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Synthesis of poly(ether ether ketone) with high content of sodium sulfonate groups and its membrane characteristics

Feng Wang*, Jianke Li, Tianlu Chen, Jiping Xu

Changchun Institute of Applied Chemistry, Changchun 130022, People's Republic of China

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Abstract

Poly(ether ether ketone) with high content of sodium sulfonate groups prepared directly from 5,5′-carbonylbis(2-fluorobenzene sulfonate), 4,4′-difluorobenzophenone and phenolphthalein via aromatic nucleophilic substitution reaction. The polymer showed excellent thermal stability, high permeability of water vapour, high permselectivity of water vapour over nitrogen, and high permselectivity of anions. © 1998 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(ether ether ketone); Sodium sulfonate; Permselectivity

1. Introduction

Among the attractive properties of the engineering thermoplastic poly(ether ether ketone)s, good solvent resistance, high thermo-oxdative stability and good mechanical properties are significant [1]. In the last decade, considerable effort was made to modify their chemical nature while maintaining their excellent physical properties to find membrane applications in electrodialysis and gas dehumidification. It has been proven that sulfonation is an effective method to increase both the permeation rate of water vapour and the separation factor of water vapour over gases [2].

A number of groups have reported the sulfonation of poly(ether ether ketone)s, using different sulfonating agents, such as concentrated sulfuric acid [3], chlorosulfonic acid [4], pure or complexed sulfur trioxide [4–6], and methane sulfuric acid/concentrated sulfuric acid [7]. Poly(ether ether ketone)s can be sulfonated with a sulfonation degree of 1.0 per repeat unit [8,9]. However, a greater degree of sulfonation is difficult to achieve due to the insolubility and side reactions such as interpolymer crosslinking and degradation. In a previous work, we reported the synthesis of sulfonated poly(ether ether ketone) with a sulfonation degree of 1.0 per repeat unit, using sodium 2,5-dihydroxybenzene sulfonate as one of the monomers for polycondensation [10]. Another monomer, sodium 5,5′-carbonylbis(2-fluorobenzene sulfonate) [11], might be employed to prepare poly(ether ether ketone) with a high degree of sulfonation. In this communication, we describe the synthesis of poly (ether ether ketone) bearing 1.2 sodium sulfonate groups per repeat unit. This is the first time that a poly(ether ether ketone) with degree of sulfonation above 1.0 was synthesized. The permeation behaviour of water vapour and nitrogen through the membranes was studied, and the ion permselectivity was determined as well.

2. Experimental

In a 100 ml three-necked round bottom flask, fitted with a Dean–Stark trap with reflux condenser, a nitrogen inlet, and a thermometer, 2.530 g (6 mmol) of 5,5′-carbonylbis(2-fluorobenzene sulfonate), 0.873 g (4 mmol) of 4,4′-difluorobenzophenone, 3.183 g (10 mmol) of phenolphthalein and 1.520 g potassium carbonate were dissolved in a mixture of dimethyl sulfoxide (16 ml) and toluene (8 ml). The entire operation was conducted under a constant stream of nitrogen. The mixture was refluxed for 3 h. After the water was essentially removed from the reaction mixture by azeotropic distillation, the temperature was raised to 175°C to distill out the toluene and kept at this temperature for 6 h. Then the reaction mixture was poured into 500 ml acetone to precipitate the polymer.

3. Results and discussion

As shown in Scheme 1, polymer I (P-I) was synthesized by the aromatic nucleophilic substitution reaction of

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* Corresponding author.

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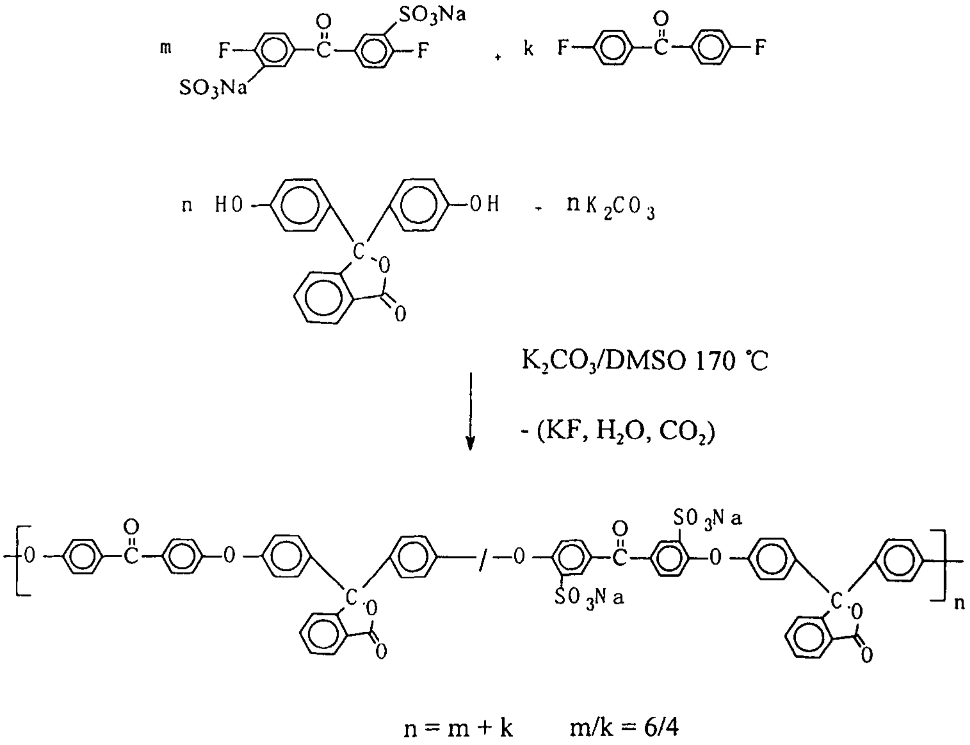

Scheme 1.

4,4′-difluorobenzophenone, sodium 5,5′-carbonylbis(2-fluorobenzene sulfonate), with phenolphthalein in the presence of potassium carbonate in dimethyl sulfoxide. The polymerization proceeded smoothly and afforded a 99% yield of P-I. The reduced viscosity of P-I is 0.74 dl g^{-1}, as measured in 0.5 g dl^{-1} *N*,*N*-dimethylformamide solution at 25 ± 0.1°C, showing that P-I was a high molecular weight polymer. To remove the residual solvents and inorganic salts, the crude polymer was dialysed using SPECTRUM cellulose acetate dialysis tubes with molecular weight cut off value of 2000. The sodium form P-I was acidified with excess 1 N HCl aqueous solution to its acid form, polymer II (P-II). Both P-I and P-II are soluble in several aprotic polar organic solvents, such as *N*,*N*-dimethylformamide, *N*,*N*-dimethylacetamide, and *N*-methyl-2-pyrrolidone. The membranes of P-I and P-II were prepared by casting a 8 wt% *N*,*N*-dimethylformamide solution on a glass plate. The membranes were dried in a desiccator at room temperature for 24 h. The inside pressure of the desiccator was kept in the range 30–50 mmHg. They were then dried at 120°C in a vacuum oven for 48 h.

The differential scanning calorimetry (d.s.c.) diagram of P-I, conducted on a Perkin-Elmer DSC-7 in nitrogen atmosphere at a heating rate of 10°C min^{-1}, showed a typical amorphous polymer. Moreover, no glass transition temperature (T_g) was observed in a temperature range of 100–350°C, indicating that the strong intermolecular interactions led to a stiff polymer segment and the glass transition should take place at a temperature higher than 350°C. Similar phenomena have also been observed for sulfonated poly(ether ether ketone)s [7,12].

As compared with one commercial poly(ether ether ketone) PEK-C, which is synthesised from phenolphthalein and 4,4′-dichlorobenzophenone [13], the introduction of sodium sulfonate groups was confirmed by the infra-red (i.r.) spectrum of P-I (Fig. 1b), where strong characteristic peaks at 1028 and 1203 cm^{-1} were assigned to the asymmetric O=S=O stretching vibration and symmetric O=S=O stretching vibration. These peaks were absent in the i.r. spectrum of the unsubstituted PEK-C (Fig. 1a). The characteristic peak of aromatic C–C at 1501 cm^{-1} was observed to split upon the introduction of sodium sulfonate groups in the phenyl rings. The splitting of this skeletal vibration is indicative of trisubstitution of the phenyl ring. No peaks attributable to the sulfone bond were observed, as shown in Fig. 1. These results suggest that no detectable sulfone crosslinking occurred in the polycondensation process. As compared with the sulfonation method, this method is more advantageous than sulfonation of the polymer, avoiding possible degradation and crosslinking.

Thermogravimetric analyses (t.g.a.) of P-I and P-II were performed on a Perkin-Elmer 7 Series Thermal Analysis apparatus at a heating rate of 10°C min^{-1} in a nitrogen atmosphere. The samples were first dried for 30 min at 150°C in the t.g.a. furnace. As shown in Fig. 2, only one weight loss stage, between 420 and 550°C, was observed in the t.g.a. curve for P-I, which is the result of the decomposition of polymer chains. The initial weight loss of P-II

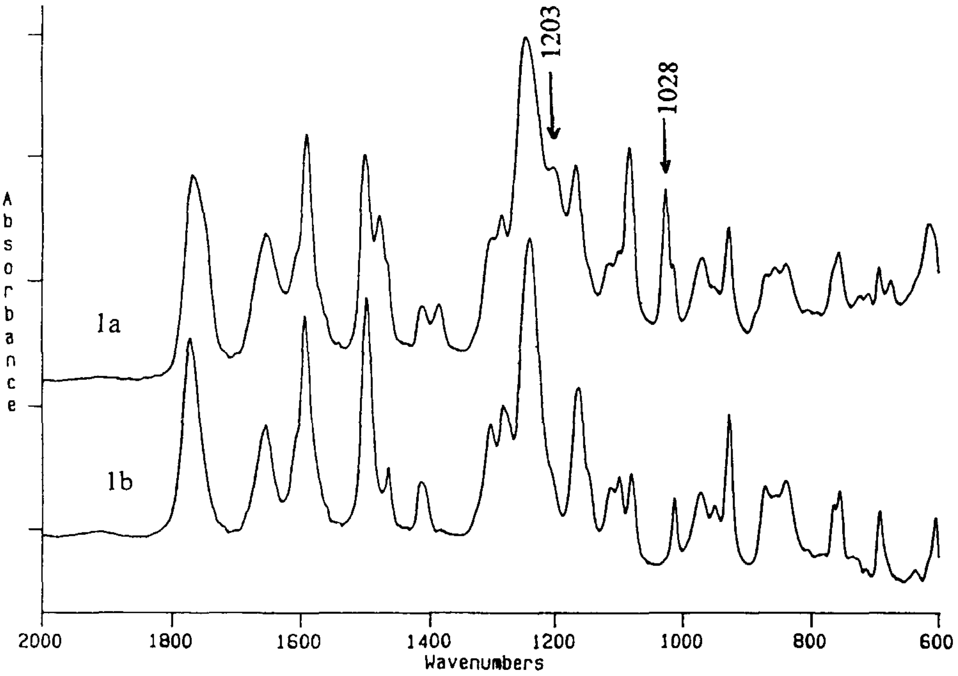

Fig. 1. I.r. spectra of P-I (a) and PEK-C (b).

between 250–420°C is only 10%, which corresponds to the loss of 1.2 sulfonic acid groups per repeat unit. The second thermal degradation above 450°C is attributed to the polymer degradation.

The permeability of nitrogen was measured on a model K315-N-03(Rikaseiki, Japan) manometric permeation apparatus and the permeability of water vapour was measured by the cup method [14]. As shown in Fig. 3, both P-I and P-II exhibit high water vapour permeation, 3.33 × 10^4, 3.11 × 10^4 barrer at 30°C, respectively. The

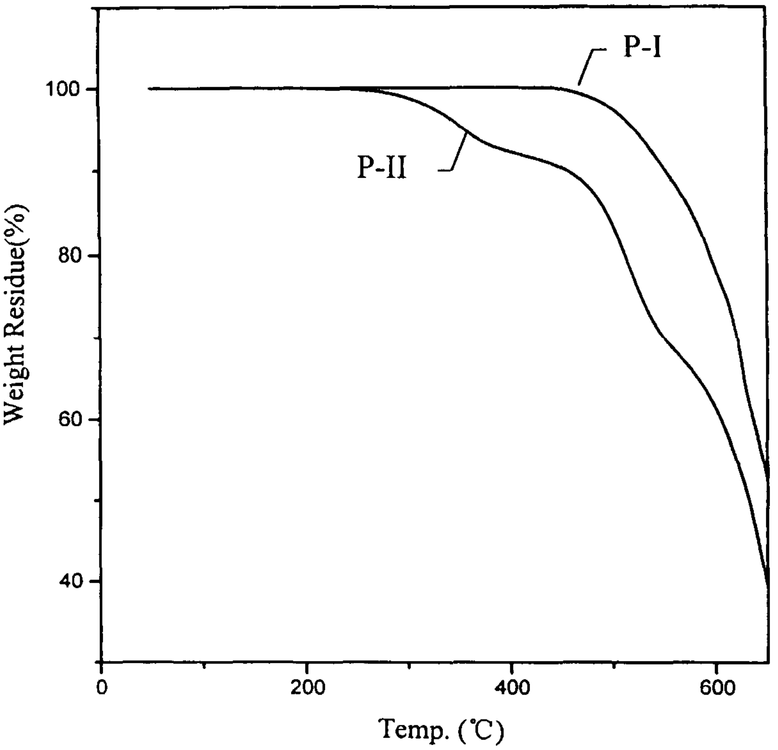

Fig. 2. T.g.a. curves of P-I and P-II.

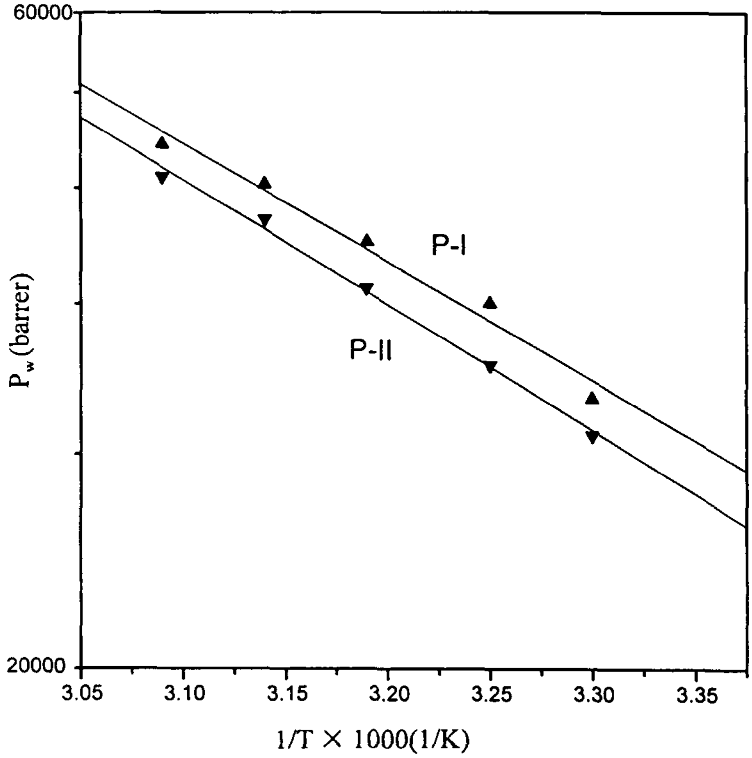

Fig. 3. The relationship between P_w and $1/T$ for P-I and P-II.

water vapour permeation (P_w) shows an approximate Arrhenius-type temperature dependence with $E_a = 18.6\ \text{kJ mol}^{-1}$ for P-I and $E_a = 16.5\ \text{kJ mol}^{-1}$ for P-II. Arrhenius plots of the permeability of nitrogen (P_N) are presented in Fig. 4. It is obvious that a linear relationship exists between $\lg P_N$ and $1/T$ in each case. The apparent activation energies of nitrogen for P-I and P-II are 16.7 and $16.8\ \text{kJ mol}^{-1}$ respectively. P-I exhibits a high

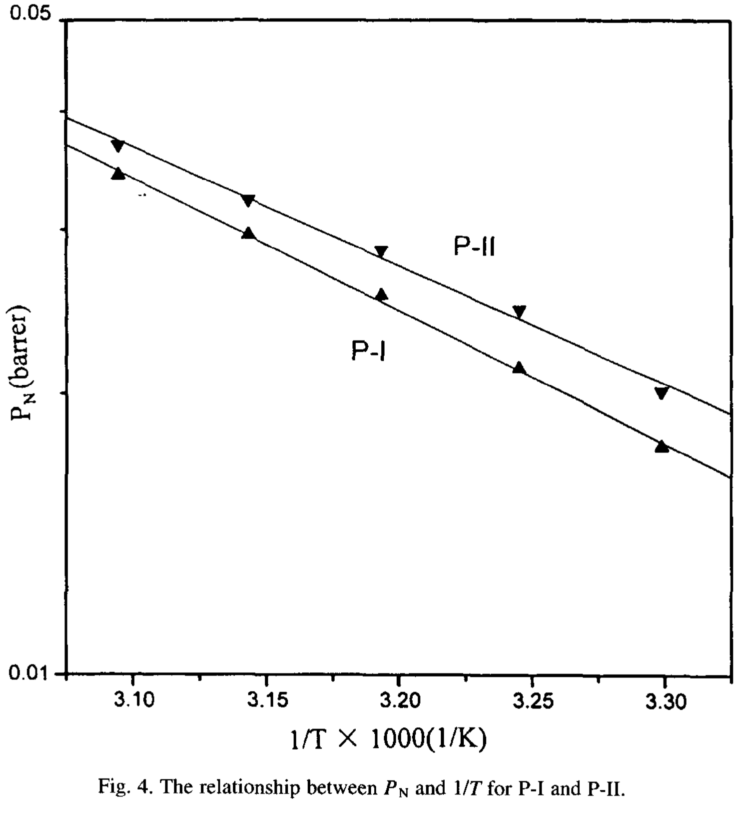

Fig. 4. The relationship between P_N and $1/T$ for P-I and P-II.

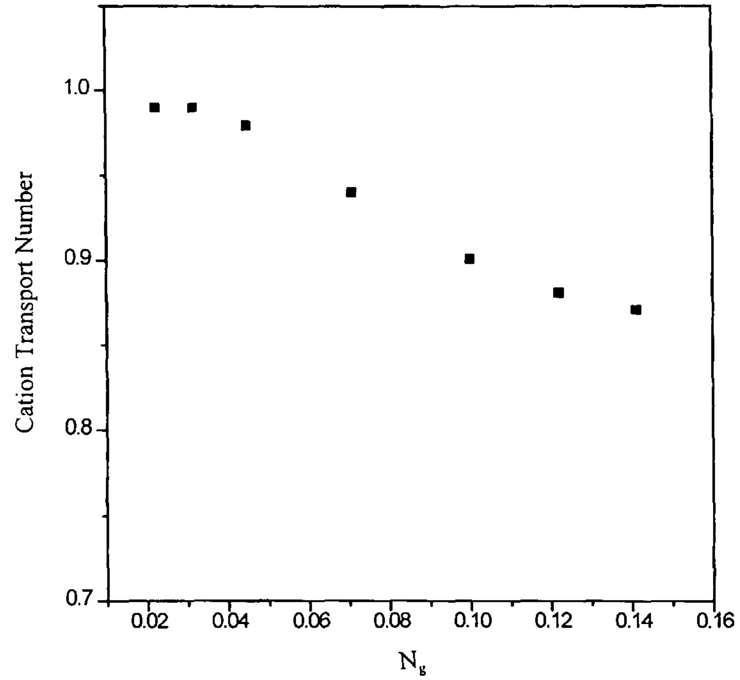

Fig. 5. Cation transport numbers across P-I membrane.

selectivity of 1.89 × 10^6 of water vapour over nitrogen at 30°C.

In order to characterize the permselectivity of P-I membrane to ions, the concentration membrane potentials in KCl solutions of different concentration (N_1 and N_2) were measured, using the conventional method as described elsewhere [15,16]. In Fig. 5, the cation transport numbers calculated from membrane potentials by the Nernst Equation are plotted versus the geometric mean (N_g) of N_1 and N_2, where N_1 was kept at a constant concentration (with $N_1 = 0.01$ N) and N_2 varied but was always maintained at a higher concentration than N_1 (with $N_2 = 0.05$–2.0 N). As shown in Fig. 5, P-I membrane had a strong screening effect for chloride ions. However, the efficiency of electrolyte exclusion decreased slightly with increasing KCl concentration, showing the lower transport selectivity for potassium ions. This can be explained by the Donnan equilibrium, i.e. the decreasing efficiency of electrolyte exclusion with increasing solution concentration is due to the increasing tendency of the electrolyte permeating by diffusion as a result of the Donnan equilibrium [17].

Acknowledgements

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