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Polymer 47 (2006) 4148–4153

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Synthesis and characterization of poly(arylene ether ketone) (co)polymers containing sulfonate groups[☆]

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Abstract

Poly(arylene ether ketone)s containing sulfonate groups were synthesized by aromatic nucleophilic polycondensation of 4,4′-difluorobenzophenone (DFK), sodium 2,5-dihydroxybenzensulfonate (SHQ) and bisphenols. Only low-molecular weight oligomer was obtained when hydroquinone (HQ) was employed as comonomer, while copolymerization of DFK, SHQ, and phenolphthalein (PL) proceeded quantitatively to high-molecular weight (reduced viscosities above 0.68 dL/g) in dimethylsulfoxide at 175 °C in presence of anhydrous potassium carbonate. The sulfonated polymers were soluble in dipolar aprotic solvents, such as *N*,*N*-dimethylactamide and *N*-methyl-2-pyrrolidinone. Tough membranes cast from *N*,*N*-dimethylformamide solution with SHQ/DFK mole ratios ≤65:35 were obtained. Both glass transition temperatures and hydrophilicity of the copolymers increased with the content of sodium sulfonate groups. The materials are candidates as new polymeric electrolytes for proton exchange membranes.

Keywords: Poly(arylene ether ketone); Sulfonation; Membrane

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1. Introduction

Poly(arylene ether ketone)s are a class of high performance polymers because of their excellent mechanical toughness, electrical/insulating, thermo-oxidative stability as well as high glass transition temperature. Two good examples of commercialized poly(arylene ether ketone)s are PEEK and PEK-C. PEEK is a homopolymer made from hydroquinone and 4,4-difluorobenzophenone, while PEK-C was manufactured from phenolphthalein with 4,4-chlorobenzophenone [1]. In contrast to hydroquinone-based PEEK, which is insoluble in most organic solvents, PEK-C has a relatively high glass transition temperature (218 °C), and is soluble in a few polar solvents such as *N*,*N*-dimethylformamide (DMF), *N*-methylpyrolidone (NMP), and chloroform [2]. These characteristics make PEK-C an excellent structural resin as well membrane material [3,4].

Sulfonation of poly(arylene ether ketone)s was extensively studied in the literature over the past few decades via the post polymer modification route. Typical sulfonating agents used for this purpose include concentrated sulfuric acid [5,6], sulfur trioxide [7], chlorosulfonic acid [8], and methanesulfonic acid [9]. Kerres et al. reported an alternative way in making sulfonated poly(arylene ether sulfone), which involved metalation of polymer with *n*-butyllihium at low temperature, sulfination with sulfur dioxide, followed by the oxidation [10]. One significant drawbacks associated with the post sulfonation procedure is the degree of sulfonation is usually not easy to control, and the reproducibility is not as good as one desired.

It is well known to polymer chemists that functional polymers can be synthesized via direct polymerization of functionalized monomers as well. For example, Ueda reported the synthesis of sulfonated poly(arylene ether sulfone)s from bisphenol A, 4,4-dichlorodiphenylsulfone, and disulfonated 4,4-dichlorodiphenylsulfone [11]. We reported the synthesis of disulfonated 4,4-difluorobenzophenone (SDFK), and sulfonated poly(arylene ether ketone) copolymers via direct polymerization of SDFK, 4,4-difluorobenzophenone, and

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[☆] For the special issue of Polymer in celebrating Dr James E. McGrath's 70th birthday.

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doi:10.1016/j.polymer.2006.02.072

different bisphenols [12–18]. Poly(arylene ether ketone) homopolymer containing sulfonate groups was also prepared from sulfonated hydroquinone and 4,4-difluorobenzophenone [19]. Moreover, considerable efforts have been paid to sulfonated poly(arylene ethers)s in the past few years due to their great potentials as proton exchange membranes for fuel cells. A large number of poly(arylene ether)s containing sulfonate groups have been prepared and characterized [20–22]. Our research results prove that the direct polymerization technique is more preferred in making sulfonated polymers. One obvious advantage of direct polymerization is the degree of sulfonation can be controlled very easily and precisely, which enables us finely tune membrane's property, and maximizes membrane's overall performance for different membrane separation processes such as fuel cells.

In this paper, we describe the synthesis and characterization of sulfonated poly(arylene ether ketone) polymers prepared from sulfonated hydroquinone, 4,4-difluorobenzonphenone, and (co)bishenols, which could be either hydroquinone or phenolphthalein.

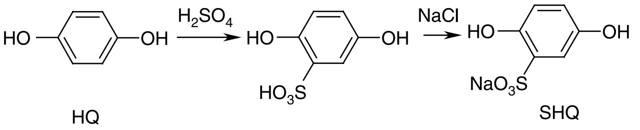
2. Experimental

2.1. Materials

Hydroquinone and 4,4′-difluorobenzophenone was purchased from Aldrich and used as received. Polymerization solvent, dimethylsulfoxide, was distilled from calcium hydride and stored under nitrogen before use. Analytical grade sulfuric acid (98%) and phenolphthalein were obtained from the Beijing Chemical Plant and were used without further purification. Potassium carbonate was dried in vacuo before polymerization. *p*-xylene and methanol were purchased from Beijing Yili Fine Chemicals Ltd.

2.2. Synthesis of sulfonated hydroquinone

Sodium salt of sulfonated hydroquinone (SHQ) was synthesized by sulfonation of hydroquinone with concentrated sulfuric acid at room temperature, followed by neutralization, according to a procedure described in the literature [14]. Polymer grade SHQ was obtained after recrystalization from the mixture of methanol and water (v/v = 9/1). ^{1}H NMR (DMSO-*d*6, 400 MHz): δ 9.942 (s, hydroxyl, ortho to –SO_3Na); 9.956 (hydroxyl, meta to –SO_3Na); 6.989, 6.982 (d, phenyl meta to –SO_3Na, 1H); 6.744, 6.737; 6.721, 6.714 (2d, phenyl para to –SO_3Na, 1H); 6.693, 6.672 (d, phenyl meta to –SO_3Na, 1H). ^{13}C NMR (DMSO-*d*6, 100 MHz): δ 149.3 (C4), 146.1 (C1), 130.7 (C3), 118.6 (C6), 117.2 (C5), 113.2 (C2) (Scheme 1).



Scheme 1. Synthesis of sulfonated hydroquinone (SHQ).

2.3. Synthesis of sulfonated poly(arylene ether ketone) copolymers with controlled degree of sulfonation

A typical aromatic nucleophilic step growth copolymerization will be described: to a dried 100 mL three-neck flask, equipped with an overhead stirrer, nitrogen inlet and a Dean Stark trap, were added 4,4′-difluorobenzophenone 2.1820 g (10.0 mmol), SHQ 1.0608 g (5.0 mmol), phenolphthalein 1.5917 g (5.0 mmol), and potassium carbonate 1.59 g (11.5 mmol). Dry DMSO was introduced to afford about a 20% solids concentration and xylene was used as an azeotropic agent. The reaction mixture was heated under reflux at 150 °C for 4 h to dehydrate the system. Then polymerization was slowly heated to 175 °C and kept at this temperature for 6 h, and a very viscous mixture was observed. After cooled to ~80 °C, the viscous mixture was diluted by ~10 mL DMSO, and filtered to remove most of the inorganic salts before precipitated in 500 mL ethanol. The fibrous polymer was washed several times with ethanol and water, and vacuum-dried at 100 °C for 12 h.

2.4. Membrane preparation

The copolymer (salt form) was dissolved in DMF (5–10% w/v) at room temperature, and filtered via 0.45 μm syringe filters. Then the solution was cast onto clean glass substrates. The films were carefully dried with infrared heat at gradually increasing temperatures (up to ~60 °C). The membranes were removed from the glass plates by submersion in water and then were dried in vacuo at 150 °C for at least 24 h.

2.5. Characterizations

Fourier transform infrared (FTIR) spectra were recorded from very thin films using Bio-RAD (FTS7) spectrometer. ^{1}H and ^{13}C NMR analyses were conducted on a Varian Unity 400 spectrometer in DMSO-*d*6 at room temperature. Reduced viscosities of salt form polymers were determined at a concentration of 0.5 g/dL in DMF at 25 °C with an Ubbelohde viscometer. Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed on Perkin–Elmer 7 Series Instruments.

The water uptake was determined from salt form membranes. The membranes were first thoroughly dried at 150 °C in vacuo to a constant weight, which was recorded. The dried film was then immersed in water at room temperature and periodically weighed on an analytical balance until a constant wet weight was obtained. The percent weight gain relative to the dried membrane is considered the water uptake.

Ion exchange capacities (IEC) of copolymers were determined by titration of acid form membranes, which were obtained by boiling the salt form membranes in excess sulfuric acid solution (1 N) for 30 min, followed by extracting free acid in boiling deionized water for 60 min. Dried acid form membranes were first neutralized by excess standard sodium hydroxide solution (1 N), followed by back titration of sodium hydroxide with standard hydrochloric acid solution (1 N).

The milli-molar difference between sodium hydroxide and hydrochloric acid divided by the dry membrane weight was regarded as the IEC of copolymer, represented as milliequivalent per gram.

3. Results and discussion

3.1. Synthesis sulfonated hydroquinone

Sodium 2,5-dihydroxybenzenesulfonate (SHQ) was made by sulfonating hydroquinone with concentrated sulfuric acid at room temperature. Highly pure SHQ was obtained as white crystals after recrystalization from methanol/water mixture. The chemical structure of SHQ was confirmed by its ^{1}H and ^{13}C NMR, as shown in Fig. 1(a) and (b). Assignments of protons and carbons of SHQ are summarized in experimental part. Other spectroscopic (FTIR and MS) and elemental analysis verified the expected structure of SHQ as well.

3.2. Synthesis of sulfonated poly(arylene ether ketone) copolymers

Poly(arylene ether ketone) (co)polymers containing sulfonated groups were synthesized via nucleophilic aromatic substitution polycondensation of sulfonated hydroquinone (SHQ), 4,4-difluorobenzophenone (DFK), a bisphenol comonomer, which could be either hydroquinone (HQ) or phenolphthalein (PL). The polymer synthesis (Scheme 2) involved condensing a controlled amount of SHQ, DFK, and bisphenol comonomer in DMSO, which contained xylene as an azeotropic agent. All the polymerization results are summarized in Table 1. The polymerizations were conducted in the sodium salt form of SHQ to take advantage of the greatly enhanced thermal stability of the sulfonic acid salt, and possible side reactions related to sulfonic acid groups generated via post sulfonation such as crosslinking and degradation were eliminated. However, since potassium carbonate was used as the base, some alkali sulfonate exchange may occur during polymerization, and the final products were probably the mixture of sodium and potassium sulfonates.

Several approaches could be used to synthesize high molecular weight poly(arylene ether)s, including electrophilic aromatic substitution, nucleophilic aromatic substitution, and metal catalyzed coupling. In the nucleophilic substitution reaction, the polymerization rate depends on the basicity of the bisphenol salt and the electron-withdrawing power of the activating group of the dihalide. For less reactive monomers, it was found that higher temperatures were necessary to achieve high molecular weight polymer [23]. The substituted hydroquinone, SHQ, is clearly less reactive than HQ, since the steric effect from the bulky sodium sulfonate group would be expected to hinder the nucleophilic attack of the phenolate. DMSO, a good solvent for all of the starting monomers with a relative high boiling point, was chosen as the reaction medium to obtain high molecular weight polymers. Very viscous polymer solutions were obtained after the condensations were kept at 175 °C for about 6 h. It is well known that poly(ether ether ketone) (PEEK) is a crystalline polymer, which can be made from HQ and DFK at very high temperature of around 300 °C. Previous study indicated that modification of PEEK, such as sulfonation, reduced its crystallinity and improved its solubility in common organic solvents [6]. The high

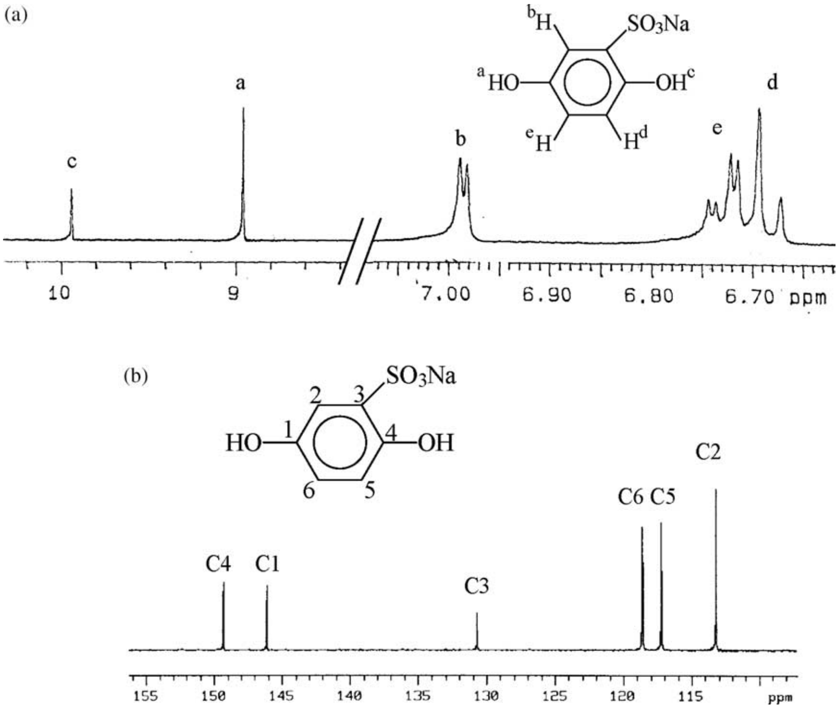
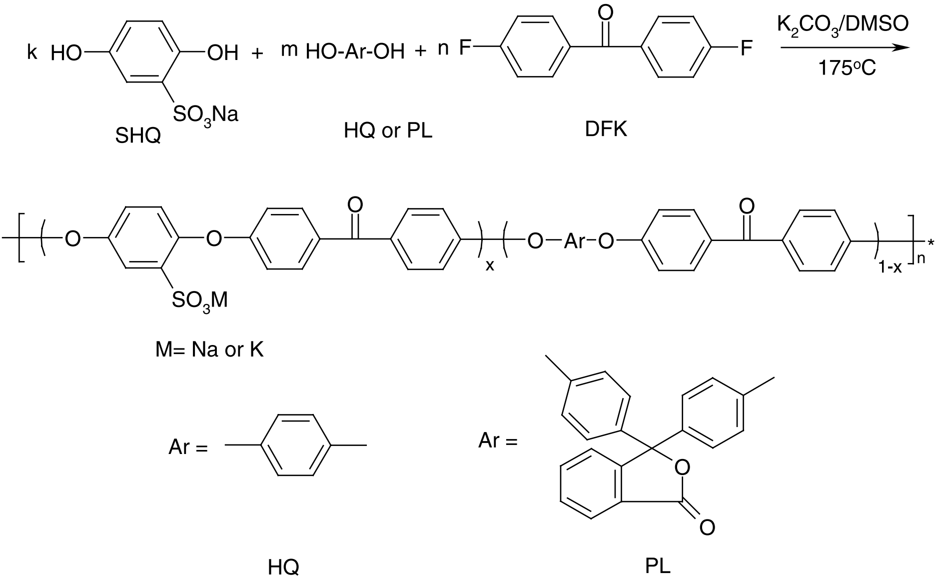


Fig. 1. NMR spectra of sulfonated hydroquinone (sodium form): (a) ^{1}H NMR and (b) ^{13}C NMR.



Scheme 2. Synthesis of sulfonated poly(arylene ether ketone) polymers.

polymerization yield, good solubility in DMSO, and high-reduced viscosity of HEK100, all suggest its high molecular weight. DSC study showed that HEK100 was indeed an amorphous polymer, as reported previously [14]. Copolymerization (HEK40) of SHQ and HQ with SHQ/DFK = 40:100 failed to give high molecular weigh copolymer. Powders precipitated from the copolymerization mixture, which was probably caused by the crystallinity of non-sulfonated poly(ether ether ketone) oligomers, and the precipitation resulted the termination polymer chain growth. The isolated powders had low reduced viscosity and poor solubility in organic solvents such as DMAc and NMP.

Poly(arylene ether ketone) copolymers were successfully synthesized from SHQ, DFK, and PL, with high recovered yields. The copolymers are listed in Table 1 as PEK-*x*, where *x* represents the molar ratio of SHQ to the total bisphenols (SHQ plus PL) from 5/100 to 65/100. For example, PEK50 is a copolymer from SHQ, PL and DFK with a molar ratio of SHQ to total bisphenols is 50/100. The fibrous copolymers demonstrated good solubility in several polar organic solvents such as DMSO, NMP and DMF. The reduced viscosities determined in DMF at 25 °C were high (Table 1). Of course, the reduced viscosities are influenced by the sulfonate groups, which is no doubt related to enhanced intramolecular stiffness and intermolecular associations. Although conventional GPC measurement failed to give exact molecular weight information of these copolymers, the high-reduced viscosities, high monomer conversion, and tough and flexible membranes obtained from all PEK-*x* copolymers proved that molecular weights of the PL-based sulfonated copolymers were high. The traditional GPC technique is not easily adapted to molecular weight characterization of sulfonated polymers, probably due to the interaction between sulfonate groups and the separation column.

3.3. Characterization of sulfonated poly(arylene ether ketone) copolymers

FTIR spectra allowed for the qualitative and quantitative determination of the functional groups of the synthesized homo and copolymers. Fig. 2 shows the FTIR spectra of PL-based sulfonated copolymers as a function of degree of sulfonation. All copolymers show absorbance at 1651 cm^{-1}, which is assigned to the carbonyl stretching of the ketone groups from DFK. Since every repeat unit in copolymer chains has one phenyl ketone group, absorbance at 1651 cm^{-1} is picked up as an internal standard for quantitative study of the degree of sulfonation. Except PEK5, all copolymers showed the characteristic symmetric stretching of sulfonate group at 1024 cm^{-1}, and the absorbance of sulfonate group increased with the higher SHQ content in the starting monomers, which confirms the successful incorporation of sulfonate groups in polymer chains. Typical sulfonate absorbance was absent in PEK5 is probably due to its very low concentration of sulfonate group. A good linear relationship was plotted in Fig. 3, between the degree of sulfonation (SHQ/DFK) and the absorbance

Table 1
Synthesis of sulfonated polymers via direct polymerization of SHQ

Copolymer	Bisphenol	SHQ/DFK (molar)	Yield (%)	RV[a] (dL/g)
HEK40	HQ	40/100	21	0.13
HEK100	HQ	100/100	93	1.0
PEK5	PL	5/100	99	1.0
PEK20	PL	20/100	90	0.8
PEK35	PL	35/100	95	0.75
PEK50	PL	50/100	89	0.76
PEK65	PL	65/100	86	0.68

[a] Salt form copolymers were measured in DMF at concentration of 0.5 g/dL at 25 °C.

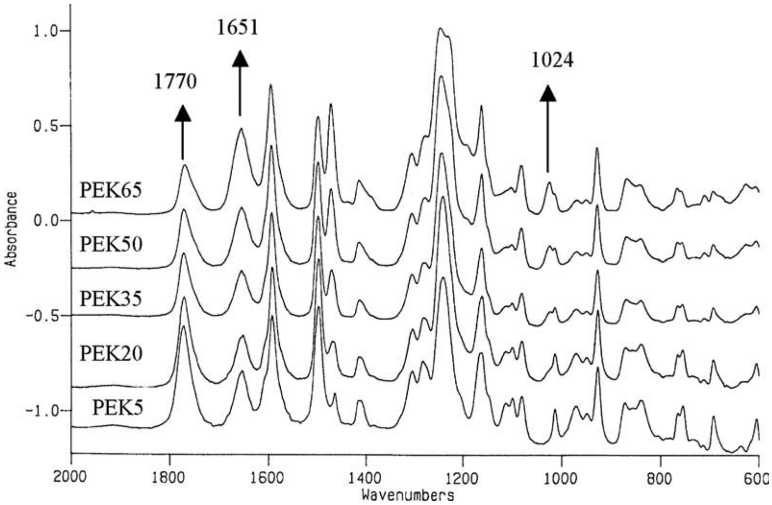


Fig. 2. FTIR spectra of sulfonated poly(arylene ether ketone) copolymers (salt form) prepared from SHQ, DFK and phenolphthalein.

ratios of sulfonate group (1024 cm^{-1}) to internal standard. Absorbance at 1770 cm^{-1}, corresponding to the vibration of cyclic ester groups from PL, decreased as SHQ increased in feed monomers, and another good linear relationship is provided in Fig. 3 as well, between the degree of sulfonation and the absorbance ratios of cyclic ester group (1770 cm^{-1}) to internal standard. All these results prove that sulfonate groups were indeed quantitatively introduced to the copolymer as designed.

Quantitative study of the degree of sulfonation was also performed by the simple titration of sulfonic acid groups. Salt form membranes were first converted into acid form by soaking in excess sulfuric acid solution, followed by titration of acid form membranes with sodium hydroxide. As shown in Table 2, the titrated ion exchange capacities (IEC) of acid form PL-based sulfonated copolymers were very close to the theoretical IEC values, assuming 100% conversion of all starting monomers. The titration results verified again that sulfonated monomer (SHQ) was quantitatively introduced to copolymer chains without any side reaction during the copolymerization.

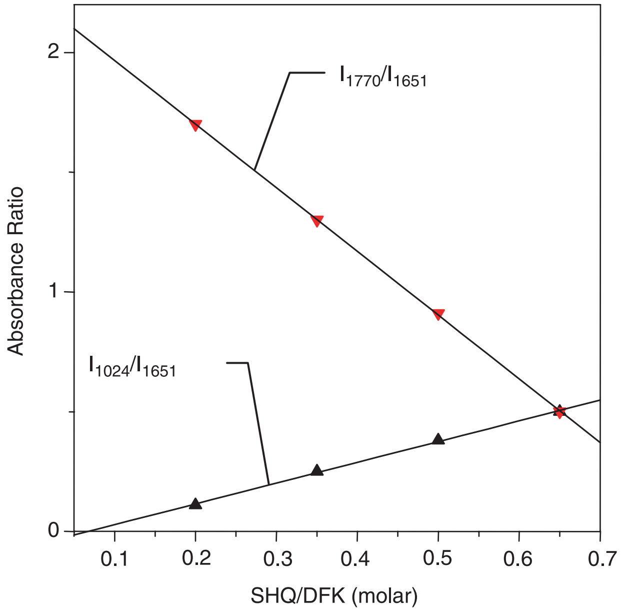


Fig. 3. FTIR correlation of sulfonate (1024 cm^{-1}), cyclic ester (1770 cm^{-1}), and internal standard (phenyl ketone at 1651 cm^{-1}) groups for PEK-*x* copolymers.

The membrane's hydrophilic character is one of the critical parameters for several membrane processes, such as reverse osmosis and proton exchange membrane fuel cells. Poly(arylene ether ketone)s are, in general, hydrophobic polymers. However, the sulfonated copolymers demonstrated hydrophilic properties due to the nature of sulfonated groups, either in acid or salt form. Water uptakes of salt form membranes, expressed in weight percent, were measured by weighting the membranes under dry and wet conditions. As shown in Table 2, the water uptake of PL-based sulfonated poly(arylene ether ketone)s increased with the increase in sulfonated monomer (SHQ) content.

Thermal properties of sulfonated poly(arylene ether ketone) copolymers were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA), and all the results are summarized in Table 3. PEK-C, a commercial poly(arylene ether ketone) made from 4,4-dichlorobenzophenone and PL, has a reported glass transition temperature (T_g) of 218 °C. When part of PL was replaced by sulfonated monomer, polymer chain interaction enhanced via the sulfonate groups leading to increased T_g. Glass transition temperatures of PEK5 and PEK20 are 229 and 235 °C, respectively, which are all higher than PEK-C homopolymer.

Table 2
Characterization of sulfonated poly(arylene ether ketone) copolymers

Polymer	Water uptake (wt%)	IEC (mequiv./g)	
		Theo.[a]	Titra.[b]
PEK5	5.0	0.09	0.10
PEK20	9.2	0.40	0.42
PEK35	15	0.75	0.76
PEK50	18	1.14	1.13
PEK65	22	1.58	1.51

[a] Calculated from the monomer compositions assuming 100% conversion.

[b] Titration of acid form membrane with sodium hydroxide (1.0 N).

Table 3
Thermal properties of sulfonated poly(arylene ether ketone) copolymers

Polymer	T_g[a] (°C)	T_{decom}[a] (°C)	
		5%	10%
PEK5	229	470	550
PEK20	235	435	510
PEK35	ND	418	490
PEK50	ND	395	480
PEK65	ND	390	420

[a] Measured form salt form membranes.

[b] Five and 10% weight loss temperature in nitrogen atmosphere, and 10 °C/min.

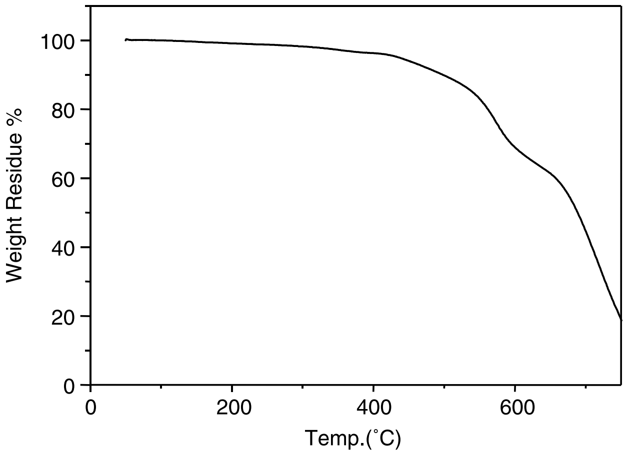


Fig. 4. TGA curves of PEK50 (salt form) in nitrogen.

However, T_g of copolymer containing 35% or more SHQ was not observed in the temperature range of 30–300 °C. One possible explanation is that the polymer chain interaction is so strong due to the high concentration of sulfonate groups that T_g is too weak to be distinguished by DSC. Another possible reason is that T_g of highly sulfonated copolymer is higher than our tested temperature. TGA experiments were conducted in nitrogen at a heating rate of 10 °C/min. All PL-based copolymers were stable up to 300 °C, however, highly sulfonated copolymers are less stable. Both 5 and 10% weight loss temperatures decreased as the increase in sulfonated units' content in copolymers. Fig. 4 shows TGA curve of PEK50, the first degradation stage between 400 and 550 °C is associated to the decomposition of sulfonated component, and the next one above 550 °C can be attributed to the main chain degradation. The remained ∼20% non-volatile substance after heated up to 700 °C is probably the inorganic sulfonate salt.

4. Conclusion

Sulfonated hydroquinone was synthesized by sulfonation of hydroquinone using concentrated sulfuric acid. Novel sulfonated poly(arylene ether ketone)s were synthesized via the direct polymerization of sodium 2,5-dihydroxybenzenesulfonate, 4,4-difluorobenzophenone with or without bisphenol comonomer. Copolymerization of SHQ with hydroquinone failed to make high molecular weight copolymer due to the crystallization of non-sulfonated oligomers. High molecular weight sulfonated poly(arylene ether ketone) copolymers were successfully prepared from SHQ, PL, and DFK. The high molecular weight of PL-based copolymers and the quantitative polymerization of sulfonated monomer were verified by reduced viscosity measurement, FTIR, and titration. The glass transition temperatures and hydrophilic property of copolymers were improved by the introduction of sulfonate group, although thermal stability was slightly decreased as compared with non-sulfonated poly(arylene ether ketone)s. Tough membranes prepared from these copolymers are good candidates as proton exchange membranes for fuel cell, and other membrane separation processes.

Acknowledgements

The authors would like to thank the National Science Foundation of China for the financial support.

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