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Evolution of Ferromagnetic Properties by Dehydrogenation of Triarylmethane Resin[1)]

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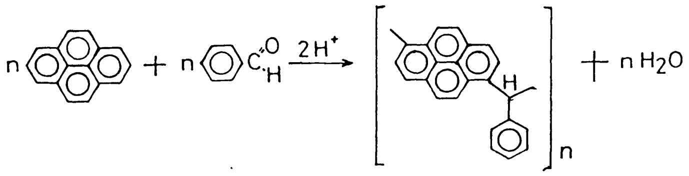
Organic ferromagnets have been successfully prepared by dehydrogenation from the triarylmethane resins and the irradiation with ultraviolet or laser light in the presence of photo-oxidizing agent is found to be effective to the dehydrogenation.

In 1988, the new organic ferromagnet was prepared by our group independently of the previous studies on the organic ferromagnetism.[2)] This compound is the resin composed of aromatic nuclei crosslinked with methine bond, and was named a "triarylmethane resin". This resin prepared under ordinary conditions is diamagnetic, but when the synthesis reaction is carried out under a magnetic field, the obtained resin exhibits ferromagnetic properties.

Through continuous efforts to improve the magnetic properties of this resin, it is found that one of the most effective method is dehydrogenation of the methine protons in order to increase the concentration of stable radical. This method is referred to as "the dehydrogenation method".[3)] The present paper aims to report the typical examples of the dehydrogenation method by irradiation with ultraviolet or laser light.

The triarylmethane resin was prepared by the method previously reported.[4)] The mixture of benzaldehyde(BA) and pyrene(Py) with molar ratio(BA/Py) of 1.25 was well-blended with 5 wt% of p-toluenesulfonic acid(PTS). The mixture was heated at 160 $^{\circ}$C for 90 min with stirring in a stream of argon. The reaction proceeds through the following equations, since the formation of methine bond is confirmed by ^{13}C NMR spectroscopy.



Heating for 90 min leads to the so-called B stage resin which has the mean molecular weight of 1500 - 1900 and is fusible and soluble in some nonpolar solvents. Further heating results in the formation of infusible and insoluble resin. The experiments in this paper mainly deal with this B stage resin. Prior to irradiation, the crude B stage resin was first purified to remove the acid catalyst, the unreacted pyrene and benzaldehyde. The resulting purified resin was transferred into a silica test tube and then dissolved into dichloromethane containing a photo-oxidizing agent such as benzoquinone(BQ) and dichlorodicyanobenzoquinone(DDQ) in molar ratio of 1 or 2 to the structural unit of the resin.

Three samples were prepared under differnt irradiation conditions. Two solutions containing the resin and BQ were irradiated with a high pressure mercury lamp at room temperature, one for 6 h and the other for 12 h. Another solution containing the resin and DDQ was irradiated with an eximer laser(wavelength of 308 nm, power of 2.5 MW, pulse repetition of 10 Hz) at room temperature for 15 min. After irradiation, these solutions were separately poured into large amounts of methanol. Only the resin component was precipitated from the solution, and the resin filtered off was washed with methanol. The two samples irradiated in the presence of BQ were yellowish-pink powders and the sample irradiated in the presence of DDQ was a gray powder.

The magnetic properties of the resulting resins was first checked by the simple method called as "moving test on the water surface" previously reported.$^{2)}$ This method is to observe the behavior of the resin powder floating on the surface of water in a Petri dish put on a permanent magnet. More quantitative measurements were carried out with a vibrating sample magnetometer(VSM model BHV-30, Riken Denshi Co., Ltd.). The magnetic properties measured by VSM are shown in Fig. 1. The unirradiated resin(Fig. 1-a) is diamagnetic. The resin irradiated with UV light in the presence of BQ for 6 h gives magnetic hysteresis with a coercive force being too small to be detected. The sample irradiated for 12 h indicates more clear ferromagnetic hysteresis(Fig. 1-b). The saturation magnetization and coercive force increased to 0.12 G and 65 Oe, respectively. The result for the sample irradiated with laser light of 308 nm in the presence of DDQ is shown in Fig. 1-c.

The coercive force increased to ca. 200 Oe, nevertheless, the saturation magnetization was still small.

Figure 2 demonstrates the result of "moving test on the water surface" for the sample irradiated with UV light for 12 h. The response of the resin powder to a permanent magnet became faster, compared with the previous sample2) prepared under magnetic field without irradiation. In this experiment, it is worth noting that all the particles were concentrated around the four points of highest magnetic flux density. These response was, however, completely disappeared as soon as the resin was exposed to hydrogen chloride gas.

This may suggests that the radicals produced by dehydrogenation are quenched by contact with hydrogen chloride.

The elemental analysis of metals of Fe, Ni, and Co were carried out with atomic absorption technique.

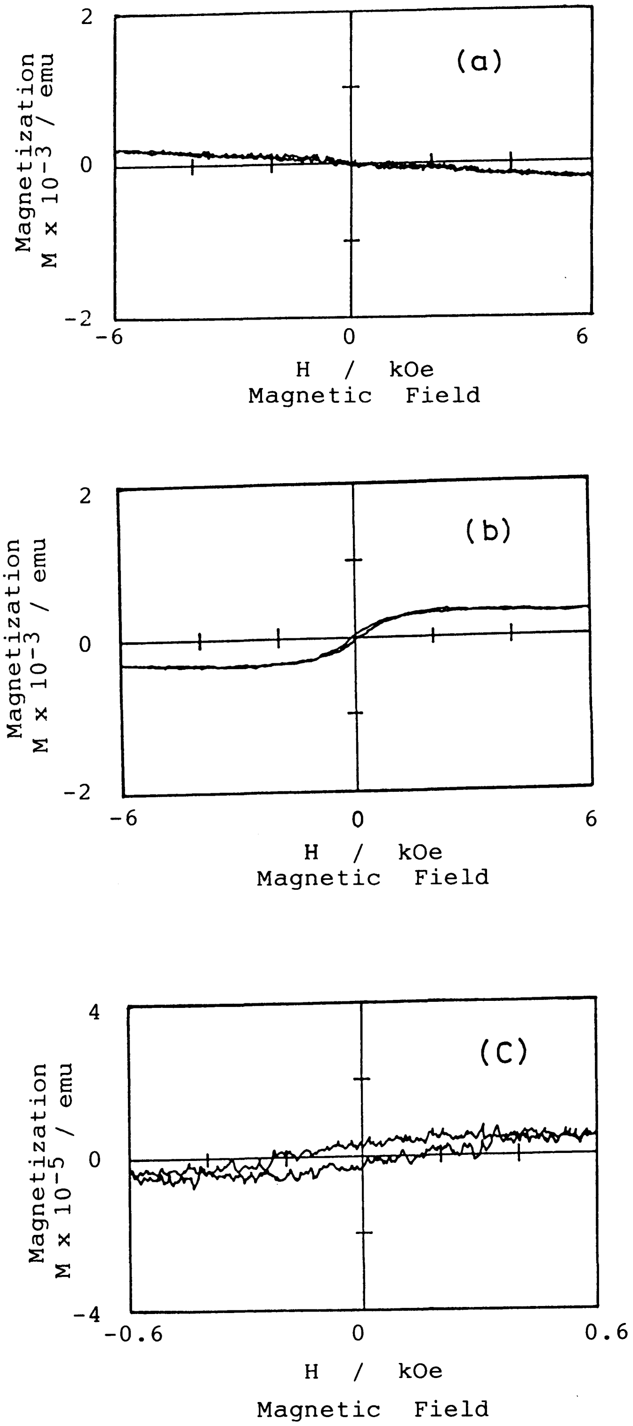


Fig.1. The magnetic properties of triarylmethane resin. (a) unirradiated, (b) 12 h (UV light), (c): 15 min (laser light)

Content of Fe was less than 20 ppm and the other two elements were not detected. The analytical values and the quenching phenomenon indicates that the ferromagnetic behavior in this study is attributed to the radicals produced by dehydrogenation. It also supports this deduction that the ferromagnetism tended to become more clear as the dehydrogenation proceeded. The effect of dehydrogenation has the different feature from the effect of the magnetic field applied at the condensation process previously reported. In the case of preparing under a magnetic field, the resin changed from ferromagnetic to diamagnetic on grinding. In the present work, these irradiated samples were obtained in a powder form from the solutions. The ferromagnetism, however, was clearly observed in spite of the powder form. Furthermore, after grinding the saturation magnetization scarcely changed through the coercive force tended to decrease.

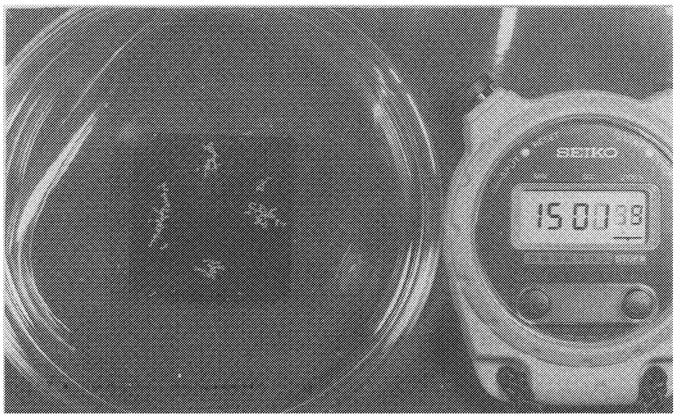


Fig. 2. Moving test on the water surface after 15 min.

These results described above may suggest that the revolution mechanism of the ferromagnetism is put under control of not only one factor but plural.

The detailed discussion such as the existence state of radical in the resin with dehydrogenation will be reported in near future elsewhere.

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