Polymer Bulletin 54, 57–64 (2005)
DOI 10.1007/s00289-005-0371-8

Polymer Bulletin

Comparison of the water uptake and swelling between sulfonated poly(phthalazinone ether ketone ketone)s and sulfonated poly(arylene ether ketone ketone)s

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Received: 23 December 2004 / Revised version: 10 March 2005 / Accepted: 28 March 2005

Summary

Sulfonated poly(phthalazinone ether ketone ketone)s (sPPEKK) and sulfonated poly(arylene ether ketone ketone)s (sPAEKK) were successfully synthesized by direct polycondensation. The water uptake and swelling of sPPEKK are much less compared with those of sPAEKK, especially in high temperature, which results from the powerful intermolecular hydrogen bonds of sPAEKK, confirmed by variable temperature IR spectra. The maximum operation temperature of proton exchange membranes made of sPPEKK is higher than 80 °C, improving the property of resistance to swelling.

Introduction

Proton exchange membrane (PEM) is one of the key integral parts of polymer exchange membrane fuel cells (PEM), the study of which now is attractive. Up to now, Nafion is the state-of-the-art used for PEM, but it has three main drawbacks, such as low conductivity at high temperature or low humidity, high cost and high methanol permeability, limiting its application in direct methanol fuel cells [1]. Therefore, more and more studies on PEM have been carried out so as to provide PEM with good overall properties [2-6]. Poly(arylene ether ketone/sulfone)s show a series of excellent properties, including excellent mechanical properties, high thermal stability, good chemical and oxidative stabilities, and so on, thus were expected to used as the bulk materials of PEM, which can be modified by introducing sulfonate groups to the benzene rings [7-9]. Works illustrated that PEM based on sulfonated poly(arylene ether ketone/sulfone)s showed a sharp increasing water uptake at 60~80 °C, then their mechanical properties became too bad to be out of operation [10]. Thereby, blending and post-modification were used to decrease the water uptake of PEM based on sulfonated poly(arylene ether ketone/sulfone)s by both physical and chemical cross-linking, resulting from the entanglements of polymer chains, van der Waals forces, intermolecular hydrogen bonds, covalent bonds and ionic bonds

[11-13]. However, studies showed that the interactions of entanglements and van der Waals forces were too low to sufficiently reduce the swelling degree; blending different kinds of components, leading to forming the intermolecular H-bonds, was complicated to carry out; the covalent cross links made blending membranes brittle, especially when drying out, though they were strong enough; the ionic cross links of acid-base blending membranes dissociate at temperature higher than 70 °C, which made the cross links weak [13]. Consequently, the routes of reducing the swelling degree of nonfluorinated PEM should be explored further. In this paper, sulfonated poly(phthalazinone ether ketone ketone)s were synthesized by direct poly-condensation, which have intermolecular H-bonds between the hydrogen of sulfonate groups and the proton acceptor of the phthalazinone groups, being expected to reduce their swelling greatly. This strategy of decreasing the swelling of nonfluorinated PEM is realized by introducing the proton acceptor of hydrogen bonds to the backbone of sulfonated ionomers, not by blending with other components containing the proton acceptor of hydrogen bonds. Sulfonated poly(arylene ether ketone ketone)s (sPAEKK) were prepared in order to compare their uptake and swelling with those of sPPEKK.

Experimental

Material

1,3-bis(4-fluorobenzoyl)-benzene, 4,4'-thiobisbenzenethiol and 4,4'-sulfonyldiphenol were purchased from Aldrich Chemical Co. 1,3-bis(4-fluorobenzoyl)-benzene was purified by recrystallization from the mixture solvent of toluene and ethanol. Dimethyl sulfoxide (DMSO) and toluene were purified by distillation and stored over 4 Å molecular sieves. Other reagents and solvents were used as received.

Measurement

NMR spectra were measured on a Varian MERCURYplus 400 MHz spectrometer. Molecular weight was recorded with a PE Series 200 gel permeation chromatography (GPC) equipped a refractive index detector. All samples were run in N,N-dimethyl formamide (DMF) at 25 °C with a flow rate of 1.0 ml/min; PS standards were used for calibration. Thermal transition was determined with a PE Pyris 1 differential scanning calorimeter under nitrogen atmosphere at a heating rate of 10 °C/min. Thermal gravimetric analysis (TGA) was measured under nitrogen flow through a PE TGA 7 thermo-gravimetric analyzer at a heating rate of 10 °C/min. IR spectra were recorded with a PE Paragon 1000 FT-IR spectrometer, equipped with a variable temperature cell. The samples were heated from room temperature to 180 °C. Sets of 4 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.

Membrane preparation

The resulting ionomers were dissolved in DMSO to produce transparent solutions and then cast on glass plates. The polymer solutions were dried at 75 °C for 12 h and successively in vacuo for 12 h. The membrane in the SO_3Na form is immersed in 1 M HCl at room temperature for 48 h in order to get its acid form membrane.

Determination of ion exchange capacity (IEC)

IEC was performed according to the following procedure: the sample (about 1g) in the SO_3H form was immersed in 50 ml saturated NaCl solution for 24 h in order to release the H^+ ions. Then the acid solution was titrated with 0.1N NaOH solution.

Water uptake content and swelling ratio

The membranes in the SO_3H form were completely dried in a vacuum oven at 120 °C for 24 h. Then membranes were immersed in de-ionized water at given temperatures for 24 h. After the surface-attached water of membranes was removed with tissue paper, the membranes were immediately weighed and measured. The water uptake and swelling ratios are calculated by the following formula:

$$Water\ Uptake(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100\% \quad Swelling\ \ ratio(\%) = \frac{l_{wet}\ -\ l_{dry}}{l_{dry}} \times 100\%$$

W_{wet} and W_{dry} are the mass of wet and dry membranes, respectively, while l_{wet} and l_{dry} represent the length of wet and dry membranes, respectively.

Monomer synthesis

The synthesis of 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)-benzene (BSFBB) was recorded in the paper [14]. The route of synthesis is displayed in Scheme 1.

Polymer synthesis

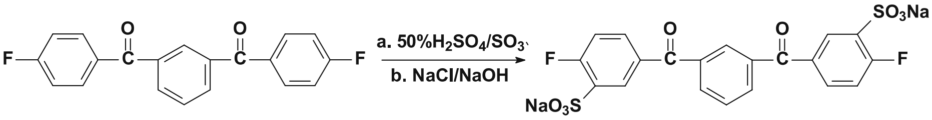
A typical polycondensation procedure was described for sPPEKK (Ia). To a 100 ml three-necked round bottom flask equipped with a Dean–Stark trap, a condenser, a nitrogen inlet, 2.5 mmol 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)-benzene, 2.5 mmol 1,3-bis(4-fluorobenzoyl)-benzene, 5 mmol 4-(4-Hydroxyphenyl) phthalazinone, 5.5 mmol K_2CO_3, 10 ml DMSO and 25 ml toluene were added. Toluene was used as an azeotropic agent. The mixture was refluxed for 3 h at 150 °C, and then toluene was completely removed from the reaction system. After continuous reaction for 20 h at 175 °C, the reaction stopped and the crude product was obtained by precipitating in water. The crude product was then washed six times with boiling water to remove inorganic salts. The purified product was dried in vacuo at 100 °C for 48 h. Yield: 99%. IR (solution casting film, cm^{-1}): 1661(-C=O), 1249, 1028, 696 (Ar-SO_3Na). ^1H NMR (400MHz, DMSO-d_6, ppm): 8.40-8.22, 8.19-7.66, 7.36-7.08, 7.08-7.00. ^{13}C NMR (400MHz, DMSO-d_6, ppm): 194.91, 194.37, 158.71, 158.15, 156.65, 147.71, 145.96, 142.62, 139.60, 137.65, 135.75, 134.23, 133.26, 132.24, 131.86, 131.51, 130.96, 129.90, 128.65, 127.66, 126.40, 125.67, 120.49, 118.49.

In similarly, sPAEKK (Ib) were prepared by polycondensation of 2.5 mmol 1,3-bis (3-sodium sulfonate-4-fluorobenzoyl)-benzene, 2.5 mmol 1,3-bis(4-fluoro -benzoyl)-benzene with 5 mmol 4,4'-sulfonyldiphenol. The purified product was also dried in vacuo at 100 °C for 48 h. Yield: 95%. IR (solution casting film, cm^{-1}): 1318, 1152 (-SO_2-), 1659(-C=O), 1246, 1029, 693(Ar-SO_3Na). ^1H NMR (400MHz, DMSO-d_6, ppm): 8.30-8.22, 8.14-7.95, 7.95-7.65, 7.36-7.14, 7.14-7.00. ^{13}C NMR (400 MHz, DMSO-d_6, ppm): 194.42, 162.19, 161.98, 160.58, 160.47, 159.63, 155.92, 140.85, 140.63, 137.89, 137.26, 136.96, 135.93, 135.53, 133.91, 133.27, 131.61, 130.80, 130.69, 130.29, 129.82, 122.58, 120.10, 120.00, 119.41.

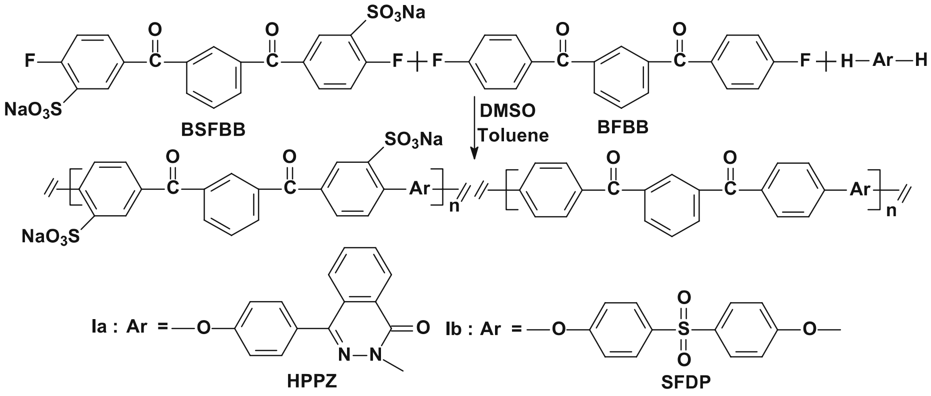
Results and discussion

Preparation of Ionomers

sPPEKK (Ia) and sPAEKK (Ib) were prepared by aromatic nucleophilic polycondensation of 1,3-bis(3-sodium sulfonate-4-fluorobenzoyl)-benzene and 1,3-bis(4-fluoro-benzoyl)-benzene with 4-(4-Hydroxyphenyl) phthalazinone and 4,4'-sulfonyldiphenol, respectively (Scheme 2). Their degrees of sulfonation are both equal to 1, that is to say, every repetitive unit has one sulfonate group on an average. They both showed high molecular weight. The results were displayed in Table 1.



Scheme 1. Synthesis of BSFBB



Scheme 2. Preparation of sPPEKK and sPAEKK

Table 1. Polycondensation results of sPPEKK and sPAEKK (in the SO_3Na form)

Polym	BSFBB (mmol)	BFBB (mmol)	HPPZ (mmol)	SFDP (mmol)	Mn (g/mol)	Yield (%)
Ia	2.5	2.5	5	0	59,391	99
Ib	2.5	2.5	0	5.	59,460	95

Thermal Properties of Ionomers

The characterization of ionomers was carried out according to the literature [15]. The samples in the salt form were dried for 30 min at 150 °C in nitrogen until their weight remained changeless, then were cooled and subjected to TGA and DSC analysis. For TGA analysis, the heating rate is 20 °C/min, the temperature range of measurement is

100 ~ 800 °C. The analysis results are listed in Table 2. The 5% weight loss temperature of the polymers is higher than 540 °C, indicating excellent thermal stability of the materials.

Table 2. Properties of Ia and Ib (in the SO_3Na form)

Polym	T_5[a] (°C)	T_g (°C)	IEC_{calc}[b] (meq/g)	IEC_{meas}[c] (meq/g)	Uptake[d] (%)	SW[d] (%)
Ia	548.3	324.8	1.606	1.574	18.1	6.9
Ib	540.0	298.2	1.576	1.551	20.8	6.3

[a] 5% weight loss temperature; [b] Calculated IEC of ionomers; [c] Measured IEC of ionomers;
[d] Measured value at 30 °C.

There is no any endothermic peak and exothermic peak in the curves of DSC in a temperature range of 50~350 °C (heating rate = 10 °C/min), indicating that the ionomers are an amorphous structure and there are no cross linking reactions between sodium sulfonate groups and benzene rings in the course of heating. Their glass transition temperatures (T_g) are both every high, which probably resulted from the powerful interaction of sulfonate groups. Tg (324.8 °C) of ionomer Ia is much higher than that (298.2 °C) of Ib because there is only one rotatable bond (ether bond) in every repetitive unit of Ia, while there are two rotatable bonds (ether bonds) in every repetitive unit of Ib, resulting in that Ib showed more flexible than Ia.

Ion exchange Capacity of Ionomers

Table 2 displays the IEC of ionomer Ia and Ib in the SO_3H form. The IEC of the ionomers is higher than 1.5 meq/g, much greater than that of Nafion 115 (0.91 meq/g). The IEC of the ionomers determined by titrating coincide with the calculated values within the experimental error, displaying that the pendant sulfonate groups were successfully attached to the polymer chains.

Water Uptake and Swelling of Ionomers

Fig. 1 shows that the water uptake and swelling of Ib in the SO_3H form are both little at 30 °C, they are 18.1% and 6.9%, respectively. In the 30~60 °C regions, the water uptake and swelling of Ib increase slightly with increasing temperature, while they enhance dramatically at 70 °C, the values are 90.0% and 31.9%, respectively. The onset of exaggerated swelling is 60 °C, which is 20 °C lower than that of sulfonated PEEKK with IEC of 1.4 meq/g [10], leading to deteriorative mechanical properties and the highest operation temperature lower than 60 °C. The water uptake and swelling of Ia in the SO_3H form are 20.8% and 6.3% at 30 °C, respectively, which are close to those of Ib in the SO_3H form. In contrast, the water uptake and swelling of Ia increase slowly with increasing temperatures in the ranging from 30 to 80 °C, the former at 80 °C is 30.6%, less than that (34%) of Nafion 115. Even in the 80 ~ 90 °C range, the water uptake and swelling also increase gradually, which are 47.6% and 17.3% at 90 °C, respectively. The former is even much less than that (90.0%) of Ib in the SO_3H form at 70 °C. Obviously, the onset of exaggerated swelling of Ia in the SO_3H form is higher than 80 °C, and also higher than that (80 °C) of sulfonated PEEKK with IEC of 1.4 meq/g, though the IEC of Ia is 1.6 meq/g, larger than 1.4 meq/g. Therefore, the highest operation temperature of Ia in the SO_3H form is

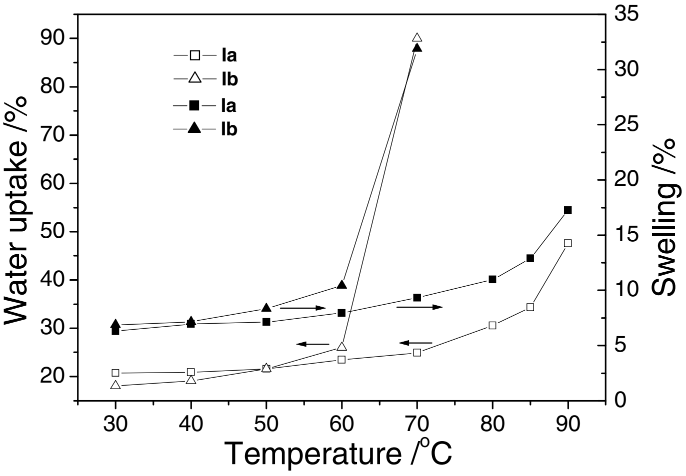


Fig. 1. Water uptake and swelling of Ia and Ib (in the SO_3H form)

higher than 80 °C in PEMFC. The higher operation temperature of Ia than that of PEM like sulfonated poly(arylene ether ketone)s with equivalent IEC is a powerful advantage for the application in PEMFC.

Studies on Hydrogen bonds

Variable temperature infrared spectrum is a good tool in the study of hydrogen bonds. Fig. 2 displays the IR spectra taken as a function of temperature for the acid form Ia and Ib. In Fig. 2, the peak of carbonyl groups of Ia in the acid form at 30 °C is broad, furthermore, a "satellite" band in the lower frequencies can be red though it is not remarkable. Generally, the bands of H-bonded carbonyl groups shift to low frequency regions. If the strength of the H-bonding is high, the "satellite" band at lower frequencies can be observed [16]. The characteristic bands of carbonyl groups are in the regions 1620~1720 cm^{-1}, the low frequencies band ("satellite" band) of carbonyl groups peak becomes more and more low with increasing temperature, which shows that their intensity (or height) of H-bonded carbonyl groups becomes more and more weak. The curve fitting procedure was used to fit the broad peaks of the carbonyl

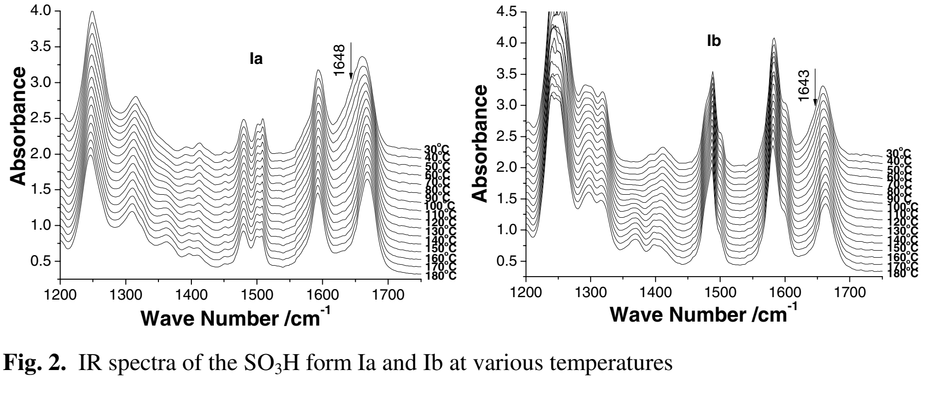


Fig. 2. IR spectra of the SO_3H form Ia and Ib at various temperatures

groups, the low frequencies peak is attributed to the H-bonded carbonyl groups, while the high frequencies peak is attributed to the non-associated carbonyl groups. Their corresponding characteristic peak tops are placed at 1648 cm^{-1} and 1669 cm^{-1}, respectively; The peak area of the associated carbonyl groups of Ia can be calculated by the Lorentzian fitting procedure, which at various temperatures is indicated in line Ia of Fig. 3. Similarly, the peaks of the H-bonded and non-associated carbonyl groups of Ib in the acid form are located at 1643 cm^{-1} and 1663 cm^{-1}, respectively; The peak area of the associated carbonyl groups of Ib as a function of temperatures is indicted in line Ib of Fig. 3. The peak area of the H-bonded carbonyl groups can be considered an indication of the strength of hydrogen bonds. In Fig. 3, The peak area of the H-bonded carbonyl groups of Ia decrease rapidly with increasing temperature in the 30~70°C regions, the strength of hydrogen bonds decreases quickly, subsequently, in the temperatures ranging from 70 °C to 180 °C, the peak area attributed to the H-bonded carbonyl groups reduces very slowly, the strength of hydrogen bonds reduces slightly. Its strength of H-bonds at 90 °C is 0.71 time as large as that at 30 °C, which means that the H-bond is still powerful even at 90 °C, resulting in that Ia showed good resistance to swelling. In contrast, the peak area corresponding to the H-bonded carbonyl groups of Ib decreases gradually with increasing temperature in the 30~80 °C regions, the strength of hydrogen bonds decreases gradually, whereafter, in the temperatures ranging from 80 °C to 180 °C, the peak area attributed to the H-bonded carbonyl groups reduces slowly, the strength of hydrogen bonds reduces slightly. Its strength of H-bonds at 90 °C is only 0.51 time as large as that at 30 °C. By comparison, the strength of H-bonds of Ib reduces more quickly than that of Ia does. The intermolecular H-bond of Ia in the acid form is still powerful even at high temperatures. Consequently, Ia showed better resistance to swelling than Ib at high temperature.

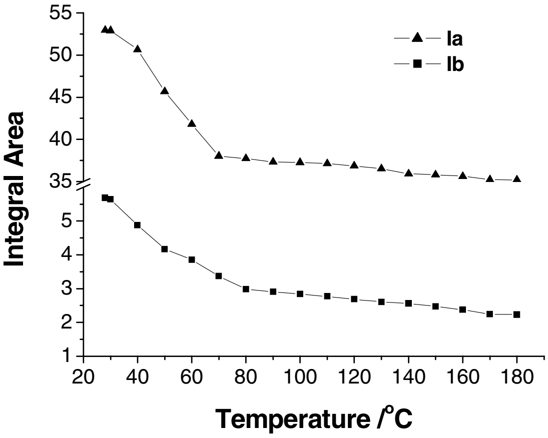


Fig. 3. Integral area of H-bonded carbonyl groups at various temperature

Conclusion

The water uptake and swelling of sPPEKK are very little compared with those of sPAEKK, especially in high temperature, which results from the more powerful intermolecular hydrogen bonds of sPPEKK than those of sPAEKK, confirmed by variable temperature IR spectra. The maximum operation temperature of PEM made of sPPEKK is higher than 80 °C, improving the property of resistance to swelling. In future work, the mechanical properties, the oxidative stability, and the electrochemistry properties will be studied in details.

Acknowledgements. The work was supported by the National Natural Sciences Foundation of China (No. 50303010) and the National High Technical Research Development Program (No. 2002AA323040).

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