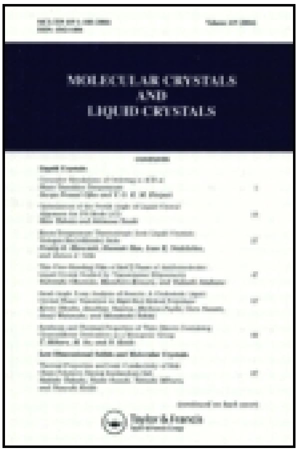

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Preparation and Magnetic Properties of Novel Triarylmethane Resin containing Ferrocene Moiety

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Abstract New triarylmethane resins were prepared by the condensation of pyrene and azulene/ferrocenecarboxaldehyde(FCA), respectively. Contrary to diamagnetic ferrocene and FCA, pyrene/FCA based resin gave weak magnetic properties. Paramagnetic behavior was observed for the azulene/FCA based resin. These magnetic properties related with characteristics of the raw aromatics.

INTRODUCTION

The network structure of meta-substituted triarylmethyl radical as a tentative model structure for the understanding of organic ferromagnet has been proposed by Mataga.[1a] Magnetic behavior of the polymer I based on the proposals of Mataga and Itoh[1b] has been reported by the present authors.[2] The structure of the polymer **I** as a network of radicals prompts us to prepare new two kinds of triarylmethane resins carrying polyradicals.

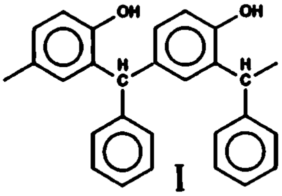
One is the polymer **IIa** replaced m-phenylene moiety of the polymer I with a metallocenylene moiety such as ferrocenylene.

Another is the polymer **IIIa** in which phenyl group in the benzylidene moiety of polymer I is replaced by a ferrocenyl group.

Ferrocene is chemically and thermally stable and is an organometallic compound possessing aromatic character.[3] As an aromatic hydrocarbon, ferrocene is as susceptible to electrophilic substitution and is easily oxidized to produce a ferrocenium ion by several acids[3] and electron acceptors[4] because of its highly electron donating property. There have been many investigations about the charge-transfer complexes of ferrocene with electron acceptors such as 2,3-dichloro-5,6-dicyanoquinone(DDQ) and 7,7,8,8-tetracyano-p-quinodimethane(TCNQ).[5]

Thus, the formation of polymers **IIb** and **IIIb** is expected by the reaction of polymers **IIa** and **IIIa** with TCNQ and so on, without causing decomposition of the ferrocene moiety.

In these polymers **IIb** and **IIIb**, radicals would form a π-conjugated system by connecting between the magnetic moments attributed to iron(III) in ferrocenium ion moieties. Thus, the alignment of the magnetic moment combined with the radicals shown in **IIb** and **IIIb** seems to be analogous to the spin arrangement characterizing ferromagnetism of metal. These results about **IIb** and **IIIb**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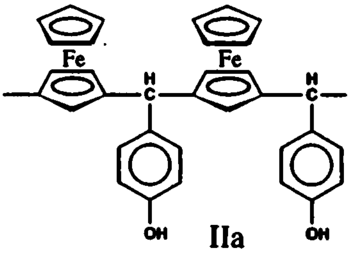
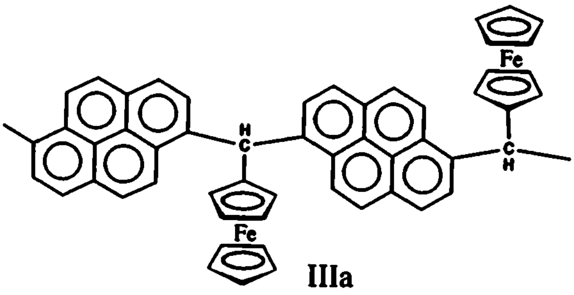
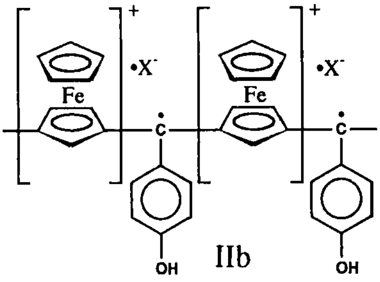


IIa

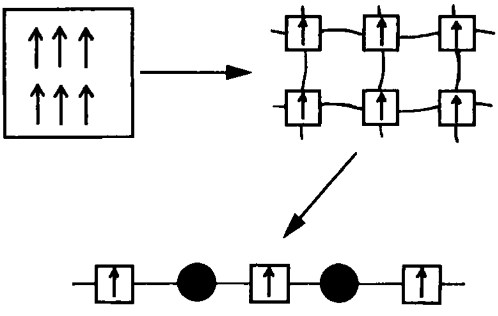


IIIa

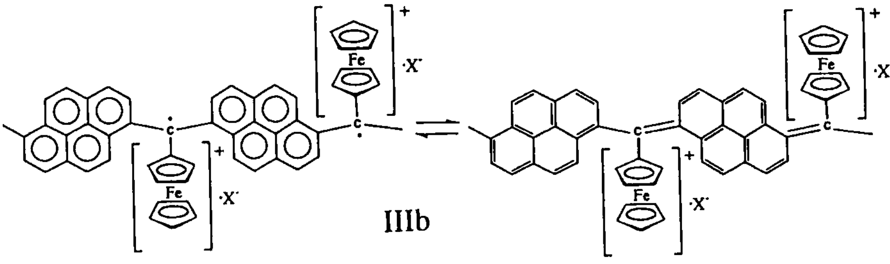


IIb

X: electron acceptor



O: π- conjugated sytem



IIIb

will be reported in detail elsewhere.

This paper describes the preparation and properties of the polymers **IIa** and **III-a**, and their magnetic properties.

EXPERIMENTAL

1. Preparation

The triarylmethane resins containing ferrocene moiety were prepared from the raw mixtures with the reaction compositions and conditions shown in Table 1 through heating with stirring under argon atmosphere.

These crude resins were purified immediately: after the resin completely dissolved in tetrahydrofuran(THF), the impurities such as the unreactant and the component of low molecular weight were filtered off through a membrane filter of 0.5 μm in pore size. The purified resins were precipitated when the filtered THF solutions were poured into hexane of 20 times volume.

2. Characterization

The structural characteristics of these purified resins were identified by IR, ^{13}C NMR, Field Desorption(FD) and Laser Desorption-Time of Flight(LD-TOF) mass spectrometry (JEOL JMS-LD1700). The molecular-weight distribution of the resins in THF solution was determined by gel permeation chromatography(GPC, polystyrene standard).

Table 1. Preparation condition of the triarylmethane resin containing ferrocene moiety.

Aromatic Compound (Aro)	FCA^{*1}/Aro (molar ratio)	Acid^{*2} (wt%)	Reaction Temp. (^{o}C)
Pyrene (Py)	1.25	2.5	160
Azulene (Az)	1.25	1	130
FCA^{*1}	——	2.5	160

*1 FCA : Ferrocenecarboxaldehyde
*2 Acid : p-Toluenesulfonic acid

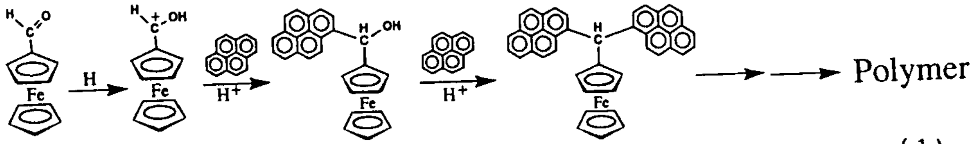
The content of iron in the resins was analyzed by using Inductively Coupled Plasma(ICP) emission spectrometer. The radical generation was detected by ESR spectroscopy, and magnetic properties were measured at room temperature with Vibrating Sample Magnetometer(VSM).

RESULT AND DISCUSSION

1. Reaction and Chemical Structure

The raw mixture of pyrene and FCA melted to give clear liquid at the reaction temperature and changed to highly viscous fluid after 2 h. On the contrary, the reaction of azulene with FCA was very fast and vigorous under the same condition as pyrene. Therefore, the reaction was carried out under the relatively mild condition shown in Table 1. The heating of FCA gave no polymer.

The condensation reaction of pyrene with FCA under acid catalyst proceeds through the eq.(1) in the same manner as the pyrene/benzaldehyde resin.[1] The polycondensation of azulene with FCA also proceeds through the similar reaction to the eq.(1).



(1)

In the purified pyrene/FCA resin, the absorption at 1700 cm^{-1} and 750 cm^{-1} in IR spectrum disappeared. These absorption bands were assigned to carbonyl group and three neighboring hydrogens on the pyrene ring, respectively. The disappearance of these hydrogens was also confirmed by ^{13}C NMR spectrum. Signals related to ferrocene nucleus from 65 ppm to 70 ppm was broadened. The purified azulene/FCA resin gave relatively sharp two signals at 67 ppm to 68 ppm to be attributed to ferrocene nucleus. These two signals suggest two patterns in the crosslinking by FCA on the aromatic rings.

The molecular-weight distribution of the purified pyrene/FCA resin by GPC was broad and symmetric around ca. 1000 of Mn.

FD and LD-TOF mass spectra of the purified pyrene/FCA and azulene/FCA resins revealed the presence of the repeating unit of polymer chain. These resins corresponding to the results of ^{13}C-NMR spectra consist of two main types which formulated such as type A and B(Figure 1). LD-TOF mass spectrum of the azulene/FCA resin **IV** is shown in Figure 1.

The content of iron in the pyrene/FCA resin was 14% according to the result of ICP emission spectrometric analysis, and this value almost agreed with the calculated value based on the structure **IIIa**.

On the basis of the above results, the most possible structures of the pyrene/FCA and azulene/FCA resins were deduced in **IIIa** and **IV** described above.

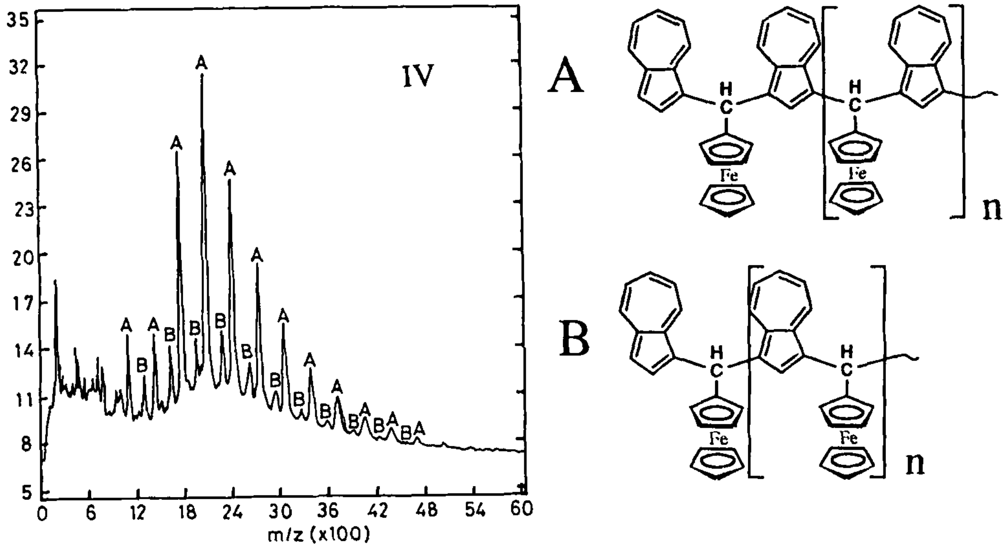


FIGURE 1. The LD-TOF mass spectrum of azulene/FCA resin.

2. Magnetic Properties

Interesting magnetic properties for the pyrene/FCA and azulene/FCA resins were observed by VSM. Contrary to diamagnetic ferrocene, the purified pyrene/FCA resin gave weak magnetic property, and magnetic curve based on magnetic saturation was found out at room temperature. However, magnetic saturation of the curve was not perfectly horizontal and was positively inclined to the right hand side, influenced by the presence of paramagnetic species. The reproducibility of the magnetic behavior was invariably good but the intensity of magnetic property somewhat depended on the delicate deviation of reaction condition.[6] This magnetic property was observed for the resin with no treatment other than purification. The component of low molecular weight which does not precipitate on purification was seemingly paramagnetic.

On the other hand, azulene/FCA resin gave weak paramagnetic property. The result of magnetic measurement of the pyrene/FCA resin is shown in Figure 2.

In ESR spectrum of the purified pyrene/FCA resin

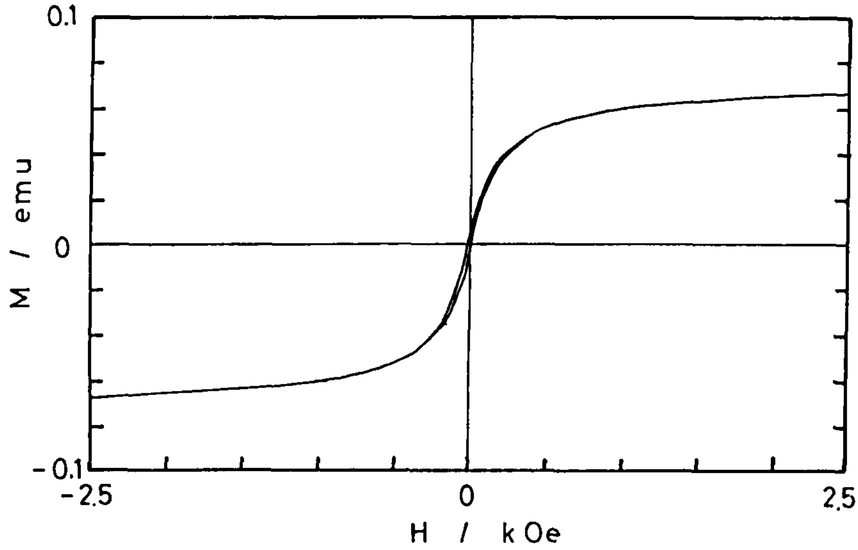


FIGURE 2. The magnetic property of pyrene/FCA resin.

shown in Figure 3, the signal for 65 mT of peak-to-peak linewidth, ΔH_{pp} at 342 mT of center field similar to that of ferrocene, possessing a sholder signal, was observed at room temperature. The signal around 342 mT therefore was attributed to FCA. We have reported on this resin[7] that the signal of π-radical(g-value=ca.2.003,ΔH_{pp}=1.4 mT at 342 mT of center field) could not be separated from the signal attributed to FCA by overlapping.

On the other hand, ESR spectra of the azulene/FCA resins shown in Figure 3 gave the signal different from that of the pyrene/FCA resin. This signal in Figure 3 consists of two kinds of signals. One is attributed to π-radical with g-value of 2.003 and ΔH_{pp} of 2 mT and another which is broad and attributed to FCA of the same as the pyrene/FCA resin. The former signal exhibits higher intensity than the later one.

The magnetic behaviors of these resins must most carefully be discussed because there are the possibilities of the isolation of iron by decomposition from the ferrocene moiety on the way to preparation and the formation of iron oxides by oxidation.

However, the formation of iron oxides was not detected

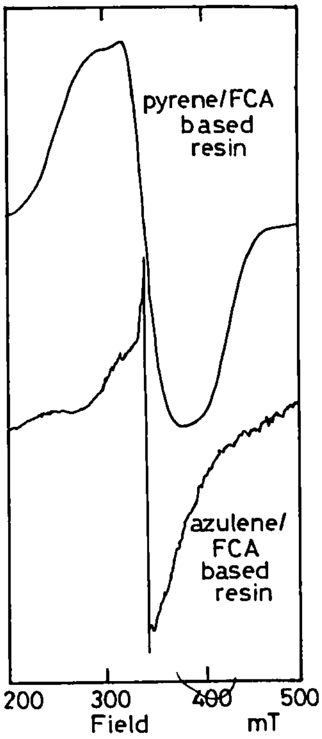


FIGURE 3. ESR spectra of the purified pyrene/FCA and azulene/FCA resins.

from ESCA spectra. The further detail investigation is under consideration by Mossbauer spectrometry and so on.

The three origins are proposed for the origin of magnetic property of the pyrene/FCA resin, that is, (i)the magnetic property essentially based on the resin, (ii)the effect of iron condensated by the decomposition on or after heating for preparation, (iii)the resulting interaction by the presence of iron atom or cluster, which dose not contribute to the macroscopic magnetism, closest to the matrix molecule of the resin.

The hypotheses (ii) and (iii) give an negative impression from our experimental results, that is, the magnetic properties of the aromatics/FCA resins seem to be essentially influenced by the kind of aromatics such as pyrene and azulene. The detectable radical could also relate to be magnetic interpretation. The characteristics of these resins is summarized in Table 2.

Table 2. The comparison between pyrene/FCA and azulene/FCA resins.

Resin	ESR*1	NMR*2	VSM*3
Pyrene/FCA	ferrocene moiety	broadening	positive*4
Azulene/FCA	π-radical	sharp	paramagnetic

*1 dominant signal of π-radical and ferrocene moiety, *2 about ferrocene nucleus; pyrene/FCA:65-70 ppm, azulene/FCA:67 and 68 ppm(two lines), *3 magnetic property by VSM measurement, *4 magnetic curve overlapped with paramagnetic line and magnetic saturation.

The properties shown in Table 2 were further regenerated by the CT complexes with TCNQ.

At the present stage, we can not reach the definite conclusion but all the factors considered in the hypothesis(i) seems to be more reasonable to account for the present magnetic property observed for the pyrene/FCA resin.

Further research is going on to understand origin of the magnetic property and interaction between the π-radical and the ferrocenium moiety of the structure **IIIb.**

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