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Synthesis and Characterization of 5, 5′, 6 ,6′-(2, 2′-Bipyridine)tetraacid

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Abstract: 5,5′,6,6′-(2,2′-Bipyridine)tetraacid, a new aza-aromatic tetraacid, was synthesizedstarting from diquinoline, and its structure was confirmed by means of mass spectrum and infrared spectrum.

Keywords: 5,5′,6,6′-(2,2′-Bipyridine)tetraacid, synthesis, diquinoline, FABMS, FT-IR.

It is well known that the dianhydride based on aromatic tetraacid plays a critical role in the preparation of polyimides, polypyrrolones or their copolymers, specially all kinds of polyimides have widely gotten applications in advanced technologies[1-3]. Polyimide exhibits a serials of excellent performances, *e.g*. high strength, modulus, heat resistance, dielectric property, chemical stability as well as radioresistance[2], meanwhile, polypyrrolone should be also a promising high performance material, which has been widely employed in the research for heat resistance, anti-radiation, gas separation, foam, as well as coating materials because of their heteroaromatic structure[1]. For the application of polyimdes, polypyrrolones and their copolymers, besides aromatic tetraacid dianhydrides that have been employed in synthesis are 4,4′-(hexafluoro-isopylidene)diphthalic anhydride(6FDA), 3,3′,4,4′-benzophenone tetracarboxylic acid dianhydride(BTDA) and 3,3′,4,4′-biphthalic anhydride(OBPA), *etc*, while a new aromatic tetraacid dianhydride will be still attended[3].

Pyridine is an aza-aromatic compound, it has excellent heat resisting property and chemical stability, and it will be interesting that pyridine is introduced in aza-aromatic polymers. Pryor *et al*.[4] synthesized 2, 2′, 6, 6′-(4, 4′-bipyridine)tetraacid, however, it can not been employed in the preparation of polyimides and polypyrrolones because it is a meta-dicarboxylic acids. In this work, a new tetraacid of bipyridine with *ortho-para* dicarboxylic acid, *i.e*. 5,5′,6,6′-(2,2′-bipyridine)tetraacid, was successfully synthesized by using diquinoline as starting reagent. Diquinoline is oxidized by potassium permanganate according to following procedure: with vigorously stirring, 11 g (0.07 mol) of diquinoline in 200 mL of 75% concentrated sulfuric acid was put into a flask, 250 g

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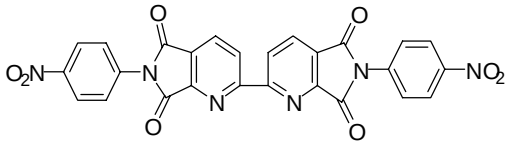
(1.6 mol) potassium permanganate was added in small portions at rate in order to maintain the temperature at 95-98°C and after that, the mixture was stirred at 95°C for 1 h. The solid was filtered off, the filtrate was neutralized with concentrated hydrochloric acid and then frozen, 5,5′,6,6″-tetraacid-2,2′-dipyridine dihydrochloride was precipitated out, it was filtered and dried, recrystallized from ammonia and hydrochloric acid subsequently. Its melting point>320°C, it dissolves in DMF, basic and part of acids aqueous solution, but is not soluble in ethanol, diethyl ether, acetone, chloroform, benzene, *etc*. The chemical shift of 5,5′,6,6″-(2,2′-bipyridine)tetraacid tetrasodium in ^{1}H-NMR is at δ 8.6, but it is feebleness, because hydrogen content in the molecule is very poor. The FT-IR indicates the signals at 3427.2 cm^{-1}($\upsilon_{O\text{-}H,}$ S), 1685.41 cm^{-1}($\upsilon_{C=O,}$ S), 1549.1, 1471.5, 1406.8 and 1355.3 cm^{-1}(pyridine). FABMS (fast atom bombard MS), *m/z*, show M^+ 407.1(6%), M^+-HCl 369.2 (18%), and others 333.1(5%), 315.1(20%), 297(5%), 223(100%) as well as 207(65%). Elemental analysis calculated for ($C_{14}H_8O_8N_2$): C 50.60, H 2.41, N 8.43, found C 50.55, H 2.48, N 8.40.

FT-IR and MS confirm the formation of 5,5′,6,6′-(2,2′-bipyridine)tetraacid, the purity of the product is not satisfy because of salt forming, however, its derivative (**Scheme I**) could be purified easily, we will report in the next work.

Scheme I



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References

1. Y. F. Li, A. J. Hu, X. C. Wang, S. Q. Gao, S. Y. Yang, *J. Appl. Polym. Sci*., **2001**, *82*, 1600.
2. J. Y. Hao, S. Y. Yang, *High Perform. Polymer,* **2001**,*13*(3), 211.
3. A. J. Hu, T. He, S. Y. Yang, *Macromolecules*, **1999**, *32*, 8046.
4. K. E. Pryor, G. W. Shipps, Jr, D. A. Skyler, *et.al.*, *Tetrahedron*, **1998**, *54*, 4107.

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