

Synthesis of Poly(m-aniline) by Dehydrohalogenation of m-Chloroaniline

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A reddish-orange colored polymer was synthesized by catalytic dehydrohalogenation of m-chloroaniline. The polymer was confirmed to have a poly(m-aniline) structure which will be of our interest as a basic skeleton for ferromagnetic polymer.

In the field of synthetic metals, which are defined as organic compounds showing metallic properties, many works concerning their electrical, optical, and magnetic properties have been reported. Recent reports¹⁾⁻⁶⁾ on the success in organic ferromagnets have attracted a great deal of attention. Torrance et al.¹⁾ have synthesized poly(1,3,5-triaminobenzene) whose iodine complex shows ferromagnetism up to 400 °C, near which the polymer is decomposed. On the other hand, Ovchinnikov et al.³⁾ have reported that what is called poly-BIPO has saturation magnetization of 0.02 G/g. On the basis of the reports of the two groups, free radicals existing on nitrogen or oxygen in π -conjugated systems might be relatively stable at room temperature.

In the present paper, we report the synthesis of poly(m-aniline) which could be an extended version of a maternal structure of ferromagnetic polymer proposed by Mataga.⁷⁾ For instance, the spin alignment in the dehydrogenated structure of poly(m-aniline) is expected to be similar to that of poly(m-phenylcarbene), the oligomer of which has been examined by Iwamura et al.⁸⁾ The synthetic method is based on the dehydrohalogenation between amine and halide,⁹⁾ namely ammonolysis.

In the presence of copper or copper(I) chloride, m-chloroaniline polymerizes to form a reddish-orange precipitate under reflux at 220-230 °C. A typical polymerization was carried out as follows: 25 g (0.20 mol) of freshly distilled m-chloroaniline and 0.5 g of copper(I) chloride were put into a flask under a high-purity nitrogen flow. After approximately 4 h at the reflux temperature, orange polymer started to appear, and it had been further refluxed for 2 h. After cooling, tetrahydrofuran (THF)

Table 1. Elemental analysis for the neutral form(1) and the salt form(2) of the polymer.

Sample	C(wt%)	H(wt%)	N(wt%)	Cl(wt%)	Total(wt%)	Composition
<u>1</u>	72.40	4.79	11.84	8.60	97.63	C ₆ H _{4.76} N _{0.84} Cl _{0.24}
<u>2</u>	65.12	4.55	10.71	16.15	96.53	C ₆ H _{5.03} N _{0.85} Cl _{0.50}

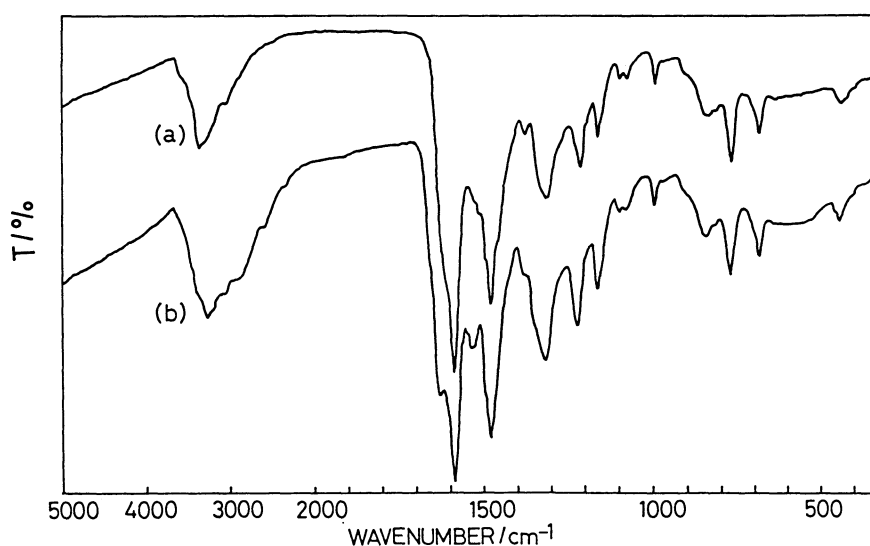


Fig. 1. IR spectra for (a) the neutral form(1) and (b) the salt form(2) of the polymer.

was poured into the flask to dissolve the lower molecular weight species, and the polymer was collected by filtration, washed with THF repeatedly, and dried under vacuum at room temperature to yield 7.5 g(30%) of brown powder. The polymer thus obtained is in the form of amine salt. In order to obtain free amine(1) and remove the catalyst, the polymer was washed five times with 5%-ammonia ethanolic aqueous solution. The salt form(2) of the polymer was prepared by treating a part of 1 with 2 mol/l-HCl ethanolic aqueous solution.

The results of the elemental analysis for 1 and 2 of the polymer are listed in Table 1. Chlorine contained in 1 is considered due to an unreacted terminal one. This interpretation is supported by the observation of the IR spectrum as follows. An absorption band at 890 cm⁻¹ due to the C-Cl stretching, which is observed in the monomer, is much weakened in the polymeric products as shown in Fig. 1. Moreover, the

three C-H out-of-plane deformation modes at 840, 770, and 685 cm^{-1} are characteristic of meta-linkage of benzene rings,¹⁰⁾ which is in striking contrast with the IR spectrum for usual polyaniline, precisely poly(p-aniline).¹¹⁾ The other vibrational bands observed in the present polymer can be similarly explained according to the analysis for poly(p-aniline): the band centered at 3400 cm^{-1} is assigned to the N-H stretching, the 3050 cm^{-1} band to the aromatic C-H stretching, the four bands at 1630, 1590, 1530, and 1480 cm^{-1} to the benzene and quinone skeletons, the 1380 and 1310 cm^{-1} bands to the C-N stretchings, and the five bands at 1210, 1160, 1100, 1075, and 990 cm^{-1} to the C-H in-plane deformation modes. All of them have a great resemblance to those observed in poly(p-aniline) except for the pattern of the C-H out-of-plane deformation modes.

Considering the results given above, the reddish-orange polymer has a poly(m-aniline) structure, and we can propose a reaction mechanism as shown in Fig. 2. A side reaction such as an elimination of ammonia could take place in the presence of acid²⁾ produced by ammonolysis, and the chain length is therefore considered not so long. Judging from the [N]/[C] and the [Cl]/[C] atomic ratios, $n=7$ or so would be anticipated.

A theoretical work¹²⁾ based on the tight-binding crystal orbital method shows that the dehydrogenated and the cationic states of poly(m-aniline), in which a hydrogen atom and an electron are extracted per each

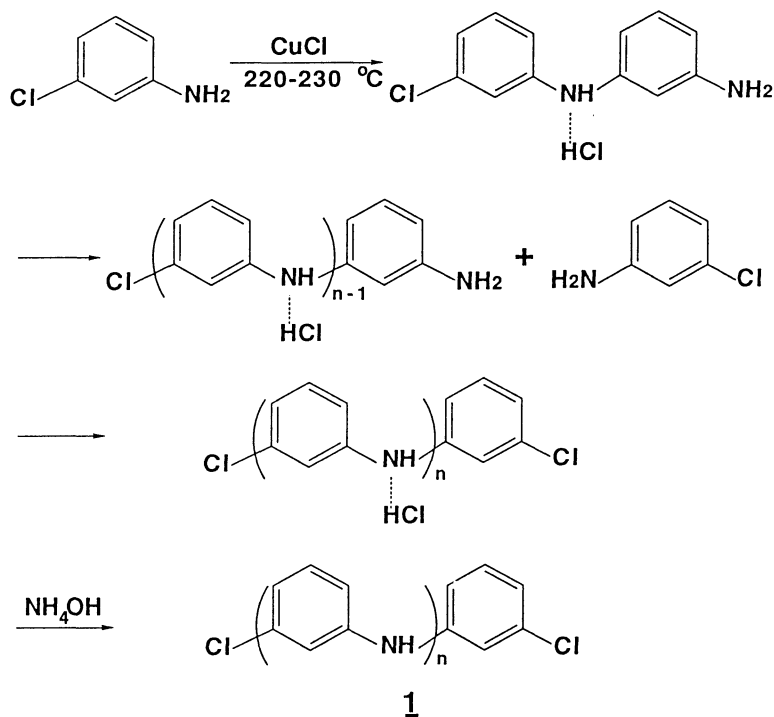


Fig. 2. Reaction mechanism toward poly(m-aniline).

unit cell, respectively, exhibit ferromagnetism when considering a single chain and have similar band structures each other. The spin distribution patterns for the two states are almost all the same. It is also clarified that the spins of these states of poly(m-aniline) are delocalized both on the nitrogen atoms and on the benzene rings in contrast to those of poly(p-aniline) being localized on the nitrogen atoms.

In conclusion, we have reported the synthetic method for the polymer with a poly(m-aniline) structure whose magnetic property will be of our interest as anticipated by the theoretical calculations.

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