

Block sulfonated poly(ether ether ketone)s (SPEEK) ionomers with high ion-exchange capacities for proton exchange membranes

Chengji Zhao, Haidan Lin, Ke Shao, Xianfeng Li, Hongzhe Ni, Zhe Wang, Hui Na*

Alan G. MacDiarmid Institute, College of Chemistry, Jilin University, Changchun 130012, PR China

Received 26 June 2006; received in revised form 27 July 2006; accepted 27 July 2006

Available online 7 September 2006

Abstract

A series of block SPEEK copolymers with high ion-exchange capacities (IEC) consisting of hydrophobic and hydrophilic blocks were synthesized successfully. Membranes were cast from their DMF solutions, and characterized by determining the ion-exchange capacity, water uptake, water retention, proton conductivity and thermal properties. Membranes exhibited conductivities from 0.027 to 0.068 S cm⁻¹ at 30 °C and from 0.049 to 0.11 S cm⁻¹ at 80 °C; water uptake from 34% to 54% and IEC from 1.25 to 1.48 mequiv. g⁻¹. Block-3 membrane with IEC 1.38 mequiv. g⁻¹ showed relatively higher proton conductivity compared to that of a random SPEEK membrane with IEC 1.37 mequiv. g⁻¹. The SAXS profiles of block SPEEK copolymers exhibited a well-defined ionomer peak at low angles due to the phase separation between ionic domains and hydrophobic domains. It is believed that their microstructure features attribute to the enhanced proton conductivity of block SPEEK membranes.

© 2006 Elsevier B.V. All rights reserved.

Keywords: SPEEK; Block copolymers; Proton exchange membrane; Phase separation

1. Introduction

The proton exchange membrane is a vital component of the solid polymer electrolyte membrane fuel cell (PEMFC), which is developing as an alternative power sources for stationary, automobile and portable power [1,2]. The commercially available membrane used in PEMFCs is Nafion[®], which is composed of perfluorinated carbon chains containing pendent perfluorinated sulfonic acid groups. It meets numerous requirements for PEMFC applications, such as excellent proton conductivity, high mechanical strength and good chemical stability. However, the high costs and the cross-over of the methanol fuel from the anode to the cathode through the membrane and consequent loss of performance at high temperature or low humidity have limited its large-scale industrial application [3]. Recently many efforts have been devoted to developing new materials for proton exchange membranes based on sulfonated aromatic polymers, such as poly(aryl ether ketone)s [4–7], poly(ether sulfone)s [8,9], polyimides [10,11]. These alternative materials are expected to have a low cost as well as adequate electrochemical properties.

The membranes' mechanical strength, water uptake and proton conductivity are not only related to the chemical structure of these polymers, but also determined by the morphology or ionic nanostructure of the membranes [12,13]. It is well known that the ion pairs form multiples that aggregate into larger clusters, which are embedded in the hydrophobic polymer matrix, leading to nanophase separation [14]. For the sulfonated aromatic polymer membranes, block copolymerization is a potential route to achieve a phase-separated morphology [15]. There are several reports on the proton exchange membranes based on block sulfonated poly(aryl ether ketone)s [16], polystyrene [17] and polyimides [18].

Recently, we presented a novel route for preparing block SPEEK membranes with various block chain lengths with low ion-exchange capacities (IEC) [19]. Interestingly, block SPEEK copolymers show a greater degree of phase separation, resulting in a higher proton conductivity than random copolymers. However, their proton conductivities are still lower than 0.03 S cm⁻¹ (80 °C), which is much lower than that of Nafion[®].

To develop the block copolymers, which can be potentially suitable for applications in fuel cell systems, the relationships between the proton conductivity and block copolymers properties, such as IEC or block chain lengths, should be systematically studied.

* Corresponding author. Tel.: +86 431 5168870; fax: +86 431 5168868.
E-mail address: huina@jlu.edu.cn (H. Na).

The purpose of this work is to prepare block SPEEK membranes with high ion-exchange capacities to obtain better performance than the random and block SPEEK membranes reported previously [19]. Specifically, the block SPEEK membranes with different IECs for the same block chain lengths or with different block chain lengths at the same IEC also allow us to focus on the structure–properties relationships in terms of water uptake and proton conductivity.

2. Experimental

2.1. Synthesis of hydrophobic fluorine-terminated PEEK oligomers (PEEK-F)

As shown in Scheme 1, the synthesis of fluorine-terminated oligomers was carried out via our previously reported procedure with n (15, 9 or 4) equivalents of 3,3',5,5'-tetramethyl-4,4'-biphenol, $n+1$ (15, 9 or 4) equivalents of 4,4'-difluorobenzophenone and 10% excess of anhydrous K_2CO_3 [19]. In Scheme 1, the symbol m representing average repeat unit numbers was 31, 16 or 9. After mixing the monomers in DMSO/toluene system, the mixture was stirred at 140 °C for 4 h and then raised to 170 °C for 6 h. The reaction mixture was cooled to room temperature and poured into acetone. The inorganic salts were removed by washing with boiling water several times. The product was dried at 100 °C under vacuum. Analysis data of oligomer-1: FT-IR (KBr, cm^{-1}): 765, 862, 926, 1604 (C=C of benzene ring), 1650 (C=O), 2930 ($-CH_3$). 1H NMR (500 MHz, DMSO, ppm): 7.79 (d), 7.55 (s), 6.93 (d).

2.2. Synthesis of block SPEEK copolymers

In this procedure, the oligomers were synthesized according to the above description, but they were not precipitated. When the preparation procedure of oligomers was completed, the solution was cooled to 120 °C, then calculated sodium 5,5'-carbonylbis(2-fluobenzene-sulfonate) and 3,3',5,5'-tetramethyl-4,4'-biphenol for the hydrophilic block were added to the first reaction flask. Potassium carbonate, toluene and DMSO were also added to afford a 20 wt.% solid concentration. The reaction mixture was heated to 140 °C for 4 h and 170 °C for another 6 h. The resulting viscous solution was poured into acetone, washed with boiling water several times and dried at 100 °C for 48 h.

2.3. Membrane preparation

Membranes of block SPEEK copolymers were prepared by solution casting at 60 °C from their DMF solutions (5–10%). The residual solvent was completely removed under vacuum at 120 °C for 12 h. Then membranes were detached from the glass plates by immersing the plates into deionized water for several minutes. To convert the membranes into acid form, they were immersed in 2.0 M HCl solution overnight. Finally, the resulting membranes were thoroughly washed with deionized water and dried under vacuum at 100 °C for 24 h.

2.4. Characterization

FT-IR spectra were recorded on a Bruker Vector 22 FT-IR spectrometer, using copolymers powder samples as KBr pellets. Intrinsic viscosities of the samples were measured at 25 °C by using an Ubbelohde viscometer. The polymer concentration was 0.5 g dl^{-1} in DMF. Gel permeation chromatography (GPC) analysis was carried with a Waters 410 instrument using tetrahydrofuran as the eluant and polystyrene as the standard.

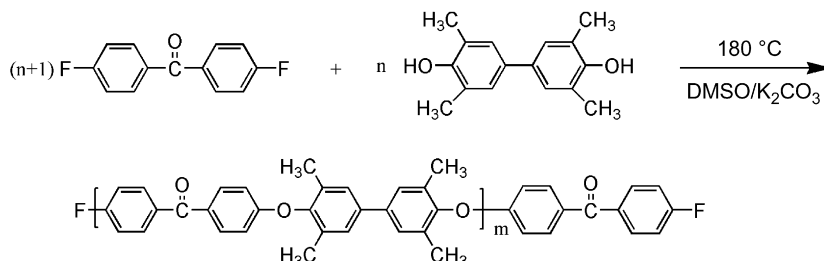
2.5. Thermal properties

The thermal stability of the SPEEK copolymers was performed on a Perkin-Elmer Pyris 1 TGA analyzer. Approximately 5–10 mg samples of the copolymers were preheated to 150 °C at 20 °C min^{-1} and kept at this temperature for 20 min to remove any residual water or solvent remaining in the copolymer films under N_2 . The samples were cooled to 80 °C and then reheated to 700 °C at 10 °C min^{-1} , the temperatures at which 5% weight loss were recorded for each sample.

2.6. Water uptake of membrane and water diffusion coefficient

The water uptake (WU) was measured after drying the membranes in acidic form at 100 °C under vacuum overnight. The dried membranes were soaked in deionized water for more than 48 h until the weight remained constant. This procedure was repeated at least three times to obtain a satisfactory data reproducibility. The water uptake was calculated as percentage by using the following formula:

$$WU (\%) = \frac{W_{wet} - W_{drying}}{W_{drying}} \times 100 \quad (1)$$



Scheme 1. Synthesis of oligomers with fluorine end-groups.

The water desorption measurements were made by a Pyris 1TGA (Perkin-Elmer) at 80 °C and at constant pressure for 60 min. The Pyris 1TGA was used to determine the weight changes of samples with time [28]. Water diffusion coefficient was calculated from the following formula:

$$\frac{M_t}{M_\infty} = 4 \left(\frac{Dt}{\pi l^2} \right)^{1/2} \quad (2)$$

where D is the water diffusion coefficient, M_t/M_∞ the water desorption, and l is the membrane thickness.

2.7. Ion-exchange capacity (IEC) of membrane

The IEC of block SPEEK membranes was determined by classical titration [9]. Membrane samples (0.5–1.0 g) were immersed in 1 M NaCl solution for at least 24 h to liberate the H⁺ ions (the H⁺ ions in the membranes were replaced by Na⁺ ions). The exchanged protons within the solutions were titrated with 0.05 N NaOH solutions by using phenolphthalein as an indicator. For each sample, at least three measurements were carried out until it had reached to a constant value. The IEC was calculated from the titration result via the following formula:

$$\text{IEC (mequiv./g)} = \frac{\text{consumed ml NaOH} \times \text{molarity NaOH}}{\text{weight dried membrane}} \quad (3)$$

2.8. Proton conductivity

The proton conductivity of the SPEEK membranes was measured via the AC impedance spectroscopy using a Philips 1260 impedance/gain-phase analyzer over a frequency range of 10 Hz to 1 MHz. The specimens were soaked in deionized water for at least 24 h prior to testing. Conductivity measurements of fully hydrated membranes were carried out with the cell immersed in liquid water, as reported in our previous work [6]. The proton conductivity was calculated by the following formula:

$$\sigma = \frac{L}{RA} \quad (4)$$

where L is the distance between the two electrodes, R the membrane resistance and A is the cross-sectional area of membrane.

2.9. Small-angle X-ray scattering (SAXS)

SAXS measurements were performed on dried SPEEK copolymers in their sodium salt form. All the measurements were carried out at room temperature, using Kratky small-angle X-ray scattering with Cu K α (Philips) radiation.

3. Results and discussion

3.1. Synthesis of oligomers

In order to obtain block SPEEKs comprised of an alternating segment of hydrophobic non-sulfonated and hydrophilic sulfonated blocks, the preparation of end-functionalized oligomers was initiated. As illustrated in Scheme 1, fluorine-terminated PEEK oligomers were synthesized by high-temperature condensation of 4,4'-difluorobenzophenone and 3,3',5,5'-tetramethyl-4,4'-biphenol. Excess of 4,4'-difluorobenzophenone was used to ensure formation of fluorine-terminated structure for the subsequent condensation. n (15, 9 or 4) equivalents of 3,3',5,5'-tetramethyl-4,4'-biphenol were reacted with corresponding $n + 1$ (16, 10 or 5) equivalents of 4,4'-difluorobenzophenone at a molar ratio of $n:n + 1$ to give different chain lengths of the fluorine-terminated oligomers, which were subsequently used to form the hydrophobic segment of the block copolymers. According to Carothers equation [20], the calculated average repeating unit numbers were 31, 19 and 9, respectively. Molecular weights for these hydrophobic blocks were estimated by GPC, as listed in Table 1. The results were consistent with the calculated M_n using Carother's equation, which indicated the hydrophobic blocks formed successfully with the desired lengths. Based on Shin's report [16], hydrophilic blocks as well as the block copolymers were prepared by step growth polymerization reactions. In our procedure, the molecular weights of hydrophilic blocks cannot be measured independently.

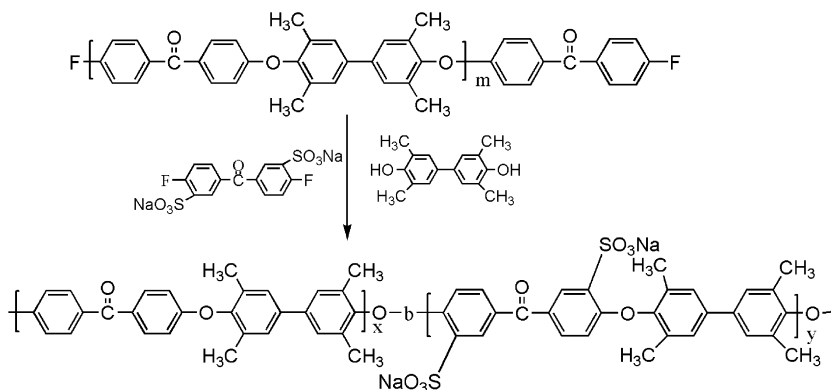
3.2. Synthesis of block SPEEK copolymer ionomers

The block SPEEK copolymers were synthesized successfully by a two-stage one-pot method as shown in Scheme 2. Firstly, the hydrophobic block was prepared with the desired length, then the monomers for the hydrophilic block were added to the reactive flask in order to form block copolymers. This approach was similar to Shin's published work [16], but in this present work the hydrophobic blocks were kept in the reactive flask and not precipitated before the polymerization, which can ensure the high molecular weights of the resulting polymers. Another improvement was that due to the better reactivity of the fluorine groups, fluorine-terminated oligomers other than phenol-terminated ones were prepared.

The problem of the block copolymers obtained by Shin was their poor solubility. But the block SPEEK copolymers either in sulfonic acid or sodium forms obtained by our one-pot method could be dissolved in common aprotic solvents, such as NMP,

Table 1
Synthesis results of oligomers for hydrophobic block

Oligomers	Ratio of $n/n + 1$	Average repeating unit number	Molecular weight (calculated)	Molecular weight (measured)	DPI
Oligomer-1	4/5	9	3410	3998	1.76
Oligomer-2	9/10	19	9403	8198	1.74
Oligomer-3	16/17	31	13729	13061	2.04



Scheme 2. Synthesis of SPEEK block copolymers.

DMF and DMAc, which allowed forming tough transparent membranes.

Block copolymers with different IEC were synthesized by varying the stoichiometry of the monomers. The molar amounts of 4,4'-difluorobenzophenone, sodium 5,5'-carbonylbis(2-fluobenzene-sulfonate) and 3,3',5,5'-tetramethyl-4,4'-biphenol used in the block preparation were summarized in Table 2. The intrinsic viscosities of the copolymers were measured in DMF at 25 °C with a polymer solution concentration of 0.5 g dl⁻¹. Block SPEEK copolymers have viscosities higher than 1.00, which indicates all copolymers possess high molecular weights.

3.3. Polymer characterization

FT-IR spectra were used for confirming functional groups in the copolymers. As illustration in Fig. 1, the successful incorporation of sulfonate groups can be confirmed by their corresponding characteristic transmitted bands. The observed bands at 1227, 1026 and 1086 cm⁻¹ are assigned to symmetric and asymmetric stretching vibrations of O=S=O. The peak at 685 cm⁻¹ is due to the stretching of the S–O. The spectroscopic results of the block SPEEKs are similar to the random ones observed by our previous work [4]. So, it is proved that the sulfonate groups were successfully introduced into both random and block copolymers as expected.

Table 2
Synthesis data of block SPEEK copolymers

Sample	Feed (mmol)				Yield (%)	Viscosity (η_{sp}/c)
	K ^a	I ^a	M ^b	I ^b		
Block-1	4.00	3.20	4.00	4.80	96	1.20
Block-2	4.00	3.75	4.00	4.25	93	1.34
Block-3	4.00	3.60	6.00	6.40	94	1.53
Block-4	4.00	3.75	6.00	6.25	92	1.13

^a The amount of 4,4'-difluorobenzophenone (monomer K) and 3,3',5,5'-tetramethyl-4,4'-biphenol (monomer I) in the oligomers preparation.

^b The amount of sodium 5,5'-carbonylbis(2-fluobenzene-sulfonate) (monomer M) and 3,3',5,5'-tetramethyl-4,4'-biphenol (monomer I') in the block SPEEK preparation.

3.4. Thermal properties of the block SPEEK

Fig. 2 shows the TGA curves of the block SPEEKs in their acid form. All the block SPEEKs exhibit a two-step degradation pattern. The first weight loss at around 300 °C is attributed to the splitting-off of sulfonic acid groups. This may be caused by the thermal degradation of sulfonic acid groups at relatively low temperature compared to the backbones of polymers. The second degradation step around 440 °C corresponds to the main chain decomposition. The 5% weight loss temperatures of block-1 to block-4 are 316, 292, 303 and 302 °C, respectively, indicating the high thermal stability of block SPEEKs copolymers.

3.5. The small-angle X-ray scattering (SAXS)

Block copolymers comprised of hydrophobic and hydrophilic blocks are well known to exhibit microphase separation of the incompatible domains [21,22]. Such microphase separation facilitates the formation of continuous ion channels, which provide the proton transport channels through the membranes and further improve their performances in fuel cells [23].

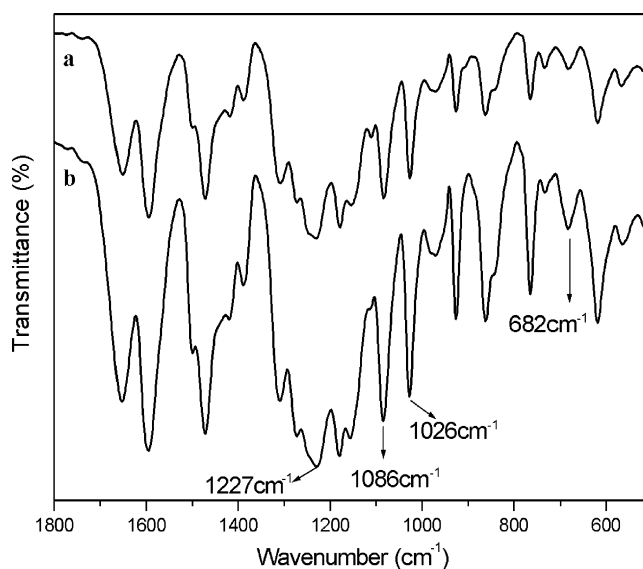


Fig. 1. The FT-IR spectrum of (a) random SPEEK and (b) block-4 SPEEK.

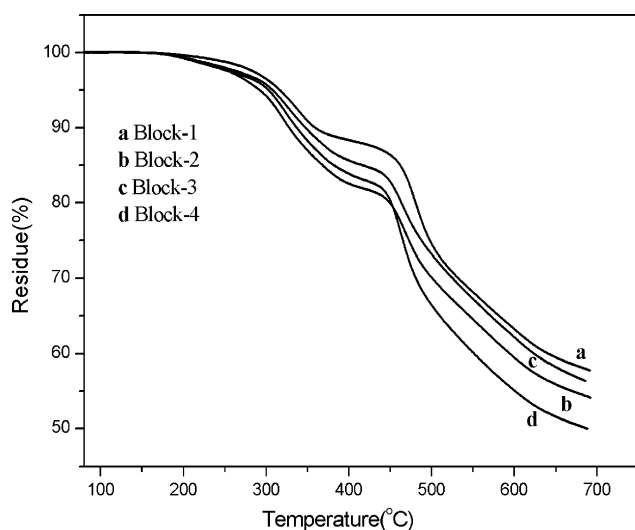


Fig. 2. TGA curves of block SPEEK copolymers in acid form.

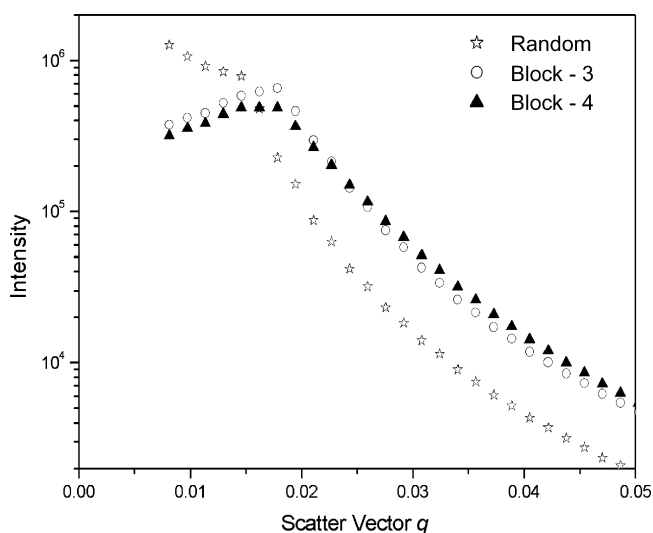


Fig. 3. The SAXS profiles of SPEEK copolymers.

SAXS was usually used to study the internal structures of the ionic polymers including the ionic clusters [24]. SAXS profiles of block-3, block-4 and random SPEEK ionomers are shown in Fig. 3. A scattering maximum (so-called “ionomer peak”) due to the phase separation between the ionic domains

and the hydrophobic domains is observed more obviously in block SPEEK ionomers than that of random SPEEK. This result reveals that the sulfonated groups in block polymers distribute more concentrated and easily aggregated to form ionic domains.

The scattering profiles of block SPEEK ionomers exhibit a well-defined peak at low angles: $q_{\max} = 0.02 \text{ \AA}^{-1}$. As previously mentioned by Essafi et al., this peak position is close to block sulfonated polyimides and very low compared to those of other ionomers such as Nafion[®], for which the peak position is located at around $q_{\max} = 0.1\text{--}0.2 \text{ \AA}^{-1}$ relying on the water content [25]. The Bragg spacing d , referring to the center-to-center distance between the two ionic clusters, can be obtained from the equation $d = 2\pi/q$. From the Bragg spacing calculated results, it can be deduced that the size of the ionic domains of block SPEEK is similar to block sulfonated polyimides and roughly 10 times larger than that of usual ionomers.

3.6. Water uptake and water desorption of membranes

As mentioned in Section 3.2, all block copolymers in their sodium or acidic form prepared by our modified approach can be soluble in common aprotic solvents, such as NMP, DMF, DMAc. Consequently, tough membranes can be obtained by casting from their DMF solutions.

The water uptake is one of the essential parameters for both proton transport and mechanical stability of proton exchange membranes [26]. The proton transporting through the membrane requires a significant amount of water to coordinate with proton. The water uptake of block SPEEKs membranes is summarized in Table 3. The water uptake shows an increasing trend with the increasing of IEC. For example, block-1 and block-4 membranes with IEC 1.25 and 1.48 mequiv. g^{-1} exhibit the value of water uptake of 34% and 54%, respectively. However, the water uptake does not seem to only depend on the IEC value but also on the special morphology of the membranes. The value shows an increasing trend with hydrophobic chain length increasing. Block-2 membrane shows higher water uptake value than block-1 membrane. This may be due to the formation of large phase separation structure.

Water retention of proton exchange membranes has significant effects on their proton conductivities, especially the water retention of membranes at high temperatures [27]. Low water retention of Nafion[®] at high temperatures is one of drawbacks, which hinders their further commercial application. Water reten-

Table 3
The water uptake, IEC and conductivity of membranes

Polymer	d^a (μm)	Water uptake (%)	IEC (mmol g^{-1})		Water diffusion coefficient ($\times 10^{-10} \text{ m}^2 \text{ s}^{-1}$)	Proton conductivity (S cm^{-1})	
			Calculated	Measured		30 °C	80 °C
Block-1	80	34	2.00	1.25	1.38	0.027	0.049
Block-2	65	40	2.00	1.27	1.48	0.04	0.065
Block-3	45	37	2.32	1.38	1.47	0.054	0.088
Block-4	65	54	2.32	1.48	6.32	0.068	0.11
Random	60	22	1.65	1.37	–	0.046	0.067
Nafion117	175	38	–	0.92	–	0.08 ^b	0.12 ^b

^a Thickness of membranes.

^b Proton conductivity measured with the same method.

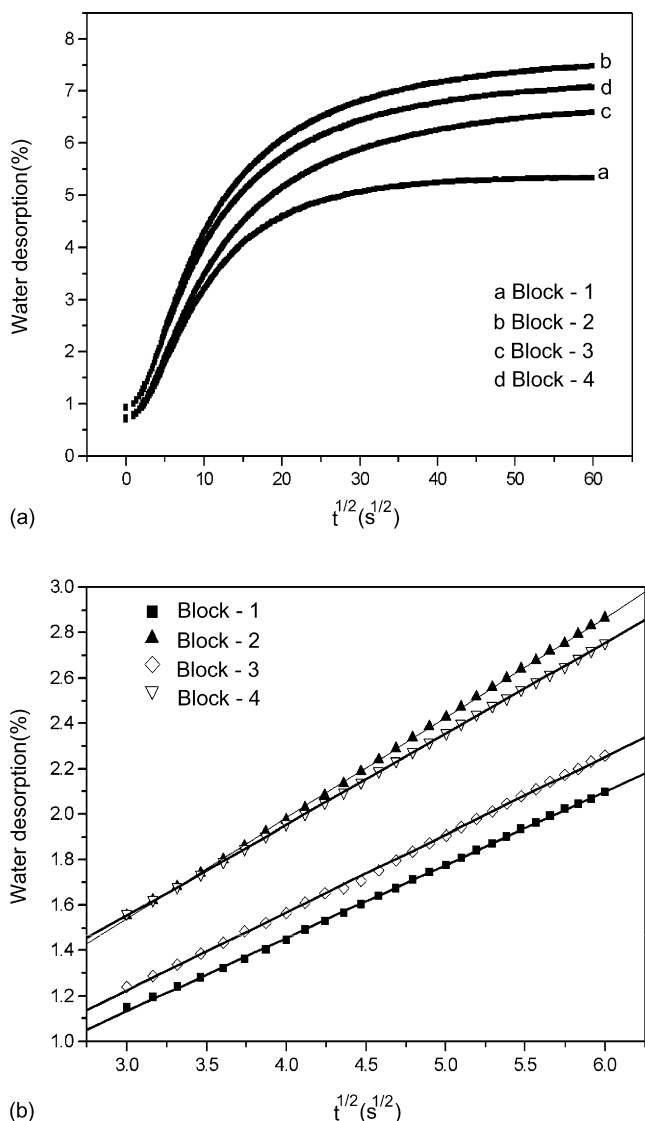


Fig. 4. The water desorption of block SPEEK membranes.

tion of membranes was closely related to the microstructure of membranes. In this section, water retention was analyzed by the velocity of water evaporation of membranes at 80 °C. Water desorption isotherm curves of block SPEEK membranes are shown in Fig. 4a. Plots of M_t/M_∞ versus $t^{1/2}$ initially are linear for Fickian diffusion laws [28], which is shown in Fig. 4b. The water diffusions of block SPEEK membranes calculated from the slope of the line are 1.38×10^{-10} , 1.48×10^{-10} , 1.47×10^{-10} and $6.52 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, respectively. From the results, the velocity of water volatilization increases with increasing IEC and increasing hydrophobic block chain lengths. More loosely bound water results in a higher self-diffusion coefficient, while more tightly bound water yields a lower self-diffusion coefficient [30]. So, the loosen structures of block SPEEK membranes generate high values of loosely bound water, and make the water easily evaporated, which results in increasing water diffusion coefficient of water in the membranes at relatively high temperature.

3.7. Ion-exchange capacities and proton conductivity of membranes

The ion-exchange capacity, or IEC, is usually defined as the moles of fixed SO_3 sites per gram of polymer. High IECs are necessary for good proton conduction because of the high charge density of the membrane. The theoretical IEC was calculated from the composition of the block copolymer ionomers. IECs determined by titration are less than the theoretical values. It indicates that loss of sulfonate groups occurs during synthesis and purification procedures. This is due to extraction of the lower molecular weight hydrophilic oligomers during workup at various stages of the membrane preparation [16].

The proton conductivity of the membranes at different temperatures was calculated from AC impedance spectroscopy measurement. Fig. 5 shows the proton conductivity of the fully hydrated (100% relative humidity) block SPEEK membranes at different temperatures. The random SPEEK membranes and Nafion[®] 117 were selected as references to compare the conductivities of membranes. All the membranes possess proton conductivity that was higher than $10^{-2} \text{ S cm}^{-1}$, which is the basically required value of practical interest for using as PEMs in fuel cells. As expected, it can be seen that the proton conductivity of the membranes increases with IEC and temperature increasing. Block-4 SPEEK membrane with the highest IEC $1.48 \text{ mequiv. g}^{-1}$ exhibits highest conductivity among these SPEEK membranes, which is close to the values of Nafion[®] 117. This can be explained that more protons that participate in conduction are derived from higher content of sulfonic acid groups.

To further reveal the difference of the proton conductivity between the random and the block SPEEK membranes with the similar IEC, and to detect the proton conductivity of the block SPEEK membranes with different block chain lengths, the conductivity data of some representative samples were analyzed. Compared to the random SPEEK membranes with IEC $1.37 \text{ mequiv. g}^{-1}$, block-3 membrane with IEC $1.38 \text{ mequiv. g}^{-1}$

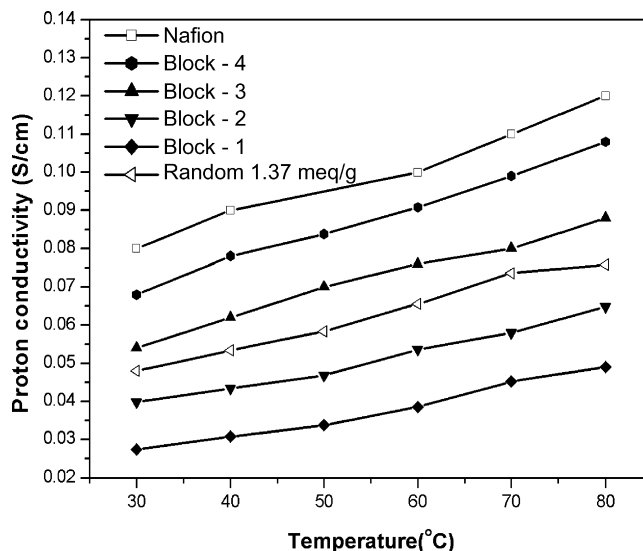


Fig. 5. Proton conductivities of block SPEEKs membranes as a function of temperature.

shows relatively higher proton conductivity. This is attributed to the different distribution of ion domains in membranes, which can be deduced from their SAXS profiles. Basically, block copolymers membranes usually contain two domain regions: the hydrophobic and hydrophilic ones. The phase of non-sulfonated blocks should provide good mechanical stability and reduce the swelling of the sulfonated blocks. On the other hand, the hydrophilic sulfonated blocks present high proton conductivity [29]. The existence of the two regions may lead to the microphase-separation structure, and concentrated sulfonate groups may provide much larger transport channels, which are beneficial to enhance the proton conductivity of the membranes. However, due to the structural characteristic of random SPEEK, the sulfonated groups were dispersed throughout the polymers matrix and not easily phase separated, which may lead to the lower proton conductivity than the block ones.

Block-1 and block-2 have similar IEC $1.25 \text{ mequiv. g}^{-1}$, but they have different hydrophobic block lengths of 9 and 31, respectively. Block-2 SPEEK membrane exhibits conductivity of 0.040 S cm^{-1} at 30°C and 0.065 S cm^{-1} at 80°C , which is higher than block-1 membrane, 0.027 S cm^{-1} at 30°C and 0.049 S cm^{-1} at 80°C , respectively. This might be attributed to the great degree of phase separation and increasing size of ionic clusters with hydrophobic block lengths increased.

4. Conclusion

Block SPEEK membranes with high ion-exchange capacities were successfully obtained. The structure and properties of the block SPEEK membranes were studied in detail. Microstructures of the block SPEEK membranes have been characterized by SAXS. The SAXS profiles of the block SPEEK ionomers exhibited a well-defined ionomer peak due to the phase separation between ionic domains and hydrophobic domains. The block SPEEK membranes showed increased water uptake and proton conductivity compared to the random SPEEK membrane at the similar IEC, which is attributed to a greater degree of phase separation. Block SPEEK membranes with high IEC exhibited proton conductivity in the range of 10^{-2} – $10^{-1} \text{ S cm}^{-1}$, which is close to that of Nafion[®] 117 under the same conditions. It appears that the block SPEEK membranes might be suitable for fuel cell applications as potential proton exchange membrane materials.

References

- [1] M. Rikukawa, K. Sanui, *Prog. Polym. Sci.* 25 (2000) 1463.
- [2] J.A. Kerres, *J. Membr. Sci.* 185 (2001) 3.
- [3] K.D. Kreuer, *J. Membr. Sci.* 185 (2001) 29.
- [4] M. Gil, X.L. Ji, X.F. Li, H. Na, J.E. Hampsey, Y.F. Lu, *J. Membr. Sci.* 234 (2004) 75.
- [5] P.X. Xing, G.P. Robertson, M.D. Guiver, S.D. Mikhailenko, K.P. Wang, S. Kaliaguine, *J. Membr. Sci.* 229 (2004) 95.
- [6] X.F. Li, C.J. Zhao, H. Lu, Z. Wang, H. Na, *Polymer* 46 (2005) 5820.
- [7] X.F. Li, C.P. Liu, H. Lu, C.J. Zhao, Z. Wang, W. Xing, H. Na, *J. Membr. Sci.* 255 (2005) 149.
- [8] M.A. Hickner, H. Ghassemi, Y.S. Kim, B.R. Einsla, J.E. McGrath, *Chem. Rev.* 104 (2004) 4587.
- [9] F. Wang, M.A. Hickner, Y.S. Kim, T.A. Zawodzinski, J.E. McGrath, *J. Membr. Sci.* 197 (2002) 231.
- [10] C. Genies, R. Mercier, B. Sillion, N. Cornet, G. Gebel, M. Pineri, *Polymer* 42 (2001) 359.
- [11] Y. Yin, J.H. Fang, Y.F. Cui, K. Tanaka, H. Kita, K. Okamoto, *Polymer* 44 (2003) 4509.
- [12] Y.S. Yang, Z.Q. Shi, S. Holdcroft, *Macromolecules* 37 (2004) 1678.
- [13] J.F. Ding, C. Chuy, S. Holdcroft, *Adv. Funct. Mater.* 12 (2002) 389.
- [14] A. Eisenberg, *Macromolecules* 3 (1970) 147.
- [15] X.P. Zhang, S.Z. Liu, J. Yin, *Polymer* 46 (2005) 1719.
- [16] C.K. Shin, G. Maier, B. Andreaus, G. Scherer, *J. Membr. Sci.* 245 (2004) 147.
- [17] Z.Q. Shi, S. Holdcroft, *Macromolecules* 38 (2005) 4193.
- [18] T. Nakano, S. Nagaoka, H. Kawakami, *Polym. Adv. Technol.* 16 (2005) 753.
- [19] C.J. Zhao, X.F. Li, Z. Wang, Z.Y. Dou, S.L. Zhong, H. Na, *J. Membr. Sci.* 280 (2006) 643.
- [20] W.H. Carothers, *J. Am. Chem. Soc.* 52 (1929) 2548.
- [21] D.J. Kinning, E.L. Thomas, D.B. Alward, L.J. Fetters, D.L. Handlin, *Macromolecules* 19 (1986) 1288.
- [22] R.F. Storey, D.W. Baugh, *Polymer* 41 (2000) 3205.
- [23] J. Won, H.H. Park, Y.J. Kim, S.W. Choi, H.Y. Ha, I.-H. Ha, *Macromolecules* 36 (2003) 3228.
- [24] M. Fujimura, T.J. Hashimoto, H. Kawai, *Macromolecules* 14 (1981) 1309.
- [25] W. Essafi, G. Gebel, R. Mercier, *Macromolecules* 37 (2004) 1431.
- [26] R.W. Kopitzke, C.A. Linkous, H.R. Anderson, G.L. Nelson, *J. Electrochem. Soc.* 147 (2000) 1677.
- [27] X.F. Li, D.J. Chen, D. Xu, C.J. Zhao, Z. Wang, H. Lu, H. Na, *J. Membr. Sci.* 275 (2006) 134.
- [28] T. Watari, H.Y. Wang, K. Kuwahara, K. Tanaka, H. Kita, K. Okamoto, *J. Membr. Sci.* 219 (2003) 137.
- [29] X. Lu, W.P. Steckel, R.A. Weiss, *Macromolecules* 26 (1993) 5876.
- [30] T.A. Zawodzinski, J. Davey, J. Valerio, S. Gottesfeld, *Electrochim. Acta* 40 (1995) 297.