CHEMISTRY LETTERS, pp. 317-318, 1991.

An Improved Synthesis of Poly(m-aniline) and the Magnetic Properties of Its HCl Salt

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An analytically satisfactory sample of poly(m-aniline) was obtained from m-bromoaniline in the presence of a copper-based catalyst. The magnetic susceptibility of the HCl salt followed a Curie-Weiss law and the spin concentration was determined to be 2.6×10^{19} spins/g.

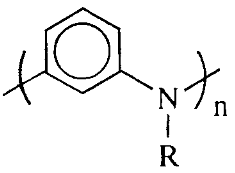
During the course of our study on poly(oxyimino-1,3-phenylene)(**1**) as a potential organic ferromagnetic material, we found that the dehydrobromination of m-bromoaniline gave poly(imino-1,3-phenylene)(**2**) (so-called "poly(m-aniline)") under modified Jourdan-Ullmann-Goldberg conditions.[1)]

A typical procedure is as follows. A mixture of 1.75 g of m-bromoaniline, 0.03 g of powdery copper, 0.09 g of Cu_2I_2, 0.06 g of I_2 and 2.76 g of anhydrous K_2CO_3 in 5 ml of diphenyl ether was vigorously stirred and refluxed for 16 h. The insoluble fraction was filtered off and washed with ca. 10 ml of CH_2Cl_2. After addition of ca. 30 ml of hexane to a combined filtrate, the precipitate was collected and purified by reprecipitation with CH_2Cl_2 and hexane, giving 0.41 g (44%) of a slightly blue white powder. Anal. Found: C, 78.22; H, 5.54; N, 15.01; Br, 0.51 (determined by gravimetry), 0.48% (by ion chromatography).

Though the apparent degree of polymerization was estimated by GPC to be rather low ($\overline{Mw}$ 850; DP. 9.3) because of strong adsorption on the polystyrene-gel column, the composition $C_6H_{5.06}N_{0.99}Br_{0.006}$ suggests it is large if a bromine atom is attached to the polymer terminal. An IR spectrum shows absorption bands of C-H out-of-plane deformation (850, 770, and 692 cm^{-1}) and a well resolved N-H stretching (3376 cm^{-1}) which confirm the structure of poly(m-aniline).[2)]

Very recently Yoshizawa et al.[2)] reported the synthesis of poly(m-aniline) resembling to **2** with a composition $C_6H_{4.76}N_{0.84}Cl_{0.24}$ from m-chloroaniline. In comparison with this, acid-free poly(m-aniline) was directly obtained in our method with some synthetic advantages: the use of more substitution-susceptible bromide instead of the chloride and removing of HBr by-produced with potassium carbonate.

Besides the research for the conditions of the selective oxidation at the nitrogens toward **1**, we also examined the synthesis and properties of poly(hydrochloride salt) of **2**. Treatment of **2** with an excess of concd HCl aq. followed by precipitation with ether gave a dark blue product which was insoluble in CH_2Cl_2 but soluble in methanol. An ESR spectrum of the sample containing 10.8% chlorine as determined by elemental analysis showed a singlet with $\Delta Hpp = 1$ mT at $g = 2.0028$. The magnetic susceptibility was measured on a Faraday magnetic balance and found to follow a Curie-Weiss law [$\chi = C / (T - \theta)$] with $C = 2.63 \times 10^{-5}$ cm^3 K g^{-1} and $\theta = -1.0$ K in the temperature range 2 - 80 K (Fig. 1). The spin concentration was estimated to be 2.6×10^{19} spins/g, that is, one spin/10^2 units, on the assumption of apparent S = 0.72 estimated from the magnetization curve at 4.1 K. The considerably low concentration is probably due to a slow oxidation under these conditions. A hypothetic polymer **2** oxidized stoichiometrically$^{3)}$ or doped with a stoichiometric amount of an electron acceptor seems to be of great interest in connection with non-Kekulé polymers containing *m*-quinone diimine moieties.



1 R = O•
2 R = H

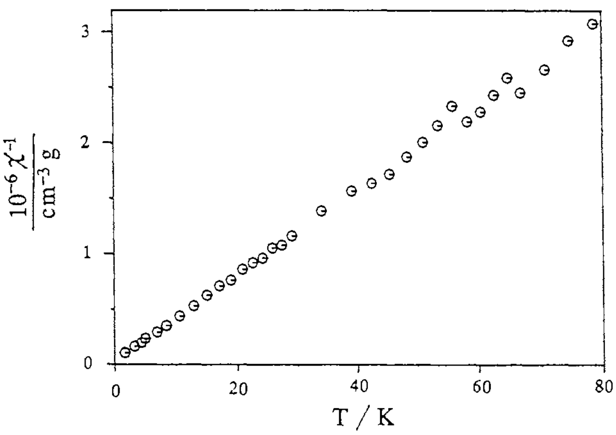


Fig. 1. Temperature dependence of the reciprocal magnetic susceptibility (1/χ) of the HCl salt of **2**.

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(Received Octorber 19, 1990)