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Synthesis of Isophthalaldehyde Polymer and ESR Detection of High Spin States

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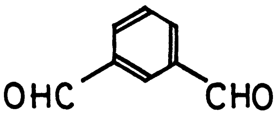
Thermal polymerization of isophthalaldehyde in the presence of a catalytic amount of p-toluenesulfonic acid gave polymer insoluble in any organic solvent. This polymer seems to possess triphenylmethyl radical as a monomer unit. It showed ESR signals of triplet and higher spin states, besides that of the organic monoradical. This type of polymer is expected to open a new field of organic ferromagnetic materials.



Isophthalaldehyde

Studies on organic ferromagnetic materials have attracted much attention for years, and several groups are currently trying to prepare them.[1)] However, only in recent year was the first organic ferromagnet reported by Ovchinnikov et al.[2)] Quite recently, Ohtani and coworkers have reported the synthesis and magnetic properties of organic resins which can be mobile by a conventional magnet at room temperature. These polymers were obtained by heating the mixture of aromatic aldehyde with aromatic hydrocarbon in the presence of a catalytic amount of p-toluenesulfonic acid.[3)] This work seems to open a new area of organic polymers possessing ferromagnetic properties. We have prepared isophthalaldehyde polymer by a similar method, and detected triplet and higher spin states by ESR both at room temperature and 4.2 K. Thus, this type of polymer seems to have a possibility of giving organic ferromagnetic polymers if the synthetic method is improved.

Isophthalaldehyde polymer was obtained by heating the mixture of isophthalaldehyde and a small amount of p-toluenesulfonic acid (1 wt%) at 170 °C for 1 h and then at 270 °C for 1 h in a quartz tube under a gentle flow of nitrogen gas. The black polymer powder was taken into an agate bowl by using a plastic spoon, acetone was added to the polymer, the polymer was crushed with a plastic spoon in acetone in order to extract the materials of low molecular weight, and the acetone solution was discarded carefully. The latter extraction process was repeated several times. The black polymer was dried under vacuum in a desiccator. It was insoluble in any organic solvent. In order to avoid the contamination of ferromagnetic impurities such as Fe_2O_3, the following precautions were taken. (1) Quartz tube was used as a reaction vessel. Pyrex glass contains more than 100 ppm of Fe_2O_3, and Fe^{2+} and/or Fe^{3+} may be dissolved in the polymer especially under such acidic reaction conditions as those described above. The quartz tube used in this study contains only less than 2 ppm of Fe_2O_3. (2) Nitrogen gas flow from an iron cylinder may contain ferromagnetic dust. Thus, nitrogen gas from the gas cyrinder was passed through a bubbler containing liquid paraffin at first, and then it was led to the quartz tube. (3) p-Toluenesulfonic acid sold as a reagent for an automatic analysis of amino acid was used, because it was found to be free from Fe_2O_3 by atomic absorption analysis. Other grades of p-toluenesulfonic acid contained about 100 ppm of Fe_2O_3. (4) All of the reagents and solvents were checked not to be contaminated with ferromagnetic impurities. The polymer obtained in this way showed no ESR signal due to Fe_2O_3 even at the highest limit of the sensitivity. The elemental analysis of polymer (C, 76.34; H, 3.83; S, 0.60%) showed that only small fractions of aldehyde groups took part in the reaction. This is in line with the FTIR spectra of the polymer; strong absorptions due to carbonyl and hydroxy groups were observed.

Figure 1 shows the ESR spectra (X band) of the polymer at 288 K[4)] and 4.2 K by using cryostat for ESR measurement (Heli-Tran model LTR-3-110 system, Air Products and Chemicals Inc). Besides the strong signal at 325 mT (g = 2.0028) due to organic monoradical, a triplet signal ($\Delta M_s = \pm 2$) was observed at 152.2 mT. The intensity of the latter signal increased with decreasing temperature, suggesting the triplet state to be a ground state. Zero-field splitting parameter D^* [5)] was estimated to be 0.093 cm^{-1}, which is close to the values reported for excited triplet states of various aromatic hydrocarbons.[6)] No $\Delta M_s = \pm 1$ transitions of triplet was detected, probably due to their anisotropic nature and/or to the much smaller intensities than the doublet signals. Small signal was observed nearly at the half-field (≈75 mT) of $\Delta M_s = \pm 2$ transition at 4.2 K. It may be attributed to a quintet signal ($\Delta M_s = \pm 4$). Triplet signals were usually observed at low

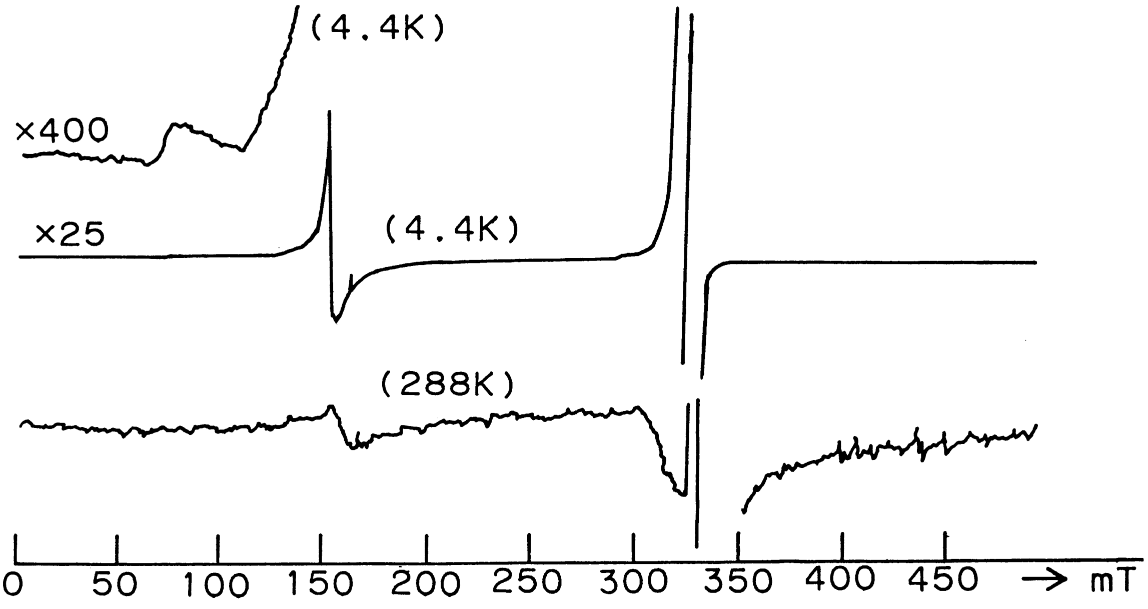


Fig. 1. ESR spectra of isophthalaldehyde polymer.

temperatures. The observation of the triplet signal in this polymer at room temperature suggests that the triplet biradical structure is stabilized by the steric effect of polymer network which protects the radical sites from further reaction. The concentration of monoradical was estimated to be 3.8 x 10^{18}/g, by comparing the ESR intensity of the doublet signal with that of 4-hydroxy-2,2,6,6-tetramethylpiperidinoxy radical.7) The measurement of the magnetization of the polymer showed no ferromagnetic behavior. The magnetic susceptibility of the polymer was -0.52 x 10^{-6} cm^3/g at room temperature. Thus, a diamagnetic contribution dominates over a paramagnetic one. Although most of the radicals exist as noninteracting monoradical species, some fractions of radical spins seem to align in parallel in the polymer, in view of the observation of the triplet and higher spin states by ESR. Thus, if the radical concentration is increased much more than in the present polymer, parallel spin fraction is also expected to increase, and it may lead to ferromagnetic organic polymers.

Figure 2 shows the possible polymerization mechanism of aromatic aldehyde in the presence of the acidic catalyst. This figure explains the polymerization of benzaldehyde for the ease of comprehension. The important points of the reaction mechanism are, (1) an electrophilic attack of the carbonium ion at the meta-position of benzaldehyde, and (2) final oxidation of the aromatic ring by the acid8) and subsequent deprotonation reaction which leads to triphenylmethyl radical. Provided that the similar reactions take place, the isophthalaldehyde polymer seems to contain the partial structures shown in Fig. 3. The partial

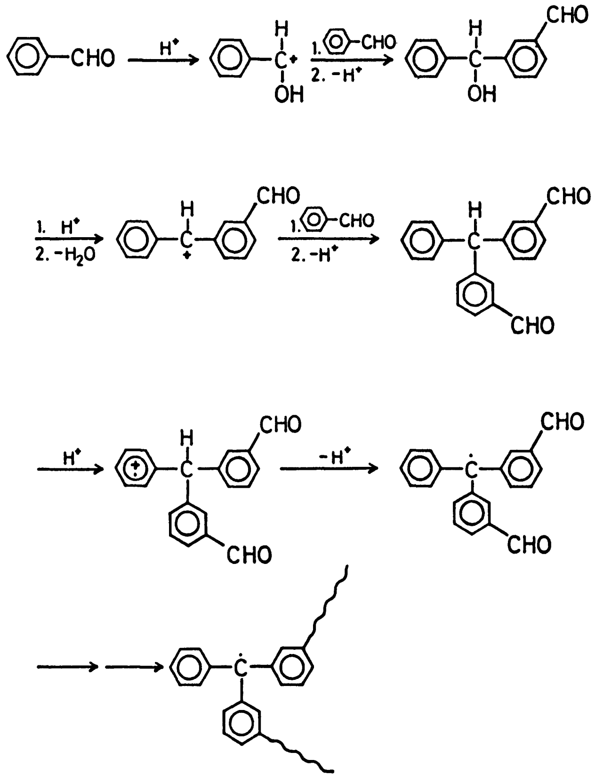


Fig. 2. Possible polymerization mechanism of benzaldehyde in the presence of an acidic catalyst.

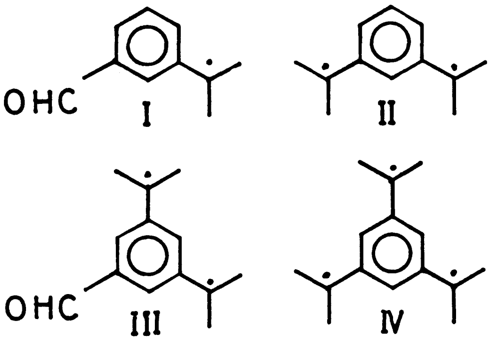


Fig. 3. Possible partial structures of isophthalaldehyde polymer.

structures (II, III) and (IV) in this figure give triplet and quartet spin states respectively. Moreover, connections of these partial structures may give much higher spin states and possibly ferromagnetic organic polymer. In general, the polymers containing odd-alternant hydrocarbons as monomer units and their linkage at the meta-position have a possibility of giving high spin states.[9)]

We are currently preparing other polymers by the same method as described above: pyrenealdehyde polymer, 4-ethylbenzaldehyde polymer, copolymer of pyrene and terephthalaldehyde, copolymer of pyrene and isophthalaldehyde, and copolymer of indole and isophthalaldehyde. All of these polymers showed triplet signals ($\Delta M_s = \pm 2$) at 4.2 K. The copolymer of pyrene and isophthalaldehyde also showed the triplet signal even at room temperature.[10)]

References

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5) $D^{*2} = D^2 + 3E^2$ (see Ref. 5).

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