadiene) have also been investigated [21,22]. The syntheses of such block copolymers are not simple and thus the production costs are greater than expected. Moreover, microphase separation of the block copolymers containing rigid aromatic moiety is not satisfactory to form a proton conducting channel.

In this study, a new proton exchange membrane, which is durable, low in cost and high in proton conductivity, is prepared. For this purpose, poly(styrene-co-styrene sulfonic acid)-*b*-poly(methyl methacrylate) [P(S-co-SSA)-*b*-PMMA] is first synthesized and then blended with poly(vinylidene fluoride) (PVDF) which imparts good thermal and chemical stability and has a favourable interaction with the poly(methyl methacrylate) (PMMA) block [23]. This blend is expected to self-assemble into a microphase-separated structure on a nanometer scale. The morphology and the proton conductivity of the membrane are examined as functions of the sulfonation

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level of the polystyrene block as well as the blend ratio. Based on these results, an attempt is made to establish a relationship between the microstructure of membrane and the proton conductivity.

2. Experimental

2.1. Materials

Symmetric polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) ($M_w \sim 130,000$; 50 wt.% styrene; Polymer Source) was used as-received. PVDF ($M_w \sim 80,000$) was provided by Solvay Korea Co. Acetic anhydride (99.5%, Aldrich), H_2SO_4 (95%, Aldrich), 1,2-dichloroethane (DCE; 99%; Aldrich), N,N-dimethylacetamide (DMAc; 99%, Aldrich), methanol (Daejung) were used as-received.

2.2. Sulfonation of PS-*b*-PMMA

Poly(styrene-*co*-styrene sulfonic acid)-*b*-poly(methyl methacrylate) was prepared by sulfonation of PS-*b*-PMMA using acetyl sulfate [12,24]. A solution of 2.5 mL of acetic anhydride in 7.5 mL of DCE was cooled below 0 °C, to which 0.75 mL of sulfuric acid was added. A 3–5 wt.% solution of PS-*b*-PMMA in DCE was heated to 55 °C, and acetyl sulfate solution was added and stirred for 3–5 h at 55 °C. Finally, methanol was added to terminate the sulfonation reaction. The product was isolated by precipitation in boiling water. The precipitate was washed with distilled water until the pH of residual water became neutral, and then dried for 3 days at 30 °C under vacuum.

2.3. Preparation of membranes

P(S-*co*-SSA)-*b*-PMMA/PVDF blends were prepared by means of the solvent-casting method. Mixtures of P(S-*co*-SSA)-*b*-PMMA and PVDF with a predetermined blend ratio (listed in Table 1) were dissolved in DMAc to yield 10 wt.% solutions. The polymer solution was cast on a glass slide to form a liquid membrane, and then the solvent was slowly evaporated for 7 days at room temperature and dried for 3 days at 60 °C under vacuum to remove the residual solvent. The film thickness of the P(S-*co*-SSA)-*b*-PMMA/PVDF blend membranes was 50–80 μm. The membranes were annealed for 3 days at 180 °C under vacuum in order to develop self-assembled microstructure.

2.4. Characterization

Sulfonation of the block copolymer was characterized by means of Fourier Transform Infrared (FT-IR) spectrometry (Perkin Elmer Spectrum 2000), and the degree of sulfonation was determined by elemental analysis.

Thermal stability of the membrane was measured with a thermo-gravimetric analyzer (TGA) (TA Instruments model 2920)

Table 1
Preparation of membranes with different sulfonation level and blend ratio.

Sample designation	Sulfonation level ^a	Blend ration of block copolymer to PVDF	Wt fraction of (PVDF + PMMA) in blend
S10F00	10	100/0	0.5
S10F22	10	78/22	0.6
S10F41	10	59/41	0.7
S24F00	24	100/0	0.5
S24F22	24	78/22	0.6
S24F41	24	59/41	0.7
S39F00	39	100/0	0.5
S39F22	39	78/22	0.6
S39F41	39	59/41	0.7

^a By elemental analysis.

at heating rate of 10 °C min⁻¹ under nitrogen. The samples were thoroughly dried for 2 days at 30 °C under vacuum prior to TGA measurement.

Water adsorption by the membrane was determined by water uptake measurement. The membrane was first weighed under a wet condition after being equilibrated in distilled water for 2 days at room temperature, and then the membrane was weighed under a dry condition after being desiccated for 2 days at 30 °C under vacuum. The water uptake of membrane was calculated as

$$\text{water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100,$$

where W_{wet} is the weight of swelled membrane and W_{dry} is the weight of dried membrane.

The ion-exchange capacity (IEC) of membrane was measured by elemental analysis and titration. The membranes were equilibrated in 2.0 M NaCl solution for 2 days and then the solution was titrated with 0.025 M NaOH solution using phenolphthalein as an indicator. After titration, the membranes were washed with distilled water and dried for 2 days at 30 °C under vacuum. The IEC was calculated according to

$$\text{IEC} = \frac{V_{\text{NaOH}} M_{\text{NaOH}}}{W_{\text{dry}}},$$

where V_{NaOH} is the volume of NaOH solution and M_{NaOH} is the molar concentration.

The impedance of the membrane was measured by an impedance analyzer (Zahner IM-6) using a four-point probe ion conductivity cell. The proton conductivity was then calculated as

$$\sigma = \frac{L}{Rwd},$$

where σ is the proton conductivity, L is the length between the electrodes, R is the impedance of the membrane, w is the width of membrane, and d is the thickness of membrane. The microphase-separated morphology of membrane was observed using transmission electron microscopy (TEM). The membrane was sliced into thin films with a thickness of 70 nm using an ultramicrotome (Leica ultracut UCT) with a diamond knife, and the sliced

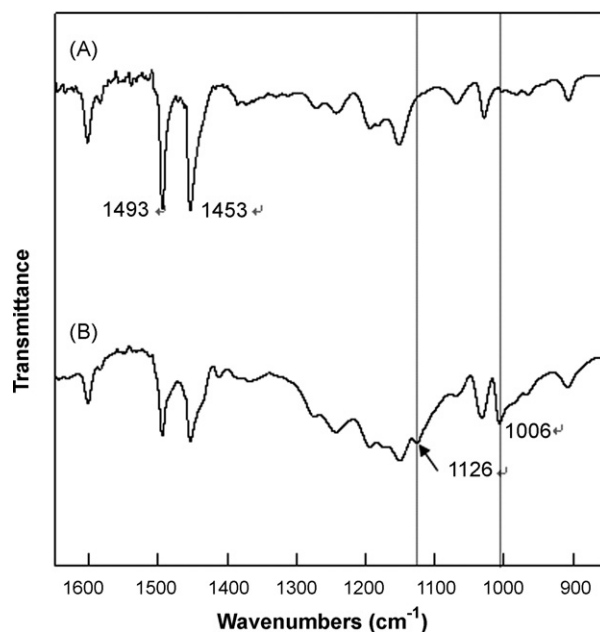


Fig. 1. FT-IR spectra of (A) PS-*b*-PMMA and (B) sulfonated block copolymer P(S-*co*-SSA)-*b*-PMMA.

Table 2
Proton conductivity, water uptake and IEC values of membranes.

Sample designation	Water uptake (wt.%)	Calculated IEC ^a (mmol g ⁻¹)	Measured IEC ^b (mmol g ⁻¹)	Proton conductivity ^c (S cm ⁻¹)
S10F00	14	0.47	0.42	3.9×10^{-3}
S10F22	8	0.37	0.30	2.0×10^{-3}
S10F41	2	0.28	0.16	6.1×10^{-4}
S24F00	34	1.15	1.09	1.1×10^{-2}
S24F22	24	0.90	0.80	8.3×10^{-3}
S24F41	15	0.69	0.51	4.2×10^{-3}
S39F00	51	1.90	1.87	3.2×10^{-2}
S39F22	43	1.48	1.41	2.5×10^{-2}
S39F41	22	1.12	0.87	7.0×10^{-3}

^a By elemental analysis.

^b By titration.

^c Measured at room temperature under 100% relative humidity.

film was mounted on a 400 mesh copper grid. The samples were exposed to RuO₄ solution for 15–20 min to stain the P(S-co-SSA) block, and the phase morphology of samples was observed by TEM (JEOL JEM 2000 EX II) at 200 kV. The RuO₄ staining solution was prepared by adding 0.01 g RuO₂ in 1.5 mL NaIO₄ solution [25].

3. Results and discussion

The PS block in PS-*b*-PMMA is sulfonated and the resulting sulfonated PS block is expected to form a proton conducting channel.

Fig. 1 compares the FT-IR spectra of PS-*b*-PMMA before and after sulfonation. The spectrum of the block copolymer after sulfonation exhibits two new peaks at 1026 and 1006 cm⁻¹ that correspond to symmetric stretching of the sulfonate group and in-plane bending of the para-substituted phenyl ring of polystyrene [26], respectively. The intensities of the two peaks at 1493 and 1453 cm⁻¹, which correspond to stretching vibrations of unsubstituted phenyl ring of polystyrene are significantly reduced and thus indicate that some of the polystyrene units are successfully sulfonated. Determination of the degree of sulfonation elemental analysis, reveals that three sam-

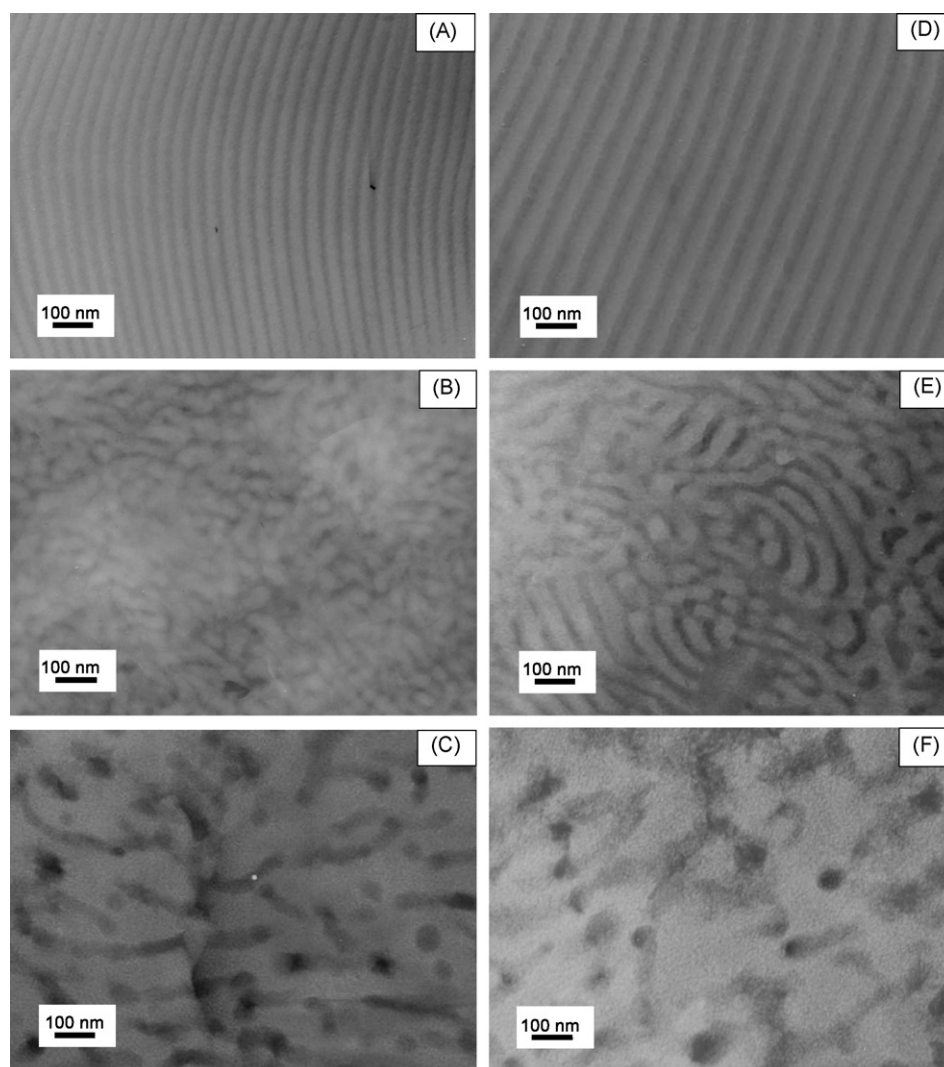


Fig. 2. TEM images of membranes with different degree of sulfonation and blend ratio: (A) S24F00; (B) S24F22; (C) S24F41; (D) S39F00; (E) S39F22; (F) S39F41.

ples with different degrees of sulfonation are prepared depending on the reaction time, as listed in Table 1.

The IEC value of the membrane was measured by an element analysis and titration. A comparison of the experimental and calculated IEC values shows that the former are always lower than the latter and that the difference between them becomes larger as the PVDF content in the blend is increased. This is probably because the microphase separation of membrane becomes poorer as the PVDF content in the blend is increased and as a result poorly microphase-separated morphology induces more readily the formation of dead-end ion channels.

The weights of hydrated and dried membranes reveal that the water uptake is proportional to the amount of sulfonic acid groups in the membrane, as listed in Table 2.

The morphology of the membrane is very important for proton conductivity. The morphology of the membrane is observed by TEM, as shown in Fig. 2, where dark and bright areas in the images represent hydrophilic and hydrophobic domains, respectively, when the membranes are stained with RuO₄. It should be noted that the hydrophobic region consists of the PMMA block and PVDF, whereas the hydrophilic region is sulfonated polystyrene block. When Fig. 2(A)–(C) are compared with Fig. 2(D)–(F), respectively, it is realized that the hydrophilic domains become larger as the degree of sulfonation is increased. This is probably because more sulfonic acid groups in the hydrophilic domain are aggregated with each other as the degree of sulfonation increases. The data in Fig. 2 also show that the morphology of the membranes changes from a well-ordered lamellar structure (S24F00 and S39F00, see Table 1 for sample code) through a less organized worm-like structure (S24F22 and S39F22) to a disordered form (S24F41 and S39F41) as the PVDF content in the blend is increased. This is easily explained by the fact that crystallization of PVDF in the blend membrane may affect self-assembly of the block copolymer [27]. It should be mentioned here that PVDF is a crystalline polymer and therefore the crystallinity of PVDF in the blend increases with increasing PVDF content.

The proton conductivity of the membranes prepared in this study and Nafion[®] 117 were measured by means of a-c impedance spectroscopy at room temperature under a relative humidity of 100%, and the results are listed in Table 1. When the proton conductivity is plotted against IEC in Fig. 3, it is found that the values are in the range of 6.1×10^{-4} to 3.2×10^{-2} S cm⁻¹ and that the conductiv-

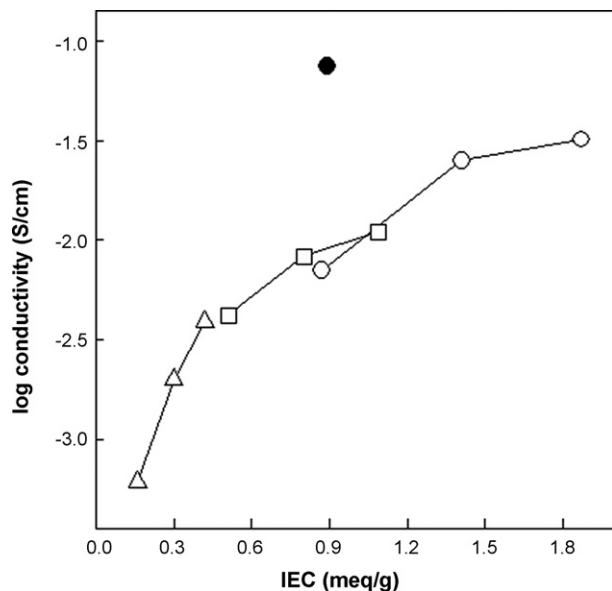


Fig. 3. Proton conductivity of membranes as function of IEC: degree of sulfonation 39% (○), 24% (□), 10% (△), and Nafion 117 (●).

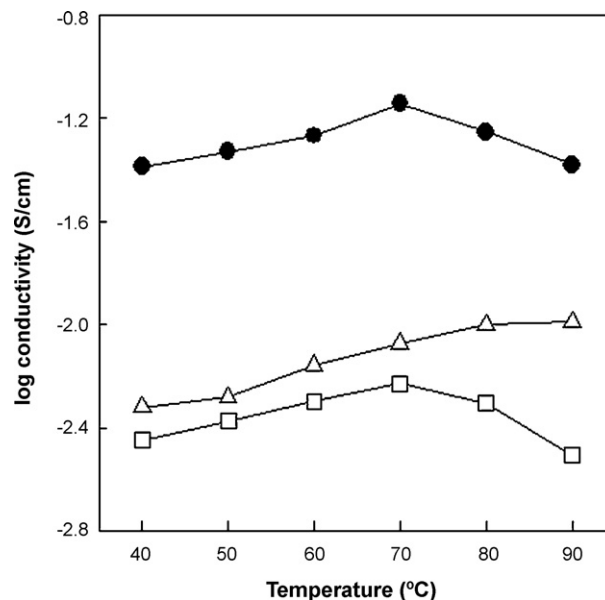


Fig. 4. Proton conductivity of membranes as function of temperature: S10F00 (□), S39F41 (△), and Nafion 117 (●) under constant humidity (60% RH).

ity increases with increase in the IEC value, which is proportional to the degree of sulfonation of the block copolymer. Comparison of the data in Fig. 2 with Table 2 shows that the proton conductivity is strongly dependent on the phase-separated morphological structure of the membrane. The S24F00 membrane has a higher proton conductivity than the S39F41 membrane, whereas the two membranes have a similar IEC value. This is primarily because the S24F00 membrane has a well-ordered microphase-separated structure compared with that of the S39F41 membrane, as shown in Fig. 2.

The temperature dependence of proton conductivity is shown in Fig. 4. The conductivity of both Nafion and the S10F00 membrane increases up to 70 °C and then decreases above 70 °C, whereas the conductivity of the blend membrane (S39F41) increases up to 90 °C. This enhancement of the thermal stability of the blend membrane is due to the good thermal stability of PVDF. The lower proton con-

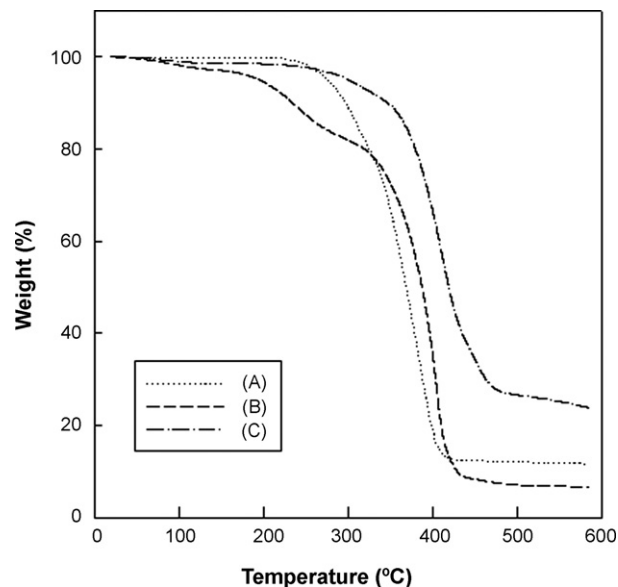


Fig. 5. TGA curves of (A) PS-*b*-PMMA, (B) P(S-co-SSA)-*b*-PMMA (S24F00) and (C) P(S-co-SSA)-*b*-PMMA/PVDF blend (S24F22).

ductivity of the block copolymer membranes compared with that of Nafion 117 may be attributed to the higher pK_a of the phenyl sulfonic acid group in P(S-co-SSA)-*b*-PMMA ($pK_a = -1$) versus that of the fluoroether sulfonic acid group in Nafion 117 ($pK_a = -6$) [9].

The thermal stability of membranes was investigated using TGA analysis. Three successive stages of weight loss are observed in the TGA of P(S-co-SSA)-*b*-PMMA, as shown in Fig. 5. This is significantly different from that of PS-*b*-PMMA, which shows only a single weight loss. The first weight loss of P(S-co-SSA)-*b*-PMMA occurs between 40 and 120 °C due to the removal of residual water, and the second weight loss at 170–220 °C is due to elimination of sulfonic acid groups. The decomposition of the block copolymer main chain starts at 330 °C. For the blend membrane P(S-co-SSA)-*b*-PMMA/PVDF, however, both the elimination temperature of sulfonic acid groups and the decomposition temperature of the block copolymer main chain increase due to the good thermal stability of PVDF [28].

4. Conclusions

In this study, a new proton exchange membrane is prepared by blending P(S-co-SSA)-*b*-PMMA and PVDF. The morphological structure of blend membranes is controlled by a blend ratio of diblock copolymer to PVDF. The proton conductivity, IEC, and water uptake of the membrane increase with the degree of sulfonation of the block copolymer and also depend on the blend ratio. It is also found that well-ordered microphase-separated membranes have better proton conductivity than membranes with randomly ordered morphology. Thus it is concluded that a well-ordered microstructure of the membrane is an important factor to optimize the performance of a proton exchange membrane in a PEMFC.

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References

- [1] M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* 25 (2000) 1463–1502.
- [2] B. Smitha, S. Sridhar, A.A. Khan, *J. Membr. Sci.* 259 (2005) 10–26.
- [3] C. Heitner-Wirguin, *J. Membr. Sci.* 120 (1996) 1–33.
- [4] P. Xing, G.P. Roberyson, M.D. Guiver, S.D. Mikhailenko, K. Wang, S. Kaliaguine, *J. Membr. Sci.* 229 (2004) 95–106.
- [5] B. Lafitte, L.E. Karlsson, P. Jannasch, *Macromol. Rapid Commun.* 23 (2002) 896–900.
- [6] M.D. Guiver, G.P. Robertson, *Macromolecules* 28 (1995) 294–301.
- [7] Y. Yin, Y. Suto, T. Sakabe, *Macromolecules* 39 (2006) 1189–1198.
- [8] B.R. Einsla, Y.S. Kim, M.A. Hickner, Y.T. Hong, M.L. Hill, B.S. Pivovar, J.E. McGrath, *J. Membr. Sci.* 255 (2005) 141–148.
- [9] K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29–39.
- [10] I.W. Hamley, *The Physics of Block Copolymers*, Oxford University Press, New York, 1998.
- [11] R.A. Weiss, A. Sen, L.A. Pottick, C.L. Willis, *Polymer* 32 (1991) 2785–2792.
- [12] R.A. Weiss, A. Sen, C.L. Willis, L.A. Pottick, *Polymer* 32 (1991) 1867–1874.
- [13] X. Lu, W.P. Steckle, R.A. Weiss, *Macromolecules* 26 (1993) 5876–5884.
- [14] J. Kim, B. Kim, B. Jung, *J. Membr. Sci.* 207 (2002) 129–137.
- [15] J. Kim, B. Kim, B. Jung, Y.S. Kang, H.Y. Ha, I.H. Oh, K.J. Ihn, *Macromol. Rapid Commun.* 23 (2002) 753–756.
- [16] J. Won, H.H. Park, Y.J. Kim, S.W. Choi, H.Y. Ha, I.H. Oh, H.S. Kim, Y.S. Kang, K.J. Ihn, *Macromolecules* 36 (2003) 3228–3234.
- [17] J. Won, S.W. Choi, Y.S. Kang, H.Y. Ha, I.H. Oh, K.T. Kim, W.H. Jo, *J. Membr. Sci.* 214 (2003) 245–257.
- [18] Y.A. Elabd, E. Napadensky, J.M. Sloan, D.M. Crawford, C.W. Walker, *J. Membr. Sci.* 217 (2003) 227–242.
- [19] Y.A. Elabd, E. Napadensky, C.W. Walker, K.I. Winey, *Macromolecules* 39 (2006) 399–407.
- [20] Z. Shi, S. Holdcroft, *Macromolecules* 38 (2005) 4193–4201.
- [21] Y. Yang, Z. Shi, S. Holdcroft, *Eur. Polym. J.* 40 (2004) 531–541.
- [22] X. Zhang, S. Liu, J. Yin, *J. Membr. Sci.* 275 (2006) 119–126.
- [23] A. Linares, J.L. Acosta, *J. Appl. Polym. Sci.* 67 (1998) 997–1004.
- [24] T.B. Norsten, M.D. Guiver, J. Murphy, T. Astill, T. Navessin, S. Holdcroft, B.L. Frankamp, V.M. Rotello, J. Ding, *Adv. Funct. Mater.* 16 (2006) 1814–1822.
- [25] B. Ohlsson, B. Tornell, *J. Appl. Polym. Sci.* 41 (1990) 1189–1196.
- [26] J.F. Ding, C. Chuy, S. Holdcroft, *Macromolecules* 35 (2002) 1348–1355.
- [27] J.K. Lee, J.S. Kim, H.J. Lim, K.H. Lee, S.M. Jo, T. Ougizawa, *Polymer* 47 (2006) 5420–5428.
- [28] N. Chen, L. Hong, *Polymer* 45 (2004) 2403–2411.