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Evolution of Ferromagnetism in the Triarylmethane Resin Synthesized under a Magnetic Field[1)]

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A thermosetting resin composed of triarylmethane structure was prepared under a magnetic field. The resulting resin exhibited ferromagnetic properties with excellent reproducibility.

The preceding work[2)] in this series has shown that a triarylmethane resin consisting of aromatic nuclei crosslinked with methine bond was successfully prepared from a mixture of pyrene and aromatic aldehyde by heating in the presence of an acid catalyst. During the course of this investigation, we had noticed that some particles of this resin slightly responded to a permanent magnet.

Since then, we have tried to improve the magnetic properties of the resin. In this paper, we will describe that the preparation under a magnetic field is effective for this purpose.

Several attempts to prepare organic ferromagnets have been actually made to date. Most of them can be roughly divided into two groups in view of the starting material used. One is the trials to get the ferromagnet from the organic compounds containing no metal element, and other is the approach from organometalic compound. The trials by Korshak et al.,[5)] Torrance et al.,[6)] and Iwamura et al.[7)] belong to the former group, and in the latter group there are the approaches by Miller et al.,[8)] Kamachi et al.[9)] and so on. The former investigations other than Iwamura's work,[7)] however, seem to involve some problems remaining to be solved, e.g. poor reproducibility of the results, small yield of the products and uncertainty in the molecular structure. Iwamura et al.[7)] have confirmed the occurence of organic ferromagnetism at an extremely low temperature. However, this ferromagnetism disapeared at room temperature.

The materials dealt with in the latter investigations are not, strictly speaking, organic ferromagnets because the transition metals in the molecule act as important triggers for ferromagnetic properties. Availability of their approaches has been discussed theoretically by Mataga,[3)] Itoh,[4)] McConnell,[10)] and so on. The new organic ferromagnets presented in this paper belongs to the former group and are thought to offer solutions to the problems involved with previous organic ferromagnets.

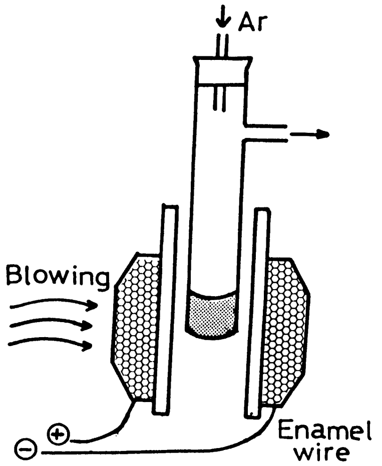

Fig. 1. Reaction apparatus
Current : 2.5 - 3.0 A, Coil : 1000 turns, Heating temp. : 130 - 140 °C

The resin was synthesized as follows. The mixture of terephthalaldehyde(TPA)/pyrene (molar ratio of 1.25 : 1) was well-blended with 5 wt% of p-toluenesulfonic acid and then put into a side-arm test tube. The test tube, which was continuously purged with argon, was placed at the center of an electromagnetic induction coil as shown in Fig. 1. The raw mixture was heated at 130 - 140 °C for 60 min under the magnetic field of ca. 440 or ca. 880 G.

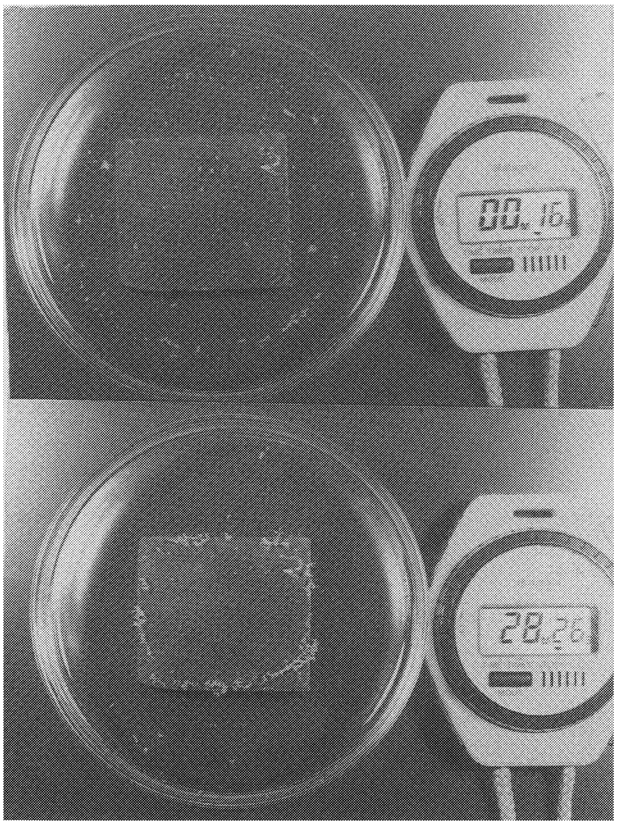

Fig. 2. Moving test of water surface.
Top: beginning
Down: after 28 min

The obtained resin was a greenish yellow solid having a mean molecular weight of 1500-1900, and was soluble and fusible. So, the resin belongs to the groups of so-called B stage resins using the technical term used in the area of thermosetting resin. The magnetic properties of the resulting resin were first checked by the following method named as "movement test on the water surface". The

the following method named as "movement test on the water surface". The granules of the resulting resin were floated on the surface of water(ca. 2 mm in in depth) in a Petri dish. Then a Petri dish was put on a permanent magnet to observe the movement of resin granules.

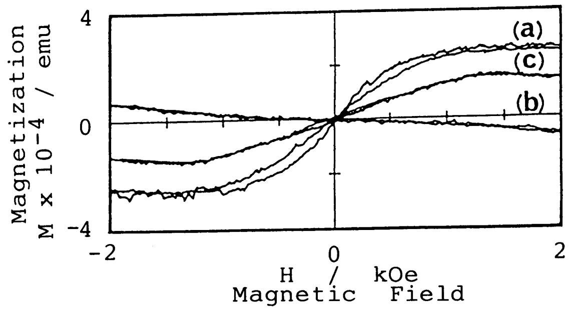

Fig. 3. The magnetic hysteresis curves of COPNA resins. (a) Bulk sample(prepared under ca. 440 G), (b) Ground sample (prepared under ca. 440 G), (c) Bulk sample(prepared under ca. 880 G)

Figure 2 demonstrates the behavior of the resin granules to the permanent magnet under the dish. The dispersed resin granules removed to form a cluster just above the edges of the magnet within 28 min. Then, the magnetic property was measured more quantitatively with a vibrating sample magnetometer(VSM model BHV-30, Riken Denshi Co., Ltd.). Small cube of the samples(2-3 mm in each side) was first used for the measurements.

The bulk samples of both resins prepared under different magnetic fields gave the ferromagnetic hysteresis curves as shown in Fig. 3(a) and (c). The saturation magnetization(Is) of the resin prepared under the lower magnetic field is ca. 0.18 G but the coercive force(Hc) is too small to be detected by this apparatus. When the bulk sample was pulverized into finer powder, however, this resin gave interestingly not a hysteresis loop but only a diamagnetic line as shown in Fig. 3(b). The bulk sample of another resin prepared under a higher magnetic field exhibited a larger value of Hc (40 Oe) as shown in Fig. 3(c), though the value of Is decreased.

The concentrations of Fe, Ni and Co in the resins were measured quantitatively by using an atomic absorption analyser. As shown in Table 1, all of the obtained values are close to the detection limits of this method. The amounts of these metals are too small to explain the ferromagnetism of these resins. In the previous report, it was indicated that the molecular structure of the resin prepared from the mixture of pyrene and TPA can be represented by

Table 1. Elemental analysis on the metals in the resins

Fe (ppm)	Ni (ppm)	Co (ppm)
15	less than 10	less than 10

the model which consists essentially of triarylmethane structure unit as shown in Fig.4.[2] From this model, it is reasonable to assume that the ferromagnetism is caused essentially by the presence of the stable triarylmethyl radicals. Therefore, the analysis of the spin state of these resins is thought to be most important for understanding the appearance of ferromagnetism. An investigation with ESR spectroscopy for this purpose is now in progress. The result will be reported before not so long. It should also be noted that the ferromagnetism of the resin disappeared after pulverization into a fine powder.

This behavior suggests that stacking and orientation of the constituent molecules in the resin consitute more substantial factor than spin concentration for the appearance of ferromagnetism.

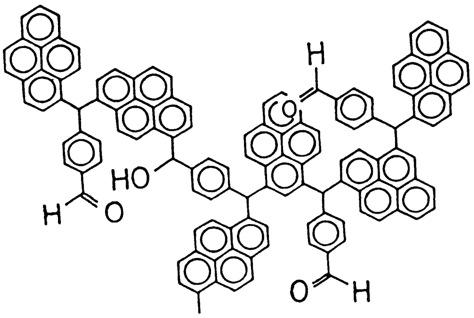

Fig. 4. The structural model of the COPNA resin.[2]

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