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Synthesis and characterization of novel sulfonated poly(arylene ether ketone)s derived from 4,4'-sulfonyl-diphenol

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Summary

Novel sulfonated poly(arylene ether ketone)s were prepared directly by aromatic nucleophilic polycondensation of 4,4'-sulfonyldiphenol with various ratios of 4,4'-difluorobenzophenone to 5,5'-carbonylbis(2-fluorobenzenesulfonate) in dimethyl sulfoxide. The resulting polyelectrolytes were characterized by IR, NMR, TGA and DSC. The 10% weight loss temperature of the products is higher than 510°C, and their glass transition temperature is above 260°C. The introduction of 4,4'-sulfonyldiphenol with powerful electron-withdrawing group, -SO_2-, into the main chain of sulfonated poly(arylene ether ketone)s improves the thermal stability against desulfonation. The ion-exchange capacity and swelling of the polyelectrolyte membranes were measured, which are higher than 1.23meq/g and not higher than 20.9%, respectively. The membranes show very good perspectives in polymer electrolyte fuel cell (PEMFC) application.

Introduction

Polymer electrolyte membrane (PEM) is one of the key components of polymer electrolyte membrane fuel cells (PEMFC) [1]. At present, Nafion® is the only one commercially available membrane successfully used in PEMFC, which is a sort of perfluorinated membranes [2]. Although it has good chemical and physical properties for the use in fuel cell fields, Nafion® has some performance limitations, including not only low conductivity at low humidity or use temperature higher than 80°C, but also high methanol permeability, which limit the application in the direct methanol polymer electrolyte membrane fuel cells. Besides, the perfluorinated membranes are very expensive, which is also regarded as a disadvantageous factor [3,4]. Thus new polymer electrolyte membranes for fuel cells are being explored.

Poly(arylene ether ketone)s are one of high-performance polymers with excellent mechanical properties, good resistance to acidity and alkali, high thermal and thermooxidative stability [5]. It is desirable to modify poly(arylene ether ketone)s to some degree while maintaining its excellent properties for the application in PEMFC which require good mechanical properties, high permselectivity, low electrical resistance, high thermooxidative stability, high hydrolytic stability, a fairly low swelling or shrinking, and so on [6,7]. Thus sulfonated poly(arylene ether ketone)s are of interest as polymer electrolyte membranes [8]. Sulfonated poly(arylene ether ketone)s were studied by Jin et al [9,10] who successfully used a post-modification procedure to sulfonate commercially available PEEK. Of course, it is convenient to prepare sulfonated poly(arylene ether ketone)s by way of post-sulfonation. However, post-sulfonation reaction results in the placement of the sulfonic acid group ortho to the activated aromatic ether linkage, where the sulfonate groups are relatively easy to hydrolyze; Moreover, only one sulfonic acid per repeat unit can be achieved [9,10]. Fortunately, Ueda et al [11] have successfully invented a new route to prepare sulfonated poly(arylene ether sulfone)s with monomer units containing sulfonate groups derived from sulfonating the dihalide monomer before polycondensation. Sulfonation of the dihalide monomers, 4,4'-dihalobenzophenone and 4,4'-dihalodiphenylsulfone, results in sulfonic acid functionallization on both deactivated phenyl rings ortho to the halogen moiety, which offer them more chemical stability against desulfonation, and allows for two sulfonic acid groups per repeat unit after polymerization [12,13,14,15]. This preparation approach of sulfonated poly(arylene ether ketone)s has obvious advantages, which may be free from any degradation and cross-linking and easy to control the content of sulfonate groups by adjusting the ratios of monomer (**1**) to monomer (**2**) as well [11]. Recently, bisphenol A-based and phenolphthalein-based sulfonated poly(arylene ether ketone)s were prepared by the same method [16,17]. Yet, the bisphenol monomer containing an electron-withdrawing group, -SO_2-, has not been used to prepared sulfonated poly(arylene ether ketone)s, and the effect of the electron-withdrawing group of the bisphenol unit on the stability of sulfonated poly(arylene ether ketone)s has not been investigated [18]. The electron-withdrawing group of the bisphenol monomer reduces the density of negative charge of the phenyl ring containing sulfonate group in main chains, which probably improves the chemical stability against desulfonation. This paper describes the synthesis and characterization of a new series of sulfonated poly(arylene ether ketone)s derived from 4,4'-sulfonyldiphenol, 5,5'-carbonylbis(2-fluorobenzenesulfonate) and 4,4'-difluorobenzophenone, devoid of aliphatic carbon prone to oxidation, pendant unstable cardo groups.

Experimental

Materials

4,4'-Difluorobenzophenone and 4,4'-sulfonyldiphenol were purchased from Aldrich Chemical Co. and used as received. 5,5'-Carbonylbis(2-fluorobenzene sulfonate) was synthesis by sulfonation of 4,4'-difluorobenzophenone according to the procedure reported by Wang et al [12], although the conditions changed slightly. Dimethyl sulfoxide (DMSO) and toluene were purified by distillation and stored over 4 Å molecular sieves. Other reagents and solvents were obtained commerically and used without further purification.

Measurement

Inherent viscosity was measured by using an Ubbelohde viscometer. IR spectra were performed on the polymer membranes from N, N-dimethyl formamide (DMF) solution with a PE Paragon 1000 spectrophotometer. NMR spectra were recorded on a Varian Gemine-2000 300Hz spectrometer. Thermal gravimetric analysis (TGA) was measured under nitrogen flow by using a PE TGA 7 thermo-gravimetric analyzer (heating rate =10°C min^{-1}). Differential scanning calorimetry (DSC) analysis was recorded on a PE Pyris-1 thermal analyzer at a heating rate of 10°C min^{-1} in a N_2 purge. Measurement of swelling was based upon the following procedure [6]: the membrane sample (0.5~1 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 membranes, M_{wet}, is determined by weighing. After the wet membranes dring at 80°C , their dry weight M_{dry} is obtained. The swelling (SW) is calculated via following formula:

$$SW = (M_{wet}-M_{dry})/M_{dry} \times 100\% \qquad (\mathbf{1})$$

Ion-exchange capacity is performed as follows: a dry weight of 0.5~1 g of the polymer membrane in the SO_3H form is stirred in 50 ml of satured NaCl solution. The H^+ ions of the polymer membrane are released by the huge excess of Na^+ ions. Then the solution containing the polymer membrane is titrated with 0.1 N NaOH solution.

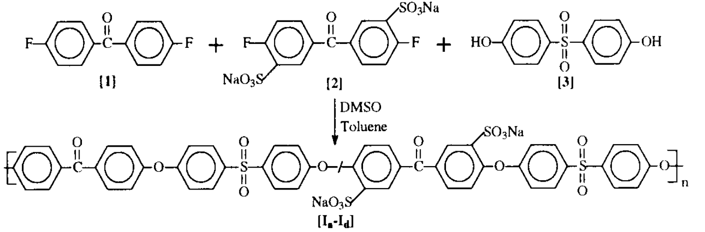
Polymer Synthesis

To a 150 ml three-necked round flask equipped with a Dean-Stark trap, a condenser and a nitrogen inlet were added to 20 mmol 4,4’-sulfonyldiphenol, a mixture of 4,4’-difluorobenzophenone and 5,5’-carbonylbis(2-fluorobenzene sulfonate) (20 mmol), DMSO (40 ml), toluene (45 ml) and K_2CO_3 (24 mmol). 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 250 ml the solution of methanol and water. The crude product was then wash six times with water to remove inorganic salts. The purified polymer was filtered and dried *in vacuo* at 80°C for 48 h. The analysis results of $\mathbf{I_c}$ were given as follows: Yield: 97%. ^1H NMR (300Hz, DMSO-d_6): δ= 8.3-8.2, 8.1-7.9, 7.9-7.7, 7.4-7.1; ^{13}C NMR (300Hz, DMSO-d_6): δ= 193.62, 193.46, 161.72, 161.57, 160.33, 158.78, 155.41, 155.33, 140.05, 136.70, 136.44, 135.60, 135.30, 133.51, 133.11, 133.06, 132.80, 132.55, 130.93, 130.35, 130.28, 129.88, 121.79, 120.15, 119.53, 119.14. Elem. Anal. Calcd. for $\mathbf{I_c}$: C, 58.86%; H, 3.00%; S, 11.31%. Found : C, 58.45%; H, 3.07%; S, 11.02%.

Results and discussion

Preparation and Characterization of Polymers

Polymers $\mathbf{I_a}$-$\mathbf{I_d}$ with different degree of sulfonation were prepared from aromatic nucleophilic substitution polycondensation of 4,4’-sulfonyldiphenol (**3**) with various ratios of 4,4’-difluorobenzophenone (**1**) to 5,5’-carbonylbis(2-fluorobenzene sulfonate) (**2**) (scheme 1). The polymerization results and the analytical data of $\mathbf{I_a}$-$\mathbf{I_d}$ are listed in Table 1. The inherent viscosity of polymers $\mathbf{I_a}$-$\mathbf{I_d}$ is higher than 0.80dL/g, which indicates high molecular weight of the resulting polymers. Table 1 displays that the higher the ratio of monomer (**2**) to monomer (**1**), the higher the inherent viscosity of the resulting polymer. This can be attributed to the fact that the electron-withdrawing group, -SO_3Na, increases the density of positive charge of the carbon atom connecting with the fluorine atom and thus enhances the nucleophilic reactivity, although the steric hindrance of sodium sulfonate group have the effect to decrease the reactivity. A similar phenomenon has been reported [16].



Scheme 1. Preparation of sulfonated poly(arylene ether ketone)s

Table 1. Polycondensation results of sulfonated poly(arylene ether ketone)s

Polym	Monomer 1		Monomer 2		Monomer 3		[η]*	Yield
	m/g	n/mmol	m/g	n/mmol	m/g	n/mmol	dL/g	%
$\mathbf{I}_a$	3.0548	14	2.5338	6	5.0055	20	0.80	98
$\mathbf{I}_b$	2.8366	13	2.9560	7	5.0055	20	0.82	97
$\mathbf{I}_c$	2.6184	12	3.3783	8	5.0055	20	0.91	97
$\mathbf{I}_d$	2.4002	11	3.8006	9	5.0055	20	0.93	96

* Inherent viscosity measured at a concentration of 0.5 g/dL in DMF at 25±0.1°C .

The IR spectra of polymer I_c are displayed in Figure 1. All IR spectra have an absorption band at 1028 cm^{-1}, 1243 cm^{-1}and 1084 cm^{-1} due to the asymmetric and symmetric O=S=O stretching vibrations of sodium sulfonate groups. The absorption bands at 1301 cm^{-1}, 1149 cm^{-1} can be attributed to the asymmetric and symmetric O=S=O stretching vibrations of the sulfone group, respectively. The absorption bands at 696 cm^{-1} can be assigned to the S-O stretching of sodium sulfonate groups. The existence of the C=O stretching is confirmed by a characteristic peak at 1652 cm^{-1}.

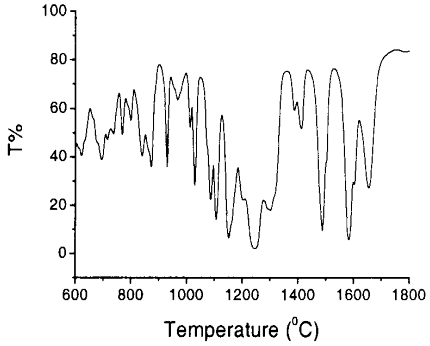


Figure 1. IR spectra of $\mathbf{I}_c$

Thermal Properties of Polyelectrolytes

Thermal gravimetric analysis (TGA) was used to characterize the thermal stability of resultant polymers. The sample was dried for 30 min at 150°C in nitrogen and subsequently subjected to TG analysis. A typical trace of TG for polymer $\mathbf{I}_a$ is shown in Figure 2. The analysis results are summarized in Table 2. The 10% weight loss temperature (T_{10}) of all the polymers is higher than 510°C , indicating excellent thermal stability of the materials. The T_{10} of polymer I_c (518°C), in which the ratio of monomer (**1**) unit to monomer (**2**) unit is 6:4, is 64°C higher than that of the bisphenol A based sulfonated poly(arylene ether ketone)s with the same ratio of monomer (**1**) to mononmer (**2**) [19]. The sulfone group of 4,4'-sulfonyldisphenol unit in the main chain is the powerful electron-withdrawing group. The density of negative charge of the phenyl ring containing sulfonate group reduces due to the induction effect of electron-withdrawing and the delocalization of electron in molecular chain. Thus the sulfonate group of phenyl ring with lower density of negative charge have higher stability against desulfonation. The TGA data show that there is a reduction in the degradation temperatures with increasing concentration of sodium sulfonate groups because of the thermal degradation of sodium sulfonate. This trend was observed in other sulfonated poly(arylene ether ketone)s and sulfonated poly(arylene ether sulfone)s [16,20,21] .

Table 2. Thermal properties of Ia-Id

Polymer	$\mathbf{I_a}$	$\mathbf{I_b}$	$\mathbf{I_c}$	$\mathbf{I_d}$
T_{10}(°C)*	524	521	518	514
T_g(°C)	268	281	288	317

*10% Weight loss temperature.

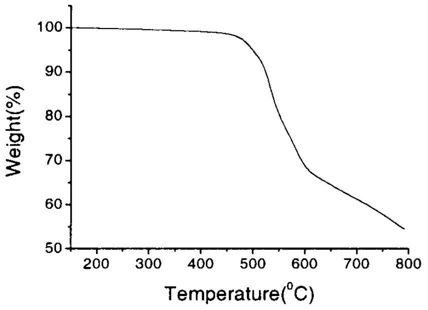


Figure 2. TG trace of I_a

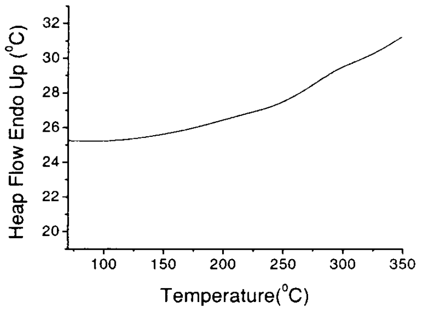


Figure 3. DSC curve of I_a

A typical trace of DSC for polymer $\mathbf{I_a}$ is displayed in Figure 3. The absence of any endothermic peak and exothermic peak in a temperature range of 60~350°C means that the polymers are an amorphous structure and there are no cross-linking reactions between sodium sulfonate groups and phenyl protons during the heating course. The glass transition temperature (T_g) of resulting polymers shown in Table 2 is higher than 260°C and much higher than that (205°C) of the corresponding poly(arylene ether ketone)s. The T_g of $\mathbf{I_a}$-$\mathbf{I_d}$ enhances with increasing the concentration of sodium sulfonate groups, as explained not only in terms of the strong intermolecular interaction of the sulfonate groups, but also in terms of the steric hindrance of segmental mobility of the main chains due to the bulky sulfonate groups.

Ion–exchange Capacity of Polymers

Table 3 shows the data of the ion-exchange content (IEC) of polymers $\mathbf{I_a}$-$\mathbf{I_d}$. The IEC of the samples (above 1.2 meq/g) is higher than that of Nafion 115 (0.91meq/g). The IEC of polyelectrolytes determined by means of titrating is in agreement with the calculated values within the experimental error, indicating that the pendant sulfonate groups were successfully attached to the polymer main chain. It is convenient to control IEC of the sulfonated poly(arylene ether ketone)s by using the appropriate ratio of monomer (**1**) to monomer (**2**) in polycondensation.

Swelling of Polymers

The swelling of resulting polymers is listed in Table 3, which is in the range of 14.4%~20.9%, while that of Nafion 115 is 34%. The swelling of polymers **I**$_a$-**I**$_d$ is less than that of Nafion 115 and they are suitable for the electrochemical application. As to expect, the swelling increases with increasing IEC. Consequently, the smallest swelling can be obtained by decreasing the IEC within the range of requirement.

Table 3. ICE and SW of **I**$_a$-**I**$_d$

Polymer	**I**$_a$	**I**$_b$	**I**$_c$	**I**$_d$	Nafion 115
ICE$_{calc}$(meq/g)*	1.23	1.40	1.57	1.73	--
ICE$_{meas}$(meq/g)#	1.20	1.37	1.54	1.71	0.91
SW(%)	14.4	15.8	18.0	20.9	34

* The calculated IEC value of ionomers; # The measured IEC value of ionomers.

Conclusions

Sulfonated poly(arylene ether ketone)s were prepared successfully by aromatic nucleophilic polycondensation of 4,4'-sulfonyldiphenol with various ratios of 4,4'-difluorobenzophenone (**1**) to 5,5'-carbonylbis(2-fluorobenzenesulfonate) (**2**). All ionomers show high molecular weight, good thermal stability, high ion-exchange capacity and low swelling. The introduction of the powerful electron-withdrawing group, -SO_2-, of 4,4'-sulfonyldiphenol into main chains of Sulfonated poly(arylene ether ketone)s improves the thermal stability against desulfonation. They show very good perspectives in PEMFC application.

Acknowledgements

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