Chinese Chemical Letters Vol. 15, No. 1, pp 17 – 18, 2004
http://www.imm.ac.cn/journal/ccl.html

Synthesis and Characterization of Ion-exchange Copolyimide

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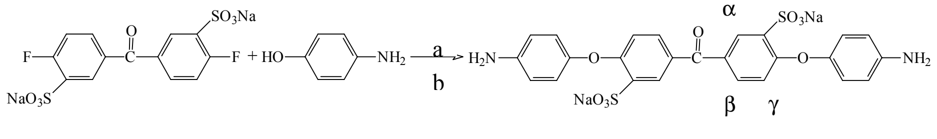
Abstract: A new diamine, disodium 4, 4′-di(4-aminophenoxy)-3, 3′-disulfonate-1, 1′- diphenylketone, was prepared from the nucleophilic substitution of disodium 4, 4′- difluoro-3, 3′-disulfonate-1, 1′-diphenylketone and *p*-aminophenol. Polymerization of this diamine and 4, 4′-diamino-1, 1′- diphenyl ether with 3, 3′, 4, 4′-tetracarboxyl dianhydride-1, 1′- diphenyl ketone gave ion-exchange copolyimide. The new diamine and its polyimide were characterized with ^{1}H-NMR and FT-IR.

Keywords: Diamine, ion-exchange polymer, polyimide.

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 **2**

a) K_2CO_3
b) DMSO

1 was synthesized according to reference 5. 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

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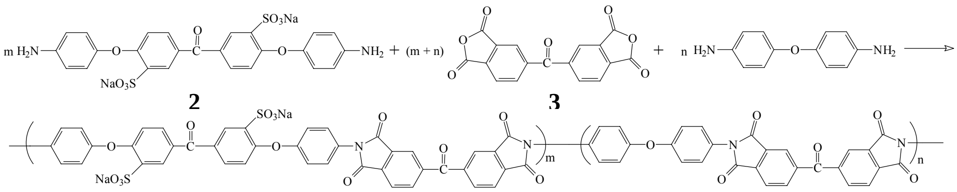
120°C under N_2 atmosphere for 2 h. Upon dehydration and removal of toluene, the reaction temperature was raised to 175°C and kept for 17 h. Then, the mixture was cooled and precipitated in ethanol. FT-IR spectrum of **2** showed the presence of Ar–NH_2 at 3435 and 1131 cm^{-1}, Ar-SO_3Na at 1193 and 1067 cm^{-1}, phenylene at 1591 cm^{-1} and 1508 cm^{-1} and C-O-C at 1246 cm^{-1}. ^1H-NMR displayed four groups of signals at δ 8.27 (d), 7.7-7.8 (dd), 7.5-7.7 (d) and 6.8-7.1(m) ppm in correspondence to protons α, β, γ (**Scheme 1**), and all other protons respectively.

Scheme 2



Copolymerization (**Sheme 2**) was conducted as follows: 0.24 g(0.4×10^{-3} mol) **2** and 0.12g (0.6×10^{-3} mol) 4, 4′-diaminodiphenylether was dissolved in a solution of 0.322g (1×10^{-3} mol) **3** in 0.25g (2.4×10^{-3} mol) triethylamine and 3g *m*-methylphenol under N_2 atmosphere. The mixture was heated at 80°C for 4 h and 180°C for 20 h; then diluted with 8 g *m*-methylphenol and precipitated in 40 mL ethyl acetate. Product was in dried vacuum at 100°C for 24 h. Yellow copolyimide has an intrinsic viscosity of 0.33 dL/g and is soluble in DMF, *m*-methylphenol, DMSO and NMP. FT-IR 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}.

Acknowledgment

This project is supported by the National Natural Science Foundation of China (Contract grant number: 20104001).

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Received 13 December, 2002