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Low-swelling proton-conducting copoly(aryl ether nitrile)s containing naphthalene structure with sulfonic acid groups *meta* to the ether linkage[☆]

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Abstract

Wholly aromatic poly(aryl ether ether nitrile)s containing naphthalene structure with sulfonic acid groups *meta* to ether linkage (*m*-SPAEEN), intended for fuel cells applications as proton conducting membrane materials, were prepared via nucleophilic substitution polycondensation reactions. The incorporation of rigid naphthalene structure with *meta*-sulfonic acid groups was with the intent of improving the aggregation of hydrophilic and hydrophobic domains and to increase the acidity and conductivities. *m*-SPAEEN copolymers were readily synthesized by potassium carbonate mediated nucleophilic polycondensation reactions of commercially available monomers: 2,6-difluorobenzonitrile (2,6-DFBN), 2,8-dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6), and 4,4′-biphenol (4,4′-BP) in dimethylsulfoxide (DMSO) at 160–170 °C. The sulfonic acid group content (SC), expressed as a number per repeat unit of polymer, ranged from 0 to 0.6 and was readily controlled by changing the feed ratio of 2,8-DHNS-6 to 2,6-DFBN. High thermal stability of *m*-SPAEEN copolymers was indicated by observed glass transition temperatures (T_gs) ranging from 223 to 335 °C in sodium salt form and from 230 to 260 °C in acid form (*m*-SPAEENH) and decomposition temperatures (T_d)s over 250 °C in acid form and over 350 °C in sodium form in both nitrogen and air. All *m*-SPAEENH copolymers exhibited reasonable flexibility and tensile strength in the range of 39–78 MPa, indicating they were mechanically stronger than Nafion®117, which had an approximate value of 10 MPa under the same test conditions. As expected, *m*-SPAEENH copolymers showed considerably reduced moisture absorption compared to previously prepared sulfonated hydroquinone based poly(aryl ether nitrile). *m*-SPAEENH copolymers also showed improved proton conductivities. Proton conductivity curves parallel to that of Nafion 117 were obtained with proton conductivity of 10^{-1} S/cm at equivalent ion exchange capacities (IEC) of 1.6 and 1.9, comparable to Nafion®117. The best compromise combining PEM mechanical strength, water swelling and proton conductivity, was achieved at SC of 0.5 and 0.6.

Keywords: Nucleophilic polycondensation; Poly(aryl ether ether nitrile)

1. Introduction

Proton exchange membrane fuel cells (PEMFC)s and direct methanol fuel cells (DMFC)s are receiving considerable attention as electrical power sources for vehicular transportation, distributed residences and institutions, and portable devices owing to their high efficiency and innocuous waste emission [1]. As one of the key components of the membrane electrode assembly (MEA), proton exchange membranes (PEM)s have to satisfy several rigorous requirements: (1) proton conductivity higher than 10^{-2} S/cm, (2) chemical and mechanical stability, (3) low permeability to fuel [2]. Perfluorosulfonic acid PEMs, such as DuPont's Nafion®, are typically used as the polymer electrolytes in PEMFCs because of their excellent chemical and mechanical stabilities as well as high proton conductivity. However, their disadvantages of high cost, low operation temperatures and high fuel permeability are stimulating an intensive search for alternative materials and numerous attempts have been made to prepare less expensive and more versatile polymer electrolytes.

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Poly(aryl ether)s, such as poly(aryl ether sulfone)s, poly(aryl ether ketone)s, poly(phenylene oxide) and poly(phenylene sulfide), have recently been attracting considerable attention in the polymer electrolyte fields due to the high proton conductivities of their protonic derivatives, which are readily available by simple polycondensations of readily prepared monomers or post modifications of commercially available high performance polymers [3–24]. It is believed that the hydrophobic backbone and the hydrophilic sulfonic acid groups nanophase separate into two domains in the presence of water. The hydrophobic domain provides the films with morphological stability in water by preventing films from over-swelling and the hydrophilic domain provides channels for transporting hydrated protons [2,25]. The selection of monomers have a profound influence on the structures of hydrophobic and hydrophilic units, which affect the aggregations of each domain and further affect the properties of resulting films. For example, Harrison [17] synthesized a series of sulfonic acid-containing poly(arylene ether sulfone)s from disodium 3,3′-disulfonate-4,4′-dichlorodiphenylsulfone (SDCDPS), 4,4′-dichlorodiphenylsulfone (DCDP) and four different bisphenols: 4,4′-bisphenol A, 4,4′-bisphenol F, 4,4′-biphenol and hydroquinone. It was found that the bisphenol structures influenced the properties of sulfonated copolymers such as solubility and water uptake. Copolymer containing relatively soft hydroquinone units did not favor hydrophobic aggregation and exhibited the highest water uptake, while more rigid bisphenol-6F improved the hydrophobicity and resulted in the lowest values for swelling.

Aromatic poly(aryl ether nitrile)s are a class of high performance thermoplastic polymers prepared by polycondensation of bisphenols and dihalobenzonitriles or dinitrobenzonitriles in dipolar solvents [26–40]. Their good mechanical properties, high chemical and thermal resistance, and strongly polar pendant nitrile groups, make poly(aryl ether nitrile)s good candidates for matrices in advanced composites in aerospace industries. It is also found that the introduction of nitrile groups into proton conductive sulfonated thermoplastics decreased their moisture absorption [41,42]. In addition, it is also believed that the presence of nitriles have the potential to promote adhesion of the polymers to heteropolyacids in composite membranes or to electrodes in the preparation of MEAs. Recently, poly(aryl ether nitrile)s containing sulfonic acid groups were prepared by our group from 2,6-difluorobenzonitrile (2,6-DFBN), potassium 2,5-dihydroxybenzenesulfonate (SHQ), and a third monomer 4,4′-biphenol or hydroquinone. They show lower water uptake than sulfonic acid containing poly(aryl ether ketone)s and poly(aryl ether sulfone)s at similar equivalent weight (EW) and ion exchange capacity (IEC) values, and proton conductivities close to or higher than that of Nafion117, reaching 10^{-1} S/cm. However, for poly(aryl ether nitrile)s with comparable conductivities to Nafion, the water swelling was still higher than that of Nafion, particularly in hot water. In the present study, a more rigid and hydrophobic naphthalene-based bisphenol containing sulfonic acid groups bonded meta to ether linkage was used instead of the more flexible and hydrophilic hydroquinone to prepare new poly(aryl ether nitrile)s. As far as we are aware, this is the first example of utilizing this inexpensive commercially available material 2,8-dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6) as a monomer in a polycondensation reaction. It was incorporated in anticipation of improving the films with in-water dimensional stability and mechanical properties. The sulfonic acid groups, which are not in a deactivated position, could potentially improve the proton conductivity and hydrolytic stability of the polymer chain. The thermal stability both in air and nitrogen, mechanical, swelling, and proton conducting properties were investigated.

2. Experimental part

2.1. Materials

2,8-Dihydroxynaphthalene-6-sulfonate sodium salt (2,8-DHNS-6) was purchased from Rintech, Inc. and recrystallized from deionized water. DMSO and 4,4′-biphenol were purchased from Aldrich and was vacuum distilled and purified by sublimation, respectively, before usage. All other chemicals (obtained from Aldrich) were reagent grade and used as received.

2.2. Copolymerization

Synthesis of the copolymers by nucleophilic substitution reactions was based on the procedure reported by McGrath [27]. In a typical reaction, 10 mmol 2,6-DFBN, 5 mmol 2,8-DHNS-6, 5 mmol 4,4′-biphenol, and 15 mmol K_2CO_3 were added into a three-neck equipped flask with a magnetic stirrer, a Dean–Stark trap, and an argon gas inlet. Then, 10 mL DMSO and 10 mL chlorobenzene were charged into the reaction flask under an argon atmosphere. The reaction mixture was heated to 130 °C. After dehydration and removal of chlorobenzene, the reaction temperature was increased to about 160–170 °C. When the solution viscosity had apparently increased, the mixture was cooled to 100 °C and coagulated into a large excess of ethanol or water with vigorous stirring. As an example, the resulting polymer was designated *m*-SPAEEN-50, where 50 refers to the 2,8-DHNS-6 content of aromatic phenol monomers. *m*-SPAEEN copolymers were washed thoroughly with water to remove salt.

2.3. Copolymer analysis and measurement

^{1}H NMR spectra were obtained on a Varian Unity Inova NMR spectrometer operating at a proton frequency of 399.95 MHz. Deuterated dimethylsulfoxide (DMSO-d_6) was the NMR solvent and tetramethylsilane (TMS) was used as the chemical shift reference (0 ppm). IR spectra were measured on a Nicolet 520 Fourier transform spectrometer with membrane film samples in a diamond cell.

A TA Instruments thermogravimetric analyzer (TGA) instrument model 2950 was used for measuring T_d. Polymer samples for TGA analysis were preheated to 150 °C at 10 °C/min in either nitrogen or air and held isothermally for

40 min for moisture removal. Samples were then heated from 90 to 750 °C at 10 °C/min for T_d measurement. A TA Instruments differential scanning calorimeter (DSC) model 2920 calibrated with tin at 231.93 °C and zinc at 419.53 °C was used for measuring T_g. Samples in sodium form for DSC analysis were initially heated rapidly at a rate of 10 °C/min under nitrogen atmosphere to 380 °C. When the DSC cell had cooled to around 50 °C, the samples were reheated at a rate of 10 °C/min to 430 °C. The procedure for samples in acid form was similar except that the end point of the initial heating was 250 °C.

Intrinsic viscosities were determined using an Ubbelohde viscometer for *N*,*N*-dimethylacetamide (DMAc) solutions of copolymer at 25 °C.

2.4. Preparation of membrane films

An amount of 1 g copolymer in the sodium salt form was dissolved in 20 mL of DMAc and filtered. The filtered solution was poured onto a leveled glass plate having a circular glass retaining wall and dried at about 40 °C under a constant purge of nitrogen for about one day. The acid form (*m*-SPAEENH) membrane films were obtained by immersing corresponding sodium form *m*-SPAEEN membrane films in 2 N H_2SO_4 for 24 h at room temperature, and then in deionized water for another 24 h during which time the water was changed several times. The thickness of all membrane films was in the range of 40–70 μm.

2.5. Water uptake content measurement and swelling ratio

The membrane films were dried at 100 °C overnight prior to the measurements. After measuring the lengths and weights of dry membranes, the sample films were soaked in deionized water for 24 h at predetermined temperatures. Before measuring the lengths and weights of hydrated membranes, the water was removed from the membrane surface by blotting with a paper towel. The water uptake content was calculated by

$$\text{Uptake content}(\%) = \frac{\omega_{\text{wet}} - \omega_{\text{dry}}}{\omega_{\text{dry}}} 100\%$$

where ω_{dry} and ω_{wet} are the masses of dried and wet samples, respectively. The swelling ratio was calculated from films 5 to 10 cm long by:

$$\text{Swelling ratio}(\%) = \frac{l_{\text{wet}} - l_{\text{dry}}}{l_{\text{dry}}} 100\%$$

where l_{dry} and l_{wet} are the lengths of dry and wet samples, respectively.

2.6. Tensile test

Tensile tests were performed on an Instron tensile tester (model 1123) at a strain speed of 50 mm/min at room temperature. Membrane films with typical size of 40 mm × 4 mm × 0.05 mm were used for testing.

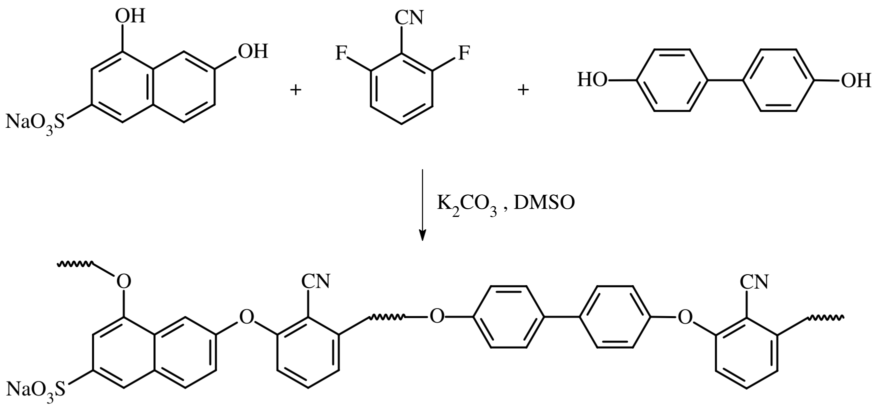
2.7. Proton conductivity

The proton conductivity measurements were performed on *m*-SPAEENH membrane films by AC impedance spectroscopy over a frequency range of 1–10^7 Hz with oscillating voltage 50–500 mV, using a system based on a Solartron 1260 gain phase analyzer. Proton conductivities in the longitudinal direction were measured. Prior to the proton conductivity measurements, membranes were immersed in 98 °C water for 36 h to attain hydration equilibrium, and then cooled to room temperature. A $20 \times 10\ \text{mm}^2$ membrane sample was lightly clamped between two electrodes and placed in a temperature controlled cell open to the air by a pinhole where the sample was equilibrated at 100% RH at ambient atmospheric pressure. The proton conductivity (σ) of the samples in the longitudinal direction was calculated from the impedance data, using the relationship $\sigma = l/Rdw$, where l is the distance between the electrodes, d and w are the thickness and width of the films, respectively, and R was derived from the low intersect of the high frequency semi-circle on a complex impedance plane with the Re(Z) axis, where Re refers to 'Real' in the complex impedance plane. The impedance data were corrected for the contribution from empty and short circuited cell.

3. Results and discussion

3.1. Synthesis and characterization of m-SPAEEN copolymers

m-SPAEEN copolymers were synthesized by copolymerization of 2,6-DFBN, 2,8-DHNS-6 and 4,4′-biphenol as shown in Scheme 1. DMSO was used as polymerization solvent instead of *N*-methyl-2-pyrrolidone (NMP), which was used in most of our previous polycondensation reactions since complete precipitation of reactants or oligomers in NMP took place at the bisphenoxide formation stage. Water generated during this stage was removed as an azeotrope with chlorobenzene. It should be noted that replacement of chlorobenzene with toluene for dehydration also caused precipitation during the bisphenoxide formation. Polymerization solutions appeared as a cloudy yellow color. Polymerization compositions, details of the resulting polymers such as equivalent weight per sulfonate group (EW), ion exchange capacity (IEC) of *m*-SPAEEN-X copolymers are summarized in Table 1. Intrinsic viscosity values of 0.62–1.0 dL/g in DMAc at 25 °C indicate the success of polymerization in producing high molecular weight *m*-SPAEEN-20 to *m*-SPAEEN-60. However, due to the angled structure of 2,8-DHNS-6, *m*-SPAEEN copolymers with SC values ≥0.7 were not obtained with high molecular weights. This was probably due to excessive entanglement in the polymer chains that contained less linear biphenol segments. Indeed, there is no need to further increase the sulfonic acid content in *m*-SPAEEN. From Table 1, it can be seen that the *m*-SPAEEN-60 already has a high IEC value. It can also be seen in Fig. 4 that *m*-SPAEENH-60 (the acid form of *m*-SPAEEN-60) has a swelling of 24% at 100 °C, which indicates that SC≥0.70 in *m*-SPAEENH copolymers will result in unacceptable swelling in membrane



Scheme 1. Synthesis of *m*-SPAEEN copolymers.

Table 1
Syntheses of *m*-SPAEEN copolymers

Polymer	4,4′-BP (mmol)	2,6-DFBN (mmol)	2,8-DHNS-6 (mmol)	$[\eta]^a$ (dL/g)	EW (IEC) expected g/mol SO_3 (Mequiv/g)	SC expected	SC from ^1H NMR data
m-PAEEN-0	5	5	0	–	–	0	0
m-SPAEEN-20	8	10	2	0.85	1480 (0.68)	0.2	0.19
m-SPAEEN-30	7	10	3	1.0	1005 (1.0)	0.3	0.31
m-SPAEEN-40	6	10	4	0.62	767 (1.3)	0.4	0.38
m-SPAEEN-50	5	10	5	0.9	625 (1.6)	0.5	0.50
m-SPAEEN-60	4	10	6	0.82	530 (1.9)	0.6	0.57

[a] Measured at 25 °C in DMAc.

at high temperatures, and result in a decrease in the membranes' morphological and mechanical stability. *m*-SPAEEN-20 to *m*-SPAEEN-60 have good solubility in *N*,*N*-dimethylacetamide and were cast into strong transparent and flexible membrane films. Since all the reactants used in the preparation of *m*-SPAEEN copolymers are commercially available and inexpensive, the present sulfonated nitrile copolymers are much cheaper to manufacture than Nafion.

The chemical structures of *m*-SPAEEN copolymers were initially confirmed by FT-IR. As seen in Fig. 1, characteristic bands of the aromatic sulfonate salt are observed at 1045, 1084, and 1108 cm^{-1} for *m*-SPAEEN copolymers compared with unsulfonated *m*-PAEEN and the intensity of these characteristic absorption bands increase with SC. The characteristic symmetric stretching band of nitrile groups was observed at 2242 cm^{-1}. The absorption bands at 1211 and 1246 $cm^{-1}$are assigned to phenoxy groups. The absorption bands at 1463 and 1495 cm^{-1} are assigned to phenyl ring and the bands at 1587 and 1606 cm^{-1} are attributed to C=C stretching.

The structural properties of the synthesized polymers were also studied by liquid phase ^1H NMR spectroscopy with DMSO-d_6 as the solvent. As an example, the ^1H NMR spectrum of the aromatic region of *m*-SPAEEN-30 is shown in Fig. 2. The benzonitrile proton signals for H-f,h (2H) appeared at the same low frequencies (6.6–6.9 ppm) as observed before in the SPAEEN polymers [21]. The intensity of the distinct signals at high frequencies (8.15–8.40 ppm) for H-b,c of the DHNS monomers were used to estimate and compare the experimental SCs with the expected SCs from the feed ratios. Using *m*-SPAEEN-30 as an example in Fig. 2, the intensity of H-b,c is 0.62, therefore, the ratio of DHNS: biphenol is 0.31: 0.69 for 1.0 DFBN hence an experimental SC of 0.31. Table 1 shows the experimental SC values obtained from NMR are in close agreement with the expected SCs from the feed ratios.

3.2. Thermal properties of m-SPAEEN

Thermal properties of *m*-SPAEEN copolymers were evaluated by their T_d and T_g data. T_ds were determined in both nitrogen and air in order to detect their inherent thermal stabilities and thermal stabilities in air. Fig. 3 shows that the TGA curves of *m*-SPAEEN copolymers in both nitrogen and air are very similar to those of other sulfonated high

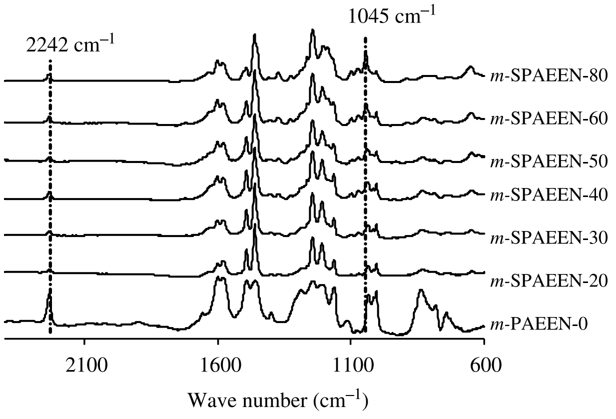


Fig. 1. FT-IR spectra of SPAEEN copolymers.

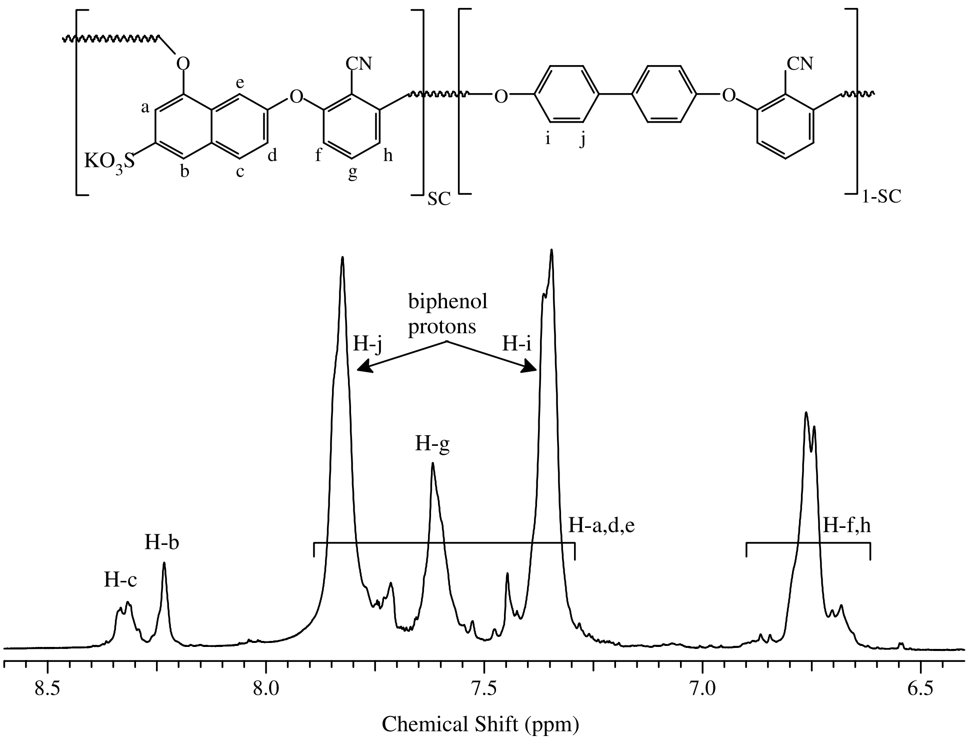


Fig. 2. ^{1}H NMR spectrum of *m*-SPAEEN in DMSO-d_6.

performance polymers reported before [18–21]. Each copolymer showed only one weight loss step for sodium form polymers at around 460–500 °C attributed to the degradation of polymer chain, and two distinct weight loss steps for acid form polymers, of which the initial weight loss at around 260–300 °C is caused by cleavage of $–SO_3H$. Fig. 3 also shows that air did not cause earlier cleavage of $–SO_3H$ than in nitrogen and *m*-SPAEEN copolymers are both thermally stable and thermo-oxidatively stable enough for PEM usage. Table 2 summarizes the observed $T_{d5\%}$ (5% weight loss) and onset weight loss temperatures (T_d) data of *m*-SPAEEN. Table 2 also summarizes T_gs of *m*-SPAEEN copolymers in both sodium and acid forms. The T_gs of copolymers increase with SC values varying from 233 to 336 °C in sodium form and from 230 to 260 °C in acid form. The T_gs of sodium form copolymers were all observed before the onset of thermal decomposition. However, the acid form copolymer *m*-SPAEENH-60 had a decomposition onset lower than its T_g and the T_g of *m*-SPAEENH-50 was observed at a temperature that decomposition had already started, so the reported value is only an approximation. The combination of T_gs and T_d values leads us to conclude that all *m*-SPAEENH copolymers have good thermal stabilities.

3.3. Water uptake, swelling ratio and proton conductivity and mechanical properties

There is a considerable body of scientific evidence to suggest that the electrostatic interactions in sulfonic

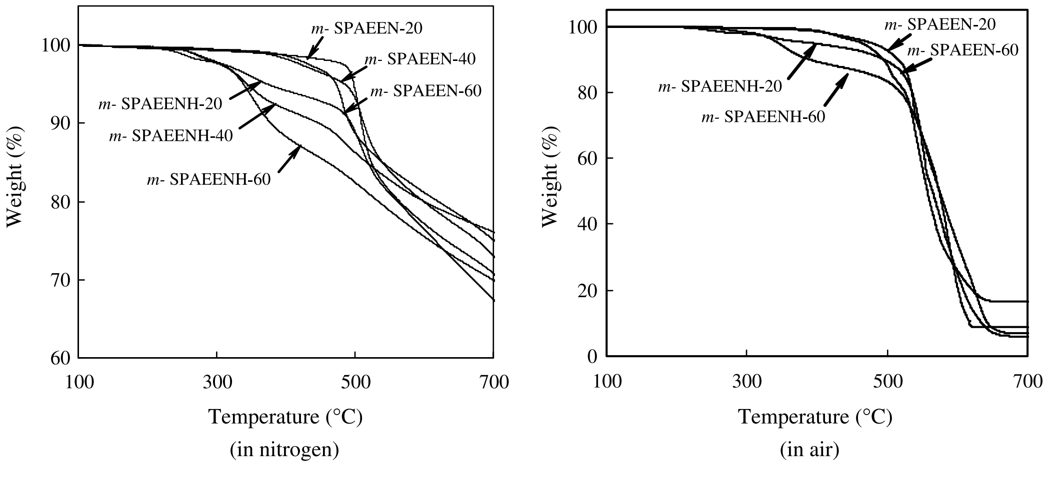


Fig. 3. TGA traces of *m*-SPAEEN copolymers in nitrogen and air.

Table 2
Thermal properties of polymers

Polymer	T_g (°C)		$T_{d5\%}$ (°C)				T_d (°C) extrapolated onset for first weight loss			
	Na form	Acid form	In nitrogen		In air		In nitrogen		In air	
			Na form	Acid form	Na form	Acid form	Na form	Acid form	Na form	Acid form
m-SPAEEN-20	233	230	498	373	477	390	491	268	521	264
m-SPAEEN-30	261	244	493	353	468	361	484	299	504	290
m-SPAEEN-40	310	247	485	345	449	352	482	300	491	290
m-SPAEEN-50	313	260[a]	468	345	467	341	488	288	489	297
m-SPAEEN-60	336	–	473	339	463	344	460	307	512	310

[a] Approximate value.

acid-containing polymers may lead to microphase separation to hydrophobic and hydrophilic regions in their membrane films. The majority of ion exchange sites and counter ions aggregate to form hydrophilic phase, which form clusters in a continuous hydrophobic phase. Upon hydration, the hydrophilic regions imbibe water and increase the clusters sizes into interconnecting channels for protons. Hydrophobic blocks of polymers are tightly packed to provide the membrane films with dimensional and mechanical stabilities. Consequently, morphology concerning the distribution of hydrophilic and hydrophobic phases is greatly affected by absorbed water, which in turn further affects the proton conductivity and mechanical properties of PEMs.

The water uptake and swelling ratio of *m*-SPAEENH membranes are plotted as functions of SC values and temperatures in Fig. 4. PEMFCs are normally operated at temperatures from RT to 80 °C based on the properties of state-of-art polymer electrolyte Nafion. However, since elevated operation temperatures will raise the tolerance ability of catalysts to CO, PEMs that can endure temperatures higher than 100 °C are preferred. Considering these experimental conditions, the water uptake and swelling ratios were tested at room temperature, 80 and 100 °C, respectively. Fig. 4 shows that the *m*-SPAEENH copolymers absorbed water in the range of 5.7–69% with increases in the 2,8-DHNS-6 content and temperature from RT to 100 °C after 24 h immersion in water and increased their linear dimensional sizes by 1.7–24%. These values of dimensional swelling compare very favorably with those of Nafion, shown in Table 3. The dimensional swelling and proton conductivity values at 100% RH of *m*-SPAEEN-60 are comparable to Nafion, whereas the *m*-SPAEEN-50 copolymer has lower swelling, while having good proton conductivity. Using these criteria, all the present *m*-SPAEENH copolymers had low or adequate dimensional swelling when fully hydrated. Fig. 4 also indicates that an SC value of ∼0.6 is the highest practical one for FC application. A further increase in 2,8-DHNS-6 content in the copolymer will result in an over-uptake of water, which will weaken the interactions of hydrophobic phase and cause excessive dimensional swelling. The present nitrile copolymers show much lower water uptakes and swelling ratios, when compared with our previously prepared sulfonic acid-containing poly(aryl ether)s (Table 3) of similar proton conductivity values, including both poly(aryl ether ketone) and poly(aryl ether nitrile) from flexible hydroquinone monomer. We attribute the lower swelling ratios to the combination of polar nitrile groups and hydrophobic naphthalene structures to network the film structure. In nano-phase separated hydrated film, the hydrophobic domains in nitrile-containing polymers are more intensively packed than other polymer films via their strong polar intermolecular actions and enhance the hydrophobic phases, which consequently improve the dimensional stability of membrane films.

All the membranes maintained good shape and were mechanically strong after the hydration pretreatment of immersion in 98 °C water for 36 h. This pretreatment differs from previous ones we employed in past studies, where the films were simply soaked in water at room temperature. This is because the nitrile copolymers were apparently more difficult

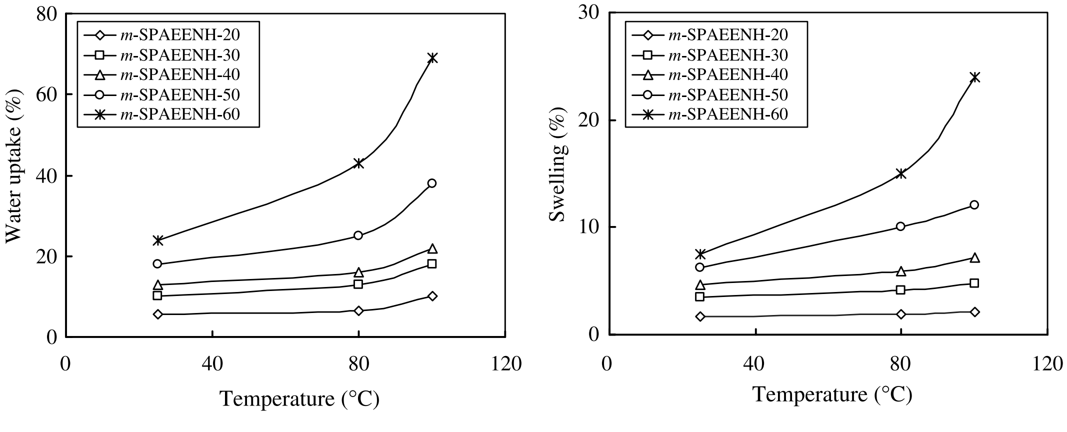


Fig. 4. Water uptake (a) and swelling (b) of *m*-SPAEENH copolymers.

Table 3
Comparisons of swelling and proton conductivities of different polymers

Polymer	EW expected g/mol SO_3	Room temperature		80 °C		100 °C	
		Swelling ratio[a] (%)	Conductivity (S/cm)	Swelling ratio (%)	Conductivity (S/cm)	Swelling ratio (%)	Conductivity (S/cm)
m-SPAEEN-50	625	6.2	3.5×10^{-2}	10	6.4×10^{-2}	12	7.8×10^{-2}
m-SPAEEN-60	530	7.5	8.3×10^{-2}	15	1.4×10^{-1}	24	1.5×10^{-1}
SPAEEKK-100 [21]	575	18	–	Excessively swollen	–	–	–
SPAEEN-B50 [43]	575	6.9	$\sim1.2\times10^{-2}$	11	3.5×10^{-2}	–	8.0×10^{-2}
SPAEEN-B60 [43]	479	9.1	$\sim4.5\times10^{-2}$	17	1.0×10^{-1}	–	2.5×10^{-1}
SPAEEN-Q50 [43]	498	9.4	$\sim3.0\times10^{-2}$	26	1.0×10^{-1}	–	–
Nafion 117	1100	13	7.5×10^{-2}	15.4–20[b]	9.6×10^{-2}	20–23[b]	1.6×10^{-1}

[a] Percentage length gain of 5–10 cm strips of thin films after 24 h.

[b] Measured in our laboratory, *x*-direction 15.4 and 20.0%, *y*-direction 20.0 and 23.3% at 80 and 100 °C, respectively.

to hydrate initially, as observed by conductivity profiles. The proton conductivity measurements of *m*-SPAEENH copolymers were run at 100% relative humidity as a function of SC and temperature in the longitudinal direction by AC impedance spectroscopy and the results are shown in Fig. 5. It shows that the proton conductivities of *m*-SPAEENH copolymers increase with both SC and temperature. However, their SC dependent tendency seems quite different from the temperature dependence. All *m*-SPAEENH copolymers display temperature-dependant proton conductivity curves parallel to that of Nafion 117, i.e. their logarithmic conductivities are linearly dependant on the reciprocal of the temperature from RT to 100 °C, indicating their similar proton transfer mechanism and activation energy to Nafion, involving hydronium ions.

An increase in SC from 20 to 30% resulted in a two orders of magnitude increase in proton conductivity. At SC > 30%, the rate of increase in proton conductivity with SC slows down gradually. When the proton conductivities were plotted against SC (Fig. 6), it is noticeable that the proton conductivity initially increases exponentially with SC and then the rate of increase diminishes. This phenomenon can be explained by channel formation upon hydration. As described previously, sulfonic acid groups form clusters in the continuous hydrophobic phase, which increase in size into interconnecting channels for protons upon hydration. At low SC values, hydrated sulfonic acid groups formed mainly distributed clusters and less connected channels, which resulted in low proton conductivities. An increase in the SC will considerably improve the connection and promote the proton conductivity greatly. At high SC values, however, obvious dimensional swelling in hydrated membranes will dilute the volume concentration of sulfonic acid groups in the membrane, which negatively affects the increase of proton conductivity with increasing SC. This is because the swelling increases at an accelerate rate with SC and retards the increase in conductivity. *m*-SPAEENH-50 and *m*-SPAEENH-60 show high proton conductivities comparable to Nafion117 from room temperature to 100 °C, ranging from

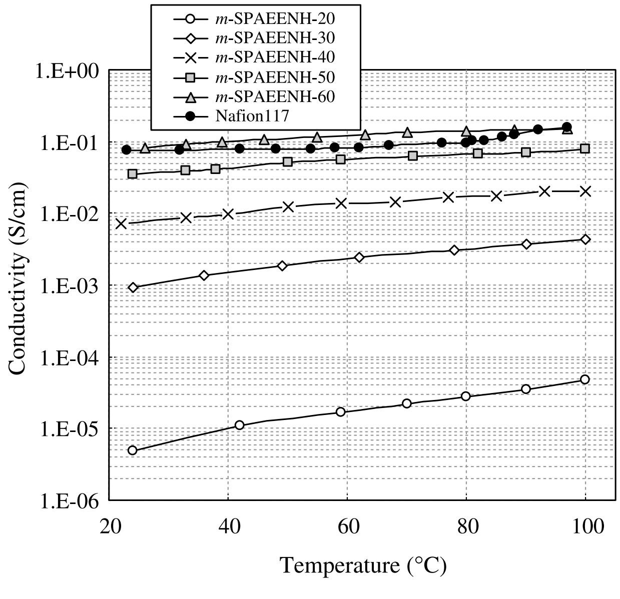


Fig. 5. Proton conductivities of *m*-SPAEENH copolymers after hydration in hot water for 36 h.

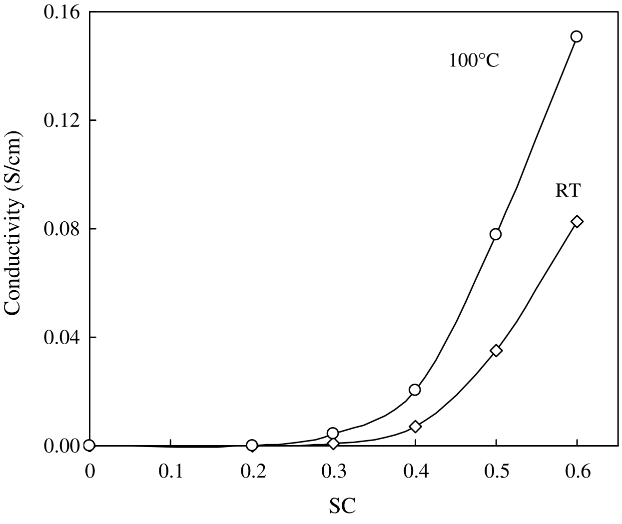


Fig. 6. SC dependence of proton conductivity of *m*-SPAEENH copolymers.

6.2×10^{-2} to 1.5×10^{-1} S/cm. The comparisons on swelling and conductivity of *m*-SPAEENH copolymers and Nafion117 in addition to our selected previously prepared sulfonic acid-containing poly(aryl ether)s are summarized in Table 3. SPAEEKK-100 prepared from 1,3-bis(4-fluorobenzoyl)benzene and sodium 6,7-dihydroxy-2-naphthalenesulfonate was reported with proton conductivities values which were lower than that of Nafion117 under the same measurement conditions [21]. It should be noted here that the proton conductivities were originally measured transversely (through the membrane), which give values significantly lower than those measured longitudinally (along the membrane). As Table 3 shows, previously reported sulfonic acid-containing poly(aryl ether)s have either Nafion-comparable proton conductivities but excessive swelling or reasonable swelling but lower proton conductivities than Nafion. However, *m*-SPAEENH copolymers, especially *m*-SPAEENH-60, have both low dimensional swellings and high proton conductivities, comparable to Nafion117. The reason for low water uptake and swelling has been discussed before. Here, the high proton conductivity is explained. Normally, post-sulfonation of poly(aryl ether)s results in the sulfonic acid group being located ortho to the ether linkage, which deactivates the acidity of sulfonic acid and lowers the proton conductivity. The sulfonated poly(aryl ether sulfone) or poly(aryl ether ketone) copolymers prepared from biphenol and SDCDPS or 3,3′-disulfonate-4,4′-difluorobenzophenone (S-DFB) also have sulfonic acid groups ortho to ether linkage, which are both deactivated by the ether linkage and activated by the SDCDS or S-DFB units at the same time. Unlike those polymers, *m*-SPAEENH has sulfonic acid groups meta to the ether linkage, which is a less deactivating position, resulting in a higher acidity of sulfonic acid groups. The effect of sulfonic acid located on different sites will be further discussed in another paper.

Kim [44] reported that high-temperature acidification of solvent-cast films gave high proton conductivities due to different microstructure formation occurring during various acidification process. In the present work, the films were all acidified at room temperature. However, they were soaked in deionized water at different temperatures before conductivity test. The results are plotted in Fig. 7. Unlike *m*-SPAEENH copolymers, which were soaked in hot water for 36 h prior to conductivity measurement, *m*-SPAEENH-50-untreated and *m*-SPAEENH-60-untreated were only immersed in deionized water at room temperature for 24 h. Fig. 7 shows that proton conductivities of hot water-soaked *m*-SPAEENH-50 and *m*-SPAEENH-60 are less temperature-dependant than those of *m*-SPAEENH-50-untreated and *m*-SPAEENH-60-untreated and at high temperatures they to converge to approximately the same values for the membranes treated differently. This is explained by taking into consideration the synergic effect of a water confinement effect of 2,8-DHNS-6 structure, the nitrile group polarity as well as the microstructure effect discussed by Kim [17]. *m*-SPAEENH-50-untreated and *m*-SPAEENH-60-untreated were not completely hydrated at low temperatures, consequently inadequately formed proton channels were improved with temperature and the proton conductivities increased more sensitively with temperature. The angled structure of 2,8-DHNS-6 increases the interchain spacing and creates permanent pores lined with $-SO_3H$ groups. Once H_2O enters the pore at elevated temperature, it is held very strongly. In addition, polar nitriles in the hydrophilic domains of nano phased separated film may also interact with the water molecules confined in the pore, which would assist in enhancing the water confinement. As a result, hot water-soaked *m*-SPAEENH-50 and *m*-SPAEENH-60 show higher proton conductivities even after having been cooled down to room temperature. At higher temperatures, water uptake and proton channels tend to be the same no matter how the membranes were treated initially; their proton conductivities tend to be the same.

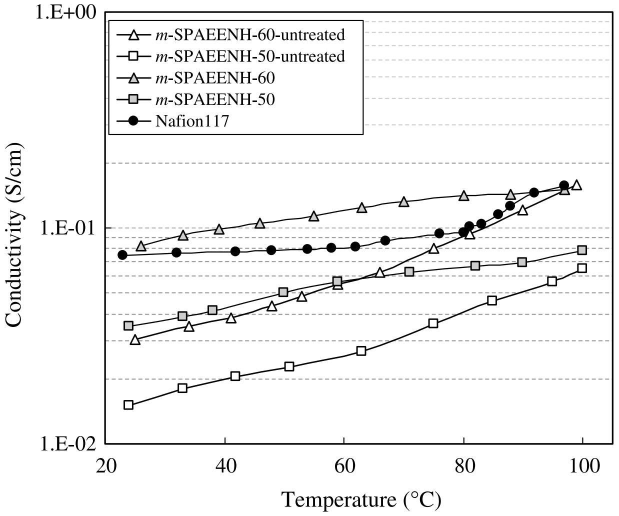


Fig. 7. Temperature dependence of proton conductivity of *m*-SPAEENH copolymers with or without hot water treatment.

Table 4
Tensile properties of *m*-SPAEENH copolymers

Polymer	Tensile strength (MPa)	Elongation at break (%)
m-SPAEEN-20	78	4.5
m-SPAEEN-30	73	10
m-SPAEEN-40	39	3.5
m-SPAEEN-50	56	4.6
m-SPAEEN-60	54	4.6
Nafion®117	10	623

The tensile properties were measured at room temperature and are summarized in Table 4. All membranes show small strain with elongation at break of 3.5–10% compared to 623% of Nafion117. Tensile strengths are from 39 to 78 MPa, several-fold higher that the 10 MPa value of Nafion117.

4. Conclusions

A series of aromatic poly(aryl ether ether nitrile)s containing sulfonic acid groups meta to ether linkage (*m*-SPAEEN) having 0–60 mol% of 2,8-dihydroxynaphthalene-6-sulfonate (2,8-DHNS-6) segment, have been successfully prepared from commercially available inexpensive monomers via one-step polycondensation reactions. *m*-SPAEENH copolymers have good thermal stabilities with decomposition temperatures higher than 250 °C and T_gs higher than 230 °C. *m*-SPAEENH membranes have tensile strength from 39 to 78 MPa, several times higher than 10 MPa of Nafion117 and elongation at break from 3.5 to 10%, several hundred times smaller than 623% of Nafion117. Pendant nitrile groups increase the dipole interactions between polymer chains and decrease the membrane swelling, even up to 100 °C. For example, the dimensional swelling and proton conductivity of *m*-SPAEEN-60 is similar to Nafion, whereas the *m*-SPAEEN-50 copolymer has lower swelling, while having good proton conductivity. The angled structure of 2,8-DHNS-6 increases the interchain spacing and confines the water molecules, which improves the proton conductivities of membranes at lower temperatures. The location of the sulfonic acid groups meta to the ether linkage results in the copolymer sulfonic acid groups being less deactivated, giving membranes with high proton conductivity due to the increased acidity. Furthermore, the meta position is expected to reduce hydrolytic instability. The combination of inexpensive monomers, high thermal stability, low dimensional swelling, good mechanical properties and high proton conductivity makes *m*-SPAEENH-50 and *m*-SPAEEN-60 attractive as PEM materials for fuel cells applications.

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References

[1] Steele BCH, Heinzel A. Nature 2001;414:345.

[2] Kreuer KD. J Membr Sci 2001;185:29.

[3] Mecerreyes D, Grande H, Miguel O, Ochoteco E, Marcilla R, Cantero I. Chem Mater 2004;16:604.

[4] Yang Y, Shi Z, Holdcroft S. Macromolecules 2004;37:1678.

[5] Wang L, Meng YZ, Wang SJ, Shang XY, Li L, Hay AS. Macromolecules 2004;37:3151.

[6] Ueda M, Toyota H, Ouchi T, Sugiyama J, Yonetake K, Masuko T, et al. J Polym Sci, Part A: Polym Chem Ed 1993;31:853.

[7] Genies C, Mercier R, Sillion B, Cornet N, Gebel G, Pineri M. Polymer 2001;42:359.

[8] Miyatake K, Hay AS. J Polym Sci, Part A: Polym Chem Ed 2001;39: 3211.

[9] Wang F, Hickner M, Kim YS, Zawodzinski TA, McGrath JE. J Membr Sci 2002;197:231.

[10] Faure S, Cornet N, Gebel G, Mercier R, Pineri M, Sillion B. In: Savadogo O, Roberge PR, editors. Proceedings of the second international symposium on new materials for fuel cell and modern battery systems. Canada: Montreal; 1997. p. 818.

[11] Nolte R, Ledjeff K, Bauer M, Mülhaupt R. J Membr Sci 1993;83:211.

[12] Kobayashi T, Rikukawa M, Sanui K, Ogata N. Solid State Ionics 1998; 106:219.

[13] Glipa X, Haddad ME, Jones DJ, Rozière J. Solid State Ionics 1997;97: 323.

[14] Kerres J, Cui W, Reichle S. J Polym Sci, Part A: Polym Chem Ed 1996; 34:2421.

[15] Soczka-Guth T, Baurmeister J, Frank G, Knauf R. International Patent WO 99/29763; 1999.

[16] Kim YS, Dong L, Hickner MA, McGrath JE. Macromolecules 2003;36: 6281.

[17] Harrison WL, Wang F, Mecham JB, Bhanu VA, Hill M, Kim YS, et al. J Polym Sci, Part A: Polym Chem 2003;41:2264.

[18] Gao Y, Robertson GP, Guiver MD, Jian X. J Polym Sci, Part A: Polym Chem 2003;41:497.

[19] Gao Y, Robertson GP, Guiver MD, Jian X, Mikhailenko SD, Wang K, et al. J Polym Sci, Part A: Polym Chem 2003;41:2731.

[20] Gao Y, Robertson GP, Guiver MD, Jian X, Mikhailenko SD, Wang K, et al. J Membr Sci 2003;227:39.

[21] Gao Y, Robertson GP, Guiver MD, Mikhailenko SD, Li X, Kaliaguine S. Macromolecules 2004;37:6748.

[22] Xing P, Robertson GP, Guiver MD, Mikhailenko SD, Kaliaguine S. Macromolecules 2004;37:7960.

[23] Xiao G, Sun G, Yan D, Zhu P, Tao P. Polymer 2002;43:5335.

[24] Xiao G, Sun G, Yan D. Macromol Rapid Commun 2002;23:488.

[25] Kerres JA. J Membr Sci 2001;185:3.

[26] Cotter RJ. Engineering plastics: handbook of polyarylethers. Basel, Switzerland: Gordon and Breach Science Publishers S.A.; 1995.

[27] Wang S, McGrath J. In: Rogers ME, Long TE, editors. Synthetic methods in step-growth polymers. Hoboken NJ: Wiley; 2003 [chapter 6].

[28] Kricheldorf HR, Meier J, Schwarz G. Macromol Chem Rapid Commun 1987;8:529.

[29] Kricheldorf HR, Berghahn M. Macromol Chem Rapid Commun 1991;12: 529.

[30] Kricheldorf HR, Garaleh M, Schwarz G. J Polym Sci, Part A: Polym Chem 2003;41:3838.

[31] Mohanty DK, Walstrom AM, Ward TC, McGrath JE. Polym Prepr 1986; 27:147.

[32] Mohanty DK, Hedrick JL, Gobetz K, Johnson BC, Yilgor I, Yilgor E, et al. Polym Prepr 1982;23:284.

[33] Blinne G, Bender H, Neumann P. US Patent 4567248; 1986.

[34] Hoehn HH, Richter JW. US Patent 3899309; 1975.

[35] Heath DR, Wirth JG. US Patent 3730946; 1973.

[36] Murakami T. US Patent 4972016; 1990.

[37] Krizan TD. US Patent 5080698; 1992.

[38] Matsuo S, Murakami T, Takasawa R. US Patent 4703104; 1987.

[39] Matsuo S, Murakami T. US Patent 4663427; 1987.

[40] Matsuo S, Murakami T. US Patent 4640975; 1987.

[41] Sakaguchi Y, Kitamura K, Nagahara S, Takase S. Polym Prepr 2004;45: 56.

[42] Sumner MJ, Harrison WL, Weyers RM, Kim YS, McGrath JE, Riffle JS, et al. J Membr Sci 2004;239:199.

[43] Gao Y, Robertson GP, Guiver MD, Mikhailenko SD, Li X, Kaliaguine S. Macromolecules 2005;38:3237.

[44] Kim YS, Wang F, Hickner M, McCartney S, Hong YT, Harrison W, et al. J Polym Sci, Part B: Polym Phys 2003;41:2816.