90. V.V.Korshak, E.S.Krongauz, and A.L.Rusanov, Izv. Akad.Nauk SSSR, Ser.Khim., 726 (1965).
91. E.S.Krongauz and A.L.Pusanov, "Abstracts of Scientific Communications, International Symposium on Macromolecular Chemistry, Prague, 1965", p.185; V.V.Korshak, E.S.Krongauz, and A.L.Rusanov, Dokl.Akad. Nauk SSSR, 166, 356 (1966).
92. A.P.Grekov, S.A.Mamotenko, and K.A.Kornev, "Khimiya Geterotsiklykh Soedinenii" (The Chemistry of Heterocyclic Compounds), 1966, p.352.
93. V.V.Korshak, E.S.Krongauz, and A.L.Rusanov, Dokl. Akad.Nauk SSSR, 166, 356 (1966).
94. C.G.Overberger and S.Fujimoto, J.Polymer Sci., B3, 735 (1965).
95. W.Prichard, U.S.P. 2395642 (1941); Chem.Abs., 40, 4915 (1946).
96. J.W.Fisher, E.W.Wheatley, and H.Bates, J.Appl.Chem., 4, 212 (1954).
97. Collected Papers, "Itogi Nauki. Khimicheskie Nauki." (Results of Science. Chemical Sciences), No.7, "Khimiya i Tekhnologiya Sinteticheskikh Vysokomolekulyarnykh Soedinenii" (Chemistry and Technology of Synthetic Macromolecular Compounds), Izd.Akad.Nauk SSSR, Moscow, 1961, p.191.
98. R.J.W.Reynolds, in "Fibres from Synthetic Polymers" (Edited by R.Hill), Elsevier, Amsterdam, 1953, p.187.
99. M.A.Shkolina, Candidate's Thesis, Institute of Inorganic and Organoelementary Compounds of the USSR Academy of Sciences, Moscow, 1959.
100. K.T.Potts, Chem.Rev., 61, 87 (1961).
101. I.Iwakura, M.Makajima, and E.Kitani, Makromol.Chem., 44–46, 408 (1961).
102. H.Botes, J.W.Fisher, and E.W.Wheatley, U.S.P. 2512599 (1950); Chem.Abs., 44, 9731 (1950).
103. H.Weidinger and J.Kranz, Chem.Ber., 96, 1064 (1963).
104. V.V.Korshak, E.S.Krongauz, and A.L.Rusanov, USSR P.175652 (1965).
105. J.W.Fisher and E.W.Whealey, B.P. 693172 (1953); Chem.Abs., 48, 1064 (1954).
106. J.W.Fisher, G.B.May, and E.W.Wheatly, B.P. 676785 (1952); Chem.Abs., 46, 10691 (1952).
107. T.Lieser and K.Kemmer, Chem.Ber., 84, 4 (1951).
108. S.B.McFarlane and A.Miller, U.S.P. 2615862 (1952); Chem.Abs., 47, 6668 (1953).
109. J.R.Holsten and M.R.Lilyquist, J.Polymer Sci., A3, 3905 (1965).
110. V.V.Korshak, T.M.Frunze, A.A.Izyneev, and T.N.Shishkina, Vysokomol.Soed., 6, 901 (1964).
111. V.V.Korshak, T.M.Frunze, and A.A.Izyneev, Izv.Akad. Nauk SSSR, Ser.Khim., 2104 (1964).
112. Y.Iwakura, K.Uno, and M.Fukui, Makromol.Chem., 77, 41 (1964).
113. O.Ya.Fedotova, I.P.Losev, N.I.Skripchenko, M.A.Okunchikova, L.V.Bykova, and M.I.Shtil'man, Vysokomol.Soed., 1, 1685 (1959).
114. A.P.Grekov, S.A.Sukhorukova, and K.A.Kornev, Vysokomol.Soed., 7, 255 (1965).
115. V.V.Korshak, E.S.Krongauz, and A.L.Rusanov, USSR P.180796 (1966).
116. C.J.Fox, J.Polymer Sci., A2, 267 (1964).
117. J.Preston and W.B.Black, J.Polymer Sci., B3, 845 (1965).
118. N.A.Adrova, A.M.Dubnova, M.M.Koton, E.M.Moskvina, and L.K.Prokhorova, "Programma XV Konferentsii po Vysokomolekulyarnykh Soedinenii" (Programme of the Fifteenth Conference on Macromolecular Compounds), Moscow, 1965, p.14.
119. P.J.Flory, J.Amer.Chem.Soc., 64, 2205 (1942).
120. M.M.Brukbaker, D.D.Cofman, and F.C.McGrew, U.S.P. 2339237 (1944).
121. V.V.Korshak, S.V.Vinogradova, M.M.Teplyakov, and Yu.A.Chernomordik, 147, 1365 (1962).
122. Plastic Technol., 9, 55 (1963).
123. B.A.Dolgoplosk, B.L.Erusalimskii, E.B.Milovskaya, and G.P.Belonovskaya, Dokl.Akad.Nauk SSSR, 120, 783 (1958).
124. T.M.Frunze and V.V.Korshak, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 344 (1958).
125. Chem.Eng.News, 42, 53 (1964).
126. Iron Age, 194, 69 (1964).
127. Materials in Design Engineering, 58, 5 (1963).
128. Space Aeronautics, 10, 146 (1963).
129. H.H.Levine, Ind.Eng.Chem., 54, 22 (1962).
130. Ind.Eng.Chem., 54, 118 (1962).
131. Fibres Plastics, 22, 125 (1961).
132. L.A.Laius, M.I.Bessonov, N.A.Adrova, and M.M.Kotov, Plastmassy Mashinostr.Mosk.Dom Nauch.-Tekhn.Propagandy, No.8, 34 (1965).
133. V.I.Kasatochkin, V.V.Korshak, V.V.Kurashev, Z.S.Smutkina, T.M.Frunze, and T.M.Khrenkova, Vysokomol.Soed., 7, 1147 (1965).
134. Chem.Eng.News, 41, 40 (1963).
135. A.H.Frazer and F.T.Wallenberger, J.Polymer Sci., A2, 1171 (1964).

Mendeleev Moscow Institute of Chemical Technology

Buryat Combined Scientific Research Institute, Ulan-Ude

U.D.C. 541.6:547.257.2

POLYMERS BASED ON FERROCENE

T.P.Vishnyakova, I.A.Golubeva, and T.A.Sokolinskaya

CONTENTS

I.	Introduction	932
II.	Ferrocene polymers obtained by polymerisation	933
III.	Ferrocene polymers obtained by polyrecombination	934
IV.	Ferrocene polymers obtained by polycondensation	935
V.	Fields of application for polymers containing ferrocene	944

I. INTRODUCTION

Ferrocene is the most accessible and stable—and hence the most thoroughly investigated—representative of a novel type of organometallic compound. Several detailed reviews[1-3] have appeared on ferrocene and its derivatives. The aromatic character of ferrocene, its structural peculiarities, the high reactivity, and the thermal stability—unusual for organometallic compounds—have attracted the attention of many research workers, and explain the attempts to use various of its derivatives for the synthesis of polymers.

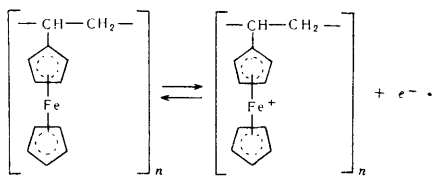
Some hundred different ferrocene-containing polymers are already known, but there has not yet been a thorough review covering this new and fairly extensive field of polymer chemistry. There has merely been mention of certain polymers of ferrocene in reviews by Haiduc on coordination polymers[4] and by Korshak[5] and by Brown[6] on organoelementary macromolecular compounds. Reviews appeared in 1966 by Zimakova[7] and by Zelenetskii[8], but these do not cover completely the vast amount of information on the chemistry of ferrocene polymers.

Ferrocene-containing polymers can be divided into three groups depending on whether they are obtained by polymerisation, polyrecombination, or polycondensation.

2. FERROCENE POLYMERS OBTAINED BY POLYMERISATION

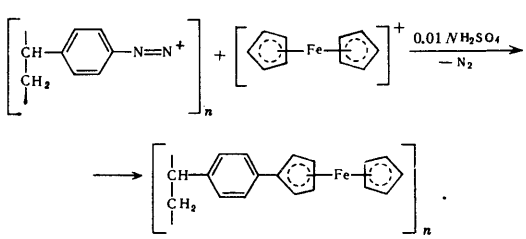
The first polymer of this type, polyvinylferrocene, was prepared from vinylferrocene by Arimoto and Haven[9] in 1955. In the presence of 85% phosphoric acid or potassium persulphate, a viscous oil, soluble in benzene, was formed. When azoisobutyronitrile was used, vinylferrocene polymerised at 80°C to form a benzene-soluble solid melting at 280–285°C. Copolymers of vinylferrocene with methyl methacrylate, styrene, and chloroprene were also obtained[9,10]. All the polymers were soluble in benzene and insoluble in methanol. Clear, brittle films could be obtained from solutions of the solid polymers.

Table 1 lists some properties of homopolymers and copolymers of vinylferrocene. Treatment of the copolymers with formaldehyde yields cross-linked products having redox properties:



Solid polymers of vinylferrocene also possess redox properties, though polyvinylferrocene is insoluble in the solvents normally used for potentiometric titration.

The electron-exchange properties of polyvinylferrocene were studied by sulphonating it in the ring[11]. Analysis showed that two sulpho-groups entered the ring linked by the polymer chain, and one entered the second ring. Sulphonated polyvinylferrocenes are soluble, but they cannot be titrated owing to their rapid decomposition. A further electron-exchange resin, a ferrocene–polystyrene analogue of a redoxite[12], has been obtained from ferrocene:



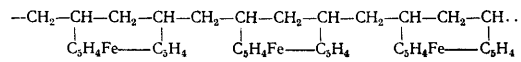
Rausch and Coleman[13] described various copolymers based on ferrocene β-styryl ketone [cinnamoylferrocene], which was synthesised in 81.5% yield from cinnamoyl chloride and ferrocene by the Friedel–Crafts reaction. The

TABLE 1. Homopolymers and copolymers of vinylferrocene.

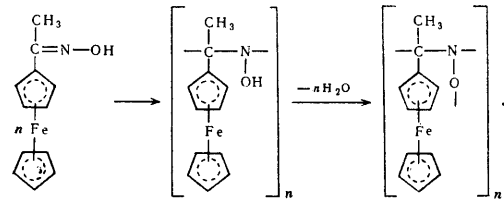
Catalyst	Comonomer	Product	M.p., °C
85% Orthophosphoric acid	—	viscous oil	—
Potassium persulphate	—	oil	—
	—	solid	280—285
Azoisobutyronitrile	methyl methacrylate	solid	190—210
	styrene	solid	158—165
Potassium persulphate	chloroprene	elastomer	—

ketone itself does not polymerise, but it forms copolymers with many vinyl and diene compounds, such as styrene, acrylonitrile, acrylates, butadiene, and isoprene[14,15]. Copolymers with vinyl monomers have been obtained by block polymerisation in the presence of benzoyl peroxide, or by polymerisation in benzene solution (in the absence of thiophen) or in dimethylformamide with azoisobutyronitrile as initiator. Copolymers with dienes were obtained by emulsion polymerisation using dodecanethiol as modifier. These copolymers were coloured powders, elastic materials, or solids melting at 130–275°C.

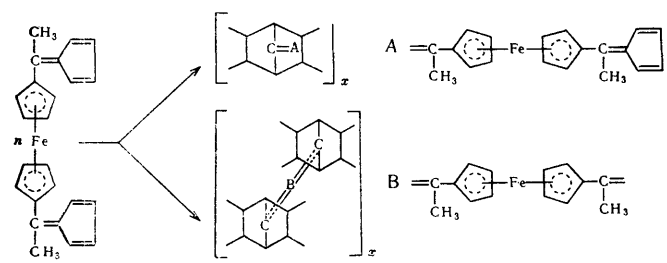
Knox and Pauson[16] attempted to prepare divinyl- and dibutadienyl-ferrocenes via the fulvenes, but were unable to isolate these derivatives, since they underwent rapid polymerisation. The polymer formed from these ferrocenes may have the structure



Ferrocene-containing polymers are formed also by the polymerisation of acetylferrocene oxime and 1,1′-bis-(1-cyclopentadienylidene-ethyl)ferrocene. The oxime undergoes polymerisation at or above its melting point to produce an almost quantitative yield of insoluble polymers[17]:



The thermal, catalytic, and radiation polymerisation of the difulvene is represented by the scheme[17]



Thermal polymerisation was conducted in sealed tubes at various temperatures for 1–8 h. Insoluble and infusible polymers were produced above 150°C. Polymerisation of the difulvene derivative in the presence of benzoyl peroxide in dioxan solution after 8 h yielded 28.2% of polymers having a linear structure and 9.1% of cross-linked polymers (with 2% of benzoyl peroxide at 65°C). With 3% of the peroxide at 100°C the polymerisation was almost quantitative.

The copolymerisation of ferrocene with hexamethylene di-isocyanate gave a 73% yield of an infusible copolymer, a polyferrocenylenepolyamide, which was insoluble in the usual organic solvents[17]. This copolymer results from the addition of ferrocene hydrogen atoms to the isocyanate groups, which suggests that these atoms are very mobile in comparison with the hydrogen atoms in benzene, for the latter does not react with di-isocyanates. The elementary composition and the infrared spectra of the copolymer indicate that it has the structure

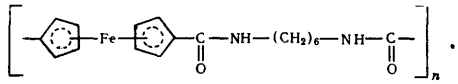
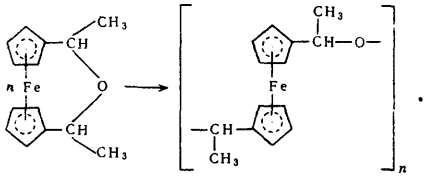
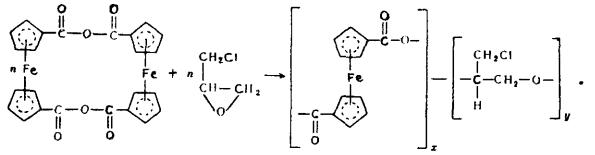


Table 2 lists the characteristics of the above ferrocene-containing polymers, obtained by the polymerisation of acetylferrocene oxime and of 1,1′-bis-(1-cyclopentadienylidene-ethyl)ferrocene, and by the copolymerisation of ferrocene with hexamethylene di-isocyanate.

A recent paper[18] has reported the synthesis, by polymerisation accompanied by ring-opening of ferrocene derivatives containing reactive bridging chains between the two cyclopentadienyl rings, of polymers containing ferrocene in the main chain. Treatment of 1,1′-(1,1′-epoxydiethyl)ferrocene with certain Lewis acids used as catalysts gave a yellow–orange polymeric product. Infrared spectroscopy showed that the polymeric product obtained by polymerisation at room temperature contained ether chains, but that obtained at 75°C did not contain them. The reaction occurred according to the scheme



Copolymerisation has been accomplished[18] also between ferrocene-1,1′-dicarboxylic anhydride and 1-chloro-2,3-epoxypropane, the products being dark brown esters insoluble in the usual organic solvents:



The polymerisation of acryloylferrocene in the presence of various initiators has been studied, as well as the copolymerisation of acrylylferrocene with acrylonitrile[19].

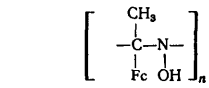
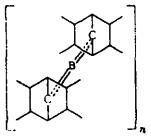
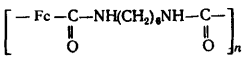
3. FERROCENE POLYMERS OBTAINED BY POLYRECOMBINATION

Polyrecombination is distinguished fundamentally from polymerisation by the fact that the starting materials are saturated compounds and that it is a stepwise reaction—not a chain reaction—although it occurs by a radical mechanism. Polyrecombination consists in treating a hydrocarbon with a peroxide, e.g. with t-butyl peroxide in an atmosphere of nitrogen at 200°C. The t-butoxyl and methyl radicals resulting from breakdown of the peroxides abstract hydrogen from the ferrocene (or α-hydrogen from its alkyl substituent), and the radicals thus formed recombine among themselves to form a polymer[20].

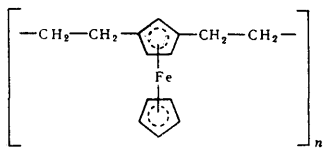
In 1958 Korshak et al. were the first to use polyrecombination to obtain a ferrocene-containing polymer based on a homoannular di-isopropylferrocene[21]. Later they made a detailed investigation of the polymer[22]. Its synthesis was conducted at 170°C with equimolecular proportions of peroxide and monomer. The polymer was a reddish powder, soluble in benzene and chloroform, with molecular weight 8200 and melting point 155–180°C.

Polyrecombination was used to obtain polymers (polyferrocenylenes) from ferrocene itself[20,23–25]. Formation of a linear polyferrocenylene, readily soluble in benzene, was accompanied by that of an insoluble polymer, probably possessing a cross-linked structure. The two polymeric forms were separated by treating the reaction mixture

TABLE 2. Characteristics of some ferrocene-containing polymers obtained by polymerisation.

Structure of polymer	Method of polymerisation	Elementary composition, wt. %								Characteristic absorption bands, cm^{-1}
		C		H		Fe		N		
		found	calc.	found	calc.	found	calc.	found	calc.	
	thermal	59.17	59.25	4.99	5.3	24.01	23	4.69	5.75	818,1000, 1100,1426, 1603
	thermal	77.85	78.6	6.14	6.01	15.1	15.3	—	—	820,1370, 1436
	catalytic	77.91	78.6	6.16	6.01	14.9	15.3	—	—	1586—1700
	radiation	77.18	78.6	6.18	6.01	14.55	15.3	—	—	
	thermal	61.5	61.1	6.72	6.20	15.25	15.8	7.2	7.9	814,1000, 1100,1360, 1450,1670

with benzene. The soluble polyferrocenylenes had molecular weights of 370–7000 and softening points of 290–300°C. The insoluble polyferrocenylene softened at 400°C, which probably indicates that cross-linkages between the chains were comparatively rare. The structure of the polyferrocenylenes, and also of the polymers obtained by the polyrecombination of di-isopropylferrocene, is supported by the infrared spectra, which contain absorption maxima, characteristic of a free cyclopentadienyl ring, in the region of 820, 1000, and 1100 cm^{-1}. On this basis the soluble polymers probably have the structure



(I).

Refinement of the polymer structure (I) permits it to be regarded as a chain of ferrocene structures linked by methylene bridges formed as a result of preliminary methylation of the ferrocene.

The work of Korshak, Sosin, and other Soviet investigators on the preparation of polyferrocenylenes by polyrecombination in the presence of t-butyl peroxide has been repeated by foreign workers [26], who have obtained under carefully controlled reaction conditions soluble polymeric compounds comparable in molecular weight and physical properties with those obtained earlier. However, the elementary composition of the products differs from that calculated for polyferrocenylenes. Spectroscopic examination and determination of the elementary composition, confirmed by the isolation not only of bi- and ter-ferrocenyl but also of diferrocenylmethane and diferrocenylmethyl t-butyl ether, substantiated the Soviet authors' results indicating that the compounds obtained were polymeric chains comprising polyferrocene segments linked by methylene and other aliphatic groups. These bridging groups result from methylene and t-butyl radicals.

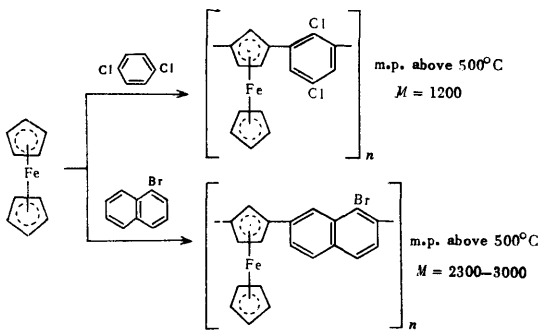
The polyrecombination of various alkyl derivatives of ferrocene was studied [27]. Polymers were obtained based on isobutylferrocene, di-isobutylferrocene, isopentylferrocene, and cyanoferrocene, as well as copolymers of ferrocene with isobutylferrocene, stilbene, and dimethyl dodecanedioate. The polyrecombination was conducted at 200°C, the molar ratio of t-butyl peroxide to the initial compound being 1.2 : 1. The alkylferrocene polymers were dark yellow and brown powders of molecular weight 3000–9000. The infrared spectra of soluble polymers exhibited in all cases absorption maxima in the region of 1000 and 1100 cm^{-1}, which are characteristic of free cyclopentadienyl rings. Hence only one of the cyclopentadienyl rings was involved in polymer formation in the above cases.

Electron spin resonance (e.s.r.) and a positive magnetic susceptibility were observed with these polymers [20,28]. However, further investigation showed [29] that the anomalous magnetic properties of ferrocene polymers were entirely due to the presence of paramagnetic and ferromagnetic impurities. Specially purified specimens of the above ferrocene polymers gave no e.s.r. signal.

The effect of preliminary heating in a vacuum at 200° and 270°C was studied on the electrical and magnetic properties of polyferrocenylenes obtained by polyrecombination [30]. Heating the polymers in a vacuum at 270°C results in a substantial change in their physical properties. The electrical resistance and the activation energy E_σ diminish appreciably, and a break appears on the conductivity–temperature straight lines. The magnetic susceptibility of polymers which have been heated in a vacuum at 270°C is much higher than that of the unheated polymers (by factors of 10^2–10^3). A marked dependence of χ on the magnetic field strength H appears, which is characteristic of ferromagnetic substances, χH exhibiting a saturation effect at the fields used. The appreciable ferromagnetism of ferrocene polymers which have been compressed and heated in a vacuum is due to the ferromagnetic properties of organometallic compounds of iron, although the possibility of thermal decomposition of the polymer with the formation of ordinary ferromagnetic compounds of ferrocene cannot be completely excluded with the preparations studied.

Paushkin, Vishnyakova, and their coworkers [31–34] investigated the polyrecombination of various alkylferrocenes and the copolyrecombination of ferrocene with 1-bromonaphthalene, *p*-dichlorobenzene, benzonitrile, salicylic acid, salicylaldehyde, benzaldehyde, phthalic anhydride, and other aromatic compounds. The reaction was conducted in the presence of various amounts of t-butyl peroxide at 175–200°C.

Copolyrecombination yields products of the following types:



Soluble (dark brown) and insoluble (black) solid polymers were obtained. The experimental results and the characteristics of the products are given in Table 3. All the specimens show a positive temperature coefficient of conductance, and the dependence of conductance on temperature is exponential in character.

4. FERROCENE POLYMERS OBTAINED BY POLYCONDENSATION

Nesmeyanov and Kochetkova prepared polymers by the polyalkenylation of ferrocene with 1,2-dichloroethane and dichloromethane in the presence of aluminium chloride at the boiling point of dichloroethane [20,28,35,36]. Interaction of ferrocene with a large excess of 1,2-dichloroethane under severe conditions in the absence of a foreign solvent yielded a series of "pentaethanopolyferrocenes" not containing halogen, soluble in chloroform and benzene and insoluble in methanol, instead of the diferrocenylethane and resins of relatively high molecular weight obtained previously [37], in which several ferrocene units were linked by CH_2–CH_2 bridges. The products obtained differed among themselves in their solubility in ether, this property being utilised for their separation. On the basis of elementary analysis the substance of lowest molecular weight, which

TABLE 3. Characteristics of ferrocene-containing polymers obtained by polyrecombination.

Initial compound (Fc = ferrocene)	Molar ratio peroxide : initial compound	Yield of polymers based on initial cpd., wt. %		Mol. wt. of soluble polymer	Melting point, °C		ΔE, eV	σ^*_{50}, ohm^{-1} cm^{-1}
		sol.	insol.		sol.	insol.		
Fc + 1-bromonaphthalene	1.36:1	5.4	23.0	2300—3000	>500	>500	0.54	$2.5 \cdot 10^{-13}$
ditto	3:1	6.6	26.0		—	—	0.54	$1.7 \cdot 10^{-13}$
Fc + *p*-dichlorobenzene	1. 6:1	5.2	23.0	1200	>500	>500	0.47	$2.83 \cdot 10^{-10}$
ditto	3:1	4.2	32.9	—	—	—	0.58	$2.5 \cdot 10^{-12}$
Fc + benzonitrile	2:1	none	27.0	—	—	>500	—	—
Fc + salicylic acid	1. 8:1	none	77.0	—	—	>500	0.33	$4.0 \cdot 10^{-9}$
Fc + salicylaldehyde	1. 5:1	3.3	35.7	—	—	>500	0.45	$3.7 \cdot 10^{-12}$
Fc + benzaldehyde	2 :1	none	34.8	—	—	>500	—	—
Monoisobutylferrocene	2 :1	39.0	none	2300	300	—	—	—
Monoisopentylferrocene	2 :1	35.5	none	1300	290—295	—	—	—
Monoiso-octylferrocene	2 :1	34.0	none	2000	290	—	—	—
Fc + naphthalene	2 :1	15.35	18.25	3000	260—270	310—320	—	—
Fc + benzophenone	1.64:1	7.0	23.0	1100	180—190	320—330	—	—
Fc + azobenzene	2 :1	13.7	none	—	>500	—	—	—
Fc + benzoic acid	1.76:1	6.55	71.3	—	> 260	>500	—	—
Fc + phthalic anhydride	1.66:1	none	30.7	—	—	>500	0.036	

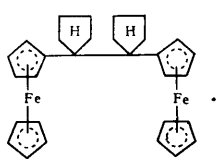
* Electrical properties given for the insoluble polymers.

decomposed at 130°C, was regarded as a pentaethanodiferrocene, containing two ferrocene units and five ethano-bridges. The products of molecular weight 1000–2000, which were less soluble in ether, contained 4–8 ferrocene residues. Their analyses were close to that of the previous substance. This suggested that they had an analogous structure.

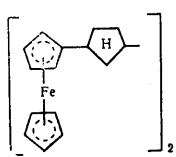
Nesmeyanov et al.[38] obtained acetyl derivatives of "pentaethanodiferrocene". The acylation of this compound with acetic anhydride in the presence of 85% phosphoric acid gives a monoacetyl derivative. Acylation with acetyl chloride in the presence of anhydrous aluminium chloride in dichloromethane (solvent) yields "diacetylpentaethanodiferrocene" and other "polyacetylpentaethanodiferrocenes". The formation of a diacetyl product confirmed the presence of two acylatable cyclopentadienyls.

In a brief communication Goldberg[39] mentioned the possibility of obtaining a substance with the same properties as "pentaethanodiferrocene" by the action of aluminium chloride on ferrocene in benzene solution in the absence of dichloroethane.

Further investigations by Nesmeyanov and Kochetkova[40] on the action of aluminium chloride on ferrocene, comparison with the action of anhydrous hydrogen fluoride on ferrocene[41], and an attempt to hydrogenate the resulting "pentaethanodiferrocene" led these workers[40] to the conclusion that their compound was 1,1′-diferrocenylbicyclopentyl

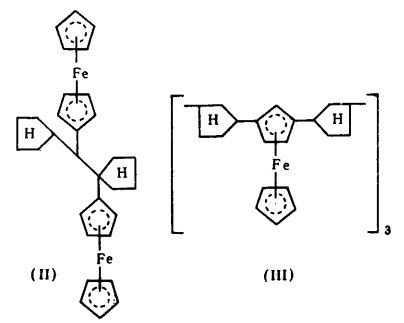


The presence of small quantities of other isomers

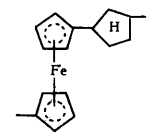


was also possible. However, the substances of molecular weight 1000 and 2000 described previously were probably polymers of cyclopentenylferrocene.

Cottis and Rosenberg[42] were able to separate the compound described earlier as "pentaethanoferrocene" into two parts—a reddish-orange rubberlike substance (II) soluble in ether and partly soluble in methanol, and a yellow solid (III)—



Other workers[43] have studied the action of $ZnCl_2$–H_2O on ferrocene in the absence of any solvent. The reaction was conducted in the melt (at 180°C) with relative proportions of ferrocene : $ZnCl_2$: H_2O = 1 : 0.3 : 0.01. The reaction gave products soluble in hexane, which were separated chromatographically and were shown by analysis to be 1,1′-(cyclopent-1,3-ylene)ferrocene and two isomers of diferrocenylcyclopentane. The product, which was insoluble in hexane but soluble in dioxan, benzene, and chlorinated hydrocarbons, had melting point 125–135°C and molecular weight 2030, and from analysis was an oligomer containing as unit

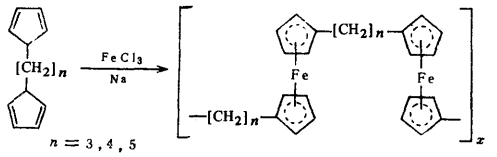


In 1961 Knobloch and Rauscher reported the preparation by interfacial polycondensation of polyamides and polyesters containing ferrocene, the starting materials being ferrocene-1,1′-dicarbonyl chloride and certain diols (2,2-diphenylpropane-*pp*′-diol, quinol, and ethylene glycol) and diamines (ethylenediamine, hexamethylenediamine, piperazine, and *p*-phenylenediamine).[44] The properties of the polyesters and polyamides are listed in Table 4. With the exception of the polymer based on *p*-phenylenediamine,

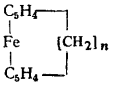
they all dissolve in the usual solvents for polyamides—*m*-cresol and 90% formic acid—and swell in 1,1,2,2-tetrachloroethane, acetone, pyridine, 1,4-dioxan, and tetrahydrofuran. Polymers obtained from hexamethylenediamine dissolve in dimethylformamide, while the polyamide based on piperazine readily dissolves in 1,1,2,2-tetrachloroethane. The polyamide obtained from hexamethylenediamine breaks down at an appreciable rate in formic acid. The molecular weights of the polymers, calculated from viscosities, were 8300–12 000.

Polyurethanes of melting points 91–225°C have been obtained by the polycondensation of ferrocene di-isocyanate with glycols—ethanediol, hexane-1,6-diol, decane-1,10-diol, *p*-phenylenedimethanol, ferrocene-1,1′-diol, and quinol—the polymers being partly soluble in dimethylformamide and dissolving well in formic acid[45].

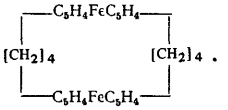
It is theoretically possible to synthesise polymers containing ferrocene in their structure from the disodium derivatives of $\alpha\omega$-dicyclopentadienylalkanes with iron(III) chloride in tetrahydrofuran[46,47]:



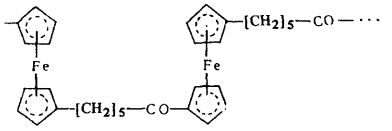
Carrying out this reaction led not only to the production of the polymers but also to the isolation of monomeric ansaferrocenes



and a small amount of cyclic dimers, e.g.

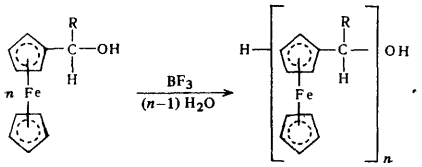


The preparation of polymers having the structure



has also been described[48].

The polycondensation of 2-hydroxyalkylferrocenes yields polymers containing alternating ferrocene and alkyl groups in the main chain[49]:



Formation of a C–C bond, which occurs very readily with the elimination of water, can be explained by the great tendency of these compounds to form ferrocenylcarbonium ions:

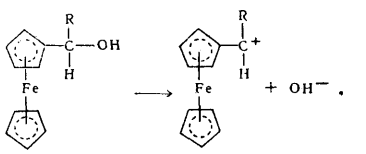


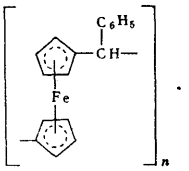
TABLE 4. Properties of polyamides and polyesters obtained from ferrocene-1,1′-dicarbonyl chloride.

Diamine or diol	Organic phase	Base	Duration of reaction, min	Yield, %	[η]	Properties of polymer
Ethylenediamine	toluene	excess of amine	1.0	–	–	–
Ethylenediamine	benzene	excess of amine	2.0	79	0.14	yellow–orange powder, dark at 180°C, brownish and rubberlike at 225°C
Hexamethylenediamine	benzene		2.0	87	0.21	yellow–orange powder decomposing at 110°C, rubberlike at 165°C, dark at 220°C
Piperazine	benzene		3.0	80	0.22	yellow–orange powder, softening at 160°C, transparent at 190°C, orange at 300°C
p-Phenylenediamine	dichloromethane		3.0	93	insol.	brown powder, dark at 230°C, black at 300°C
2,2′-Diphenylpropane-*pp*′-diol	dichloromethane		3.0	70	0.10	orange powder, m.p. 165°C
Quinol	dichloromethane		3.0	63	insol.	brown powder, dark at 200°C

The stability of ferrocenylcarbonium ions has been referred to in other papers[50,51]. By treating ferrocenylmethanol with an acid solution of alumina in benzene Schlögl and Mohar[52] obtained liquid polymers, to which they attributed the above structure (the molecular weight of the products was not stated). The polymer from hydroxybenzylferrocene was a yellow-green powder soluble in the usual solvents, brittle films of which could be obtained from the solution in benzene.

A product, insoluble as a consequence of possible cross-linking, is formed (in 3% yield) by the polycondensation of 1,1′-bis-(1-hydroxyethyl)ferrocene in benzene solution[52]. It is an infusible yellow-green powder, insoluble in the usual solvents, and decomposing at 170–180°C.

Neuse and Trifan[53] studied the polycondensation of ferrocenylmethanols having the structure FcCH(OH)R, where R = H, CH_3, C_6H_5. The polycondensation was conducted in the presence of Lewis acids, the best result being obtained in the presence of zinc chloride, the yield of polymer being 96%. The polycondensation of α-ferrocenylbenzyl alcohol[54] leads to the formation of polymeric ethers of low molecular weight, which in the presence of Lewis acids at elevated temperatures yield products of higher molecular weight having the structure



From 1954 papers began to appear on the condensation of ferrocene with aldehydes in the presence of strong acids (sulphuric, hydrochloric, hydrofluoric) and Lewis acids, leading to the formation of products of low molecular weight (diferrocenylmethane and bisferrocenylphenylmethane) and ferrocene-containing polymers of molecular weight up to 5000. Nesmeyanov and Kritskaya[55] found that ferrocene reacts with aqueous formaldehyde and with benzaldehyde in the presence of concentrated sulphuric acid at 65–70°C, with equimolecular proportions of ferrocene and aldehyde. The total yield of condensation products then reached 65–75% of theoretical. Diferrocenylmethane was obtained, a substance soluble in benzene, chloroform, and dioxan and melting at 191°C, as well as bisferrocenylphenylmethane, soluble in acetone and melting

at 218–220°C. The interaction of ferrocene with benzaldehyde yielded a compound of m.p. 268–270°C, having the composition

$$(C_5H_4)_2Fe[CH(C_6H_5)][CH(OH)C_6H_5]Fe(C_5H_4)(C_5H_5)\ . \qquad (IV)$$

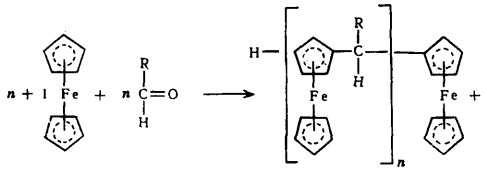
Valot[56] points out that the condensation of ferrocene with formaldehyde in sulphuric acid yields, in addition to diferrocenylmethane and traces of 1,2-diferrocenylethane, a polycondensation product which is a light brown powder of molecular weight 4800, readily soluble in benzene, toluene, and pyridine, sparingly soluble in dimethylformamide, and insoluble in ether and acetone. This product partly darkens at 150°C, and at 170°C is converted into a brownish-red viscous mass. It was proposed[57] that the condensation of ferrocene with formaldehyde and with benzaldehyde should be accomplished in the presence of a large quantity of anhydrous hydrogen fluoride. Analysis suggests that the compound obtained is formed by the condensation of two ferrocene molecules with two aldehyde molecules, accompanied by the elimination of two molecules of water. It is noteworthy that the melting point of this compound corresponds to that of the product (IV) obtained by Nesmeyanov and his coworkers[55].

A considerable quantity of insoluble products were formed by the condensation of ferrocene with benzaldehyde and with formaldehyde in the presence of sulphuric acid and hydrogen fluoride, but these were not isolated or investigated.

The condensation of ferrocene with benzaldehyde has been accomplished also in the presence of 1 ml of concentrated hydrochloric acid in glacial acetic acid at room temperature[58]. The mixture is allowed to stand without stirring for a week, and is then processed. A black powder of indefinite melting point is obtained, its elementary composition corresponding to the empirical formula $C_{17.8}H_{15.3}FeO_{1.4}$. The possibility is mentioned of condensing ferrocene with other aldehydes—such as acetaldehyde, propionaldehyde, butyraldehyde, chloral, *p*-nitrobenzaldehyde, etc.—with ferrocene : aldehyde ratios of 1 : 1–10 and above. The catalysts used are strong acids—phosphoric, sulphuric, hydrobromic, toluene-*p*-sulphonic, hydrochloric, and trichloroacetic—the quantity of which should not exceed 1 part in 10–1000 parts of ferrocene.

The polycondensation of ferrocene with benzaldehyde has been conducted also in the presence of the complex catalyst $ZnCl_2$–HCl(gas) [59] at temperatures ranging from −20° to +140°C.

Neuse and Trifan[60,61] have studied the polycondensation of ferrocene with aldehydes in the presence of Lewis acids (mainly zinc chloride), in amounts of 3–30% on the weight of ferrocene. These workers assume that condensation proceeds via the formation of intermediate ferrocenylmethanols and the corresponding carbonium ions, the final product of the reaction having the structure (V):

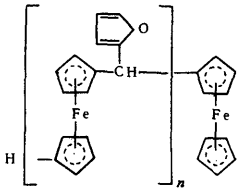


(V)

The condensation was conducted in an atmosphere of nitrogen in an autoclave at 130–180°C. Soluble, readily fusible polymers of molecular weight 2500 were obtained having the structure (V) with R = H, CH_3, C_6H_5; the yield reached 70%. Crotonaldehyde also yields polymers having the structure (V) under the same conditions, but owing to side-reactions at the double bonds in the aldehyde the yield does not exceed 20–30%.

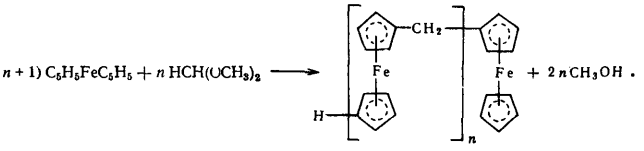
The condensation of ferrocene with furfuraldehyde and with the *o*-methoxy-, *p*-hydroxy-, *p*-carboxy-, and *p*-cyano-derivatives of benzaldehyde at atmospheric pressure gave soluble polymers of molecular weight up to 5000. In these cases the elementary composition differed slightly from that expected for the structure (V), owing to steric and electronic effects of the substituent groups and their tendency to undergo competing side-reactions.

The polycondensation of ferrocene with furfuraldehyde has since been studied in greater detail[62]. Lewis acids were used as catalysts. The molecular weight of the resulting polymers

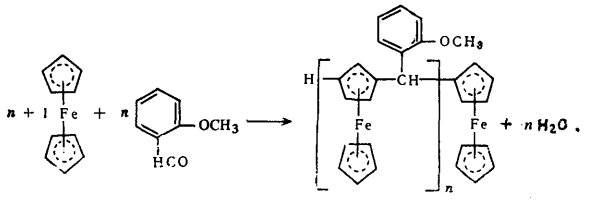


lay within the range 800–4500.

The polycondensation of ferrocene with dimethoxymethane in the presence of zinc chloride at 150–170°C for 8 to 12 h gave a polymer of the structure indicated below[63]:



The polycondensation of ferrocene with anisaldehyde was effected with various proportions of the starting materials in the presence of zinc chloride at 135° and 165°C for 0.9–13 h:[64]

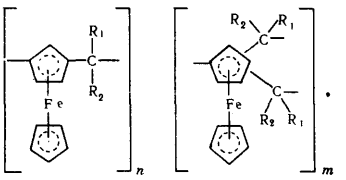


A yield of soluble polymers of 54–78% has been obtained by the polycondensation of ferrocene with *p*- and *o*-formylbenzoic acids, with a molar ferrocene : aldehyde ratio of 0.9 : 3.0, at 115–170°C for 0.4–1.7 h.[65]

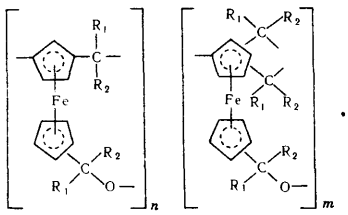
Kotrelev et al.[66] have obtained products of the polycondensation of ferrocene with diazotised benzidine (with various proportions of the starting materials) and of 1,1′-diacetylferrocene with furfuraldehyde. Determinations were made of the thermomechanical properties of the resulting polymers and of their moulding compositions with kaolin.

The polycondensation of ferrocene with various ketones —acetone, butan-2-one, cyclohexanone, acetophenone, and benzophenone—has been studied in the presence of the complex catalyst $ZnCl_2$ + HCl(gas). With relative proportions of ferrocene : ketone = 1 : 2 the yield of ferrocene-containing polymers varied from 29.1% to 76.5%.[67] From

a study of the properties of the polymers it is suggested that with these proportions of the reactants the polycondensation involves the elimination of water, perhaps via intermediate ferrocenylmethanols, with the formation of soluble and insoluble polymers. In the soluble polymers one molecule of ferrocene is associated with 1.5–2 $>CR_1R_2$ groups: i.e. the polymers probably have the structure



On the basis of the elementary analysis the insoluble polymers are assigned the structure

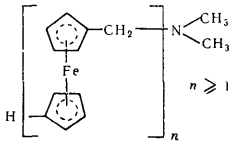


In the absence of ferrocene the condensation of ketones in the presence of $ZnCl_2$ + HCl as catalyst proceeds only as far as formation of dimers and trimers. Addition of 5 mole % of ferrocene to this mixture enhances the activity of the system, so that liquid and solid polymers not containing iron are formed, and also polymeric ferrocene-containing products.

Interaction of ferrocenyl cyanide with ferrocenyl-lithium[68] gives a diferrocenyl ketone in 55–60% yield, and reaction of the latter with ferrocenyl-lithium leads to the formation of triferrocenylmethanol (yield 60%). Reduction of the carbinol with zinc dust in acetic acid gives triferrocenylmethane:

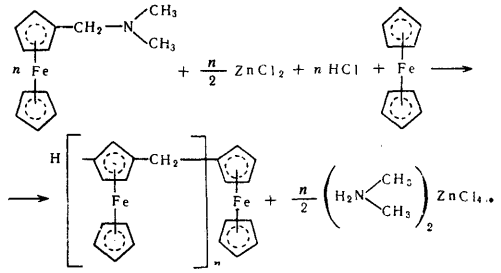
$$C_5H_5FeC_5H_4CN \xrightarrow{C_5H_5FeC_5H_4Li} (C_5H_5FeC_5H_4)_2CO \xrightarrow{C_5H_4FeC_5H_4Li} \rightarrow (C_5H_5FeC_5H_4)_3COH \xrightarrow{Zn+CH_3COOH} (C_5H_4FeC_5H_4)_3CH .$$

The condensation of *NN*-dimethylaminomethylferrocene has also been studied[69,70], in the presence of the $ZnCl_2$–HCl catalytic system in the melt. Polymers



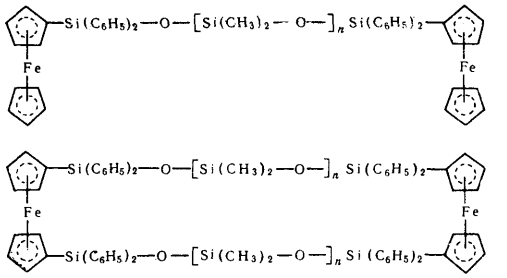
were obtained, containing ferrocenylene structures separated by methylene groups. The products had molecular weights lying in the range 4000–8000. The optimum molar proportions were Mannich base : $ZnCl_2$: HCl = 2 : 1 : 2.

NN-Dimethylaminomethylferrocene has been subjected also[71] to polycondensation with ferrocene:



The structure of the resulting polymer has been confirmed by elementary analysis and the infrared spectra.

The synthesis of several derivatives of ferrocene containing silicon has been described[72]. Various compounds have been obtained containing two ferrocene molecules linked by chains containing silicon atoms

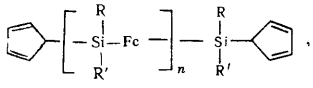


The patent claims[72] that these compounds can be used as lubricants and as defoaming agents for several organic substances.

A series of symmetrical silanylferrocenes—1,1′-bis-(3-phenyltetramethyldisiloxanyl)ferrocene, 1,1′-bis-(5-phenylhexamethyltrisiloxanyl)ferrocene, 1,1′-bis-(7-phenyloctamethyltetrasiloxanyl)ferrocene, etc.—have been obtained. These silanylferrocenes possess good lubricating properties and high thermal stability[73].

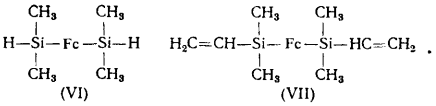
Various unsymmetrical siloxanylferrocene derivatives have also been synthesised[74], by a very complicated multistage method.

The preparation has been described[75] of polymers containing alternating ferrocen-1,1′-ylene and disubstituted silylene groups



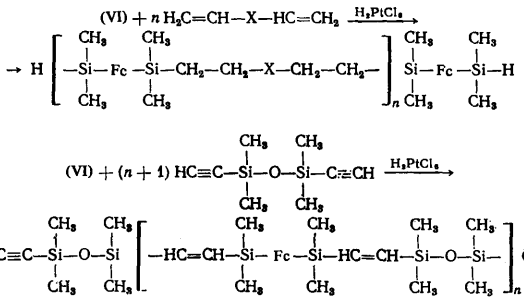
where Fc is a ferrocene residue, and R and R′ are hydrocarbon radicals containing aliphatic, cycloalkyl, aromatic groups and halogenated derivatives, alkoxy-groups, or halogens. These polymers maintain their chemical and thermal stability over a wide range of temperatures.

The reduction of 1,1′-bisethoxydimethylsilylferrocene with lithium tetrahydroaluminate gave a yield exceeding 90% of 1,1′-bisdimethylsilylferrocene (VI), which added acetylene to form 1,1′-bisvinyldimethylsilylferrocene (VII):



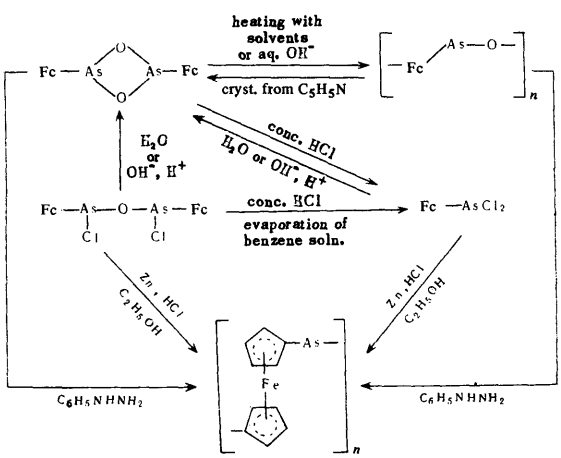
(VI) (VII)

The polyaddition of (VI) to (VII) or to other organosilicon compounds containing two unsaturated terminal groups, and also the addition of (VII) to organosilicon compounds having two $SiHR_2$ terminal groups, lead to the formation of thermostable polymers in which ferrocene is located in the main chain. By varying the proportions of the components it is possible to obtain macromolecules containing two $SiHR_2$ or two unsaturated terminal groups[76]. The reaction proceeds according to the scheme

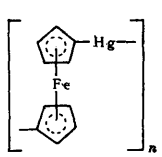


where X = $-Si(CH_3)_2.O.Si(CH_3)_2-$ and Fc = $-C_5H_4FeC_5H_4-$.

Arsenic trichloride[77] gives macromolecular compounds as well as new monoferrocene derivatives of arsenic. The polymers were readily obtained by heating dimeric arsenoferrocene in aqueous alkali, this being explained by thermal hydrolysis of the ferrocenearsonite anion. The conversion of the dimer into a polymer in various solvents is explained by these workers[77] as due to solvolysis of the As–O bond by the solvents. The formation of polymers is represented by the scheme



The synthesis has been described[78] of macromolecular mercury compounds of ferrocene of the type



Products having the composition $(C_{10}H_8FeHg)_x$ were obtained by treating 1,1′-bischloromercuriferrocene with a solution of sodium iodide in a mixture of ether and alcohol or with an aqueous solution of sodium thiosulphate.

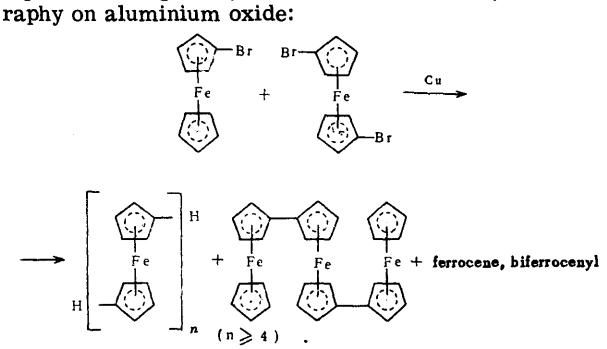
The polycondensation of ferrocene and its derivatives yielded polymers having a system of conjugated double bonds, which possessed semiconductor properties.

Several polyferrocenylenes have recently been synthesised by various methods (besides the polyrecombination reaction described above).

Nesmeyanova and Perevalova[79] obtained ferrocene polymers insoluble in organic solvents and also biferrocenyl by heating diferrocenylmercury with palladium black. Later Rausch[80] used silver in this reaction. Biferrocenyl was isolated as a byproduct of the interaction of a mixture of ferrocenyl-lithium and ferrocen-1,1′-ylenedilithium with tri-n-hexylbromosilane[81].

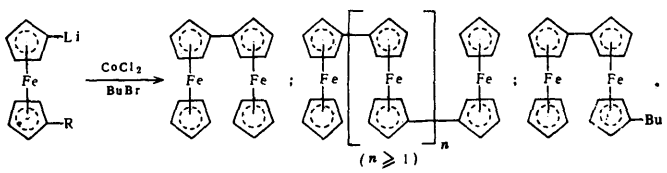
Nesmeyanov et al.[82] found that the action of an ammoniacal solution of silver oxide or of copper sulphate solution on ferrocenylboronic acid yields biferrocenyl together with ferrocene. According to Perevalova and Nesmeyanova[83] and also Rausch[80,84,85] halogenated ferrocenes undergo the Ullmann reaction with copper to give a high yield of biferrocenyl.

Rausch[80] and Nesmeyanov et al.[86] synthesised various derivatives of biferrocenyl. Reaction of a mixture of bromoferrocene and 1,1′-dibromoferrocene with copper at 105–120°C yielded biferrocenyl, 1,1′-terferrocenyl, and higher homologues[86], which were isolated by chromatography on aluminium oxide:



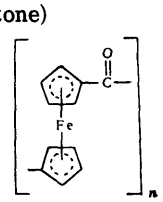
When only 1,1′-dibromoferrocene was used, 1,1′-terferrocenyl was formed in lower yield. The disubstituted terferrocenyl-1,1′-diferrocenyl-3,3′-diferrocenylferrocene was also obtained.

The preparation of a polyferrocenyl directly from ferrocenyl-lithium has been described[87,88]. The latter compound and cobalt chloride react, in the presence or in the absence of n-butyl bromide, to give various polyferrocenyls and butylated polyferrocenyls:

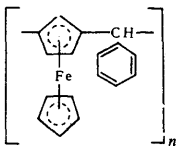


Many polyferrocenyls, butylated polyferrocenyls, and also biferrocenyl, terferrocenyl, and butylated biferrocenyl were isolated.

Pohl [? (Ed. of Translation)] reports the semiconductor properties of several ferrocene-containing polymers[89,90]. The poly(ferrocene ketone)

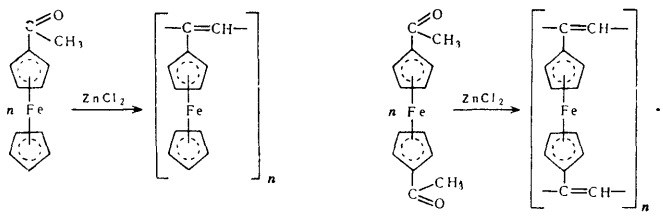


containing ferrocene molecules linked by carbonyl groups, has a conductivity of 10^{-13}–10^{-12} ohm^{-1} cm^{-1}†. The polymer having the highest conductivity is able to rectify a current in the presence of a silver–platinum couple. The polymer obtained by the condensation of ferrocene with benzylidene derivatives



exhibits a conductivity of 10^{-7}–10^{-8} ohm^{-1} cm^{-1}. Several of these polymers are thermoplastic materials.

Conjugated ferrocene-containing polymers possessing semiconductor properties were prepared by Paushkin, Vishnyakova, and their coworkers[31-33] by the polycondensation of acetyl- and 1,1′-diacetyl-ferrocene in the presence of zinc chloride in an autoclave at 200°C. Polyferrocenylvinylenes were obtained in good yields. The bulk of the polymers was insoluble and did not melt up to 500°C, while the benzene-soluble fraction melted at 260–270°C. The synthesis of the polyferrocenylvinylenes can be represented by the scheme



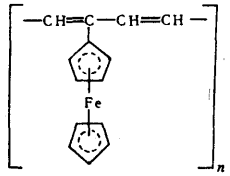
All these polymers exhibit signals in the e.s.r. spectrum and an exponential temperature dependence of the electrical conductivity, which is characteristic of semiconductors. An interesting temperature dependence is shown by the polymer obtained by the polycondensation of 1,1′-diacetylferrocene. Heating this specimen at 10^{-4} mm to 250°C leads to a sharp increase in its conductivity by a factor of 10^{7}, the activation energy being 1.5 eV. Subsequent heating and cooling of the specimen at 10^{-4} mm does not produce any appreciable change in its conductivity. The activation energy in such a process is 0.05 eV, which lies at the limit of accuracy of the measurements.

Polyferrocenylvinylenes, as well as several ferrocene-containing polymers obtained by polyrecombination, have been investigated by means of Mössbauer spectroscopy, which will make it possible to obtain information both on the electronic state of the iron atoms present in the polymers and on the general structure of the polymer[91].

A method has also been elaborated for synthesising polyferrocenylvinylenes from acetyl- and 1,1′-diacetylferrocene and calcium carbide[92]. The explanation is that the calcium carbide, while abstracting water from the acetylferrocene, is hydrolysed by it. The acetylene thus liberated may give polymers containing conjugated double bonds with the starting materials and with the initial products of the reaction.

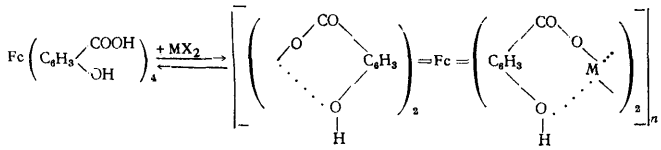
† The Russian original has 10^{-3}–10^{-12} Ω^{-1} cm^{-1} (Ed. of Translation).

The polymer is an infusible black powder, for which elementary analysis indicates the structure



Several papers have been published recently on the synthesis of polymeric chelate compounds and on their thermal stability and specific properties[93,94]. Until a few years ago, however, there was no information on polymeric chelates based on ferrocene or any other non-benzenoid aromatic compounds. Attempts to synthesise such polymers from the corresponding tetraketones of ferrocenes were in vain owing to intramolecular cyclisation[95]. Berlin and Kostroma[96] obtained polymeric chelate compounds of salicylic derivatives of ferrocene, using mainly ferrocenedisalicylic and ferrocenetetrasalicylic acids[95,97], which were treated with methyl acetylacetonates or with solutions of the corresponding salts.

Chelate compounds of ferrocenedisalicylic acid with silver and copper and polychelates of ferrocenetetrasalicylic acid with copper, magnesium, aluminium, beryllium, and tervalent iron were synthesised in yields[64] of 99%, these being almost black powders, insoluble in organic solvents and decomposed by water and alkalis. The tetrasalicylic acid, in contrast to the disalicylic acid, exhibits a strong tendency to polycondensation:



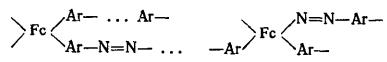
where Fc represents a ferrocene residue.

Examination of the thermal stability of the resulting polymeric chelate compounds of ferrocenetetrasalicylic acid at temperatures from 150° to 300°C showed that the beryllium complexes were the most stable, losing less than 5% of their weight when heated at 200°C for 5 h. The presence of conjugated bonds, ferrocene units, and metal atoms of variable valency in these polymeric chelates is responsible for their specific magnetic and electrical properties. Monomeric ferrocenedisalicylic and ferrocenetetrasalicylic acids are diamagnetic. When the temperature is raised (to 165°C) they acquire paramagnetic properties. The magnitude of the magnetic susceptibility of the polymeric chelate compounds is determined to a considerable extent by the nature of the metal forming part of the ring.

The electrical properties of polymers containing conjugated double bonds can be improved by including in the conjugated chain nitrogen atoms, the lone electrons of which participate in the π-electron system of the conjugated double bonds.

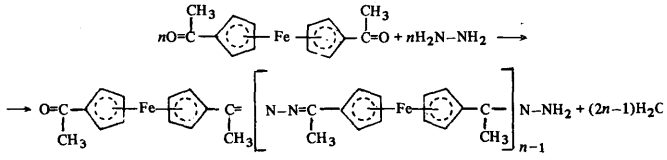
Berlin et al.[98] prepared ferrocene polymers containing nitrogen and a conjugated system by the interaction of ferrocene with biphenyl-4,4′-bisdiazonium and 3,3′-dicarboxybiphenyl-4,4′-bisdiazonium derivatives. From the elementary analysis, infrared spectra, solubility, and viscosity of the resulting polymers these workers considered that

the most probable structure had a parallel arrangement of the biphenyl or biphenyldicarboxylic acid residues:



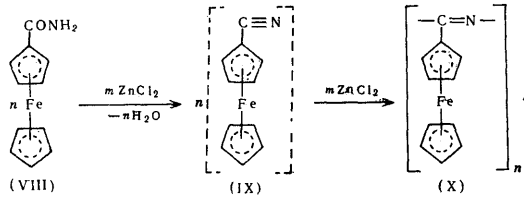
The fractions of the resulting polymers which were insoluble in organic solvents were infusible and thermostable in an inert atmosphere, losing ~ 8% of their weight at 700°C. On the admission of oxygen the polymers ceased to be thermostable. The polyazophenyleneferrocenes obtained give e.s.r. signals and possess static paramagnetism. Their electrical conductivity at room temperature is 10^{-16}–10^{-10} ohm^{-1} cm^{-1}.

The polycondensation of 1,1′-diacetylferrocene with hydrazine yields a ferrocene-containing polyazine, in which nitrogen atoms are linked together directly[99]:

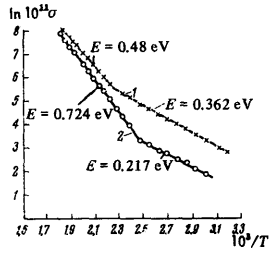


1,1′-Diacetylferrocene has been subjected to polycondensation also with diamines (*p*-phenylenediamine, benzidine, and hexamethylenediamine).[100] Conjugated ferrocene polymers containing nitrogen have been obtained by the polycondensation of ferrocene with hydroxylamine hydrochloride in the presence of zinc chloride[101].

Poly(ferrocenyl cyanide) has been obtained[102] by the polycondensation of ferrocenylformamide in the presence of zinc chloride. The first stage of the reaction involves the formation of ferrocenyl cyanide (IX), this being followed by complex formation and the ordering of its molecules with zinc chloride, and subsequent polymerisation at the C≡N bond leads to the formation of poly(ferrocenyl cyanide) (X):



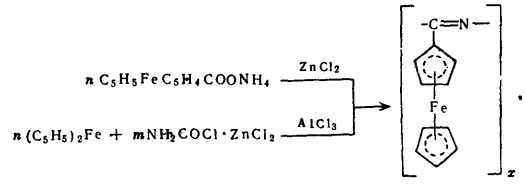
The reaction was carried out, with molar proportions of monomer : catalyst = 1 : 0.2–1, at temperatures of 80–170°C for 1½–5 h.



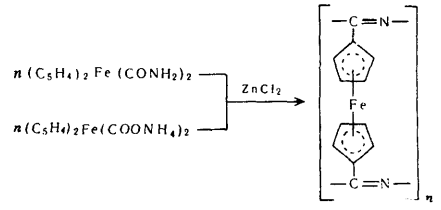
Temperature dependence of electrical conductivity of poly(ferrocenyl cyanide) after: 1) conditioning up to 50°C; 2) conditioning up to 50° and three conditionings up to 300°C.

All the insoluble products remain unmolten up to 500°C, are soluble in dimethylformamide, decompose over the range 420–500°C, and have a molecular weight of 1200. The poly(ferrocenyl cyanide) obtained gives an e.s.r. signal. The number of electrons having unpaired spins is 10^{18} g^{-1}. The temperature dependence of the electrical conductivity is exponential in character (see diagram).

Poly(ferrocenyl cyanide) has since been obtained by the polycondensation of ammonium ferrocenecarboxylate, and also directly from ferrocene and carbamoyl chloride (in the form of its zinc chloride complex)[103]. The infrared spectra and the elementary composition of the polymers were the same as for the poly(ferrocenyl cyanide) synthesised by the polycondensation of ferrocenylformamide. The reaction was conducted in an autoclave under various conditions.



The polycondensation of the diamide and of the diammonium salt of ferrocene-1,1′-dicarboxylic acid in the presence of zinc chloride yields poly(ferrocenylene dicyanide)[103,104]:

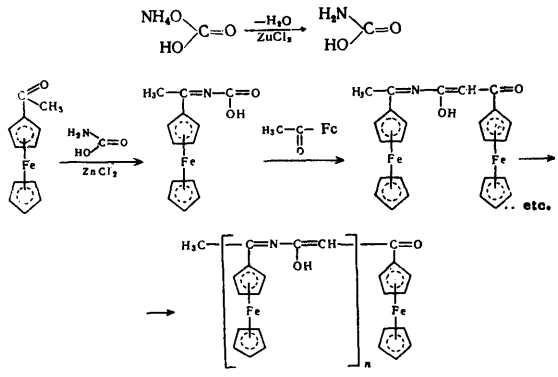


Poly(ferrocenyl cyanides) are dark coloured powders. The insoluble fractions do not melt up to 500°C, and the soluble fractions change colour at 350–500°C. The molecular weight of the soluble fractions determined isopiestically lies between 1200 and 1600. All the polymers give a narrow signal in the e.s.r. spectrum (10^{17}–10^{20} spins g^{-1}). The conductivity of the specimens is 10^{-14}–10^{-8} ohm^{-1} cm^{-1} at 50°C.

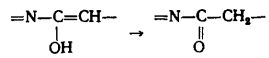
A ferrocene polymer containing nitrogen and a conjugated system has been obtained also by the polycondensation of acetylferrocene with urea in the presence of zinc chloride[105]. It give a single symmetrical signal in the e.s.r. spectrum having an integral intensity of 10^{18} spins g^{-1}, and its conductivity is 4.7×10^{-7} ohm^{-1} cm^{-1}.

An investigation has been made also of the polycondensation of acetylferrocene with ammonium hydrogen carbonate in the presence of zinc chloride, as a result of which novel ferrocene polymers have been obtained containing nitrogen, conjugated double bonds, and hydroxy-groups in the side-chains[106]. The reaction was conducted with various proportions of monomers and catalyst in an autoclave and at atmospheric pressure at 100–300°C for several hours. The yield of reaction products was 28–80% of theoretical.

The initial stage of the process probably involves conversion of the ammonium hydrogen carbonate into carbamic acid, which then reacts with the acetylferrocene:



It is possible also that the polymer chains may be cross-linked by means of the hydroxy-groups with the formation of ether links. The rearrangement



probably does not take place, since analyses show the presence of hydroxy-groups in the polymers.

Conjugated ferrocene polymers containing nitrogen have been obtained also by the polycondensation of ferrocenylformamide with acetaldehyde and butyraldehyde[107]. The reaction was conducted with various proportions of monomers and catalyst (zinc chloride) at 100–350°C for 3–10 h. The resulting polymers were paramagnetic. They give single symmetrical e.s.r. signals having a g-factor of ~ 2, a width of 2.7–5.4 oersteds, and an integral intensity of 10^{16}–10^{18} spins g^{-1}. The conductivity at 50°C is 10^{-10}–10^{-11} ohm^{-1} cm^{-1}.

TABLE 5. Electrical properties of conjugated ferrocene polymers obtained by polycondensation.

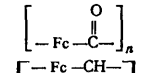
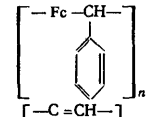
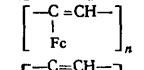
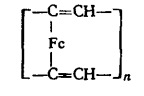
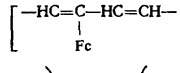
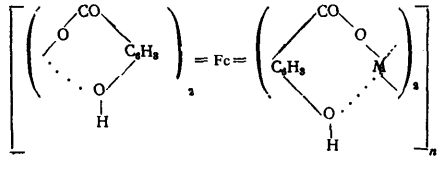
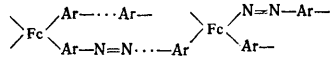
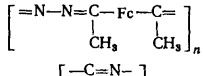
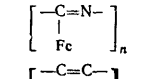
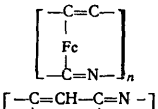
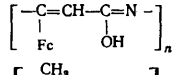
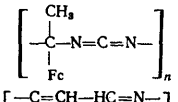
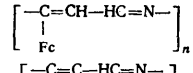
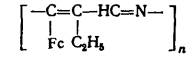
Structure of polymer	Concn. of unpaired electrons, g^{-1}	Conductivity σ_{50}, ohm^{-1} cm^{-1}	Activation energy ΔE, eV
	—	10^{-9}—10^{-13}	—
	—	10^{-7}—10^{-8}	—
	10^{17}	10^{-10}	1.45
	10^{17}	10^{-11}	0.42
	10^{16}	—	—
	signal in e.s.r. spectrum	10^{-8}—10^{-10}	—
	ditto	10^{-10}—10^{-10}	—
	10^{15}	—	1.48—2.78
	10^{17}—10^{19}	10^{-10}—10^{-12}	0.190—0.620
	10^{17}—10^{18}	10^{-11}—10^{-12}	0.115—0.630
	10^{17}	10^{-10}	0.05—0.350
	10^{20}	10^{-8}	0.070—0.455
	10^{18}	10^{-10}	0.047—0.271
	10^{18}	10^{-10}	0.158—0.230

Table 5 gives some electrical properties of the conjugated ferrocene polymers obtained by polycondensation.

5. FIELDS OF APPLICATION FOR POLYMERS CONTAINING FERROCENE

Polymers containing ferrocene are novel, as yet little studied macromolecular compounds. But the possibility of using these polymers for various purposes has already been demonstrated.

Several ferrocene-containing polymers exhibit the properties of electron-exchange resins[9-12], which can be used for the preparation of hydrogen peroxide, the removal of dissolved oxygen from water, the preparation of free iodine, the reduction of noble metals in solutions of their salts, etc.

Various silicon-containing polymers of ferrocene[75] can be used as the chief or secondary components of lubricants, hydraulic liquids, elastomers, plastics, and additives. It is possible also to formulate from them a series of compositions which can be employed as intermediates for the synthesis of resins, elastic materials, and organic metal carriers.

Ferrocene-containing polymers having conjugated double bonds, e.g. poly(ferrocene ketone)[89,90], possess the properties of organic semiconductors.

The possibility has been shown of using conjugated ferrocene polymers[102-107] as inhibitors of the degradation of rubbers by heat and oxidation and of the polymerisation of styrene[108]. Such polymers containing nitrogen are capable of forming complexes with salts of noble metals, which makes possible their use for extracting the latter from solutions.

Conjugated ferrocene polymers are catalysts of semiconductor type for the decomposition of alcohols and the synthesis of ammonia.

Several ferrocene polymers, e.g. products of the polycondensation of ferrocene with aldehydes and ketones[67], can be used as oxidation catalysts.

The diverse fields of application of ferrocene-containing polymers explain the ever increasing interest taken in these compounds, and make it certain that researches on these lines will lead to important practical results.

1. A.N.Nesmeyanov and E.G.Perevalova, Uspekhi Khim., 27, 3 (1958).
2. A.N.Nesmeyanov, Zhur.Vses.Khim.Obshch., 7, 249 (1962).
3. E.Grinsburg (Editor), "Nonbenzenoid Aromatic Compounds" (Translated into Russian), Inostr.Lit., Moscow, 1963, pp.119–142.
4. I.Haiduc, Uspekhi Khim., 30, 1124 (1961) [Russ.Chem.Rev., 498 (1961)].
5. V.V.Korshak, Zhur.Vses.Khim.Obshch., 7, 129 (1962).
6. D.Brown, Angew.Chem., 73, 197 (1961).
7. E.A.Zimakova, "Uspekhi v Oblasti Sinteza Elementoorganicheskikh Polimerov" (Progress in the Synthesis of Organoelementary Polymers), Izd.Nauka, Moscow, 1966, pp.212–223.
8. A.Zelenetskii, Khim.Tekhnol.Polimerov, No.8, 21 (1966).
9. F.S.Arimoto and A.C.Haven, J.Amer.Chem.Soc., 77, 6295 (1955).
10. A.C.Haven, U.S.P. 2821512 (1958).
11. Y.H.Chenn, M.F.Refojo, and H.G.Cassidy, J.Polymer. Sci., 40, 433 (1959).
12. B.Sansoni and O.Sigmund, Angew.Chem., 73, 299 (1961).
13. M.D.Rausch and L.E.Coleman, J.Org.Chem., 23, 107 (1958).
14. L.E.Coleman and M.D.Rausch, J.Polymer Sci., 28, 207 (1958).
15. L.E.Coleman and N.A.Meinhardt, Fortschr.Hochpolym.-Forsch., 1, 172 (1959).
16. S.R.Knox and P.L.Pauson, J.Chem.Soc., 4610 (1961).
17. Ya.M.Paushkin, T.P.Vishnyakova, F.F.Machus, T.A.Sokolinskaya, and I.A.Golubeva, Abstracts of Papers at the International Symposium on Macromolecular Chemistry, Prague, 1965.
18. K.Ban, T.Saecusa, and S.Furukawa, J.Chem.Soc.Japan, Ind.Chem.Sect., 69, 148 (1966); Index Chemicus, 221, No.63287 (1966).
19. V.V.Korshak, S.L.Sosin, T.M.Frunze, and I.I.Tverdokhlebova, Abstracts of Papers at the International Symposium on Macromolecular Chemistry, Brussels, 1967.
20. A.N.Nesmeyanov, V.V.Korshak, V.V.Voevodskii, N.S.Kochetkova, S.L.Sosin, R.B.Materikova, T.N.Bolotnikova, V.M.Chibrikin, and N.M.Bazhin, Dokl.Akad.Nauk SSSR, 137, 1370 (1961).
21. V.V.Korshak, S.L.Sosin, and M.V.Chistyakova, Vysokomol. Soed., 1, 931 (1959).
22. V.V.Korshak, S.L.Sosin, and M.V.Chistyakova, Vysokomol. Soed., 1, 937 (1957).
23. V.V.Korshak, S.L.Sosin, and V.P.Alekseeva, Dokl.Akad. Nauk SSSR, 132, 360 (1960).
24. V.V.Korshak, S.L.Sosin, and V.P.Alekseeva, Vysokomol. Soed., 3, 1332 (1961).
25. V.V.Korshak, S.L.Sosin, and V.P.Alekseeva, "Sbornik Mezhdunarodnogo Simpoziuma po Makromolekulyarnoi Khimii" (Proceedings of an International Symposium on Macromolecular Chemistry), Moscow, 1960, Section 1, pp.141–149.
26. H.Rosenberg and E.W.Neuse, J.Organometallic Chem., 6, 76 (1966).
27. S.L.Sosin, V.V.Korshak, and V.P.Alekseeva, Dokl.Akad. Nauk SSSR, 149, 327 (1963).
28. A.N.Nesmeyanov, A.M.Rubinshtein, G.L.Slonimskii, A.A.Slinkin, N.S.Kochetkova, and R.B.Materikova, Dokl. Akad.Nauk SSSR, 138, 125 (1961).
29. Yu.S.Karimov and I.F.Shchegolev, Dokl.Akad.Nauk SSSR, 146, 1370 (1962).
30. A.A.Dulov, A.A.Slinkin, and A.M.Rubinshtein, Vysokomol. Soed., 5, 1441 (1963).
31. Ya.M.Paushkin, L.S.Polak, T.P.Vishnyakova, I.I.Patalakh, T.A.Sokolinskaya, and F.F.Machus, Dokl.Akad.Nauk SSSR, 149, 856 (1963).
32. Ya.M.Paushkin, L.S.Polak, T.P.Vishnyakova, I.I.Patalakh, F.F.Machus, and T.A.Sokolinskaya, J.Polymer.Sci., C4, 1481 (1964).
33. Ya.M.Paushkin, L.S.Polak, T.P.Vishnyakova, I.I.Patalakh, F.F.Machus, and T.A.Sokolinskaya, Vysokomol.Soed., 6, 545 (1964).
34. T.A.Sokolinskaya, T.P.Vishnyakova, and Ya.M.Paushkin, Vysokomol.Soed., B9, 237 (1967).
35. A.N.Nesmeyanov and N.S.Kochetkova, Dokl.Akad.Nauk SSSR, 126, 307 (1959).
36. A.N.Nesmeyanov and N.S.Kochetkova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 242 (1958).
37. A.N.Nesmeyanov and N.S.Kochetkova, Dokl.Akad.Nauk SSSR, 109, 543 (1956).
38. A.N.Nesmeyanov, N.S.Kochetkova, and R.B.Materikova, Dokl.Akad.Nauk SSSR, 136, 1096 (1961).
39. S.I.Goldberg, J.Amer.Chem.Soc., 84, 3022 (1962).
40. A.N.Nesmeyanov, N.S.Kochetkova, P.V.Petrovskii, and E.I.Fedin, Dokl.Akad.Nauk SSSR, 152, 875 (1963).
41. V.Weinmayr, J.Amer.Chem.Soc., 77, 3009 (1955).
42. S.G.Cottis and H.Rosenberg, J.Polymer Sci., B2, 295 (1964).

43. E.W.Neuse, R.K.Grossland, and K.Koda, J.Org.Chem., 31, 2409 (1966).
44. F.W.Knobloch and W.H.Rauscher, J.Polymer Sci., 54, 651 (1961).
45. P.Petrovitch and H.Valot, Compt.rend., C263, 214 (1966).
46. A.Lüttringhaus and W.Kullick, Makromol.Chem., 44-46, 669 (1961).
47. A.Lüttringhaus and W.Kullick, Angew.Chem., 70, 438 (1958).
48. K.Schlögl and H.Seiler, Monatsh., 91, 78 (1960).
49. A.Wende and H.-J.Lorkowski, Plaste Kautschuk, 10, 32 (1963).
50. H.J.Richards and E.A.Hill, J.Amer.Chem.Soc., 81, 3484 (1959).
51. A.Berger, E.A.Kleinberg, and W.F.McEwen, Chem.and Ind., 204 (1960).
52. K.Schlögl and A.Mohar, Monatsh., 92, 219 (1961).
53. E.W.Neuse and D.S.Trifan, J.Amer.Chem.Soc., 85, 1952 (1963).
54. E.W.Neuse and E.Quo, Bull.Chem.Soc.Japan, 38, 931 (1965).
55. A.N.Nesmeyanov and I.I.Kritskaya, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 253 (1956).
56. H.Valot, Compt.rend., 258, 5870 (1964).
57. P.J.Graham, U.S.P. 2 709 175 (1955).
58. V.Weinmayr, U.S.P. 2 694 721 (1954).
59. T.A.Sokolinskaya, T.P.Vishnyakova, and Ya.M.Paushkin, "Tematicheskie i Analiticheskie Obzory, TsNIITEneftekhim, Poluprovodnikovye Polimery s Sopryazhennymi Svyazyami" (Thematic and Analytic Reviews, Central Scientific Research Institute for Technical Information and Economics of Petroleum Chemistry, Semiconductor Polymers having Conjugated Bonds), 1966, p.84.
60. E.W.Neuse and K.Trifan, J.Amer.Chem.Soc., 85, 1952 (1963) [This is identical with Ref.53 (Ed. of Translation)].
61. E.W.Neuse, Nature, 204, 178 (1964).
62. E.W.Neuse, K.Koda, and E.Carter, Makromol.Chem., 84, 213 (1965).
63. E.W.Neuse and E.Quo, Bull.Chem.Soc.Japan, 39, 1508 (1966).
64. E.W.Neuse and K.Koda, J.Organometallic Chem., 4, 475 (1965).
65. E.W.Neuse and K.Koda, J.Polymer Sci., [A-1], 4, 2145 (1966).
66. V.N.Kotrelev, S.P.Kalinina, and T.I.Kuznetsov, Plast. Massy, No.3, 24 (1961),
67. T.P.Sokolinskaya, T.P.Vishnyakova, Ya.M.Paushkin, and Ya.A.Popova, Vysokomol.Soed., B9, 677 (1967).
68. A.N.Nesmeyanov, E.G.Perepalova, L.P.Yur'eva, and L.I.Denisovich, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 2241 (1962).
69. E.W.Neuse and E.Quo, Nature, 205, 494 (1965).
70. E.W.Neuse and E.Quo, J.Polymer Sci., A3, 1499 (1965).
71. E.W.Neuse and K.Koda, Bull.Chem.Soc.Japan, 39, 1502 (1966).
72. R.A.Benkeser, U.S.P. 2 831 880 (1958).
73. R.L.Schaaf, C.T.Lenk, and H.Rosenblum, U.S.P. 3 010 982 (1961).
74. R.L.Schaaf, U.S.P. 3 036 105 (1962).
75. H.Rosenblum and M.D.Rausch, U.S.P. 3 060 215 (1962).
76. G.Greber and M.L.Hallensleber, Makromol.Chem., 83, 148 (1965).
77. G.P.Sollott and W.P.Peterson, J.Org.Chem., 30, 389 (1965).
78. M.D.Rausch, J.Org.Chem., 28, 3337 (1963).
79. O.A.Nesmeyanova and E.G.Perevalova, Dokl.Akad.Nauk SSSR, 126, 1007 (1959).
80. M.D.Rausch, J.Amer.Chem.Soc., 82, 2080 (1960).
81. S.I.Goldberg and D.W.Mayo, Chem.and Ind., 671 (1959).
82. A.N.Nesmeyanov, V.A.Sazonova, and V.N.Drozd, Dokl. Akad.Nauk SSSR, 126, 1007 (1959).
83. E.G.Perevalova and O.A.Nesmeyanova, Dokl.Akad.Nauk SSSR, 132, 1093 (1960).
84. M.D.Rausch, U.S.P. 3 010 981 (1961).
85. M.D.Rausch, J.Org.Chem., 26, 1802 (1961).
86. A.N.Nesmeyanov, V.N.Drozd, V.A.Sazonova, V.I.Romanenok, A.K.Prokof'ev, and L.A.Nikonova, Izv.Akad.Nauk SSSR, Otd.Khim.Nauk, 667 (1963).
87. K.Hata, I.Motoyama, and H.Watanabe, Bull.Chem.Soc. Japan, 37, 1719 (1964).
88. H.Watanabe, I.Motoyama, and K.Hata, Bull.Chem.Soc. Japan, 39, 790 (1966).
89. Pohl, Khim.Tekhnol.Polimerov, No.9, 22 (1963).
90. G.F.Dvorko (Editor), "Organicheskie Poluprovodniki" (Organic Semiconductors), Izd.Mir, Moscow, 1965, p.170.
91. V.F.Belov, T.P.Vishnyakova, V.I.Gol'danskii, E.F.Makarov, Ya.M.Paushkin, T.A.Sokolinskaya, R.A.Stukan, and V.A.Trukhtanov, Dokl.Akad.Nauk SSSR, 159, 831 (1964).
92. Ya.M.Paushkin, B.V.Bocharov, A.P.Smirnov, T.P.Vishnyakova, F.F.Machus, and I.S.Panidi, Plast.Massy, No.9, 3 (1964).
93. A.A.Berlin and N.G.Matveeva, Uspekhi Khim., 29, 277 (1960) [Russ.Chem.Rev., 119 (1960)].
94. V.V.Rode, E.G.Rukhadze, and A.P.Terent'ev, Uspekhi Khim., 32, 1488 (1963) [Russ.Chem.Rev., 666 (1963)].
95. S.G.Tripathi and S.Prakush, J.Indian Chem.Soc., 35, 445 (1958).
96. A.A.Berlin and T.V.Kostroma, Vysokomol.Soed., Geterotspnye Vysokomol.Soed., 53 (1964).
97. A.A.Berlin and T.V.Kostroma, USSR P. 129 018 (1959).
98. A.A.Berlin, B.I.Liogon'kii, and V.P.Parini, Vysokomol. Soed., 5, 330 (1963).
99. Yu.V.Korshak, Candidate's Thesis, Topchiev Institute of Petroleum Chemical Synthesis of the USSR Academy of Sciences, 1964.
100. I.A.Golubeva, Candidate's Thesis, Gubkin Moscow Institute of the Petroleum Chemical and Gas Industry, 1966.
101. P.M.Belash, Ya.M.Paushkin, V.F.Belov, et al., Neftekhimiya, Trudy Moskov.Inst.Neftekhim.Gaz.Prom., No.51, 48 (1964).
102. T.P.Vishnyakova, I.A.Golubeva, and Ya.M.Paushkin, Vysokomol.Soed., 7, 713 (1965).
103. T.P.Vishnyakova, I.A.Golubeva, and Ya.M.Paushkin, Vysokomol.Soed., 8, 181 (1966).
104. I.A.Golubeva and T.P.Vishnyakova, "Neftekhimiya i Pererabotka Nefti i Gaza" (Petroleum Chemistry and the Processing of Petroleum with Gas), "Tematicheskie i Analiticheskie Obzory, TsNIITEneftekhim" (Thematic and Analytic Reviews), Central Scientific Research Institute for Technical Information and the Economics of Petroleum Chemistry, 1966, p.36.
105. I.A.Golubeva and T.P.Vishnyakova, Plast.Massy, No.12, 10 (1965).
106. I.A.Golubeva and T.P.Vishnyakova, in Collected Papers, "Polimery s Poluprovodnikovymi Svoistvami" (Polymers having Semiconductor Properties), Central Scientific Research Institute for Technical Information and the Economics of Petroleum Chemistry, Moscow, 1966, p.87.
107. T.P.Vishnyakova, I.A.Golubeva, and R.P.Shabashova, Vysokomol.Soed., A9, 144 (1967).
108. Ya.M.Paushkin, T.P.Vishnyakova, A.F.Lunin, I.A.Golubeva, and A.G.Liakumovich, Prom.Sintet.Kauchuka, No.2, 16 (1966).

Gubkin Institute of the Petroleum
Chemical and Gas Industry, Moscow