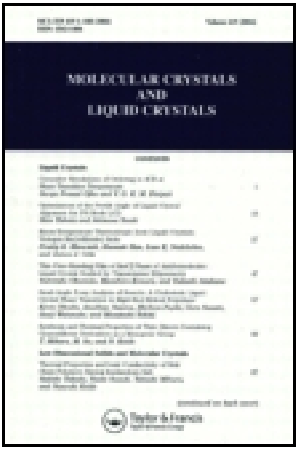

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Magnetic Properties of Triarylmethane Resins

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Abstract Triarylmethane resins dehydrogenated by irradiatation exhibited the ferromagnetic behavior.

Introduction

At 1983, the present authors have started to study novel thermosetting resins prepared by using the fused aromatic compounds and a cross-linking agent.[1] Our initial efforts were devoted to develop the thermostable resins composed of aromatic nuclei such as pyrene, anthracene and naphtharene crosslinked with p-xylylene bond.[2] These resins called as "COPNA resin"[3] were successfully prepared from the mixture of the aromatic compound and p-xylyleneglycol, and are now evaluated highly as engineering plastic and carbon precursor.[4]

This successful work prompt us to study the preparation of resin with a different type of new linkage forms other than p-xylylene bond. After some trials, the new resins crosslinked with methine bond were sucessfully prepared using aromatic aldehydes as a crosslinking agent. A structural feature of these new resins is to be composed of triarylmethyl unit, and these new resins were named as "triarylmethane resin".[5]

This triarylmethyl structure allows to imagine that the ferromagnetic property appears by dehydrogenating a proton on methine carbon in triarylmethyl unit.

This expectation was first realized by using the mixture of pyrene and aromatic aldehyde.[6,7] Later it has been found that the ferromagnetism also appeared in two other triarylmethane resins. One was prepared from the mixture of phenol and benzaldehyde, and another from seilf-condensation of p-hydroxybenzaldehyde .

Possibility of organic ferromagnet has been discussed theoritically by Mataga,[8] Itoh,[9,10] McConnell,[11] and so on.[12,13] Several attempts to synthesize such materials have been actually tried to date.[14,15,16,17]

The dehydrogenated triarylmethane resins presented in this paper are characterized by the following points, i.e. (1) synthesis under the most mild condition, (2) a relatively distinct molecular structure and (3) good reproducibility.

In this paper, we will describe the magnetic properties of three kinds of the resins prepared from the each mixture of pyrene/benzaldehyde (Py/BA), phenol/benzaldehyde (Ph/BA) and from p-hydroxybenzaldehyde (PHBA) alone.

EXPERIMENTAL AND RESULTS

1. Synthesis of Triarylmethane Resins

The triarylmethane resins were prepared from the raw mixtures with the compositions shown in Table 1 through heating with stirring in a stream of argon.

The raw mixtures melted to become clear liquid by heating and were finally converted to infusible and insoluble solid via highly viscous state. The resins obtained after the reaction periods shown in Table 1 were the viscous liquid at the reaction temperature and changed into solid after cooling to room temperature. The resin having such behaviors is usually called as "B stage resin". The Py/BA based B stage resin was soluble in dichloromethane, benzene, tetrahydrofurane etc. but insoluble in methanol and ethanol. The Ph/BA and PHBA based resins were insoluble in some nonpolar solvents but soluble in polar solvents. The present paper mainly deals with these B stage resins.

The B stage resin from Py/BA was subjected to purification to remove the acid catalyst and the unreacted components remained. The yield of the Py/BA based B stage resin was ca. 80 %. The mean molecular weight was ca. 1700 to 2000. Both Ph/BA and PHBA based B stage resins were used without purification.

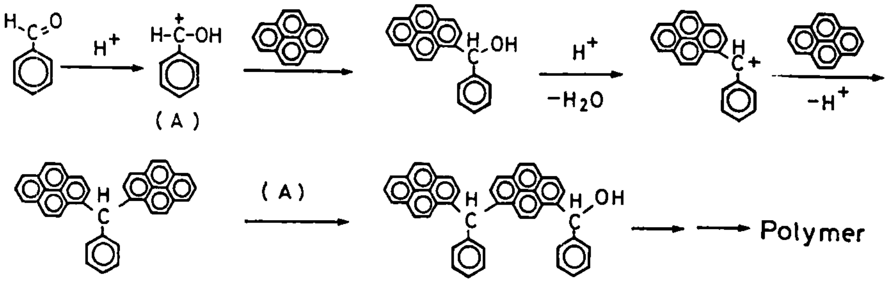
TABLE 1 Composition of raw material and preparation condition.

Raw material	Composition of raw material			Condition	
	Aromatic compound (mol)	Crosslinking agent (mol)	Acid catalyst* (%)	Temp. (K)	Period (min)
Py/BA	Py (1)	BA (1.25)	PTS (5)	433	90
Ph/BA	Ph (1)	BA (1.25)	PTS (1)	403	90
PHBA	PHBA	----	PTS (1)	403	30

* p-toluenesulfonic acid

2. Synthetic Reaction and Molecular Structure

When the molar ratio of benzaldehyde to pyrene is larger than one, the reaction proceeds through the following equation under the presence of an acid catalyst.



(1)

The absorption at 1700 cm^{-1} in IR spectra assigning to carbonyl group weakened as the reaction proceeds. The decrease of carbonyl group was also confirmed by ^{13}C NMR spectra. On the contrary, the peak around 50 ppm assigning to methine carbon appeared insteadly.

The group of peaks related to pyrene nucleus in the range from 125 ppm to 132 ppm have a relatively simple pattern. It is well known that four positions of 1, 3, 6 and 8 in pyrene are much more reactive than other positions for electrophilic attack by carbocation(A).

Therefore such simple pattern may indicate that the substitution to pyrene occurs mostly at two positions among 1, 3, 6 and 8.

On the basis of the above results, the most possible molecular structure of Py/BA based resin was deduced as shown in Figure 1, though with some ambiguity on the position of substitution.

Phenol, as well as pyrene, reacts also with

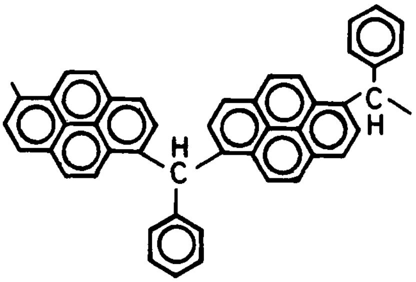


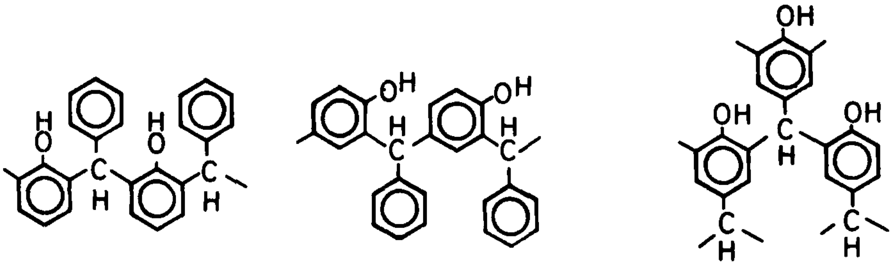
FIGURE 1. Proposed model of Py/BA based resin.

benzaldehyde through the same electrophilic reaction by carbocation. Hydroxy group exhibits strongly ortho and para orientations from which two possible molecular structures shown in Figure 2(a) and (b) are deduced. The ^{13}C NMR spectra of this resin gave two peaks at 47 ppm and 54 ppm assigning to methine carbon. This fact may indicate that the resin is mainly consisted of the ortho-para structure as shown in Figure 2 (b).

The structure of the PHBA based resin after curing is thought to be as shown in Figure 2(c) though with need of further examination.

3. Dehydrogenation from The Resins

The Py/BA based resin was dissolved into dichloromethane together with benzoquinone (BQ) as a photo-oxidizing agent. The Ph/BA or PHBA based resins were dispersed into dichloromethane or cyclohexane together with BQ, respectively. The amount of BQ was 1 or 1.5 times in molar ratio to structural unit of the resin. The solutions containing the mixture of resin and BQ were dehydrogenated by irradiating with the high pressure mercury lamp for 12 h at room temperature.



(a) ortho-ortho strucutre(Ph/BA)

(b) ortho-para structure(Ph/BA)

(c) meta-meta structure(PHBA)

FIGURE 2. Possible molecular structures of Ph/BA and PHBA based resin.

The solution of the Py/BA resin after the irradiation was poured into a large amount of methanol to separate the unreacted BQ and hydrogenated one. The suspension of the Ph/BA or PHBA was poured into a large amount of dichloromethane or cyclohexane, respectively. The precipitated resin was filtered off and then washed with methanol. The irradiated Py/BA based and Ph/BA based resins after irradiation were yellowish-pink and deep red respectively.

The elemental analysis of Fe, Ni and Co in each resin was carried out with atomic absorption technique. Content of Fe was less than 20 ppm and other elements were not detected.

4. Measurement of Magnetic Properties

The magnetic property of dehydrogenated resins was measured at room temperature with Vibrating Sample B-H Curve Tracer (VSM model BHV-30, Riken Denshi Co., Ltd.).

The unirradiated Py/BA based resin, as well as the unirradiated Ph/BA and PHBA, was confirmed to be diamagnetic as shown in Figure 4. While, all of the irradiated samples gave the magnetic hysteresis as shown in Figure 5, 6 and 7.

The magnetic hysteresis curve of the Py/BA resin irradiated with UV light for 6 h was not so clear that a coercive force was too small to be detected. The hysteresis curve, however, became more clear by extending the irradiation period up to 12 h as shown in Figure 5. The saturation magnetization and coercive force were 0.12 gauss and 65 Oe, respectively.

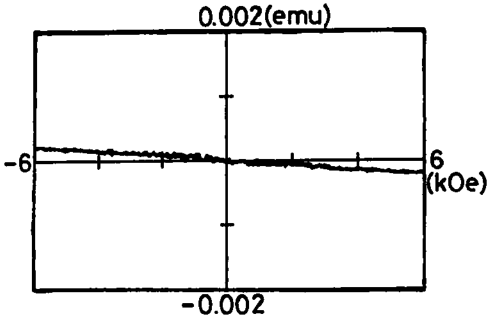


Fig. 4 Py/BAresin before irradiation.

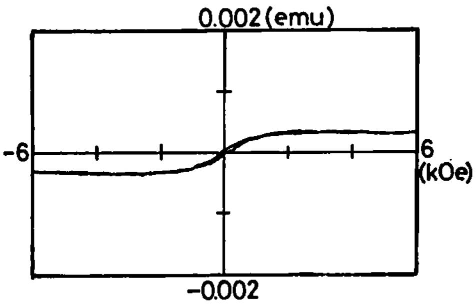


Fig. 5 Py/BAresin irradiated with UV for 12 h.

The magnetic hysteresis couves of the Ph/BA and PHBA based resin are shown in Figure 6 and 7. The Ph/BA based resin irradiated with UV light indicated the magnetic hysteresis with Hc of ca. 90 Oe and Is of ca. 0.2 gauss as shown in Figure 6. This Is value is clearly larger than that of the Py/BA based resin. The hysteresis curve of the irradiated PHBA resin (Figure 7) is characterized by lower Hc of 10 Oe and larger Is of 0.5 gauss, comparing with two other resins.

We devised the "moving test on the water surface" which is easy way to check qualitatively the magnetic properties in the place of VSM method. This testing method is to observe the behavior of resins powder floating on the surface of water in a Petri dish put on a parmanent magnet.

The unirradiated resin powder on the water surface did not conduct any special movement, but in the case of the irradiated resins, all particles were concentrated around the points of the highest magnetic flux density within 15 min.

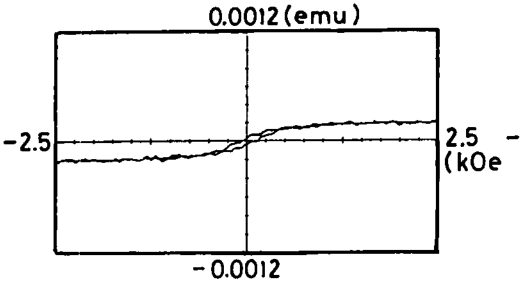


Fig. 6 Ph/BA resin irradiated with UV for 12h.

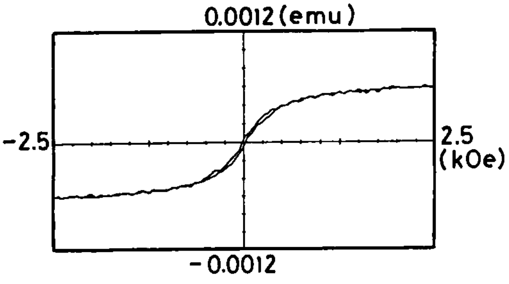


Fig. 7 PHBA resin irradiated with UV for 12 h.

DISCUSSION

On the way of investigation, we had noticed that the reaction between aromatic compounds and aldehydes containing aromatic aldehyde was known as "Baeyer's Reaction". But, as far as we know, this reaction has been limited to synthesis the such low molecular weight compounds as dyes possessing triarylmethane structure and have never adopted to prepare the polymers. The spectroscopical results obtained in this study indicate that the Baeyer's reaction is useful to prepare the high molecular weight molecule such as triarylmethane polymers. Therefore we have not the least doubt about the reaction path and the model of molecular structure proposed in this paper, although we can't determine exactly yet the positions of pyrene substituted with methine bond.

The results obtained on the ferromagnetism are summerized as follows.

1) The ferromagnetism was observed in the irradiated resins alone and increased with extending of irradiation period from 6 h to 12 h.
2) The ferromagnetism disappeared suddenly by contact with hydrogen chloride gas.
3) Content of Fe was less than 20 ppm.
4) In the "moving test on water surface", all of the resin particles were concentrated at the points of the highest magnetic flux density.
5) The magnetic properties of three irradiated resins seem to be somewhat different from each other in the values of Hc and Is as shown in Table 2.

When the resin composed of pyrene nuclei crosslinked with p-xylylene bond was treated with the same procedure and conditions as in the case of the Py/BA resin, the ferromagnetism did not appear. Therefore, the facts described in the item(1) indicate that the dehydrogenated triarylmethane structure is most essential for the appearance of ferromagnetism.

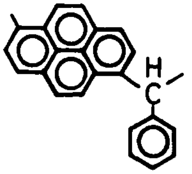
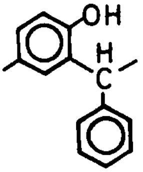
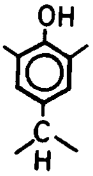
TABLE 2 Summary of the magnetic properties.

Resin	Hc(Oe)	Is(G)	Ratio of Is
Py/BA	65	0.12	1
Ph/BA	104	0.19	1.6
PHBA	10	0.59	4.3

The following fact also supports this conclusion. The Is values shown in Table 2 seems to be closely related to the formular weight of unit structure of resins shown in Table 3. That is, the Is values are inversely proportional to the formular weights.

A source of constant anxiety to confirm the organic ferromagnet is the effects of contamination with metals. On the basis of the above results described in items(2), (3) and (4) items, however, it is reasonable to conclude that the ferromagnetism is not due to the metals, but the dehydrogenated triarylmethane resins themselves.

TABLE 3 The unit structure and formula weight of resins

Resin	Unit structure	Formular weight(a)	Ratio of (1/a)
Py/BA		290	1
Ph/BA		182	1.6
PHBA		104	2.8

The final conclusion will be given by the analysis of the radicals in dehydrogenated resins.

The detail discussion on the spin existance state of the resins is now in progress by the co-working with Prof. K. Itoh's group in Osaka City University.

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