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Syntheses and Properties of Crosslinked Ferrocene Polymers

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The polycondensation reaction of acetylferrocene and furfural was investigated in the presence of concentrated H_2SO_4 as a catalyst without solvent. Stoichiometric reaction took place with 2 mol of acetylferrocene and 5 mol of furfural. Polycondensation afforded satisfactory results when 1 mol of acetylferrocene was treated with 2—7 mol of furfural. The structural evidence for these products was derived from chemical and infrared analyses. Density, micro Vickers hardness, magnetic susceptibility, and thermal behavior of these products were measured in comparison with those of other resins.

In recent years efforts have been made to obtain polymers with properties differing from those of conventional organic polymers, the ultimate objective being polymers with better electrical and magnetic properties with abrasion resistance, thermal stability and opaqueness to certain types of radiation. Organometallic compounds have been suggested as starting materials for the synthesis of these polymers; they have been polymerized by means of various procedures.[1] The organometallic polymer is expected to have properties characteristic of both organic compounds and metals, since it contains a metal as the organometallic complex. Ferrocene ($C_{10}H_{10}Fe$) is stable against acid and base, and easily undergoes aromatic substitution reactions.[2] Synthetic studies of ferrocene polymers have been carried out in the past two decades.[3] Emphasis was placed on soluble products possessing linear chain structures. However, very few attempts have been made to synthesize crosslinked ferrocene polymers (resins).[4–7]

From ferrocene, iron atoms are released by heat treatment above 400°C and then coagulate to metallic iron.[8] In the case of ferrocene resins, iron atoms would be also released from ferrocene skeletons by heat treatment. It appears that the released iron atoms do not coagulate and are isolated in the form of atoms or ultra-fine particles above room temperature due to networks of the resins. The preparation of metal atoms was reported by Barrett *et al.*[9,10] An inert gas and vapourized metal were condensed on a Be disk at liquid helium temperature, iron atoms being frozen into an inert gas matrix. The isolated iron atoms could only be present near liquid helium temperature. Preparation of ultra-fine particles of metals and their compounds has been sought by Mulay *et al.*[11,12]

Our studies deal with the synthesis of resins containing ferrocene. Reports were given on the preparation of free iron atoms or ultra-fine particles of an iron metal by pyrolysis of the ferrocene resin.[13,14] The resin used was synthesized by polymerization of furfural (II) and a ferrocene derivative. Furfural (II) was polycondensed with acetone.[15] Acetylferrocene (I) is considered to serve as a ketone derivative of ferrocene for the polycondensation. Acetylferrocene (I) was polycondensed with various proportions of furfural (II) in the presence of concentrated sulfuric acid. The structure of the synthetic resin was elucidated by chemical and infrared spectroscopic analyses. Density, micro Vickers hardness and magnetic susceptibility were measured and thermal behavior was observed.

Experimental

Materials. Polycondensation was carried out with acetylferrocene, furfural and concentrated sulfuric acid. Ferrocene was synthesized according to the method given by Hata *et al.*[16] Acetylferrocene was prepared by reacting ferrocene with acetic anhydride in anhydrous dichloromethane.[17] It was then purified by recrystallization from *n*-hexane and sublimation *in vacuo*; mp 85—86 °C (Ref. 17, 85—86 °C). Furfural was redistilled prior to use; bp 67—68 °C/20 mmHg. Concentrated sulfuric acid (reagent grade) was used.

Preparation of Resins. Concentrated sulfuric acid which was used for the preparation of furfural-acetone resins was used as the catalyst of polycondensation.[15] Polycondensation temperature was fixed at 45 °C, since low temperature is preferable for preventing the decomposition of ferrocene skeletons by acid. Acetylferrocene was dissolved in furfural in a test tube. Concentrated sulfuric acid was added to this solution at certain wt% of acetylferrocene and furfural. The reaction mixtures were stirred and then heated at 45 °C for a certain period of time. After polycondensation, synthetic resins were dried *in vacuo* at room temperature and then heated up to 100 °C for 24 hr in order to remove volatile materials.

Elemental Analysis and Measurement of Properties. Iron determination was carried out with a Hitachi-207 atomic absorption spectrophotometer. IR spectra were measured with a Nihonbunko Jasco IR-S grating IR spectrometer using potassium bromide disks. Apparent densities were calculated from the weight and size of resins. Micro Vickers hardness was measured with an Akashi Model MVK Type D instrument with a load of 200 g. Magnetic susceptibility was recorded on a Shimadzu MB-10A magnetic balance. A helical spring microbalance was used for thermogravimetric analysis (TGA), the heating rate being 2 °C/min. Powdered samples with initial weight of 100 mg were used, the determination being performed *in vacuo* (1×10^{-3} mmHg).

Results and Discussion

Polycondensation Reaction and Resin Structure. The results are summarized in Tables 1—3. Polycondensation seems to be affected by experimental conditions. Effects of (a) amount of a catalyst and (b) the length of reaction time were investigated using a mixture of 1 mol of acetylferrocene and 5 mol of furfural. Forty-hour polycondensation data are given in Table 1 for (a),

Table 1. Effect of amounts of H_2SO_4 on polycondensation[a)]

Amounts of Concd H_2SO_4 (wt%)	Yield (wt%)	Density (g/cm^3)	Elemental analysis (wt%)			Furfural (mol) / Acetylferrocene (mol)
			Fe	C	H	
2	58.5	1.42	11.7	65.52	4.03	2.81
3	81.6	1.41	9.55	65.02	4.13	3.93
4	83.9	1.43	9.08	64.01	3.77	4.16
5	82.7	1.40	8.71	64.24	3.75	4.46
6	85.2	1.40	8.64	63.96	3.81	4.48

a) Acetylferrocene; 1 mol, furfural; 5 mol, time; 40 hr, temperature; 45 °C.

Table 2. Effect of reaction time on polycondensation[a)]

Reaction time (hr)	Yield (wt%)	Density (g/cm^3)	Elemental analysis (wt%)			Furfural (mol) / Acetylferrocene (mol)
			Fe	C	H	
6	71.7	1.45	10.8	62.62	4.10	2.99
11	72.4	1.44	10.2	63.19	4.15	3.36
20	76.9	1.43	9.97	63.27	3.97	3.50
40	83.9	1.43	9.08	64.01	3.77	4.16
72	82.2	1.40	9.05	64.84	3.83	4.26
96	85.0	1.43	8.80	63.82	3.82	4.34
137	83.4	1.40	8.28	64.31	3.95	4.71

a) Acetylferrocene; 1 mol, furfural; 5 mol, concd H_2SO_4; 4 wt%, temperature; 45 °C.

Table 3. Effect of different ratios of acetylferrocene and furfural on polycondensation[a)]

Samples	Acetyl-ferrocene (mol)	Furfural (mol)	Yield (wt%)	Density (g/cm^3)	Elemental analysis (wt%)			Furfural (mol) / Acetylferrocene (mol)
					Fe	C	H	
2-Resin	1	2	93.1	1.43	12.2	64.98	4.29	2.55
3-Resin	1	3	89.3	1.43	11.6	64.50	4.29	2.77
5-Resin	1	5	83.9	1.43	9.08	64.01	3.77	4.16
7-Resin	1	7	74.5	1.43	7.85	63.12	4.02	5.08
10-Resin	1	10	61.6	1.02	7.51	62.50	3.95	5.34
12-Resin	1	12	55.4	0.878	6.87	60.72	3.32	5.82
15-Resin	1	15	52.2	0.758	6.28	60.18	3.35	6.51

a) Concd H_2SO_4; 4 wt%, time; 40 hr, temperature; 45 °C.

The yields of resins were constant when more than 3% of the catalyst was used, their density being independent of the amount of the catalyst. Molar ratios of furfural to acetylferrocene (F/A) in resins could be calculated from elemental analyses of carbon, hydrogen and iron contents. The molar ratios of F/A increased with the amount of catalyst. The effects of the reaction time were investigated with 4% catalyst (Table 2). Yields of resins were approximately constant when polycondensation was continued for 40 hr or longer. The density of resins was independent of the reaction time. The molar ratios of F/A in resins increased with an increase in the reaction time. The behavior of polycondensation was considered to be influenced by the molar ratios of F/A in starting materials. The influence was investigated under experimental conditions where the catalyst was 4% and reaction time was 40 hr. In Table 3, the notation of resins shows the number of moles of furfural per mole of acetylferrocene in the starting materials. No resins were formed when the concentration of the acetylferrocene component was reduced to below 15 of F/A. Yield of resins decreased in proportion to the decrease in acetylferrocene. The density of resins was invariable for 2- to 7-Resins, but reduced rapidly for 10- to 15-Resins. The molar ratio of F/A in the resin of the 2-Resin was greater than that in the starting material. For other resins, the relation between the molar ratios of the starting material and the resin was reversed. The stoichiometry of polycondensation was thus considered to be as follows. In the case of the 2-Resin, excess acetylferrocene not capable of reacting with furfural was removed. On the other hand, furfural in the starting material of the 3-Resin was more than enough to react with acetylferrocene. The excess furfural was removed, but what remained might have become partially incorporated into resins according to the progress of polycondensation. Thus, the stoichiometry of polycondensation was decided to be a reaction of 2 mol of acetylferrocene and 5 mol of furfural (2-Resin). The mechanism of the stoichiometric reaction was estimated on the chemical reactivities of acetylferrocene and furfural. Furfural could not be subject to polycondensation without the presence of other compounds.[15] Furfuryl alcohol has been established to be a versatile polymer precursor.[18] Thus, if furfural is converted into the form of furfuryl alcohol in the course of polycondensation process, the polycondensation reaction would successfully proceed to give resin. The initial step in polycondensation involves 1 mol of acetylferrocene and 2 mol of furfural to undergo aldol condensation and Friedel-Crafts reactions to yield oligomer (III). The oligomer was in the form of furfuryl alcohol containing four reaction points (1, 2, 3, 4); with further reactions with each other and 1 mol of furfural, it produces polymers (IV), as shown in Fig. 1. The polymer was reactive with

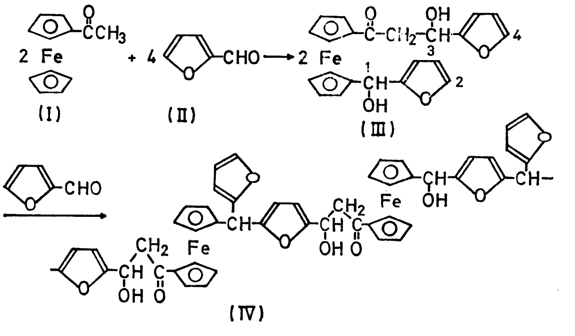

Fig. 1.

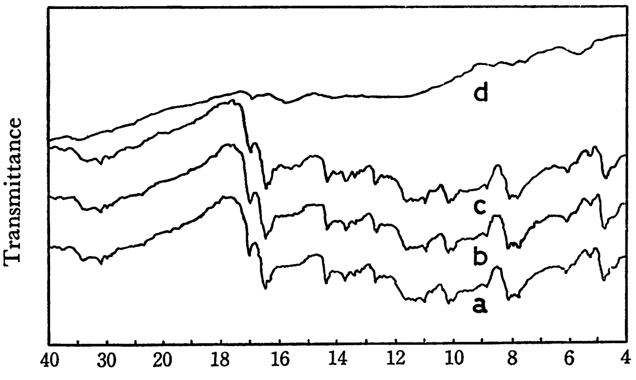

Fig. 2. IR spectra of 2-Resin, the heat-treated at various temperatures; (a) 2-Resin, (b) 200 °C, (c) 300 °C, (d) 400 °C.

Table 4. IR bands of 2-resin and their assignments

Absorption band (cm^{-1})	Assignment	Reference
3080	Ferrocene C–H stretching	19
2930 2850	Aliphatic C–H stretching	20
1655	νC=O of ferrocenyl ketone	21
1445	δCH of methylene or methyl	20
1375	δCH of methyl	20
1160	Furan	22
1103	In-plane bending of ferrocene C–H	23
1017	C–O–C Vibration	22
818	Out-of-plane bending of ferrocene C–H	23
780	Out-of-plane bending of furan C–H	22
478	Ring metal stretching of ferrocene	19

furfural or became crosslinked with each other, after removal of hydroxy groups.

The IR spectrum of the 2-Resin, shown in Fig. 2, exhibited absorption bands at 3080, 2930, 2850, 1700, 1655, 1445, 1375, 1273, 1160, 1103, 1017, 818, 780, and 478 cm^{-1}. Assignments of all bands except for those at 1700 and 1273 cm^{-1} were referred to those of ferrocene polymers available in literature (Table 4). The 1700 cm^{-1} band corresponded to one of the absorption bands in the IR spectrum of furfural.[24] It is therefore considered to be due to a ketone conjugated with a furan ring (furyl ketone). The 1273 cm^{-1} band would be assigned to the acetylated cyclopentadienyl ring since this absorption band was observed in the IR spectrum of acetylferrocene[25] but not in that of ferrocene.[19] Rosenblum and Woodward reported that two bands near 1000 and 1100 cm^{-1} indicated the presence of unsubstituted cyclopentadienyl rings.[26] In the case of the 2-Resin, unsubstituted cyclopentadienyl rings were not contained in its structure because of the lack of the 1000 cm^{-1} band of those bands in the resin. Results of IR spectrum studies are in accord with the structure (IV) of the 2-Resin predicted here. However, its actual structure might partially deviate from structure (IV) owing to the effect of the furyl ketones and the acetylated cyclopentadienyl rings remaining in the structure. For 3-Resin to 15-Resin, the excess furfural which exceeded the stoichiometric composition in the starting material would be expected to lead to a Diels-Alder addition reaction in furyl side-groups of the polymer structure (IV)[22] and a substitution reaction with the hydroxyl groups. Thus, structures of these resins were considered to decrease in crosslinkages. Holliday suggested that the connection number is useful in describing crosslinkages and it can be derived from the density of the polymer.[27] From the relationship between density and connection number, 1.43 density was found to correspond to 2.3 (connection number). Since the maximum connection number is 2.5 for CH polymer, 2.3 shows a considerably high value of crosslinkages. Low density of 10- to 15-Resins as compared to other resins corresponded to the decrease in crosslinkages. The densities of 2- to 7-Resins were higher than those of phenolic novolac resins.[28]

Micro Vickers Hardness. Micro Vickers hardness measurements were carried out for the mechanical properties of resins. The values of hardness were approximately the same for 2-Resin to 7-Resin. The hardness of 10-Resin to 15-Resin decreased with the decrease in density. A linear relationship was obtained between hardness and density (Fig. 3). Close packed resins (2- to 7-Resins) are assumed to have high hardness characteristics. Hardness of these resins was similar to that of phenolic novolac and melamine resins.[29]

Magnetic Properties. Magnetic susceptibilities of 2-Resin, 5-Resin and 15-Resin are given in Table 5. The observed values of magnetic susceptibility were all positive and of the order of 10^{-6} irrespective of iron content. The paramagnetism should be discussed in connection with the structure of resins since the magnetic susceptibility of ferrocene has been reported

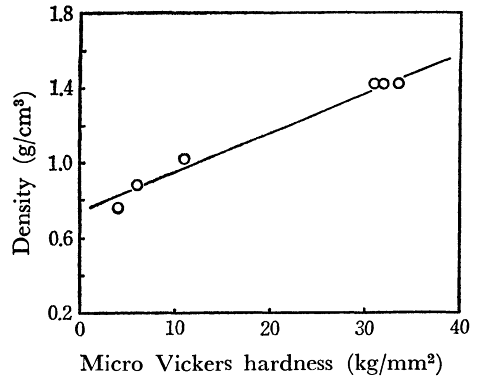

Fig. 3. Relation between density and micro Vickers hardness of resins.

TABLE 5. MAGNETIC SUSCEPTIBILITY OF THE RESINS AT 20 °C

Samples	χ_g cgs units
2-Resin	2.91×10^{-6}
5-Resin	2.74×10^{-6}
15-Resin	2.88×10^{-6}

to be $\chi_a=-99.0\times10^{-6}$ cgs units.[30] Kalimov and Shchegolev demonstrated that the products can be converted from paramagnetic into diamagnetic with the use of paramagnetic ferrocene polymers[31] described by Nesmeyanov *et al.*[32] Since the present specimens could not be purified because of insolubility, the paramagnetism does not seem to arise from the structure of the resins; instead, it might be related to magnetic contaminants. However, it is evident that no ferromagnetic iron compounds are contained in the resins.

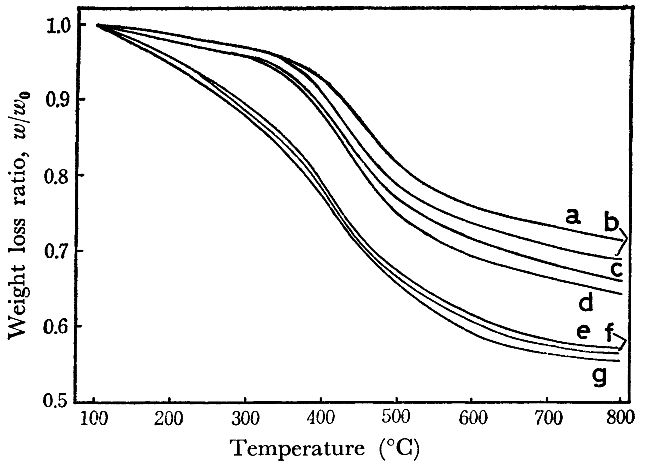

Fig. 4. Thermograms for resins; (a) 2-Resin, (b) 3-Resin, (c) 5-Resin, (d) 7-Resin, (e) 10-Resin, (f) 12-Resin, (g) 15-Resin.

TABLE 6. RESIDUE AND REDUCED RESIDUE OF THE RESINS HEAT-TREATED AT 800 °C

Samples	Residue (wt%)	Fe in residue (wt%)	Reduced residue[a] (wt%)
2-Resin	71.4	19.1	52.3
3-Resin	69.0	16.9	52.1
5-Resin	66.0	13.8	52.2
7-Resin	64.3	13.0	51.3
10-Resin	57.3	12.1	45.2
12-Resin	56.4	11.5	44.9
15-Resin	55.4	9.40	46.0

a) Reduced residue=Residue-Amounts of Fe.

Thermal Behavior. Structural changes of resins were investigated by means of IR spectroscopy. IR spectra of heat-treated 2-Resin (200 and 300 °C) do not differ from those of 2-Resin (Fig. 2). From the IR spectrum of 2-Resin heat-treated at 400 °C, we see that the structure was decomposed on heating at 400 °C. This structural change corresponded to carbonization of resins, since carbonization of organic compounds starts near 400 °C.[33] Thermal behavior was investigated by means of a thermobalance. The thermograms of resins, heated up to 800 °C, are shown in Fig. 4. The weight losses were remarkable above 300 °C for 2- to 7-Resins and above 100 °C for 10- to 15-Resins. Residues at the end of thermogravimetric analysis are given in Table 6. The reduced residues are derived by subtraction of the amounts of iron from the residues. The residues of 2- to 7-Resins differ from each other, but no difference is seen in their reduced residues. In the case of 10- to 15-Resins, no such difference was observed in the reduced residue. Thermograms and reduced residues of 2- to 7-Resins are similar to those of phenolic novolac resins.[34] We see that the thermal behavior of the resins was not affected by the presence of iron. It is known that the residues of organic polymers heat-treated above 600 °C increase with the formation of crosslinkages.[35] A decrease in reduced residues of 10- to 15-Resins as compared with 2- to 7-Resins is considered to correspond to the decrease in crosslinkages. Thermograms of 10- to 15-Resins show that the decrease of their reduced residues mainly results from the weight loss at low temperatures (100—300 °C).

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