A New Polymerization Reaction: 2,5-Dichlorothiophen–Aluminium Chloride–Cupric Chloride

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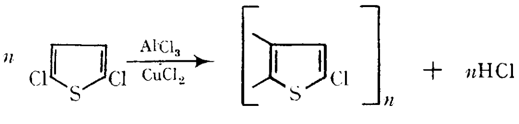
WE report a novel type of polymerization which yields a product of unique structure. A mixture of 2,5-dichlorothiophen, aluminium chloride, and cupric chloride (1:4:2 molar ratio) in carbon disulphide, stirred for 2 hr. at 12—29°, gave a solid in 93% yield. The reaction appears to be:



The material is a brown powder, m.p. *ca.* 115—150°, soluble in hot trichlorobenzene, but not completely soluble in common solvents at room temperature. The structure is based on elemental analysis (after extraction with hexane), i.r. spectral data (characteristic bands at 790, 815, and 860 cm.$^{-1}$), and the n.m.r. spectrum (broad signal at δ 6·7—7·5 in tetrachloroethylene at 80—90°). 90% of the theoretical amount of hydrogen chloride (based on one mole of gas per mole of monomer) was collected.

Distillation of the product gave a little yellow liquid of dimer-type constitution, $C_8H_3Cl_3S_2$. Column chromatography of the ether-soluble fraction of the polymer afforded a yellow solid, m.p. 197—199°, which possesses the characteristics of a tetramer-type entity, $C_{16}H_6Cl_4S_4$. The evidence was derived from molecular weight, elemental, i.r. analyses, as well as n.m.r. studies of the dimer-type fraction.

Polythienylenes coupled through the 2,3-positions have not been reported. The net effect of the reaction is nuclear coupling by dehydrohalogenation. We believe that the mechanism involves a cationic polymerization[1] accompanied by loss of hydrogen chloride. Some related methods have been reported, *e.g.* oxidative cationic conversion of benzene to *p*-polyphenylene under similar conditions,[1] transformation of quinol to polyhydroxyphenylene by exposure to zinc chloride,[2] and treatment of bromophenol with copper in basic solution to form polyphenylene oxide.[3]

2,3,5-Trichlorothiophen underwent an analogous reaction in trichlorobenzene at 90—100°, but 2-chlorothiophen and thiophen gave complex products. Since we have experienced difficulties in obtaining chemical evidence of the nature of the principal polymer, the structural assignment should be regarded as tentative.

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