Polymer 42 (2001) 3293–3296

polymer

www.elsevier.nl/locate/polymer

Polymer Communication

Novel sodium sulfonate-functionalized poly(ether ether ketone)s derived from 4,4′-thiodiphenol

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Received 22 August 2000; received in revised form 6 October 2000; accepted 11 October 2000

Abstract

Novel sodium sulfonate-functionalized poly(ether ether ketone)s derived from 4,4′-thiodiphenol with degree of sulfonation up to 2.0 were synthesized by nucleophilic polycondensation of various amount of 5,5′-carbonylbis(2-fluorobenzenesulfonate) (**1**) and 4,4′-difluorobenzophenone (**2**) with 4,4′-thiodiphenol (**3**). Component and structure of the polymers were confirmed by IR, NMR and elemental analysis. Wide angle X-ray diffraction patterns indicated an amorphous structure of the polymers. All the polymers showed excellent thermal stability and poor solubility in water.

Keywords: Poly(ether ether ketone); Sodium sulfonate-functionalized; 4,4′-Thiodiphenol

1. Introduction

Poly(ether ether ketone)s with sodium sulfonate groups have received extensive attention for their potential usage as high performance gas dehumidification and ion exchange membrane materials [1–4]. Several sulfonating agents have been used in sulfonation of poly(ether ether ketone)s in the last two decades [5–8]. Since Ueda et al. [9] first synthesized sodium sulfonate-functionalized poly(ether ether sulfone)s with degree of sulfonation up to 0.8 directly from a sulfonated monomer, sodium 5,5′-sulfonylbis(2-chlorobenzensulfonate), this method has been proven to be more advantageous than postsulfonation methods since the side reaction could be avoided and the degree of sulfonation can be easily controlled [10,11].

Increasing content of sodium sulfonate groups in polymers inproves both ion permeability and separation factor of water vapor over gases due to the increased hydrophilicity and ion exchange content [12,13]. But the highest reported sulfonation degree of sulfonated poly(ether ether ketone)s was no more than 1.2 until our report of synthesis of sodium sulfonate-functionalized poly(ether ether ketone)s derived from bisphenol A with degree of sulfonation up to 2.0 [3,14], which severely swell and even dissolve in water at room temperature when the degree of sulfonation is higher than 1.2, thus prohibiting their further use in watery environments, such as in gas dehumidification and electrodialysis.

In this paper, we describe the synthesis of novel sodium-functionalized poly(ether ether ketone)s derived from 4,4′-thiodiphenol with degree of sulfonation up to 2.0, which are insoluble in water at room temperature even when sulfonation degree is 2.0, indicating a potential usage as high performance gas dehumidification and ion exchange membrane materials.

2. Experimental

2.1. Materials and measurements

4,4′-Difluorobenzophenone and 4,4′-thiodiphenol were purchased from Aldrich Chemical Co. and used as received. 5,5′-Carbonylbis(2-fluorobenzene sulfonate) was obtained by sulfonation of 4,4′-difluorobenzophenone [11]. Dimethyl sulfoxide (DMSO) and toluene were purified by distillation and stroed over 4 Å molecular sieves. Potassium carbonate was dried at 180°C for 10 h prior to use. Other reagents and solvents were obtained commercially and used without further purification.

IR spetra were recorded on a Bio-Rad FTS7 spetrometer. Elemental Analysis was performed on a MOD-1106 Elemental Analyzer. Wide-range X-ray diffraction (WAXD) patterns were recorded on a D/Max-IIB spectrometer. NMR spetra were recorded on a Unity 400 spectrometer.

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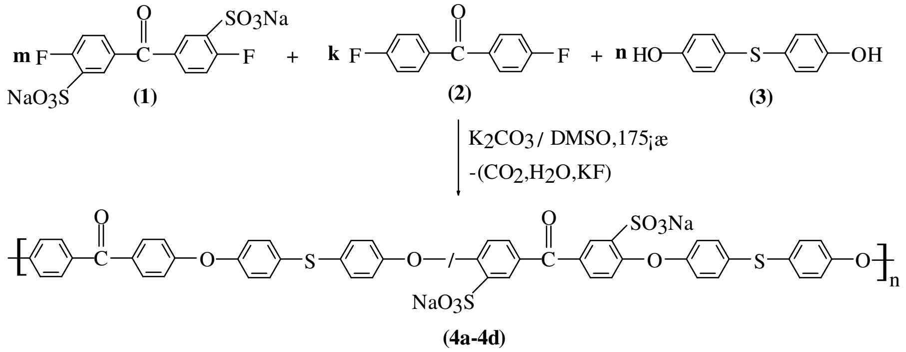
PII: S0032-3861(00)00748-5



Scheme 1.

Thermogravimetric analysis was conducted on a Perkin–Elmer 7 Thermal Analysis System at a heating rate of 10°C/min.

2.2. Synthesis of polymers *4a–4d*

In a 100 ml three-necked round bottom flask, equipped with a Dean–Stark trap with reflux condenser, a nitrogen inlet and a thermometer, 10 mmol 4,4′-thiodiphenol, 5,5′-carbonylbis(2-fluorobenzene sulfonate) + 4,4′-difluorobenzophenone(10 mmol), and potassium carbonate(11 mmol) were added into a mixture of 20 ml dimethyl sulfoxide and 12 ml toluene. The mixture was refluxed for 4 h at 150°C. After the water was essentially removed from the reaction mixture by azeotropic distillation, toluene was distilled out and the temperature was raised to 175°C and kept at this temperature for 6 h. Then the reaction mixture was cooled to room temperature and poured into 500 ml methanol to precipitate the copolymer. The crude product was then washed twice with water to remove inorganic salts, filtered and dried in a vacuum oven at 100°C for two days.

3. Results and discussion

3.1. Polymer synthesis and characterization

Polymers with different degree of sulfonation were obtained by aromatic nucleophilic polycondensation of 5,5′-carbonylbis(2-fluorobenzenesul-fonate) (**1**) and 4,4′-difluorobenzophenone (**2**) with 4,4′-thiodiphenol (**3**), by changing the ratio of monomers **1** and **2**, provided the amount of monomer **3** is fixed (Scheme 1; Polymerization of **4a**–**4d**).

The polymerization results and the analytical data of **4a**–**4d** are summarized in Table 1.

The specific viscosity of all the polymers is above 0.71 dl/g, indicating high molecular weight of the polycondensates. Sulfonation degree of polymers **4a**–**4d** determined by titration is in good agreement with the calculated values, indicating that the sodium sulfonate groups were successfully incorporated into the polymer chain. Three major factors are assumed to compete with each other to affect the results. First, the electron-withdrawing group, $-SO_2-$, favors the nucleophilic polycondensation due to the increasing density of positive charge of the carbon atom connecting with the fluorine atom. Second, the steric hindrance of sodium sulfonate group reduces the reactivity. Third, the solubility of polymers in DMSO has a great effect on polymerization. All the polymers dissolve well in DMSO when degree of sulfonation is not more than 1.6, and in this range of sulfonation degree, the first factor is in predominance. Precipitation occurs in the polymerization of **4d** when the polymerization reaches a certain extent, indicating the poor solubility of **4d** in relatively high specific viscosity, which gives rise to lower specific viscosity of **4d** than that of **4c**.

Polymer **4d** was chosen to illustrate component and structure of the polymers. Fig. 1 shows the IR spectrum of polymer **4d**. The absorption bands at 1028, 1254 and 1084 cm^{-1} can be assigned as the asymmetric and symmetric O=S=O stretch of sodium sulfonate groups. And the absorption band at 710 cm^{-1} can be assigned as the S–O stretch of sodium sulfonate groups. No peaks attributed to the aromatic sulfone group were observed for **4d** in a range of 1140–1110 cm^{-1},indicating no detectable crosslinking in copolymerization, due to the sodium form of sulfonic acid in polymerization. The elemental analysis of **4d** is in good

Table 1
Polymerization results and the analytical data of 4a–4d

Polymer	**4a**	**4b**	**4c**	**4d**
m/k	4/6	6/4	8/2	10/0
Degree of sulfonation[a]	0.78(0.80)	1.23(1.20)	1.62(1.60)	1.99(2.00)
Yield in %	98	98	96	93
$\eta_{sp/c}$[b] (dl/g)	0.71	0.82	0.99	0.93

[a] Number of sodium sulfonate groups per repeating unit. Determined by titration with standard NaOH aqueous solution in DMF. Values in parentheses are the expected degree of sulfonation according to the ratio of reactants. Polymers are acidified to their acid form with excess 1 N HCl aqueous solution before titration.

[b] Specific viscosity: measured at a concentration of 0.50 g/dl in DMF at 25 ± 0.1°C.

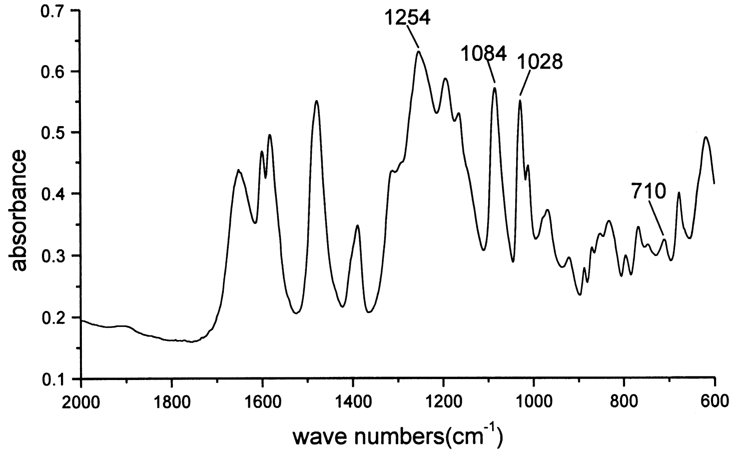


Fig. 1. IR spectrum of **4d**.

agreement with the calculated values: Cal. C 50.01, H 2.35, S 16.01. Found C 49.92, H 2.33, S 16.11.

NMR spectroscopy was used for structure confirmation of polymer **4d**. The ^{1}H, ^{13}C and dept NMR spectra of **4d** (Fig. 2), along with its peak assignments, were extremely clean. The dept NMR spectrum of **4d** reflects the non-substituted carbon in aromatic rings.

Wide-angle X-ray diffraction patterns of polymers **4a**–**4d** (Fig. 3) show no crystalline behavior, indicating an amorphous structure of the polymers. It can be seen that polymers **4a**–**4d** exhibit diffused diffraction peaks at about 17°. This indicates there should be some long distance ordered structure in polymer system. And with the increasing of degree of sulfonation, the intensity of diffused diffraction peaks of polymers decreases gradually, indicating the increased disordered arrangement of polymer chains in polymer system. This can be explained by the decreased ordered structure caused by the incorporation of the bulk groups of sodium sulfonate.

3.2. Thermal properties of polymers

The thermal properties of polymers **4a**–**4d** are listed in Table 2.

No glass transition temperature was observed in a temperature range of 100–400°C, probably because of the strong intermolecular interaction due to the high content of sodium sulfonate groups. All the polymers were stable up to 430°C both in air and nitrogen atmosphere, indicating excellent thermal stability of the materials. It is obvious that the 10% weight loss temperature decrease as the content of ionic groups therein increases. This could be explained by the thermal degradation of sodium sulfonate at a relative

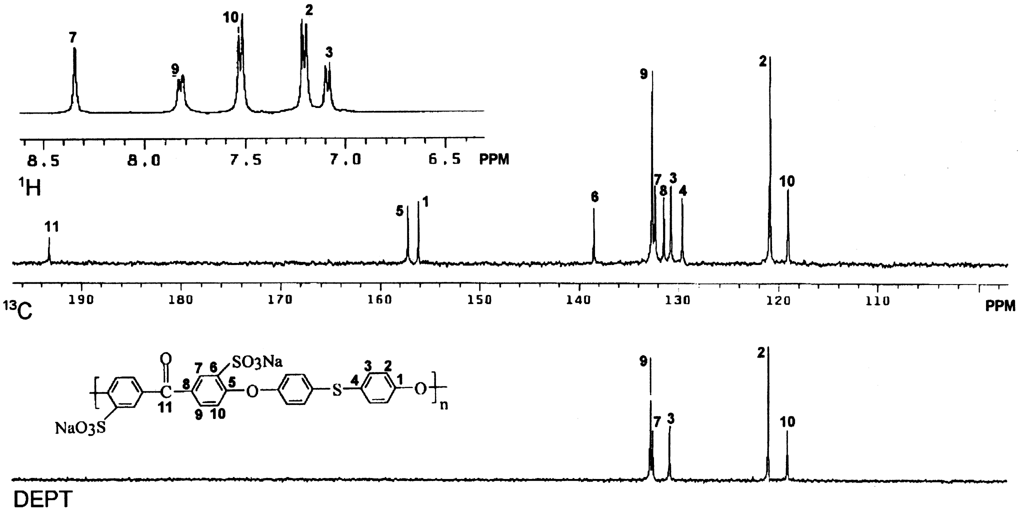


Fig. 2. NMR spectra of **4d**.

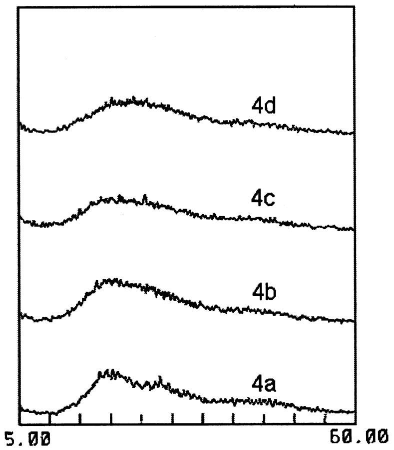


Fig. 3. WAXD patterns of **4a**–**4d**.

Table 2
Thermal stabilities of polymers **4a**–**4d**

Polymer	**4a**	**4b**	**4c**	**4d**
T_g(°C)[a]	Nd[b]	Nd[b]	Nd[b]	Nd[b]
T_{10}(°C)[c] (in air)	472	460	451	443
T_{10}(°C) (in N_2)	450	443	438	432

[a] Determined in nitrogen atmosphere.
[b] Not detected.
[c] 10% weight loss temperature.

Table 3
Solubility of Poly(ether ether ketone)s (Solubility: (+) soluble on heating, (++) soluble at room temperature (SW) swollen, (−) insoluble)

Solvent	Poly(ether ether ketone)s			
	4a	**4b**	**4c**	**4d**
N,N-Dimethylformamide	+	+	+	+
Dimethyl sulfoxide	+	+	+	+
Chloroform	SW	−	−	−
Water	−	−	−	+
Methanol	−	−	−	SW
Methanol + Water (1:1)	−	+	++	++

low temperature, as noted for other sulfonated polymers [15].

3.3. Solubility of polymers

Solubility of polymers **4a**–**4d** in selected solvents is listed in Table 3.

It shows that increasing content of sodium sulfonate groups in polymers improves the solubility of polymers in protonic polar solvents such as methanol and water, which is attributed to the solvation between the strong electron-donating sodium sulfonate groups and the strong electrophilic solvents, water and methanol. The solvation increases with the increase of content of sodium sulfonate groups in polymers. And as an extreme case, polymer **4d** is soluble in water under severe heating. Polymer **4b** and **4c** are insoluble either in water or in methanol. However, they are both soluble in a mixed solvent of water and methanol in a volume ratio of 1:1, which cannot be explained by the conventional theory on polymer solution. Further research on nature of the solubility of polymers will be taken and will be reported in an individual paper.

All the polymers are readily solution cast into tough membranes. Due to their high content sodium sulfonate groups and poor solubility in water, they look promising for use as high performance gas dehumidification and ion exchange membrane materials. Work on water vapor and gas permeation behaviors, and ion permselectivity through membranes prepared from these functionalized polymers is currently under investigation and will be reported in the near future.

Acknowledgements

This project was financially supported by Polymer Chemistry Laboratory, Chinese Academy of Sciences and China Petro-Chemical Corporation.

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