BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 44, 207—210 (1971)

Ferrocene Polymers Obtained by the Polycondensation of Ferrocene with Dicarboxylic Acid Chlorides

Teruzo ASAHARA, Manabu SENŌ, Keiryo MITSUHASHI[1], and Yohsuke ICHIKAWA
The Institute of Industrial Science, The University of Tokyo, Roppongi, Minato-ku, Tokyo

(Received July 24, 1970)

The polycondensation reactions of ferrocene with terephthaloyl and adipoyl chloride were investigated in the presence of $AlCl_3$, $ZnCl_2$, or $FeCl_3$ as the catalyst and in dichloromethane, *n*-hexane, carbon tetrachloride, or dioxane as the solvent. With terephthaloyl chloride, the highest polymer yield was obtained when $AlCl_3$ in *n*-hexane was used, and the product was mainly of a polyketone structure. The polycondensation with adipoyl chloride afforded the most satisfactory result when ferrocene was treated in liquid adipoyl chloride with neither catalyst nor solvent, and a product with the expected structure was obtained. The average molecular weights of the products are in the range of 3000—7000. Polymers obtained by polycondensation with terephthaloyl and succinyl chloride are paramagnetic and show the temperature dependence characteristic of semi-conductivity.

Ferrocene possesses a high reactivity toward electrophilic substitution, especially toward the Friedel-Crafts acylation, and the acylation of monoacylated ferrocene affords 1,1′-disubstituted ferrocene as the main product. Therefore, it may be expected that a polyketone containing ferrocene nucleus will be produced through the polycondensation of ferrocene with a dicarboxylic acid chloride.

Recently, Neuse and Koda reported their findings on the polycondensation of ferrocene with terephthaloyl chloride.[2] They obtained the expected product, together with various by-products formed through the cleavage of the ferrocene nucleus and oxidation-reduction processes.

In the present investigation, the formation of polyketone was examined, under several sets of reaction conditions with various catalysts and solvents, by using adipoyl chloride or terephthaloyl chloride as the bifunctional acylating agent. The electric and magnetic properties of the products obtained were also measured. The results will be presented in this paper.

Experimental

Materials. Ferrocene was prepared according to the method reported by Hata *et al.*[3] and was purified by sublimation *in vacuo*; mp 172—173°C.

Terephthaloyl chloride and adipoyl chloride were prepared by the reaction of the corresponding acids with thionyl chloride in the presence of a small amount of pyridine; the former was purified by recrystallization from dry *n*-hexane, mp 81—82°C, and the latter by distillation at a reduced pressure, bp 120—123°C/12 mmHg.

Aluminum chloride, zinc chloride, and ferric chloride were dried and stored in a desiccator.

The solvents were purified by the usual methods.

Polycondensation Reactions. Ferrocene, dicarboxylic acid chloride, and a Lewis acid catalyst were mixed in a molar ratio of 1 : 1 : 2 (or >2) in a solvent and were heated at the prescribed temperature with stirring under a stream of

---

[1] Present Address: Faculty of Engineering, Seikei University, Kichijoji, Musashino-shi, Tokyo.

[2] E. W. Neuse and K. Koda, *J. Macromol. Chem.*, **1**, 595 (1966).

[3] K. Hata, I. Motoyama, and H. Watanabe, This Bulletin, **38**, 853 (1965).

Table 1. Solution polycondensation of ferrocene with terephthaloyl chloride
[Ferrocene 0.02 mol, Terephthaloyl Chloride 0.02 mol]

Exp. No.	Solvent	Catalyst	(mol)	Temp. (°C)	Time (hr)	Yield of polymer[a] (%) Sol. in $CHCl_3$	Insol. in $CHCl_3$
1	dichloromethane	$AlCl_3$	0.04	35	3	3	52
5	carbon disulfide	$AlCl_3$	0.04	47	3	1.5	2
6	carbon disulfide	$AlCl_3$	0.04	47	6	2	3
7	carbon disulfide	$ZnCl_2$	0.04	47	6	<1	<1
8	carbon disulfide	$ZnCl_2$	0.04	47	20	1.5	1
9	*n*-hexane	$AlCl_3$	0.054	69	20	27	19
10	*n*-hexane	$AlCl_3$	0.054	69	30	33	25
11	*n*-hexane	$ZnCl_2$	0.073	69	10	<1	<1
12	*n*-hexane	$FeCl_3$	0.04	69	30	2	3.5
15	dimethylacetamide	$AlCl_3$	>0.04	5	100	0	0
31	cyclohexane	$AlCl_3$	0.06	83	7.5	15	5

a) The yield of product was calculated according to Eq. (1).

nitrogen gas. After a definite period, the reaction mixture was poured onto ice-water; the solid product was then collected by filtration and washed successively with water, dilute hydrochloric acid, a dilute sodium hydroxide solution, water, and hot methanol. After being dried, this product was fractionated into a soluble part and an insoluble part in chloroform. The soluble part was subsequently represipitated from methanol or *n*-hexane.

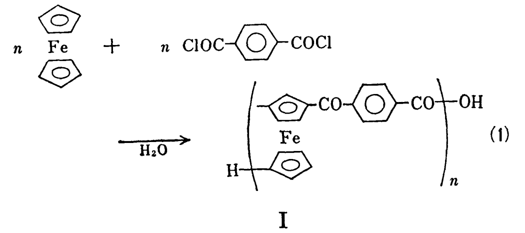
Analytical Procedures. The structure was analysed by means of a study of its IR spectrum (KBr disc). The molecular weight was measured with a vapor-pressure osmometer.

The electric conductivity and the magnetic susceptibility were measured using powdered samples packed under 1.5 kg/cm^{-1}.

Results and Discussion

Solution Polycondensation with Terephthaloyl Chloride. The results of polycondensation using various solvents and catalysts are summarized in Table 1. Each product is a reddish or dark brown powder. The products soluble in chloroform, obtained from polycondensation using $AlCl_3$ and *n*-hexane, were analysed to be as is shown in Table 2. The IR spectra of the soluble and insoluble products are shown in Fig. 1.

From these results, the main reaction to afford a soluble product may be assumed to be as follows:



(1)

I

However, the results of the elemental analysis show a higher H content than the value calculated for I, and the IR spectrum shows a strong absorption at 2900 cm^{-1} which is assignable to a methylene group. These results suggest the occurrence of side reactions involving the cleavage of ferrocene nucleus and the reduction of carbonyl group to afford the compounds with structures II and III. This is in accord with the results obtained by Neuse and Koda.[1] They used sulfolane as the solvent.

Table 2. Analyses of polycondensation products of ferrocene with terephthaloyl chloride, soluble in $CHCl_3$

Exp. No.	Average mol wt	Degree of polymerisation[a]	Calcd for I (%) C	Calcd for I (%) H	Found (%) C	Found (%) H
9	3300	10	68.00	3.87	70.19	4.83
10	3600	11	86.03	3.86	68.57	5.13

a) calcd from mol wt by assuming structure I.

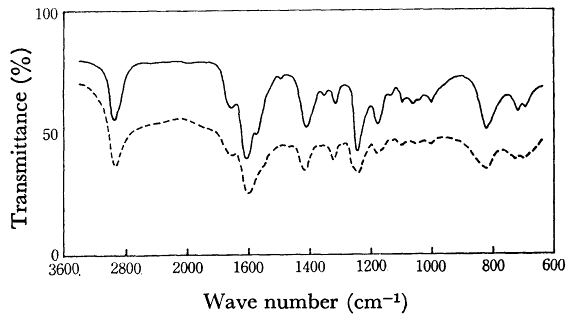
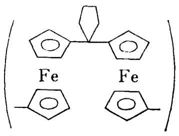
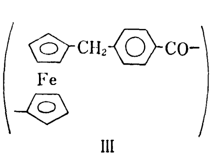


Fig. 1. IR spectra of polycondensation products of ferrocene with terephthaloyl chloride (Exp. No. 10).
—— : Sol. in $CHCl_3$, ------ : Insol. in $CHCl_3$



II



III

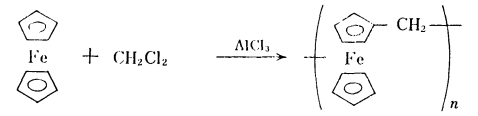
Such a dipolar aprotic solvent was considered to be favorable for this reaction, but no noticeable difference was observed in the present results, which were obtained using *n*-hexane, a nonpolar solvent.

When dichloromethane was used as a solvent, the product was mostly insoluble in chloroform. This solvent acts as a Friedel-Crafts alkylating agent to lead to cross-linking products. A similar reaction has been reported on ferrocene and dichloroethane.[4] Therefore,

---

[4] A. N. Nesmeyanov and N. S. Kochetkova, *Dokl. Akad. Nauk SSSR*, **109**, 543 (1956); *ibid.*, **126**, 307 (1959).

an attempt to obtain a soluble methylene-bridged ferrocene polymer was made; such a polymer was indeed obtained, in 35% yield, from the reaction of ferrocene with dichloromethane catalysed by $AlCl_3$; mp 210—220°C; average molecular weight, 1600.



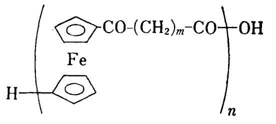
(Methylene group links at 1,1′-, 1,2-, or 1,3-position.)

Melt Polycondensation with Terephthaloyl Chloride. The polycondensation of ferrocene in liquid terephthaloyl chloride was carried out at 85°C without any solvent; the results are shown in Table 3. When $AlCl_3$ was used as a catalyst, a violent reaction occurred to give a decomposition product with a large carbon content. In the case of $ZnCl_2$ catalyst, a rather moderate reaction proceeded, with a low yield of polymers.

TABLE 3. MELT POLYCONDENSATION OF FERROCENCE WITH TEREPHTHALOYL CHLORIDE
[Ferrocene 0.01 mol, Terephthaloyl Chloride 0.01 mol, Temp. 85°C, Time 2 hr]

Exp. No.	Catalyst	(mol)	Yield of polymer (%) Sol.	Insol. in $CHCl_3$
20	none	—	0	0
21	$AlCl_3$	0.01	—	—
22	$ZnCl_2$	0.015	3	4

Polycondensation with Adipoyl Chloride. Ferrocene reacted with adipoyl chloride in a certain solvent or without any solvent in the manner shown in Eq. (1). The rseults are shown in Table 4.



IVa: $m=4$ IVb: $m=2$

The products, the structures of which were assumed to be IVa, are pale or dark brown solids. The highest yield was obtained in the reaction at 80—100°C without any catalyst or solvent, whereas no polymeric product was obtained from the reaction with terephthaloyl chloride under similar conditions. This is likely to be the result of the difference in the solubility of ferrocene in liquid dicarboxylic acid chloride and the homogeneity of the reaction mixture.

The product (Exp. No. 43), purified by recrystallization from chloroform - *n*-hexane, was analysed as follows:

Average molecular weight, 7000 (Degree of polymerization assuming structure IVa, 24).

Found: C, 62.56; H, 5.48%. Calcd for IVa: C, 64.72; H, 5.46%.

The IR spectrum of this product shows absorptions at 2900 (CH_2), 1660 (C=O), 3050, 1440, 810 (ferrocene nucleus), 1100, and 1000 cm^{-1} (the unsubstituted cyclopentadienyl ring of terminal ferrocene) (Fig. 2). These results are in good accord with structure IVa.

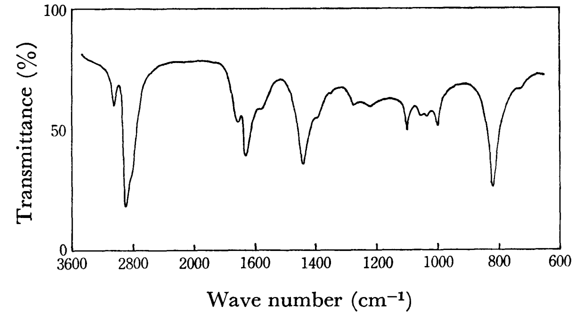


Fig. 2. IR spectrum of polycondensation product of ferrocene with adipoly chloride (Exp. No. 43).

TABLE 5. ELECTRIC CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY OF FERROCENE POLYMERS

Exp. No.	Compound	Yield of polymer (%)	σ (at room temp.) $ohm^{-1} \cdot cm^{-1}$	χ_g cgs units.	ΔE[a] eV
1	I	52	9×10^{-9}	7.3×10^{-6}	0.12
3	IV_b	75	7×10^{-9}	3.2×10^{-6}	0.52

a) ΔE was calculated from Fig. 3 by the following equation: $\rho = \rho_0 \exp (\Delta E/2kT)$ *i.e.* $\log \rho = (\Delta E/4.6k)(1/T) + \text{const.}$ where k is Boltzmann constant.

TABLE 4. POLYCONDENSATION OF FERROCENE WITH ADIPOYL CHLORIDE
[Ferrocene 0.02 mol, Adipoyl Chloride 0.02 mol]

Exp. No.	Solvent	Catalyst	(mol)	Temp. (°C)	Time (hr)	Yield of plolymer (%) Sol.	Insol. in $CHCl_3$
31	carbon tetrachloride	$AlCl_3$	0.04	30	15	12	5
32	carbon tetrachloride	$AlCl_3$ pyridine	0.04 0.02	30	15	15	7
33	diethyl ether	$ZnCl_2$	0.04	0	140	0	0
34	dioxane	$ZnCl_2$	0.04	20	30	—[a]	0
40	none	$ZnCl_2$	0.02	r.t.	80	0[b]	0[b]
41	none	none	—	r.t.	45	—[a]	0
42	none	none	—	160	—[c]	—[c]	—[c]
42	none	none	—	80—100	4	55	0

a) dissolved in hot methanol.
b) As ferrocene was oxidized to ferricinium ion, condensation reaction didn't proceed to polymeric product.
c) A violet reaction proceeded to decomposition product with a large carbon content.

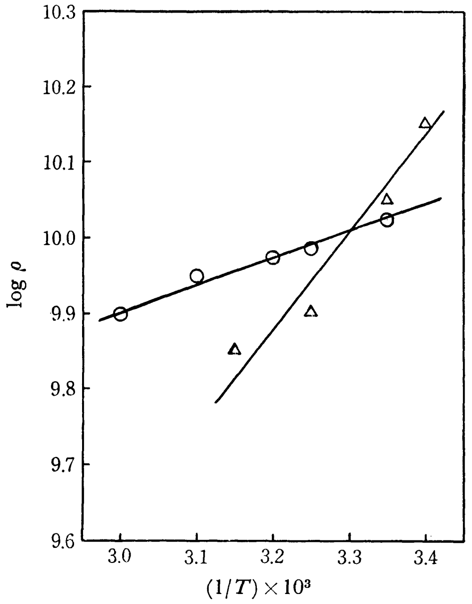


Fig. 3. The temperature dependences of specific resistance of ferrocene polymers.
○ : I, △ : IVb; T : °K

Electric and Magnetic Properties of Ferrocene Polymers. The electric conductivity and magnetic susceptibility of the products from the polycondensation reactions of ferrocene with terephthaloyl and succinyl chloride in dichloromethane are shown in Table 5. The temperature dependences of specific resistance, ρ, are shown in Fig. 3. This is characteristic of semi-conductive substances, and the order of specific conductivity agrees with the expected one. The magnetic susceptibility of ferrocene has been reported to be $\chi_a = -99.0\times 10^{-6}$ cgs units,[5] while Karimov and Shchegolev stated that the magnetic properties of ferrocene polymers varied from paramagnetic to diamagnetic according to the method of preparation and purification.[6] Since the present specimens could not be completely purified because of insolubility, it was not possible to examine the relation of the magnetic properties to the chemical structures. In this respect, more detailed examinations are now in progress.

The authors wish to express their thanks to Professor Hiroo Inokuchi of The Institute for Solid State Physics for his kind suggestions regarding the measurement of the electric and magnetic properties.

---

5) L. N. Mulay and M. E. Fox, *J. Chem. Phys.*, **38**, 760 (1963).
6) Yu. S. Karimov and I. F. Shchegolev, *Dokl. Akad. Nauk SSSR*, **146**, 1370 (1962).