CHEMISTRY LETTERS, pp. 419-420, 1976. **Published by the Chemical Society of Japan**

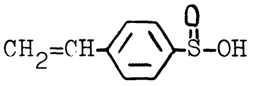
SYNTHESIS OF POLYMERIZABLE p-STYRENE SULFINATE

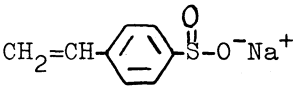
Hiroyoshi KAMOGAWA, Tsuyoshi HAYASHI, and Masato NANASAWA
Department of Applied Chemistry, Yamanashi University, Takeda 4, Kofu 400

Sodium p-styrene sulfinate, a novel redox monomer, was synthesized starting with 2-bromoethylbenzene with intention of preparing a novel class of redox polymer. The monomer was found to afford soluble polymers of high molecular weights by radical polymerization.

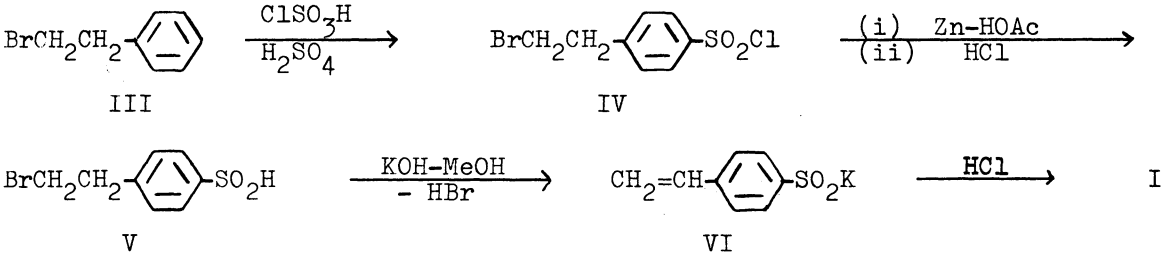
It is well known that aromatic sulfinic acids are useful nucleophiles as well as reductants[1]. When this functional groups are incorporated into vinyl polymers as side chains, the resulting polymers will constitute a novel class of reactive polymers.

In this letter, we wish to report the first synthesis of polymerizable p-styrene sulfinic acid(I) and its sodium salt(II).


I


II

Compounds I and II were synthesized as follows.



2-Bromoethylbenzene sulfinic acid(V) was synthesized according to the method of Spinner-Yannopoulos-Metanomski[2] starting with 2-bromoethylbenzene(III). Thus, 2-bromoethylbenzene sulfonyl chloride(IV) was prepared by the reaction of compound III with chlorosulfonic acid to give colorless crystals in 76.8% yield.

Compound IV was then converted to compound V in 63.2% yield by the reduction with zinc powder in acetic acid, followed by HCl-treatment.

Compound V thus synthesized(5.0 g, 20 mmol) was dissolved in 100 ml of methanol containing 3.4 g(60 mmol) of potassium hydroxide. A small amount of hydroquinone was added and the solution was refluxed for one hour to afford a dark solution with white precipitates. The reaction mixture was evaporated in vacuo at 40°C and poured into water to afford a homogeneous solution. Crude p-styrene sulfinic acid(I) was isolated by the acidification of the solution with hydrochloric acid. Recrystallization from water provided colorless crystals of mp 53 -54.5° in 38.8% yield.

Anal. Found: C, 57.59; H, 4.57%. Calcd for $C_8H_8SO_2$: C, 57.12; H, 4.79%. IR(KBr): 3080, 3040, 2800(br), 2480(br), 1620, 1580, 1480, 1380(s), 1300(s), 1080, 1065, 1030(s), 1010, 990, 940, 915, 840(s), 740, 640 cm^{-1}. NMR($CDCl_3$): δ 7.7(s 1H $-SO_2H$), 7.2 - 7.7(2d

4H aromatic), 6.7(q 1H vinyl), 5.8(d 1H vinyl), 5.3(d 1H vinyl) ppm. Mass: m/e 168 (M^+ 54), 170(M+2 7), 78(100).

Since monomer I was unstable, it was converted to more stable sodium salt.

Sodium p-styrene sulfinate(II) was prepared in the form of colorless crystals by dissolving monomer I in water containing an equivalent of sodium hydroxide and by subjecting the resulting solution to freeze-drying. Iodometric titrations provided the stoichiometric redox capacity. IR(KBr): 3400(br), 3080, 3040, 3000, 1620, 1440(s), 1380, 1060, 1050(s), 1025, 990(s), 975, 910, 880, 840(s), 745, 645 cm^{-1}. NMR(D_2O): δ 8.0(s 4H aromatic), 7.2(q 1H vinyl), 6.3(d 1H vinyl), 5.7(d 1H vinyl), 4.7(s water) ppm.

Monomer II was polymerized in aqueous solutions to afford polymers of high molecular weights. Thus, a solution of 0.5 g of monomer II and 0.005 g of potassium persulfate in 5 ml of water was put into a glass ampoule, which was evacuated and sealed off in a conventional manner, followed by standing at 70°C for 24 hours. The viscous solution thus obtained was poured into methanol to precipitate a polymer, which was freeze-dried from water to afford a white solid in 25% yield. Intrinsic viscosity in water at 30°C was 3.70 dl/g. IR(KBr): 3350(br water), 3040, 2930, 2850, 1640, 1590, 1440, 1400, 1380, 1360, 1120(br), 1080, 1025(s), 975, 910, 840(s), 640 cm^{-1}.

Radical polymerization behaviors of monomers I and II are interesting due to the possible participation of the sulfinic acid group in radical initiation. The pendant sulfinic acid groups in polymers are also the sources of nucleophilic substitution as well as redox reactions, which may make this novel polymer group useful as a reactive polymer.

References

(1) Sandler-Karo, "Organic Functional Group Preparations" Academic Press, New York, 1968, p.519.

(2) H. Spinner, J. Yannopoulos, and W. Metanomski, Can. J. Chem., 39 2529 (1961).

(Received March 13, 1976)