The Synthesis of New Type Sulfonated Polyimide*

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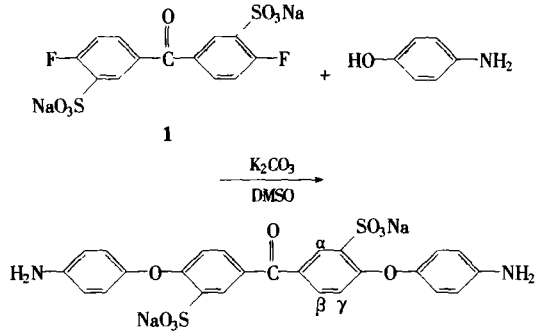
Abstract: Proton conductor ion exchange membrances, because of their high ionic conductivity and excellent resistant, are used in solid polymer H_2/O_2 fuel cells. But their too high cost has limited their application on market. Researches have been undertaken to provide cheaper alternative productions. Sulfonated polyimides are thought of as the possible alternatives. A new aromatic diamine was synthesized by using sodium 5,5-carbonylbis(2-flurobenzensulfonate) and 4-aminophenol, then a series of sequenced sulfonated polyimides were prepared by one step in *m*-cresol using the new aromatic diamine and dianhydride, which avoided the crosslink and degradation of polymeric chain when the polymer was sulfonated. New aromatic diamine was characterilized by H NMR and IR spectroscopies, while sulfonated polyimides were characterilized by IR spectroscopies. The influence of degree of sulfonation on the properties of copolymers, such as component, solubility and inherent viscosity were studied. The results show that the new polyimides are soluble in the solutions such as DMF, DMAc, NMP etc.

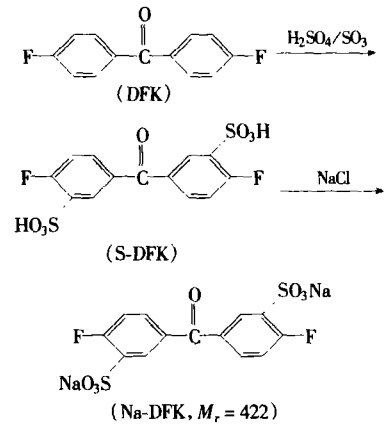
Key words: diamine; ion-exchange polymer; polyimide
CLC number: TQ323.6; O632.6 **Document code**: A **Article ID**: 0529-6579(2003)S1-0088-03

Sulfonated polyimides are recently developed as ion-exchange polymers intended for use in fuel cell as a substituent for Nafion, which has high performances and a long life, but is too expensive and complicate for most usage. The first sulfonated polyimides were prepared from 4, 4′-diamino-biphenyl 2, 2′-disulfonic acid, 4, 4′-oxydianiline and oxy-diphthalic dianhydride[1]. Although some other attempts have also been made in recent years on sulfonated polyimides, the sulfonic acid groups are all attached to benzyl rings activated by amino groups[2-4]. Here we design and synthesize a new diamine with sulfonate attached to benzyl ring deactivated by carbonyl groups (Scheme 1), which may enhance the stability of polymer and cause a little bit higher acidity.



Scheme 1

1 was synthesized according to scheme 2[5]. A three-necked round bottom flash containing 10 g 4,4′-difluorobenzophenone and 20 mL fuming sulfuric acid (50% SO_3) were fitted with a magnetic stirrer, condenser, nitrogen pad and thermometer. This mixture was heated to 100 ℃ for 10 h, then cooled to room temperature and poured to neutralize the excess fuming sulfuric acid. After the mixture was cooled, 20 g NaCl was added to precipitate the white solids. The precipitated white solids were filtered, recrystsllizated from an ethanol/water mixture. Then the solids was filtered and dried at 80 ℃ under vacuum.



Scheme 2

The condensation reaction of 2.110 g (5×10^{-3} mol) **1** with 1.270 g (1.17×10^{-2} mol) *p*-aminophenol was firstly conducted in 20 mL dimethylsulfoxide and 40 mL toluene containing 1.685 g (1.22×10^{-2} mol) K_2CO_3 at 120 ℃ under N_2 atmosphere for 2 h. Upon

* Received 10 December 2002; Accepted 18 April 2003
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dehydration and removal of toluene, the reaction temperature was raised to 175 ℃ and kept for 17 h. Then, the mixture was cooled and precipitated in ethanol. FTIR spectrum of **2** (Fig. 1) showed the presence of Ar-NH_2 at 3435 and 1131 cm^{-1}, Ar-SO_3Na at 1193 and 1067 cm^{-1}, phenylene at 1591 cm^{-1} and 1508 cm^{-1} and C—O—C at 1246 cm^{-1}. ^1H NMR (Fig. 2) displayed four groups of signals at δ8.27 (d), 7.7 ~ 7.8 (dd), 7.5 ~ 7.7 (d) and 6.8 ~ 7.1 (m) in correspondence to protons α, β, γ (Scheme 1), and all other protons respectively.

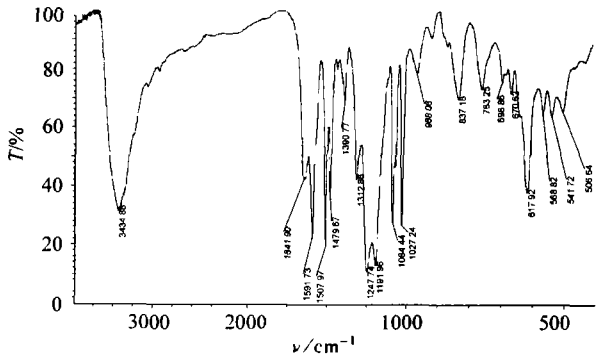


Fig. 1 FTIR spectrum of diamine

Copolymerization (Sheme 3) was conducted as follows: 0.24 g(0.4×10^{-3} mol) **2** and 0.12 g(0.6×10^{-3} mol) 4,4′-diaminodiphenylether was dissolved in a solution of 0.322 g(1×10^{-3} mol) **3** in 0.25 g(2.4×10^{-3} mol) triethylamine and 3 g *m*-methylphenol under N_2 atmosphere. The mixture was heated at 80 ℃ for 4 h and 180 ℃ for 20 h; then diluted with 8 g *m*-methylphenol and precipitated in 40 mL ethyl acetate.

Product was in dried vacuum at 100 ℃ for 24 h. Yellow copolyimide has an intrinsic viscosity of 0.33 dL/g and is soluble in DMF, *m*-methylphenol, DMSO and NMP. FTIR spectrum showed the presence of —CO— in —CO—N—CO— at 1772 cm^{-1}, —CO— at 1663 cm^{-1}, C—N at 1663 cm^{-1}, C—O—C at 1241 cm^{-1} and SO_3Na at 1083 cm^{-1}.

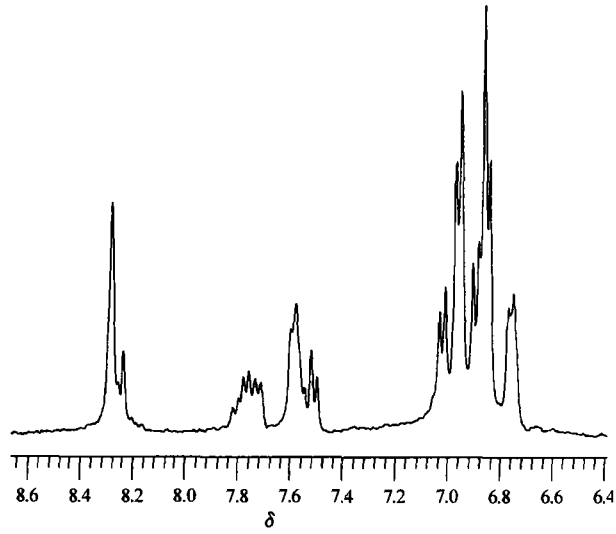


Fig. 2 ^1H NMR spectrum of diamine

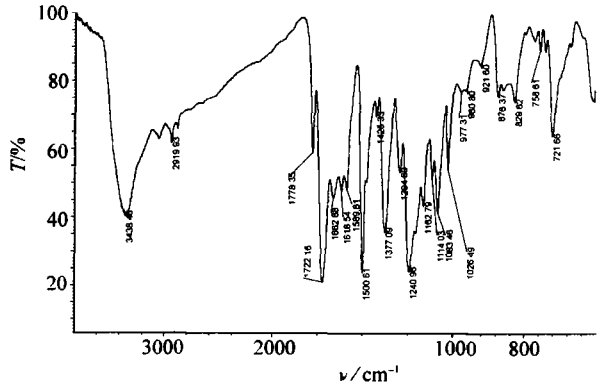
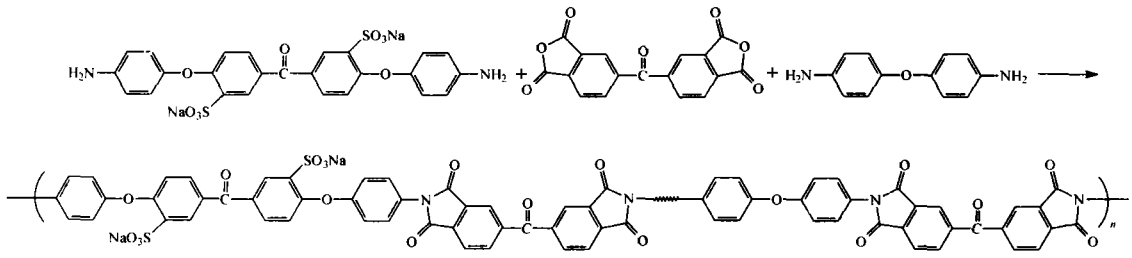


Fig. 3 FTIR spectrum of copolyimide



Scheme 3

Acknowledgement: This project is supported by National Natural Science Foundation of China through grant 20104001.

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新型磺化聚酰亚胺的合成

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摘 要:质子导电离子交换膜由于其高导电率和优异的化学性质而广泛应用于 H_2/O_2 燃料电池,但是全氟化膜的昂贵的价格限制了它的市场应用,为此,研究者尝试生产廉价的代替品,磺化聚酰亚胺就是被人们看好的代替品之一。用 3,3′-二磺酸钠基-4,4′-二氟二苯酮和对氨基苯酚为原料合成一种新型芳香族二胺,再将新型芳香族二胺和二酐以间甲酚为溶剂一步法合成一系列具有不同磺化度的聚酰亚胺,从而避免了由聚合物磺化改性引起的聚合物链的交联与降解。用红外吸收光谱和 H NMR 核磁共振光谱对新型芳香族二胺单体进行了表征,并用红外吸收光谱表征了聚合物。研究了共聚物的组成结构,溶解性,及磺化度对共聚物的影响。结果表明 DMF,DMAc,NMP 等均是该磺化聚酰亚胺的良溶剂,聚合物粘度随着磺酸基含量的增加而降低。

关键词:聚酰亚胺;质子交换膜; 燃料电池
中图分类号:TQ323.6;O632.6 **文献标识码**:A