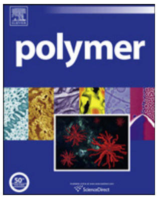
Polymer 50 (2009) 6001–6008

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Synthesis and properties of novel sulfonated poly(phenylquinoxaline)s as proton exchange membranes

Feixiang Gong [a,b], Nanwen Li [a,b], Suobo Zhang [a,*]

[a] State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China
[b] Graduate School of Chinese Academy of Sciences, Beijing 100039, China

ARTICLE INFO

Article history:
Received 13 June 2009
Received in revised form
28 September 2009
Accepted 2 October 2009
Available online 31 October 2009

Keywords:
Sulfonated poly(phenylquinoxaline)s
Proton exchange membrane
Sulfonated tetraamine

ABSTRACT

Two series of sulfonated poly(phenylquinoxaline)s (SPPQ-*x* and SPPQ(O)-*x*, *x* refers to molar percentage of sulfonated tetraamine monomer) were first synthesized from a sulfonated tetraamine (4,4′-bis(3,4-diaminophenoxy)biphenyl-3.3′-disulfonic acid) and two aromatic bisbenzils (4-phenylglyoxalylbenzil and *p*,*p*′-oxydibenzil) in a mild condition. The structures of SPPQ-*x* and SPPQ(O)-*x* were characterized by IR and ^{1}H NMR spectra. The properties of these polymer films, such as water uptake, water swelling ratio, proton conductivity, thermal properties, methanol permeability, hydrolytic and oxidative stability were also investigated. The resulting polymers generally showed good solubility in DMAc and DMSO. Flexible and tough membranes with high mechanical strength were prepared. They show very high thermal, thermooxidative, hydrolytic stabilities and low methanol permeability. SPPQ-100 with the IEC value (2.41 mmol/g) displays the conductivity of 0.1 S/cm and a swelling ratio of 7.3% at 100 °C. The low swelling was attributed to the high rigid of polymer backbones and the strong intermolecular interaction between the basic nitrogen atoms of quinoxaline units and sulfonic acid groups. Moreover, we found that the conductivities of SPPQ(O)-*x* membranes were higher than SPPQ-*x* membranes at the similar IEC value. The highest conductivity of 0.2 S/cm was obtained for SPPQ(O)-100 at 140 °C. A combination of excellent dimensional and hydrolytic stabilities indicated that the SPPQ ionomers were good candidate materials for proton exchange membrane in fuel cell applications.

1. Introduction

Ion-conducting polymers are of interest for a variety of applications, such as sensors, actuators, batteries, and ion exchange membranes or resins. Particularly, recent progress in the area of polymer electrolyte membrane fuel cells (PEMFCs) has stimulated considerable interest in proton conductive polymer membranes [1]. Polymer electrolyte membrane (PEM) plays a key role in a PEFC system, namely to provide a barrier to the fuel gas cross-leaks between the electrodes and to transfer protons from the anode to the cathodes. Currently, perfluorinated ionomers such as Nafion are the state of the art materials because of their excellent chemical stability and high proton conductivity. However, high cost, high fuel and oxygen crossover and lower operation temperature limit their wide application. In the past decade, a variety of proton conductive materials, especially the nonfluorinated aromatic hydrocarbon ionomers, have been proposed as alternative membranes [2]. Although each of them has its own advantages, most of them have failed to meet the requirements of high conductivity and durability under fuel cell operating conditions. The perfluorinated ionomers still stand as the state-of-the-art membranes [3].

One of the key issues to be emphasized on nonfluorinated aromatic ionomers is their poor hydrolytic stability or the balance between conductivity and dimensional stability in fuel cell operating conditions. To make hydrocarbon ionomers less susceptible to water swelling or hydrolysis, the selection of a suitable chemically and mechanically stable aromatic polymer as a base skeleton is very important. Poly(phenylquinoxaline)s (PPQs) are high performance thermoplastics well known for their excellent thermal and chemical stability and widely used in microelectronics and aerospace applications [4]. These polymers have also been shown to possess excellent thermohydrolytic stability and good dimensional stability over a wide temperature range [5], which are required properties for PEMs. Zhang et al. [6] first reported the preparation of conducting poly(phenylquinoxalines) films through the electrolysis of PPQ solution with corresponding supporting electrolytes under controlled potential. The conductivity of these PPQ films varies from 10^{-7} to 10^{-12} S/cm depending on dopant

---

* Corresponding author. Tel.: +86 431 85262118.
E-mail address: sbzhang@ciac.jl.cn (S. Zhang).

0032-3861/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.polymer.2009.10.033

anions in electrolytes. Kopitzke et al. [7] has successfully synthesized sulfonated poly(phenylquinoxaline) through the post-sulfonation method and reported that the sample with the highest water uptake had a room temperature conductivity of 9.8×10^{-2} S/cm. However, postsulfonation reactions are usually restricted due to their lack of precise control over the degree and location of sulfonic groups, the possibility of side reactions, or degradation of the polymer backbone [8].

In this article, we first report the synthesis of sulfonated poly(phenylquinoxaline)s by the direct copolymerization method using the corresponding monomers 4,4′-bis(3,4-diaminophenoxy)-biphenyl-3,3′-disulfonic acid, 4,4′-bis(3,4-diaminophenoxy)biphenyl and two aromatic bisbenzils (4-(phenylglyoxalyl)benzil and *p*,*p*′-oxydibenzil). The properties of these novel sulfonated copolymer films, such as water uptake, water swelling ratio, proton conductivity, thermal properties, methanol permeability, hydrolytic and oxidative stability were also investigated.

2. Experimental

2.1. Materials

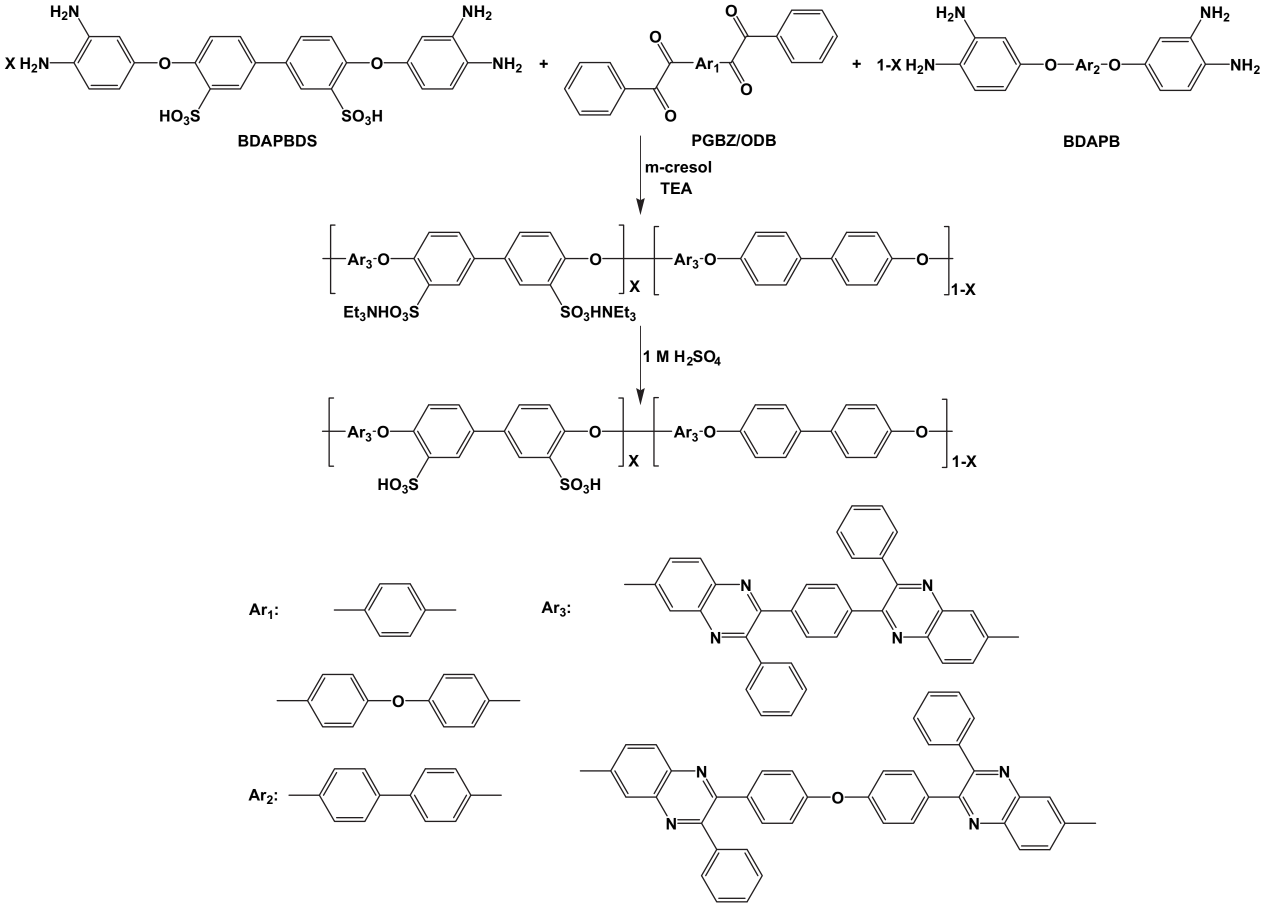
4-(Phenylglyoxalyl)benzil (PGBZ) was synthesized according to the literature [9]. *p*,*p*′-oxydibenzil (ODB) was synthesized according to the literature [10]. 4,4′-Bis(3,4-diaminophenoxy)biphenyl-3.3′-disulfonic acid (BDAPBDS) and 4,4′-bis(3,4-diaminophenoxy)-biphenyl (BDAPB) were synthesized according to the literature [11]. Triethylamine and *m*-cresol were distilled under reduced pressure. All other regents were used as received without further purification.

2.2. Polymer synthesis and membrane preparation

SPPQ-100 (100 refers to molar percentage of sulfonated tetraamine in total tetraamine): To a 100 mL completely dried three-necked flask were added 0.5586 g (1 mmol) of BDAPBDS, 8 mL of *m*-cresol and 0.68 mL of TEA successively under nitrogen flow. After the BDAPBDS was completely dissolved, 0.3423 g (1 mmol) of PGBZ was added. The mixture was stirred at room temperature for 2 h and then heated at 80 °C for 20 h. Then cooling to 30 °C, additional 6 mL of *m*-cresol was added to dilute the highly viscous solution, and then the solution was poured into 200 mL of acetone. The precipitate was filtered off, washed with acetone thoroughly, and dried in vacuum oven for 12 h at 150 °C (yield: >96%).

Tough, ductile ionomer membrane was prepared with a controlled thickness of 20–45 μm. The triethylamine salt form of the polymer was dissolved in DMSO to form a 5–8% solution at room temperature. The solution was then filtered with a fine glass frit filter funnel and cast directly onto clean glass plates. After carefully dried at 80 °C for 12 h and vacuum dried at 120 °C for 12 h, tough and flexible TEA-form film was obtained. The TEA-form PPQ membrane was transformed to their acid form by proton exchange in 1 M H_2SO_4 for 48 h at room temperature. The acidified film was then washed thoroughly with deionized water and dried under vacuum at 120 °C for 12 h.

The SPPQ-80, SPPQ-60, SPPQ-40, unsulfonated PPQ and SPPQ(O) copolymers were prepared following the same procedure as above,



Scheme 1. Synthesis of SPPQ copolymers.

Table 1
Inherent viscosity, solubility behaviors of SPPQs copolymers.

Polymer	η_{inh} (dL/g)		Solvents							
			m-Cresol	NMP	DMSO	DMAc	DMF	$CHCl_3$	CH_2Cl_2	Acetone
SPPQ-100	1.25[a]	1.03[b]	++[d]	++	++	++	++	++	−−	−−
SPPQ-80	1.18[a]	1.01[b]	++	++	++	++	++	++	−−	−−
SPPQ-60	0.93[a]	0.86[b]	++	++	++	++	++	++	−−	−−
SPPQ-40	0.91[a]	0.85[b]	++	++	++	++	++	++	−−	−−
SPPQ(o)-100	1.38[a]	1.13[b]	++	++	++	++	++	++	−−	−−
SPPQ(o)-80	1.36[a]	1.13[b]	++	++	++	++	++	++	−−	−−
SPPQ(o)-60	1.30[a]	1.08[b]	++	++	++	++	++	++	−−	−−
SPPQ-0	0.81[c]	–	++	++	−−[e]	−−	−−	++	−−	−−

[a] 0.5 g/dL in DMSO solution at 30 °C.
[b] 0.5 g/dL in DMSO + LiBr solution at 30 °C.
[c] 0.5 g/dL in m-cresol solution at 30 °C.
[d] ++: soluble at room temperature.
[e] −−: insoluble.

except that 4,4′-bis(3,4-diaminophenoxy)biphenyl was used to adjust the sulfonated level.

2.3. Polymer characterization

2.3.1. Measurements

^{1}H NMR spectra were measured at 300 MHz on a Bruker AV300 spectrometer (Germany). FT-IR spectra of SPPQ and PPQ were obtained with a Bio-Rad digilab Division FTS-80 FT-IR spectrometer (Cambridge, MA). The inherent viscosities were determined on 0.5 g/dL concentration of polymer in DMSO and in DMSO + LiBr (The molar concentration of LiBr was one half of the concentration of –SO_3H for each polymer.) with an Ubbelohde capillary viscometer at 30 ± 0.1 °C. The thermogravimetric analyses (TGA) were obtained in nitrogen with a Perkin-Elemer TGA-2 thermogravimetric analyzer (Inspiratech 2000 Ltd., UK) at a heating rate of 10 °C/min. Tensile measurement were performed with a mechanical tester Instron-1211 instrument (Instron Co., USA at a speed of 2 mm/min at ambient humidity ~50% relative humidity).

2.3.2. Ion exchange capacity

Two methods for ion exchange capacity (IEC) determination were conducted for comparison. Method 1 (M1): protonated membrane was soaked in 1.0 mol/L NaCl solution for 48 h, and thoroughly washed with deionized water. The NaCl solution combined with washed water from membrane was titrated by standard 0.01 mol/L aqueous NaOH to get IEC_{M1}. Method 2 (M2): protonated membrane was immersed in a certain volume of 0.01 mol/L NaOH solution for 24 h. The resulting NaOH solution was titrated with 0.01 mol/L HCl solution to estimate the amount of base consumed by sulfonic acid groups (IEC_{M2}).

2.3.3. Water uptake and dimensional change

The membrane sample (30–40 mg per sheet) was dried at 80 °C under vacuum for 6 h until constant weight as dry material was obtained. It was immersed into deionized water at given temperature for 4 h and then quickly taken out, wiped with tissue paper, and quickly weighted on a microbalance. Use the Equation (1) to calculate the water uptake (WU):

$$\mathrm{WU} = (W_s - W_d)/W_d \tag{1}$$

where W_s and W_d are the weight of dry and corresponding water-swollen membranes, respectively.

The dimension changes of the membranes were measured in thickness and in the plane direction, which were characterized by Equation (2):

$$\begin{aligned} \Delta T_c &= (T - T_s)/T_s \\ \Delta L_s &= (L - L_s)/L_s \end{aligned} \tag{2}$$

where T_s and L_s are the thickness and diameter of the membrane equilibrated at 70% relative humidity (RH), respectively; T and L refer to those of the membrane equilibrated in liquid water for 5 h.

2.3.4. Proton conductivity

The proton conductivity (σ, S/cm) of each membrane (size: 1 cm × 4 cm) was obtained using $\sigma = d/L_sW_sR$ (d: distance between reference electrodes, and L_s and W_s are the thickness and width of the membrane respectively). Here, ohmic resistance (R) was measured by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes were sandwiched between two pairs of gold-plate electrodes. The membranes and the electrodes were set in a Teflon cell and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h before the conductivity measurements. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10-min interval until no more change in

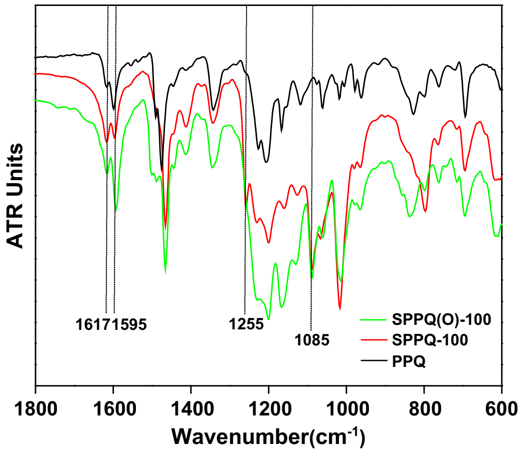


Fig. 1. The IR spectra of SPPQ-100, SPPQ(O)-100 and PPQ.

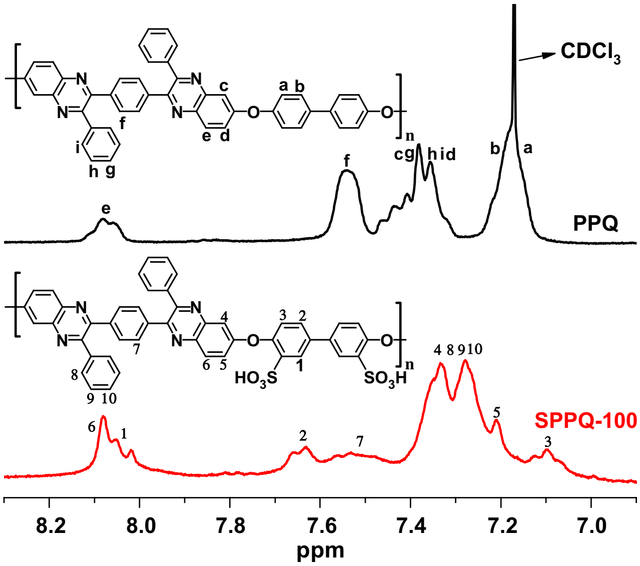


Fig. 2. The ^{1}H NMR spectra of SPPQ-100 in DMSO-d_6 and PPQ in CDCl$_3$.

conductivity was observed. For the measurement above 100 °C at 100% RH, a pressure-resistant closed chamber was used. At a given temperature, the samples were equilibrated for at least 30 min before any measurements.

2.3.5. *Methanol permeability*

The methanol permeability was determined by using a cell basically consisting of two half-cells separated by the membrane, which was fixed between two rubber rings. Methanol (2 mol/L) was placed on one side of the diffusion cell, and water was placed on the other side. Magnetic stirrers were used on each compartment to ensure uniformity. The concentration of the methanol was measured by using a Shimadzu GC-1020A series gas chromatograph. Peak areas were converted into methanol concentration with a calibration curve. The methanol permeability was calculated by the following equation:

$$C_B(t) = \frac{A}{V_B} \cdot \frac{DK}{L} \cdot C_A \cdot (t - t_0) \qquad (3)$$

where C_A and C_B are the methanol concentration of feed side and permeated through the membrane, respectively. A, L, and V_B are the effective area, the thickness of membrane, and the volume of permeated compartment, respectively. DK is defined as the methanol permeability, and t_0 is the time lag.

Table 2
IEC and mechanical properties of SPPQs membranes.

	IEC (mmol/g)			Maximum of stress (MPa)	Elongation at break (%)	Young's modulus (GPa)
	IEC$_{Cal}$	IEC$_{M1}$	IEC$_{M2}$			
SPPQ-100	2.41	2.17	2.38	75.1	21.0	1.39
SPPQ-80	2.01	1.68	2.00	64.5	30.1	1.08
SPPQ-60	1.57	1.13	1.55	56.9	57.8	1.15
SPPQ-40	1.09	0.76	1.06	51.2	48.2	0.92
SPPQ-0	–[a]	–	–	75.9	17.1	1.43
SPPQ(o)-100	2.17	2.01	2.15	81.5	5.6	1.75
SPPQ(o)-80	1.8	1.61	1.81	80.0	9.3	1.67
SPPQ(o)-60	1.4	1.19	1.38	79.1	34.8	1.62

[a] Not measured.

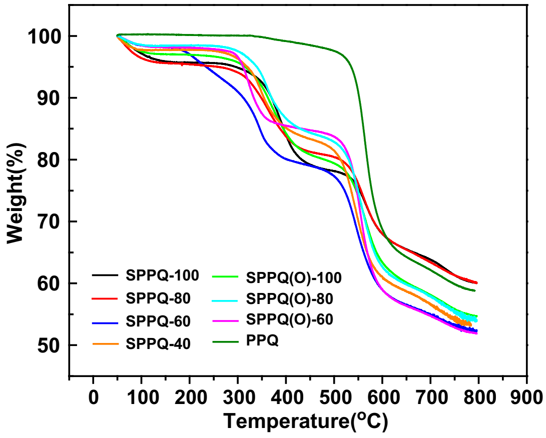


Fig. 3. The TGA curves of SPPQs copolymers.

3. Results and discussion

3.1. *Synthesis and characterization of polymers*

The preparation of SPPQ and SPPQ(O) copolymers was carried out through one-pot polymerization method in m-cresol as shown in Scheme 1. TEA was used to liberate the protonated amino groups of sulfonated tetraamine for polymerization with PGBZ or ODB. The degree of sulfonation (DS) of the copolymer was readily controlled through the monomer feed ratios of sulfonated tetraamine to non-sulfonated tetraamine, so that a series of copolymers with different IEC values could be obtained. The copolymers as synthesized were denoted as SPPQ-*x* and SPPQ(O)-*x* where *x* was the molar fraction of sulfonated tetraamine BDAPBDS in the feed. The copolymerization was initially run at room temperature for 2 h. Then the temperature was raised slowly to 80 °C and maintained at that temperature for 20 h. The SPPQs were obtained almost in quantitatively yields (yields were above 96%) and had inherent viscosity values ranging between 0.81 and 1.38 dL/g (Table 1). The solubility behavior of SPPQs in common organic solvents was listed in Table 1. All copolymers are soluble in polar aprotic solvents such as DMAc, DMF, and DMSO. Meanwhile, we found that polymers derived from ODB, BDAPB and BDAPBDS were soluble more quickly than polymers derived from PGBZ, BDAPB and BDAPBDS. Apparently, such an improvement in solubility can be attributed to the flexible ether

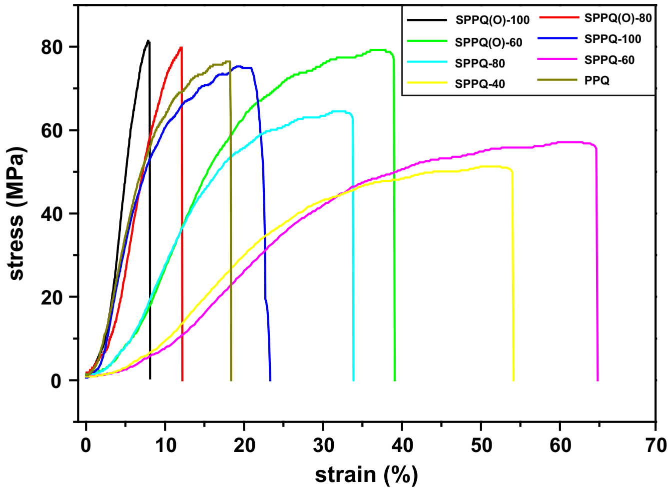


Fig. 4. Stress–strain curves of SPPQs membranes.

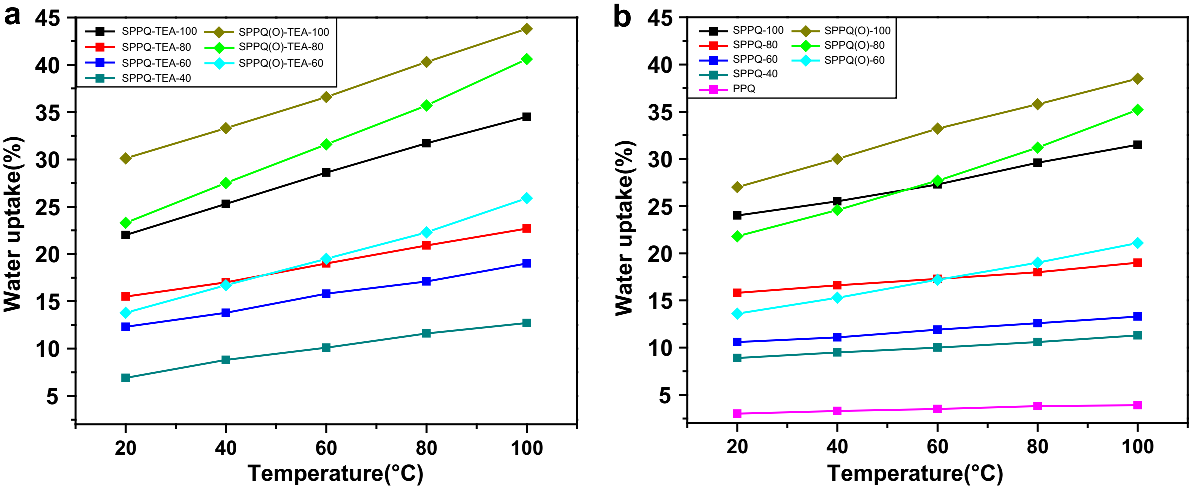


Fig. 5. Water uptake curves of SPPQs in triethylammonium salts (a) and acid form (b) at different temperatures.

moieties introduced. No partial dissolved phenomenon was observed during the solubility testing progress, indicating that the crosslinking often occurred in postsulfonation progress was avoided successfully by the direct copolymerization using the sulfonated monomer [7]. Flexible, tough and ductile membranes (in triethylammonium salt form) could be obtained from these copolymers by solvent-casting method. The obtained membranes were treated with 1.0 M sulfuric acid at room temperature for 2 days and then washed with deionized water.

The copolymers were characterized by IR and ^{1}H NMR spectra. Fig. 1 showed the IR spectra of SPPQ-100, SPPQ(O)-100 and PPQ. The absorption bands at 1617 and 1595 cm^{-1} were assigned to the typical of the C=C=N group vibrations. The symmetric and asymmetric vibrations of the O=S=O bond of the sulfonic acid group appeared at 1085 and 1255 cm^{-1}, respectively. There were no absorption bands from 1900 cm^{-1} to 1650 cm^{-1} which were corresponded to the C=O group stretching vibration, indicating a high degree of cyclization of quinoxaline. Fig. 2 showed the ^{1}H NMR spectra of SPPQ-100 in DMSO-d_6 and PPQ in $CDCl_3$ (because of poor solubility of PPQ in DMSO, so $CDCl_3$ was used). All of aromatic protons were well assigned to the supposed chemical structure. The integration ratio of the peaks corresponded to the polymer composition expected from the feed monomer. Aromatic protons located at the electron-rich ortho-ether position were strongly shielded, and their signals appeared at low frequency (7.0–7.25 ppm) area, while the protons located at ortho-positions of –C=N–, and sulfonate groups were deshielded due to their strongly electron-withdrawing effects, and their signals appeared at high frequency area (7.9–8.15 ppm). No characteristic chemical shift of $-NH_2$ (around 5 ppm) was observed, which also indicated that a fully cyclization of quinoxaline has been attained through the polymerization progress.

3.2. Ionic exchange capacity

The IEC of the copolymers synthesized was determined by titration. The protonated membrane was soaked in 1.0 mol/L NaCl solution for 48 h, and thoroughly washed with deionized water. The NaCl solution combined with washed water from membrane was titrated by standard 0.01 mol/L aqueous NaOH to get IEC_{M1}. As listed in Table 2, it was found that the experimental IEC (IEC_{M1}) was lower than the theoretical IEC (IEC_{Cal}). The similar behavior was observed by Roziere et al. with *N*-benzysulfonated-grafted PBI [12]. It was attributed to the formation of an acid-base complex between benzimidazole and the sulfonic acid groups of the polymer which make the acid protons less accessible to the exchange with Na^{+}. To overcome this uncompleted exchange problem, protonated membrane was immersed in a certain volume of 0.01 mol/L NaOH

Table 3
Water uptake, swelling ratio and conductivity of SPPQ membranes.

	Water uptake (%)				Swelling ratio (%)								Counductivity (S/cm)	
					H^{+}[c]				TEA[d]					
	H^{+}[c]		TEA[d]		Δt		Δl		Δt		Δl		20 °C	100 °C
SPPQ-100	24.0[a]	31.5[b]	22.0[a]	34.5[b]	5.6[a]	6.7[b]	4.5[a]	7.3[b]	8.9[a]	27.5[b]	9.1[a]	13.4[b]	0.034	0.1
SPPQ-80	15.8[a]	19.0[b]	15.5[a]	22.7[b]	5.3[a]	6.2[b]	3.4[a]	5.2[b]	7.8[a]	25.0[b]	4.3[a]	8.6[b]	0.021	0.058
SPPQ-60	10.6[a]	13.3[b]	12.3[a]	19.0[b]	4.9[a]	5.7[b]	2.7[a]	3.9[b]	6.2[a]	20.1[b]	3.0[a]	6.9[b]	0.015	0.04
SPPQ-40	8.9[a]	11.3[b]	6.9[a]	12.7[b]	4.4[a]	5.2[b]	1.1[a]	2.1[b]	4.0[a]	16.0[b]	1.6[a]	3.5[b]	0.01	0.03
SPPQ-0	3.0[a]	3.9[b]	–[e]	–	–	–	–	–	–	–	–	–	–	–
SPPQ(o)-100	27[a]	38.5[b]	30.1[a]	43.8[b]	8.6[a]	10.1[b]	8[a]	9.3[b]	11.3[a]	43.0[b]	9.8[a]	18.5[b]	0.05	0.13
SPPQ(o)-80	21.8[a]	35.2[b]	23.3[a]	40.6[b]	7.8[a]	9.1[b]	6.5[a]	7.6[b]	10.6[a]	37.8[b]	7.9[a]	16.3[b]	0.042	0.117
SPPQ(o)-60	13.6[a]	15.5[b]	13.8[a]	25.9[b]	4.6[a]	5.8[b]	4.1[a]	5.2[b]	6.8[a]	24.3[b]	4.7[a]	9.5[b]	0.02	0.057

[a] Measured at 20 °C.
[b] Measured at 100 °C.
[c] Membrane in acid form.
[d] Membrane in triethylammonium salts form.
[e] Not measured.

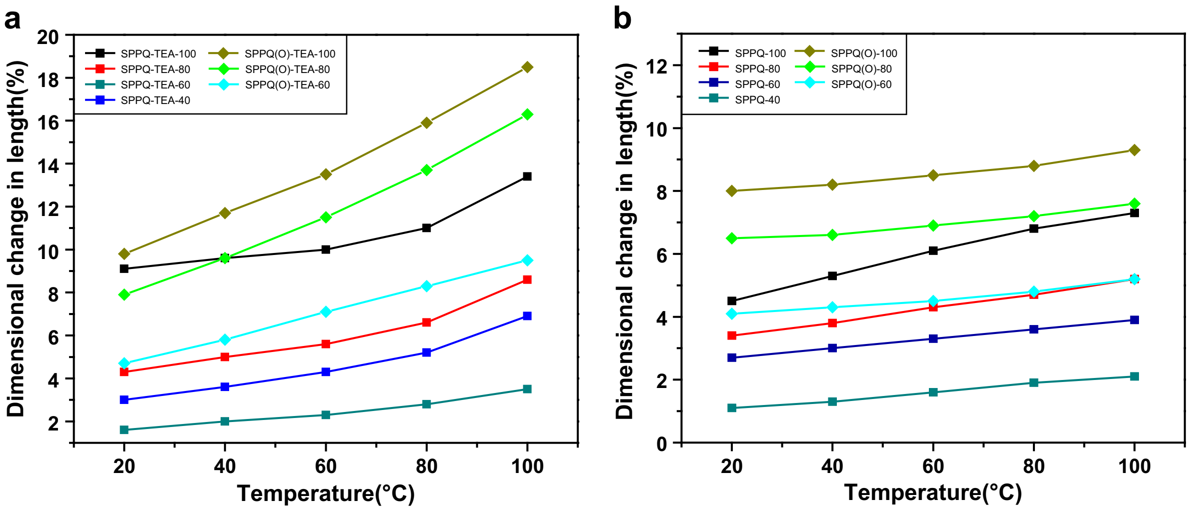


Fig. 6. Dimensional changes in length of SPPQs in triethylammonium salts (a) and acid form (b) at different temperatures.

solution for 24 h. The resulting NaOH solution was then titrated with 0.01 mol/L HCl solution to estimate the amount of base consumed by sulfonic acid groups (IEC_{M2}). It was observed that the experimental IEC_{M2} was close to theoretical IEC_{Cal}. The result indicated that the acid-base complex between quinoxaline ring and the sulfonic acid group was formed. Hence, the acid proton of SPPQ was more difficult to exchange with Na^+. Compared with sulfonated poly(ether ether ketone-benzimidazole)s (SPEEK-BI) [13], the difference between IEC_{M1} and IEC_{Cal} was much smaller for SPPQs. This may suggest that the acid-base interaction for SPPQs was much weaker than that for SPEEK-BI.

3.3. *Thermal and mechanical properties*

Fig. 3 shows the thermal stability of the PPQ, SPPQ and SPPQ(O) copolymers investigated by thermogravimetric analysis (TGA) in a nitrogen atmosphere. It can be seen that the SPPQs membranes exhibited a typical three-step degradation pattern. The first weight loss up to 200 °C was ascribed to the loss of water molecules, absorbed by the highly hygroscopic –SO_3H groups. The second weight loss around 340 °C was due to the cleavage of the sulfonic acid groups. Compared with the weight loss temperature of PPQ, the third stage weight loss of SPPQs around 530 °C was assigned the decomposition of polymer main chain. Moreover, it was easily to be seen that the temperature of the second weight loss and third weight loss for SPPQ was a little higher than SPPQ(O) at the near sulfonation lever. From the results above, it is concluded that the SPPQs are thermally stable to satisfy the requirement of thermal stability for the use in PEMFC (>200 °C).

The mechanical properties of the SPPQs membranes were measured at room temperature. The stress–strain data are shown in Table 2 and Fig. 4. The membranes have tensile stress at maximum load of 51.2–81.5 MPa, Young's moduli of 0.92–1.75 GPa, and elongation at break of 5.6–57.8%, which indicated that these SPPQs membranes were strong and tough enough for fuel cell application even at high sulfonation degree. Meanwhile, it was found that the tensile strength and Young's modulus both for the SPPQ and SPPQ(O) copolymers increased with the increase of IEC. This result may be attributed to the increased interactions of polymer molecules induced by the acid–base interactions between the N atoms of quinoxaline ring and the –SO_3H groups.

3.4. *Water uptake, dimensional change*

The water content has a great effect on the properties of PEMs. High water content can facilitate the transport of protons, but too much water absorption results mechanically less stable membrane. The water uptake of the copolymer membranes in acid form was determined by measuring the changes in the weight of hydrated and dehydrated films at desired temperature. As shown in Fig. 5b, the water uptake of SPPQs membranes increased with IEC and temperature. The water uptake of SPPQs membranes with IEC from 1.09 to 2.41 was in the range of 8.9–38.5%. The highest water uptake for SPPQ(O)-100 in acid form was only 27% at 20 °C and 38.5% at 100 °C respectively. Compared with other nonfluorinated aromatic ionomers [14–21], the water uptake of SPPQs is much lower and does not vary much from 20 °C to 100 °C. We believe that there are two reasons for this: one is the high rigidity of the aromatic polymer backbone, the other one is the strong interactions between the N atoms of quinoxaline ring and the –SO_3H groups. A combination of these two effects resulted in the restriction of free volume and hygroscopic –SO_3H groups for water adsorption and a decrease in the water uptake of SPPQs. Simultaneously, due to the low water uptake, the swelling ratio of SPPQs in acid form was also low and no obvious changes from 20 to 100 °C as shown in Table 3.

In order to investigate the influence of acid-base complex on water uptake and swelling ratio of SPPQ membranes, the water uptake and swelling ratio of SPPQ membrane in triethylammonium salt form were also determined. As shown in Figs. 5–7, the swelling ratio and water uptake of SPPQ membranes in triethylammonium salt form were much higher than those of acid form, especially for dimensional changes in thickness. For example, the SPPQ-100 membrane in triethylammonium salt form showed about 4 times larger swelling in thickness direction (27.5%) than that in acid form (6.7%) at 100 °C (Table 3). The results confirmed that there was an acid-base interaction between the N atom of quinoxaline ring and the sulfonic acid group. The conversion of the sulfonic acid groups to triethylammonium sulfonate lead to the decreased interaction, thus the increased water uptake and water swelling.

3.5. *Proton conductivity*

The proton conductivities of SPPQ-*x*, SPPQ(O)-*x* copolymers along with that of Nafion 117 were measured under fully hydrated

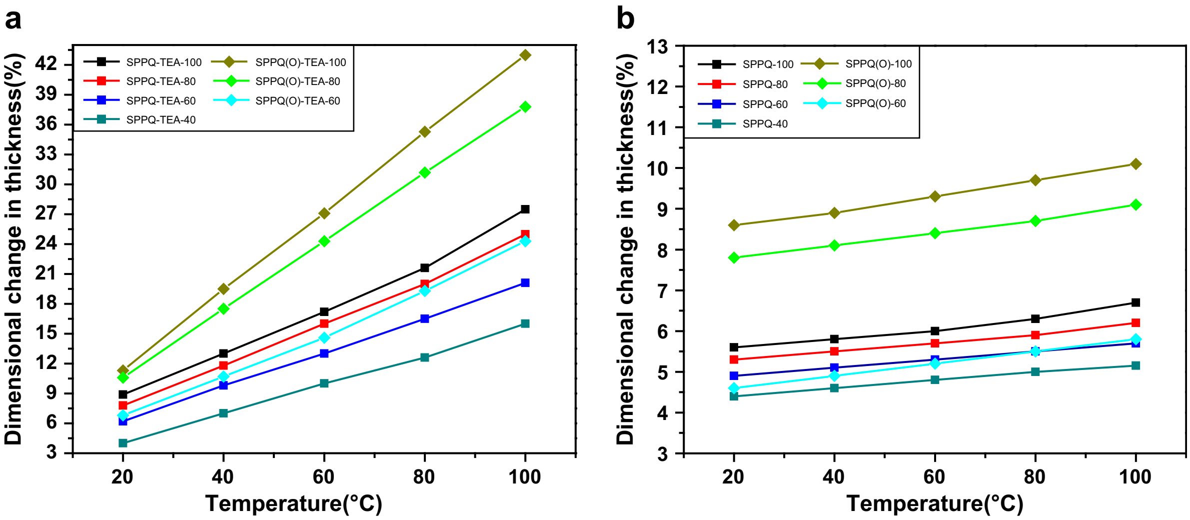


Fig. 7. Dimensional changes in thickness of SPPQs in triethylammonium salts (a) and acid form (b) at different temperatures.

condition. As shown in Table 3, SPPQ-*x* showed the proton conductivities in the range of 0.01–0.05 S/cm at 20 °C. Their proton conductivities increased with IEC and water uptake. The temperature dependence of the proton conductivities of SPPQ-*x*, SPPQ(O)-*x* and Nafion-117 measured in liquid water are summarized in Fig. 8. The proton conductivity of sulfonated copolymers showed a linear dependence on the temperature. SPPQ-100 with the highest IEC showed the proton conductivity of 0.1p S/cm at 100 °C, which was slightly lower than that of Nafion 117 at the same test conditions. However, SPPQ-100 showed much higher proton conductivity (0.034 S/cm, at 20 °C, IEC = 2.41 mmol/g) than sulfonated polybenzimidazole (SPBI) (1.7×10^{-4} S/cm, at 20 °C, IEC = 2.41 mmol/g). Mercier et al. [22] explained that the low proton conductivity of SPBI is due to the formation of a strong acid-base complex between benzimidazole and the sulfonic acid groups in SPBI. As a result, the acid proton of the –SO_3H groups is no longer available for proton conduction. Compared with SPBI, SPPQ showed a decreased basicity of the N atoms of quinoxaline ring than that of benzimidazole ring as confirmed by measuring the pK_a of PPQ-acid and BPI-acid complexes [23]. This explains the improved proton conductivity of SPPQ-*x*. At the same time, it was found that the conductivity of SPPQ(O) copolymers were higher than SPPQ series at near IEC value. This may be attributed to the higher water uptake and swelling ratio of SPPQ(O) series. It is noteworthy that the novel SPPQs membranes achieved high proton conductivity while retained a low swelling ratio even under high temperature and IEC value which is desirable for requirement of PEMFC applications.

3.6. Methanol permeability

In DMFC, the PEM is required to have low methanol diffusion coefficient because the diffusion of methanol from the anode to the cathode lead to power loss and other undesirable consequences. The membranes with lower methanol diffusion coefficient may allow for higher methanol feed concentration, thereby increasing the effective energy density of the fuel cell system. The methanol permeability through the SPPQ membranes was estimated using Equation (3) and results are illustrated in Table 4. The methanol diffusion coefficient was in the range of $(0.8–2.7) \times 10^{-7}$ cm^2/s, which is much lower than Nafion 117 (2.4×10^{-6} cm^2/s) at the same test condition. The low methanol permeability may be attributed to strong interaction between acid and base moieties. This will lead membranes to be of high crosslink, which effectively suppressed membrane water absorption and inhibited chain mobility and methanol passage, and hence resulted in the reduction of methanol diffusion coefficient.

3.7. Membrane stability toward water and oxidation

The water stability test was carried out by immersing the membranes into water at 90 °C and the stability was characterized by the elapsed time when the hydrated membranes start to loss of mechanical properties. After 1000 h, all of the SPPQ membranes were still ductile and flexible when shaking drastically and bending iterative for many times. The result revealed that SPPQ-*x* and SPPQ(O) had excellent hydrolytic stability.

The oxidative stability of the SPPQs was investigated by immersing the membranes (the size of each sheet: 0.5×1.0 cm^2) into Fenton's reagent (30 ppm $FeSO_4$ in 30% H_2O_2) at room temperature. The oxidative stability of the membranes was

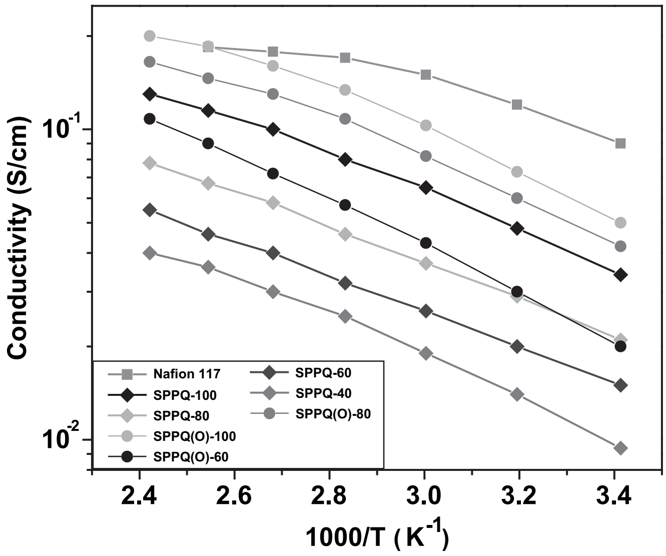


Fig. 8. Temperature dependence of proton conductivity of SPPQs membranes.

Table 4
Methanol permeability and durability of SPPQ membranes under hydrolytic and radical attack.

	IEC (mmol/g)	Methanol permeability (cm^2/s)	Hydrolytic stability (h)	Oxidative stability (h)	
				τ_1[b]	τ_2[c]
SPPQ-100	2.41	2.3×10^{-7}	>1000[a]	13	25
SPPQ-80	2.01	1.5×10^{-7}	>1000[a]	17	29
SPPQ-60	1.57	1.1×10^{-7}	>1000[a]	21	31
SPPQ-40	1.09	8.0×10^{-8}	>1000[a]	27	39
SPPQ(o)-100	2.17	2.7×10^{-7}	>1000[a]	15	20
SPPQ(o)-80	1.80	1.9×10^{-7}	>1000[a]	23	35
SPPQ(o)-60	1.40	1.3×10^{-7}	>1000[a]	38	60

[a] Measured at 90 °C in water.
[b] The time when the membranes were broken while being lightly bent.
[c] The time when the membrane dissolved completely.

characterized by the expended time that the membranes started to become a little brittle (τ_1, the membranes were broken when being lightly bent), and the membranes were dissolved completely in the solution (τ_2). Table 4 showed the testing results of SPPQ membranes. As shown in Table 4, all of the SPPQ membranes generally showed fairly good oxidative stability which was better than that of poly(arylene ether)s [24]. The oxidative stability decreased with the increase of IEC values.

4. Conclusions

A series of sulfonated poly(phenylquinoxaline) copolymers were successfully synthesized from novel sulfonated tetraamine, unsulfonated tetraamine and 4-phenylglyoxalylbenzil (or *p*,*p*′-oxydibenzil) in a mild condition. The copolymer membranes prepared by a solution casting method showed very high thermal, thermooxidative, hydrolytic stabilities and low methanol permeability. They also displayed good water swelling resistance because of the formation of acid-base complex between the N atoms of quinoxaline ring and the –SO_3H groups. SPPQs membranes showed much higher proton conductivities than the previously reported sulfonated benzimidazole. The highest conductivity of 0.2 S/cm was obtained for SPPQ(O)-100 at 140 °C. Through a comprehensive consideration of all properties of SPPQs, these materials will be hopeful candidates for polymer membrane electrode in fuel cells.

Acknowledgements

We thank the National Basic Research Program of China (No. 2009CB623401), the National Science Foundation of China (No. 50673087 and 50825303) and the Development of Scientific and Technoloical Project of Jilin Province (No. 20080620) for the financial support.

References

[1] Miyatate K, Chikashige Y, Higuchi E, Watanabe M. J Am Chem Soc 2007;129:3879–87.
[2] Lafitte B, Jannasch P. Adv Funct Mater 2007;17:2823–34.
[3] Asano N, Aoki M, Suzuki S, Miyatake K, Uchida H, Watanabe M. J Am Chem Soc 2006;128:1762–9.
[4] Fang T. Macromolecules 1991;24:444–9.
[5] Hedrick JL, Labadie JW. Macromolecules 1990;23:1561–8.
[6] Zhang C, Lai Z, Lu F. Polymer 1991;32:3075–85.
[7] Kopitzke RW, Linkous CA, Nelson GL. J Polym Sci Part A Polym Chem 1998;36:1197–9.
[8] Hickner MA, Ghassemi H, Kim YS, Einsla BR, McGrath JE. Chem Rev 2004;104:4587–612.
[9] Ogliaruso MA, Becker EI. J Org Chem 1965;30:3354–60.
[10] Hergenrother PM. J Polym Sci Part A Polym Chem 1969;7:945–57.
[11] Li NW, Cui ZM, Zhang SB, Xing W. Submitted.
[12] Roziere J, Jones DJ, Marrony M, Glipa X, Mula B. Solid State Ionics 2001;145:61–8.
[13] Wang JL, Song YL, Zhang C, Ye ZB, Liu H, Lee MH, Wang DH, Ji JB. Macromol Chem Phys 2008;209:1495–502.
[14] Liu B, Robertson GP, Kim D, Guiver MD, Hu W, Jiang Z. Macromolecules 2007;40:1934–44.
[15] Kim DS, Shin KH, Park HB, Chung YS, Nam SY, Lee YM. J Membr Sci 2006;278:428–36.
[16] Harrison WL, Wang F, Mecham JB, Bhanu VA, Hill M, Kim YS, et al. J Polym Sci Part A Polym Chem 2003;41:2264–76.
[17] Fang JH, Guo XX, Harada S, Watari T, Tanaka K, Kita H, Okamoto K. Macromolecules 2002;35:9022–8.
[18] Chen SW, Yin Y, Kita H, Okamoto K. J Polym Sci Part A Polym Chem 2007;45:2797–811.
[19] Bai ZW, Houtz MD, Mirau PA, Dang TD. Polymer 2007;48:6598–604.
[20] Zhong SL, Liu CG, Dou ZY, Li XF, Zhao CJ, F TZ, et al. J Membr Sci 2006;285:404–11.
[21] Li YX, Wang F, Yang J, Liu D, Roy A, Case S, et al. Polymer 2006;47:4210–7.
[22] Jouanneau J, Mercier R, Gonon L, Gebel G. Macromolecules 2006;40:983–90.
[23] Song EH, Paik WK. J Electrochem Soc 1998;145:1193–6.
[24] Wang L, Meng YZ, Li XH, Xiao M, Wang SJ, Hay AS. J Membr Sci 2006;280:108–15.