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Synthesis of sulfonated poly(phthalazinone ether sulfone)s by direct polymerization

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Abstract

Sulfonated poly(phthalazinone ether sulfone)s with high molecular weight were directly prepared by polycondensation of 4-(4-hydroxyphenyl) phthalazinone with various ratios of disodium 5.5′-sulfonylbis(2-fluoro-benzenesulfonate) to 4-fluorophenyl sulfone. The resulting ionomers with high IEC showed low swelling. The low swelling originates from intermolecular hydrogen bonds, which is confirmed by variable temperature IR spectroscopy. The membranes show very good perspectives in PEMFC applications. © 2002 Elsevier Science Ltd. All rights reserved.

Keywords: Sulfonation; Poly(phthalazinone ether sulfone)s; Direct polycondensation

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1. Introduction

Polymer electrolyte membrane (PEM) is one of the most important integral parts of the PEM fuel cells (PEMFC) [1]. The current state-of-the-art used for PEMFC is perfluorosulfonic acid copolymer produced by Du Pont called Nafion® [2]. Although it has good chemical and physical properties for use in fuel cell applications, Nafion® has three technical limitations in terms of high cost, low conductivity at low humidity or high temperature, and high methanol permeability, which could decrease the cell efficiency [3,4]. Thus new PEMs for fuel cells are being explored.

Poly(aryl ether sulfone)s are interesting engineering materials due to their high glass transition temperatures, good mechanical properties, excellent thermal, oxidative, and chemical stability [5,6]. Thus sulfonated poly(aryl ether sulfone)s are of interest as PEMs [7]. It is convenient to prepare sulfonated poly(aryl ether sulfone)s by post-sulfonation. However, post-sulfonation brings on the placement of the sulfonic acid group *ortho* to the activated aromatic ether linkage, where the sulfonic acid groups are relatively easy to hydrolyze. Moreover, only one sulfonic acid per repeat unit can be achieved [8,9]. Recently, Ueda et al. [10] have successfully invented a new strategy to prepare sulfonated poly(aryl ether sulfone)s with sulfonated monomer derived from sulfonating the dihalide monomer. Sulfonation of the dihalide monomer, 4,4′-difluorobenzophenone and 4-chlorophenyl sulfone, results in sulfonic acid functionallization on both deactivated phenyl rings *ortho* to the halogen moiety, which offers them more chemical stability against desulfonation, and allows for two sulfonic acid groups per repeat unit of the resulting polymer [11–14]. The novel route shows other advantages, which include being free from any degradation and cross-linking, and easy to control the content of sulfonate groups by adjusting the ratios of the dihalide monomer to the sulfonated dihalide monomer [10]. Recently, 6F-bisphenol-based and 4,4′-biphenol-based sulfonated poly(aryl ether sulfone)s were prepared by the new approach [15–17]. Generally, most of the homogeneous ionomers have the problem of very high swelling degree at reasonable conductivity [18]. So other components were required to be blended in order to obtain composite membranes with lower swelling not only by forming physical cross-linking, which results from Van der waals forces or hydrogen bonds [19,20], but also by forming covalent bonds [21,22]. Up to now, the bisphenols monomer containing carbonyl group and nitrogen heterocycle has not been found to prepare sulfonated poly(aryl ether sulfone)s via direct condensation. Unfortunately, high molecular weight resulting ionomers

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cannot be achieved by condensation of 4-(4-hydroxyphenyl) phthalazinone (HPPT) with disodium 5,5′-sulfonylbis (2-chlorobenzenesulfonate) and 4-chlorophenyl sulfone. Probably, it results from the poor reaction activity of the dichloride monomer, so the sulfonated difluoride monomer, disodium 5,5′-sulfonylbis(2-fluorobenzenesulfonate) (SBFBS), was synthesized in order to take the place of the sulfonated dichloride monomer. This paper describes the synthesis and characterization of a new series of sulfonated poly(phthalazinone ether sulfone)s derived from HPPT, 5,5′-sulfonylbis(2-fluorobenzene-sulfonate), and 4-fluorophenyl sulfone (FPSF). The new ionomer membranes show low swelling, which may be used directly as PEM in fuel cell applications without blending with other components. Low swelling originates from hydrogen bonding, which was confirmed via variable-temperature IR spectroscopy.

2. Experimental part

2.1. Materials

FPSF was purchased from Aldrich Chemical Co. and used as received. HPPT (supplied by Dalian University of Technology) was used without further purification. Dimethyl sulfoxide (DMSO) and toluene were purified by distillation and stored over 4 Å molecular sieves. Other reagents and solvents were obtained commercially and used as received.

2.2. Instruments

Inherent viscosity was measured by using an Ubbelohde viscometer. NMR spectra were performed on a Varian Gemine-2000 300 MHz spectrometer. Mass spectrum was carried out with a HP 1100 liquid chromatography–mass spectrograph detector (LC–MSD). IR spectra were recorded for the polymer membranes, made from DMSO solution, with a Bruker Equinox-55 FTIR spectrometer equipped with a variable temperature cell. The sample was heated from room temperature to 160 °C at 4 °C/min. Sets of four scans were used for signal averaging. The curve fitting procedure was used to resolve the stretching band of H-bonded carbonyl groups and determine the area under the peaks.

2.3. Monomer synthesis

SBFBS was synthesized by heating a mixture of FPSF (25.4 g, 0.1 mol) and SO_3 (50.8 ml) at 120 °C for 9 h. The mixture was cooled and poured into ice water (400 ml), then was neutralized with enough amount of Na_2CO_3, filtered and dried. Recrystallization from methanol/ ethanol/water gave the scale-like crystal. Yield: 58% (26.6 g). IR (KBr, cm^{-1}): 1325, 1143 ($Ar-SO_2-Ar$), 1237, 1071, 695 ($Ar-SO_3Na$). ^1H NMR (300 MHz, D_2O, ppm): 8.40–8.44 (s, 1H), 8.20–8.26 (s, 1H), 7.50–7.60 (s, 1H). ^{13}C NMR (300 MHz, D_2O, ppm): 163.49 (d, $J_{CF} = 259.5$ Hz), 137.06 (d, $J_{CF} = 3.0$ Hz), 135.07 (d, $J_{CF} = 10.5$ Hz), 133.35 (d, $J_{CF} = 17.25$ Hz), 130.19 (d, $J_{CF} = 3.75$ Hz), 120.52 (d, $J_{CF} = 24.0$ Hz). Elem. Anal. Calcd for $C_{12}H_6F_2O_8S_3Na_2$: C, 31.45%, H, 1.32%, S, 20.99%. Found: C, 30.92%, H, 1.49%, S, 20.32%. MS (m/z): 481 ($M + Na^+$), 939 ($2M + Na^+$), 1397 ($3M + Na^+$).

2.4. Polymer synthesis

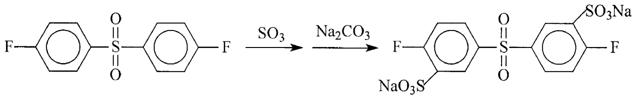
In a 150 ml three-necked round flask, equipped with a Dean–Stark trap, a condenser, a nitrogen inlet, 7 mmol HPPT, a mixture of disodium 5,5′-sulfonylbis(2-fluorobenzene sulfonate) and FPSF (7 mmol), and 8.4 mmol Na_2CO_3 were dissolved in a mixture of 25 ml DMSO and 25 ml toluene. The mixture was refluxed for 3 h at 150 °C, and then excess toluene was distilled off. The mixture was heated at 175 °C for 20 h. Then the reaction mixture was cooled to room temperature and poured into water to precipitate the copolymer. The crude product was then washed six times with hot water to remove inorganic salts. The purified polymer was filtered and dried in vacuo at 100 °C for 48 h. Analysis data of ionomer **Ie** are as follows: Yield: 96% (3.59 g). IR (solution casting film, cm^{-1}): 1324, 1153 ($Ar-SO_2-Ar$), 1245, 1074 695 ($Ar-SO_3Na$): 1669 (C=O). ^1H NMR (300 MHz, DMSO-d_6, ppm): 8.48–8.38, 8.38–8.30, 8.20–8.10, 8.10–8.02, 8.02–7.85, 7.85–7.64, 7.38–7.04. ^{13}C NMR (300 MHz, DMSO-d_6, ppm): 161.33, 161.05, 158.60, 158.28, 157.99, 157.17, 156.46, 155.73, 147.32, 147.12, 146.44, 145.98, 145.80, 144.51, 143.00, 142.68, 141.42, 140.61, 140.00, 139.43, 139.00, 135.83, 135.30, 135.04, 134.46, 132.61, 131.85, 131.57, 131.19, 130.35, 129.06, 128.55, 128.23, 128.14, 126.89, 120.41, 120.09, 118.70. Found: C, 58.01%; H, 3.02%; N, 5.31%; S, 10.53%. Calcd for **Ie**: C, 58.47%; H, 2.87%; N, 5.24%; S, 10.81%.

2.5. Preparation of membranes

Ionomer membranes (**Ia**–**Ie**) were prepared by casting a 3% solution in DMSO on a glass plate in a dust-free environment. Membranes were dried at 85 °C for 10 h and successively dried in a vacuum oven at 100 °C for 48 h.

2.6. Determination of the ion-exchange capacity

Ion-exchange capacity is performed as follows: a dry weight of 0.5–1.0 g of the polymer membrane in the SO_3H form is immersed in 50 ml of saturated NaCl solution. The H^+ ions of the membrane are released by huge excess of Na^+ ions. Then the solution containing the polymer membrane is titrated with 0.1N NaOH solution.



Scheme 1. Synthesis of SBFBS.

2.7. Measurement of swelling

Measurement of swelling was based upon the procedure [6,22]: the membrane sample (0.5–1.0 g) in the SO_3H form is swollen in water at room temperature until equilibrium is reached (about 48 h). Then the membranes are removed, and surface-attached water is quickly removed with tissue paper. The wet weight of the membrane (M_{wet}) is determined by weighing. After the wet membranes drying at 100 °C for 48 h, their dry weight M_{dry} is determined. The swelling (SW) is calculated via following formula:

$$SW = (M_{wet} - M_{dry})/M_{dry} \times 100\%$$

3. Results and discussion

3.1. Monomer synthesis

SBFBS was synthesized by sulfonation of FPSF with SO_3 (Scheme 1), which is an aromatic electrophilic reaction. The sulfonic acid is *ortho* to fluorine atom because of the *o*, *p*-orienting effect of the fluorine atom in the phenyl ring. NMR spectra of SBFBS are displayed in Fig. 1, which indicates the assignment of the peaks. The molecular structure was also confirmed by IR and element analysis. Fig. 2 is the mass spectrum of SBFBS. The peaks at $m/z =$ 481, 939, 1397 were found, which were attributed to $M + M_{Na}$ ($M = 458$ g/mol, $M_{Na} = 23$ g/mol), $2M + M_{Na}$, $3M + M_{Na}$, respectively. Thus the molecular structure was further confirmed by the mass spectrum.

3.2. Preparation and characterization of ionomers

Ionomers with different degree of sulfonation (**Ia–Ie**) were prepared from aromatic nucleophilic polycondensation of 4-(4-Hyrdroxyphenyl) phthalazinone with various ratios of SBFBS to 4-difluorophenyl sulfone (Scheme 2). The polymerization outcomes and the characterization data of **Ia–Ie** are displayed in Table 1.

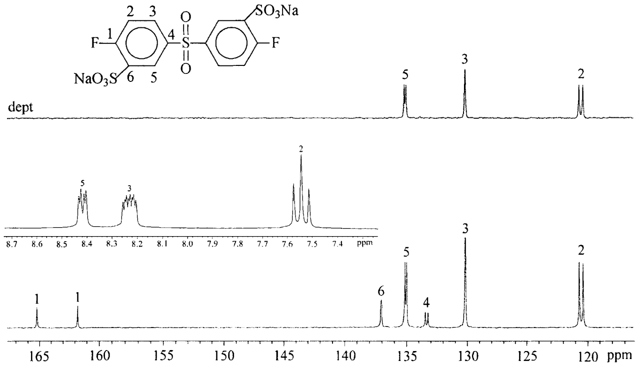


Fig. 1. ^{1}H NMR and ^{13}C NMR spectra of SBFBS.

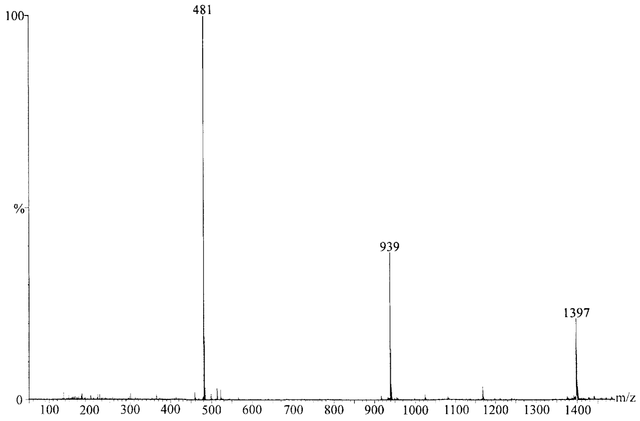


Fig. 2. Mass spectrum of SBFBS.

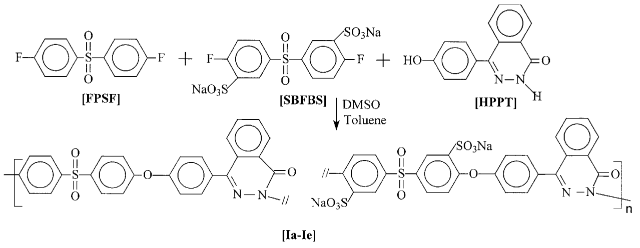
The inherent viscosity of polymers (**Ia–Ie**) is higher than 1.0 dl/g, which indicates high molecular weight of resulting polymers. Table 1 displays that higher the ratio of SBFBS to FPSF, higher the inherent viscosity of the polymer, since the electron-withdrawing sulfonate groups, $-SO_3Na$, increase the density of positive charge of the carbon atom connecting with the fluorine atom and thus enhance the electrophilic reactivity, although the steric hindrance of sodium sulfonate groups decreases the reactivity. The similar situation has been mentioned in the literature [15].

3.3. Ion-exchange capacity of ionomers

Table 1 shows the IEC of polymer **Ia–Ie**. The IEC of the ionomers, except **Ia**, is greater than that of Nafion 115 (0.91 meq/g). The IEC of the ionomers determined by titration is in agreement with the calculated values within the experimental error, illustrating that the pendant sulfonate groups were successfully attached to the polymer chains.

3.4. Swelling of ionomer membranes

The swelling of ionomer membranes are displayed in Table 1. According to expectation, the swelling of ionomer membranes increases with increasing IEC. The swelling of all the polymers is in the range of 14.0–22.9%, which is



Scheme 2. Preparation of ionomers **Ia–Ie**.

Table 1
Polycondensation conditions and characterization data of sulfonated poly(phthalazinone ether ketone)s

Polym	EPSF (n/mmol)	SBFBS (n/mmol)	HPPT (n/mmol)	$[\eta]^a$ (dl/g)	Yield (%)	$\text{IEC}_{\text{calc}}{}^b$ (meq/g)	$\text{IEC}_{\text{meas}}{}^c$ (meq/g)	SW (%)
Ia	5.60	1.40	7	1.08	98	0.811	0.794	14.0
Ib	5.25	1.75	7	1.40	98	0.993	0.971	16.8
Ic	4.90	2.10	7	1.45	97	1.17	1.14	17.7
Id	4.55	2.45	7	1.60	98	1.34	1.32	20.6
Ie	4.20	2.80	7	1.74	96	1.50	1.46	22.9

[a] Inherent viscosity measured at a concentration of 0.5 g/dl in DMSO at 25 ± 0.1 °C.
[b] Calculated IEC of ionomers.
[c] Measured IEC of ionomers.

much less than that of Nafion 115 (34%), while their IEC is much higher than that of Nafion 115 (0.91 meq/g). Therefore, sulfonated poly(phthalazinone ether sulfone)s show excellent resistance to swelling. Generally, Sulfonated poly(aryl ether ketone)s and sulfonated poly(aryl ether sulfone)s have rather high swelling degree at reasonable conductivity, which limit the application in the PEMFC. So other components were blended in order to obtain ionomer membranes with lower swelling by forming physical cross-linking or by forming covalent bonds [18]. On the contrary, sulfonated poly(phthalazinone ether sulfone)s with low swelling can be directly used as PEMs without blending with other components. The reason for low swelling will be analyzed later.

3.5. Study on hydrogen bonds

IR spectroscopy is a powerful technique in the study of hydrogen bonds [23]. IR spectra taken as a function of temperature for the membrane **Ie** (in the H^+ form) in the frequency regions 1200–1750 cm^{-1} are indicated in Fig. 3. The spectral mode in 'free' form is placed at 1669 cm^{-1} for carbonyl groups of hydroxyphenyl phthalazinone unit, while the spectral mode in H-bonded form is placed at 1650 cm^{-1}. Generally, this band shifts to lower frequency when forming hydrogen bonds, which results from a decrease of the force constant of the covalent bond with the H donor. It is obvious that the height of the band at 1650 cm^{-1} decreases with increasing temperature in Fig. 3.

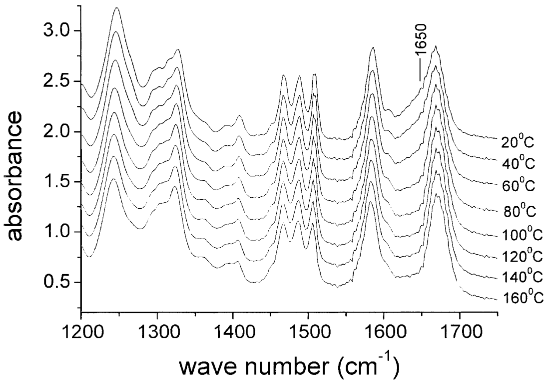


Fig. 3. IR spectra of **Ie** at various temperatures.

The normalized area of carbonyl groups forming hydrogen bonds can be considered an indication of the strength of hydrogen bonding. Fig. 4 shows the normalized area of associated carbonyl groups at various temperatures. As to expect, the normalized area decreases with increasing temperature, which reduces slowly in a temperature ranging from 20 to 60 °C and from 100 to 120 °C and reduces abruptly at 60–100 °C. This case illustrates that associated carbonyl groups transformed into non-associated carbonyl groups with increasing temperature, and that the hydrogen bonding changed greatly in intensity at 60–100 °C. The hydrogen bonding is strong between 20 and 100 °C because the integral area of H-bonded carbonyl groups is fairly great in the temperature range (Fig. 4). The strong hydrogen bonding results in low swelling of membranes cast from the solution of sulfonated poly(phthalazinone ether sulfone)s.

4. Conclusions

Sulfonated poly(phthalazinone ether sulfone)s were directly synthesized by aromatic nucleophilic polycondensation of 4-(4-hydroxyphenyl) phthalazinon with various ratios of SBFBS to FPSF. The resulting ionomers displayed high molecular weight, high ion-exchange capacity and low swelling. The low swelling originates from the hydrogen bonding between hydrogen atoms of sulfonic acid and carbonyl groups, which was validated by variable

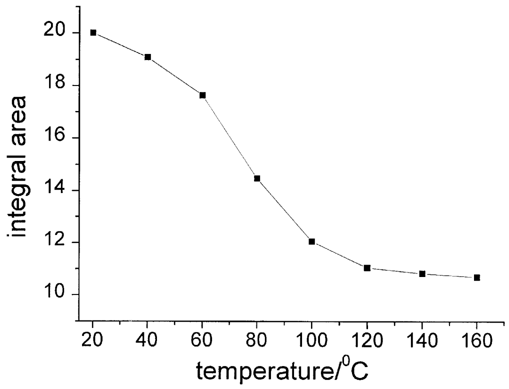


Fig. 4. Normalized area of H-bonded carbonyl groups at various temperatures.

temperature IR spectra. The ionomers show good perspectives in PEMFC applications. In future work the mechanical properties, the thermal properties, and the electrochemistry properties will be studied in detail.

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