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METALLOCENE MONOMERS AND POLYMERS. FERROCENYL AND FERROCENYLENE DERIVATIVES

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Summary

The synthesis and study of some polyenes, polyiminoimides and Schiff polybases with ferrocene obtained by either polymerization or polycondensation are reported.

The following monomers were used: ethynylferrocene, 1-chloro-1′-ethynylferrocene, α-chloro-β-formyl-*p*-ferrocenylstyrene, *p*-ferrocenylphenylacetylene, *p*-ferrocenylacetophenone, 1,1′-diacetylferrocene and 1,1′-bis[β-(2-furyl)acryloyl]ferrocene which were characterized by spectral and thermodifferential analyses and Hückel MO calculations. The polymerization was performed in the presence of benzoyl and lauroyl peroxides, triisopropylboron and complex catalysts of $[P(C_6H_5)_3]_2NiX_2$ type. The ferrocene derivatives were polycondensed with biuret, 4,4′-diaminodiphenyl ether, 4,4′-diaminodiphenyl thioether, 4,4′-diamino-2,2′-dinitrodiphenyl disulphide in the presence of metallic salts and *p*-toluene sulphonic acid as catalysts.

Polymers with either linear or tridimensional structure showing good thermal stability and semiconducting properties have been obtained. Some polymers show catalytical activity in the polymerization of chloroformylated vinylic derivatives.

Among the polymers of metallocenes, especial attention is paid to those of ferrocene and its derivatives, due on the one hand to the ready availability of monomers and on the other to the particular properties of the ferrocenic system: stability toward air, oxygen, acids and alkalies, thermal stability and propensity to electrophylic substitution reactions. Homo and heterochain polymers containing ferrocene units either in the backbone or as a substituent show special electric and magnetic properties. They have been studied as accelerators in redox systems, as catalysts for polymerization and dehydration reactions, as thermo- and photo-sensitizers, etc. Ferrocene-containing polymers have been

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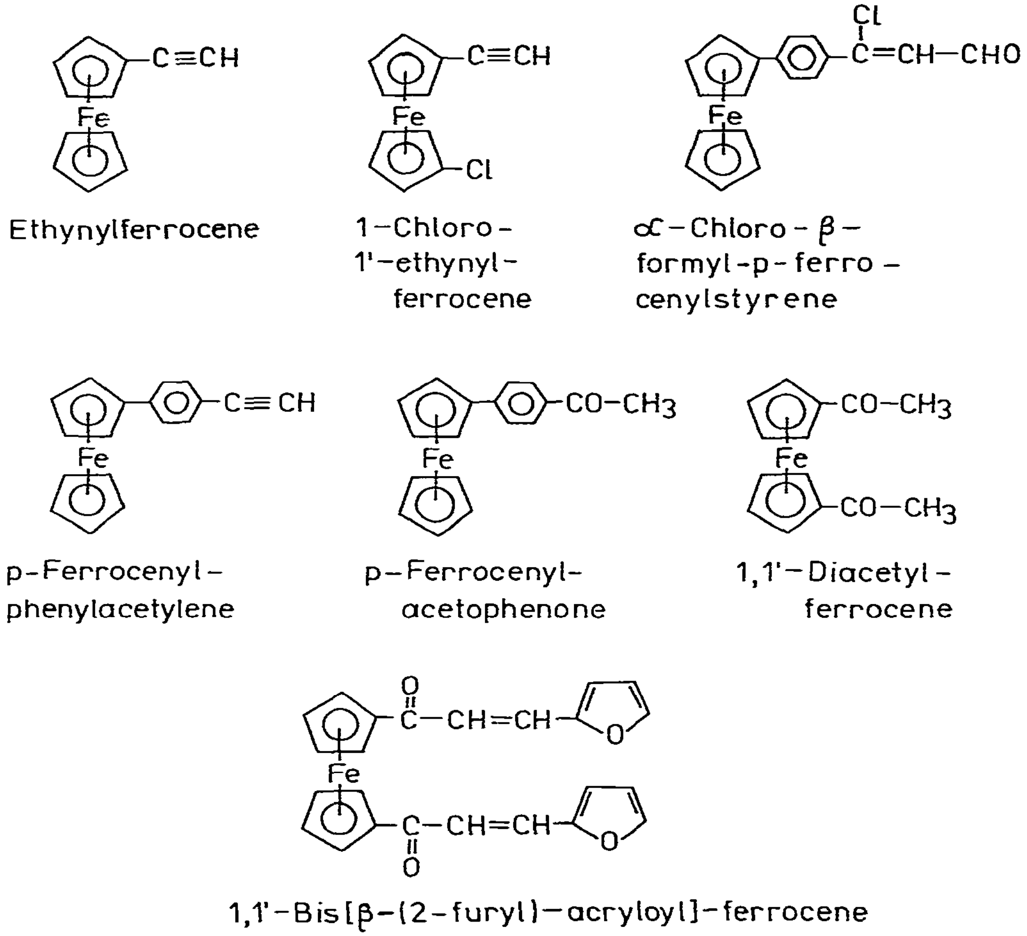


Fig. 1. Ferrocene derivatives as monomers in polymerization and polycondensation reactions.

synthesized by almost all the classical reactions of macromolecular chemistry: polymerization, polycondensation, polyaddition, polyrecombination as well as some special methods.

The present paper contains some results on the synthesis and characterization of polyenes, polyiminoimides and Schiff polybases of particular characteristics, obtained by polymerization and polycondensation of certain substituted ferrocene derivatives, i.e. ethynylferrocene, 1-chloro-1'-ethynylferrocene, α-chloro-β-formyl-p-ferrocenylstyrene, p-ferrocenylacetylene, p-ferrocenylacetophenone, 1,1'-diacetylferrocene and 1,1'-bis[β-(2-furyl)acryloyl]ferrocene.

Results and discussion

1. *Synthesis and characterization of monomers*

Ethynylferrocene was obtained according to Rosenblum's method [1] from acetylferrocene [2—5] with Vilsmeier's complex, via α-chloro-β-formyl-vinylferrocene, which in alkaline medium gives ferrocenylacetylene, as in Fig. 2.

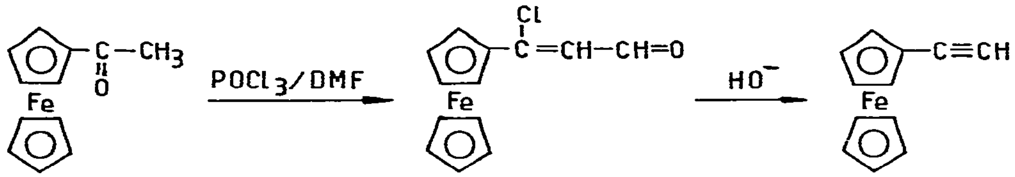


Fig. 2. Synthesis of ethynylferrocene.

Taking into account the possible influence of substituents of the ferrocene rings on the polymerization reaction of ferrocenylacetylene the following new derivatives have been synthesized in the same manner: 1-chloro-1′-ethynylferrocene [6], α-chloro-β-formyl-*p*-ferrocenylstyrene [7] and *p*-ferrocenylphenylacetylene [8].

p-Ferrocenylacetophenone used in the synthesis of poly-*p*-ferrocenylphenylacetylene was obtained from *p*-aminoacetophenone and ferrocene, according to Nesmeyanov's method for the preparation of *p*-tolylferrocene [9]. 1,1′-Diacetylferrocene was synthesized by the Friedel-Crafts acylation of ferrocene [10—12]. 1,1′-Bis[β-(2-furyl)acryloyl]ferrocene was obtained by condensation of diacetylferrocene with furfurol [13,14].

The monomers were characterized by IR and NMR spectroscopy and elemental and thermodifferential analyses. Spectral characteristics of the monomers are given in Table 1. Their reactivity was estimated by means of some molecular characteristics (i.e. change distribution, free valence indices, resonance energy and bond order) determined by M.O. calculations (Hückel approximation).

The molecular characteristics of the ferrocene-containg monomers are presented in comparison with those of other acetylenic and vinylic monomers in Table 2. The resonance energy and free valence indices attest that ethynylferrocene is more reactive than phenylacetylene or *p*-ferrocenylphenylacetylene, due to the strong electron-donating effect of the ferrocenyl group. It may be remarked that the presence of chlorine increases the stability of the halogenated monomer, as compared to that of ethynylferrocene. Taking into account the same indices for *p*-ferrocenylacetophenone [18] and acetophenone, one can note a decrease of reactivity for the former due to the electron-donor effect of the ferrocenyl group. By the same method the reactivity of α-chloro-β-formyl-*p*-ferrocenylstyrene by comparison with other chloroformilated vinylic monomers was also established.

The values of the resonance energy and the free valence indices for the olefinic carbon atoms indicate a decrease of reactivity in the following order: α-chloro-β-formylvinylferrocene > α-chloro-β-formyl-*p*-ferrocenylstyrene > α-chloro-β-formyl-*p*-bromostyrene > α-chloro-β-formylstyrene > α-chloro-β-formyl-*p*-nitrostyrene > α-chloro-β-formyl-*p*-chlorostyrene. These data are in good agreement with results obtained in the thermal polymerization of vinyl monomers [7,19,20]. The reactivity of these monomers was also estimated from the values of copolymerization parameters obtained by copolymerization of ferrocenylacetylene and *p*-ferrocenylphenylacetylene with phenylacetylene [8] and α-chloro-β-formyl-vinylferrocene and α-chloro-β-formylstyrene with

TABLE 1

SPECTRAL CHARACTERISTICS OF MONOMERS

No.	Monomer	IR		NMR		Ref.
		Type of vibration	(cm^{-1})	H$^+$ from	δ (ppm)	
1	Ethynylferrocene	ν(C=C)	2100	C_5H_4	4.48	16
		ν(≡C—H)	3280			
		ferrocenyl group	815, 1105, 1185, 1405			
2	1-Chloro-1′-ethynyl ferrocene	ν(C≡C)	2120			6
		ν(≡C—H)	3320			
3	α-Chloro-β-formyl-*p*-ferrocenylstyrene	ν(C=C)	1600	C_6H_4	7.48; 7.19	7
		ν(C=O)	1680	C=C	6.65	
		Cl	720	C_5H_4	4.50	
		ferrocenyl group	830, 1130 1190	C=O	10.30	
4	*p*-Ferrocenylphenyl-acetylene	ν(C=C)	1610			8
		ν(C≡C)	2115			
		ν(≡C—H)	3300			
		ferrocenyl group	840, 890, 1110, 1415			
5	*p*-Ferrocenylacetophenone	ν(C=O)	1685	C_5H_4	4—5	
		aromatic ring	1067	C_6H_4	7.95	
				CH_3	2.7	
		ferrocenyl group	840, 1020, 1100		7.55	
6	1,1′-Bis[β-(2-furyl)-acryloyl]ferrocene	ferrocenyl group	830—855,	C_5H_4	4.92	13, 14
			1090, 1190		4.50	
			1380, 1450	furyl	6.63	
			1545		6.42	
					7.35	
		furyl group	680, 735—745	C=C	7.45	
					6.87	
			1010—1030			
			1240—1290			
		ν(C=C)	1590			
		ν(C=O)	1650			

TABLE 2

MOLECULAR CHARACTERISTICS OF THE MONOMERS

No.	Monomer	Total energy (β)	Resonance energy (β)	F_{mean} [a]	p [a]	Ref.
1	Phenylacetylene	—	2.4242	0.6176	0.9334	15
2	Ethynylferrocene	31.1949	1.6519	0.6323	0.8791	16
3	*p*-Chlorophenylacetylene	—	—	—	0.9318	15
4	1-Chloro-1′-ethynylferrocene	37.0054	4.0054	0.6251	0.9222	17
5	*p*-Ferrocenylphenylacetylene	40.3257	4.3257	0.6232	0.9339	8
6	Acetophenone	11.7780	3.7780	1.4630	0.6533	18
7	*p*-Ferrocenylacetophenone	40.7600	14.7600	—	—	18
8	α-Chloro-β-formylstyrene	19.5636	9.5636	0.3977	0.7941	7
9	α-Chloro-β-formyl-*p*-chlorostyrene	24.6642	12.1642	0.3968	0.7911	19
10	α-Chloro-β-formyl-*p*-bromostyrene	24.3663	9.4663	0.4477	0.7940	19
11	α-Chloro-β-formyl-*p*-methylstyrene	23.5436	12.2436	0.3944	0.7850	20
12	α-Chloro-β-formyl-*p*-nitrostyrene	24.7919	10.7919	0.4125	0.7903	20
13	α-Chloro-β-formylvinylferrocene	40.1824	5.1824	0.3936	0.7498	7
14	α-Chloro-β-formyl-*p*-ferrocenylstyrene	48.5490	7.5490	0.3985	0.7828	7

[a] F = free valence index, p = π-electronic bond order.

styrene, α-chloro-β-formyl-*p*-chlorostyrene and α-chloro-β-formyl-*p*-bromostyrene [7].

2. *Synthesis of polymers*

2.1. *Polymerization*

Polymerization and copolymerization of ferrocenylacetylene and related monomers have been scarcely studied, and only in the last ten years. The first attempts to polymerize thermally or catalytically ferrocenylacetylene were made by Rosenblum [21] and Schlögl [22,23] and were unsuccessful. The only product obtained by these authors was the cyclic trimer. We synthesized polyferrocenylacetylene by polymerization of ferrocenylacetylene and its derivative in the presence of benzoyl or lauroyl peroxide, triisopropylboron and a complex catalyst of $[P(C_6H_5)_3]_2NiX_2$ type [24,25]. Concomitantly, polymerization of this monomer and separation of the cyclic trimer were reported by Korshak et al. [26,27] and Nakashima et al. [28]. Pittman accomplished the polymerization of ferrocenylacetylene in the presence of AIBN and $RbCl_2$ [29]. Ferrocenylacetylene was readily copolymerized with phenylacetylene [30], isobutene [31] and isoprene [32].

The comparative values for radical polymerization of ethynylferrocene and 1-chloro-1′-ethynylferrocene are presented in Table 3.

TABLE 3

RADICAL POLYMERIZATION OF ETHYNYL- AND 1-CHLORO-1'-ETHYNYL-FERROCENE

No.	Monomer	Initiator	Initiator concn. (%)	Temp., (°C)	Conversion, (%)	$\overline{P}$	Ref.
1	EFc	PB	1.00	140	14.83 [a]		24
2	EFc	PB	1.00	190	91.67 [b]	4 [a]	24
3	EFc	PL	1.00	170	40.20 [b]		25
4	EFc	PB	1.00	230	94.15 [b]		24
5	EFc	PL	1.00	200	76.70		25
6	EFc	$B(i\text{-}C_3H_7)_3$	5.32	190	25.87 [a]	7	25
7	EFc	$B(i\text{—}C_3H_7)_3$	2.72	230	29.46 [a]	13	25
8	Cl-EFc	PB	1.00	140	11.46 [a]	6	17
9	Cl-EFc	PB	1.00	190	41.50 [b]		17

[a] Amount of benzene-soluble polymer. [b] Amount of benzene-insoluble polymer. EFc = ethynylferrocene, Cl-EFc = 1-chloro-1'-ethynylferrocene, PB = benzoyl peroxide, PL = lauroyl peroxide, $\overline{P}$ = average degree of polymerization of the benzene-soluble fraction.

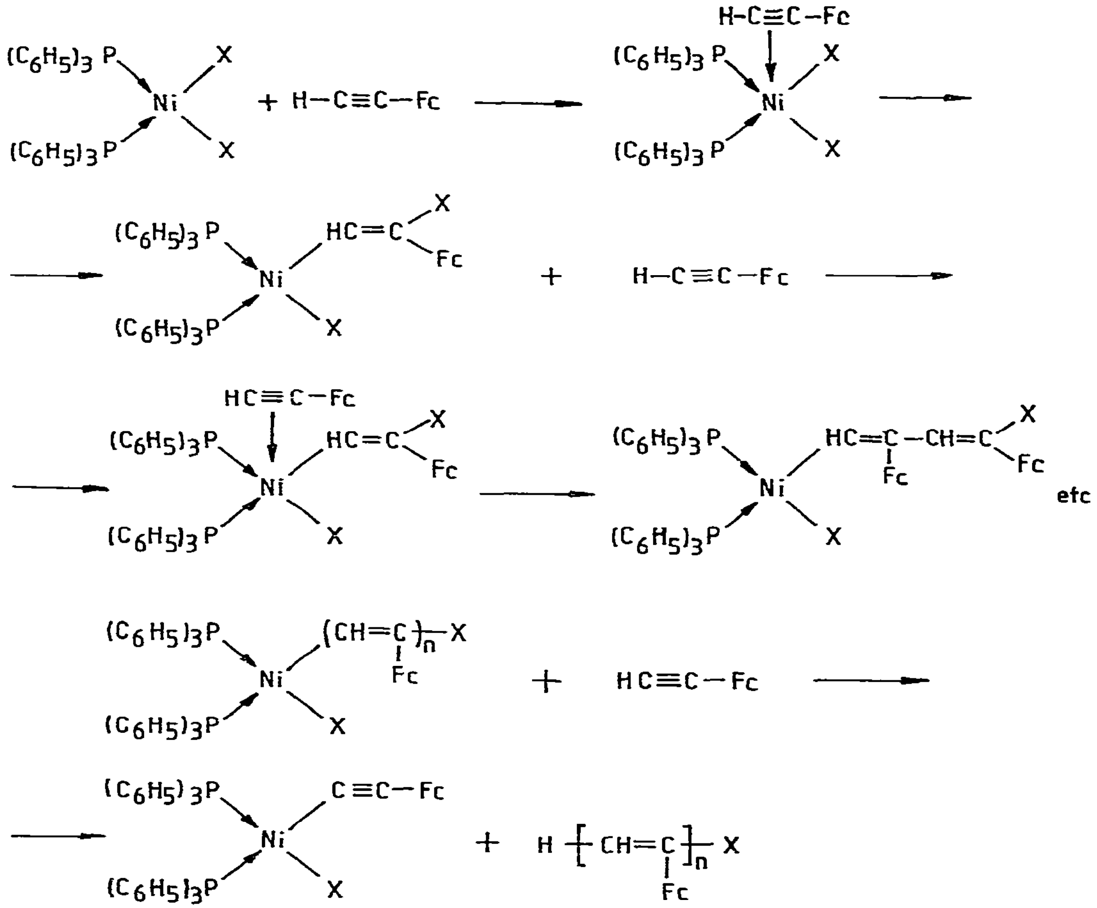


Fig. 3. Polymerization mechanism of ferrocenylacetylene with $[P(C_6H_5)_3]_2 \cdot NiX_2$.

By polymerization at 140, 190 and even at 230°C (the initiator is triisopropylboron), both benzene-soluble and insoluble fractions were obtained, while at higher reaction temperatures, only insoluble and infusible (up to 350°C) compounds were formed. High temperatures promote thus the formation of polymers with a threedimensional structure. The conversions increase with the reaction temperature and initiator concentration. The lower conversion observed in case of 1-chloro-1'-ethynylferrocene attests the fact that the halogen atom decreases the monomer reactivity, in accordance with the results obtained by MO calculations. The polymerization degree (cryoscopic method) of soluble fractions ranged between 4 and 13.

The polymerization is a first order reaction with activation energy $E = 41.8$ kJ/mol, much smaller than that found by Barkalov for the polymerization of phenylacetylene with the same initiator (88.0 kJ/mol) [33]. This relatively low value of activation energy demonstrates the influence of the electron-donating ferrocenyl group on the reactivity of the triple bond in polymerization reaction.

Polymerization of ferrocenylacetylene in the presence of the $[P(C_6H_5)_3]_2 \cdot NiX_2$ (X = Cl or Br) catalytic system was carried out in benzene solution under inert atmosphere. The yields were good (50% and higher) but the products were insoluble. The assumed reaction mechanism is similar to that suggested by Daniels [34] and Furlani [35] for polymerization of acetylene and phenylacetylene.

We tried to anchor the ferrocenyl group to polyphenylacetylene not by chemical reactions used in the synthesis of poly-*p*-ferrocenylstyrene by Sansoni and Sigmund [36], but by polymerization of *p*-ferrocenylphenylacetylene or polycondensation of *p*-ferrocenylacetophenone.

p-Ferrocenylphenylacetylene was polymerized in the same way as ferrocenylacetylene. The increase of the conversion with the temperature was noticed in this case also. Thermal polymerization at 200°C gave a higher conversion than that obtained in the presence of initiators at the same temperature. One may conclude that initiators favor soluble oligomers; in their absence the cyclic trimer is mainly formed as in the thermal polymerization of ferrocenylacetylene [23].

TABLE 4

COMPARATIVE DATA FOR THE THERMAL POLYMERIZATION OF α-CHLORO-β-FORMYL-*p*-X-STYRENE

No.	X	Temperature (°C)								Ref.
		180		200		230		300		
		Conv. (%)	M.p. (°)	Conv. (%)	M.p. (°)	Conv. (%)	M.p. (°)	Conv. (%)	M.p. (°)	
1	Br	35.08	230	43.79	250	43.98	266	51.72	294	19
2	Cl	6.98	204	8.03	218	18.10	195	35.82	249	19
3	CH_3	18.50	256	27.80	210	31.80	256	44.50		20
4	NO_2	68.30	185	79.00	>350	76.40	>350	59.60	>350	20
5	Fc	94.70	>350	95.00	>350	95.20	>350	91.80	>350	7

Fc = ferrocenyl.

The thermal polymerization of α-chloro-β-formyl-*p*-ferrocenylstyrene led to insoluble and infusible (up to 350°C) products which proved to be copolymers containing the *p*-ferrocenylphenylacetylenic group [7].

Table 4 presents comparative data for the thermal polymerization of some *p*-substituted chloroformylated vinylic derivatives.

The high conversions obtained in the polymerization of α-chloro-β-formyl-*p*-ferrocenylstyrene, irrespective of temperature, attest the high reactivity of this monomer, as resulted from Hückel MO calculations.

2.2. *Polycondensation*

A. Polyferrocenylacetylenes. Although polycondensation reactions yield, generally regular polymers, the homo- or hetero-polycondensation of acetyl- and diacetylferrocene is rather less studied due to the multiple reaction pathways for these compounds. Starting from ferrocene-containing monomers, polyenes [28,29,37—40], polycyclotrimers [22,23], polyazines [41,42] and Schiff polybases [42] have been synthesized.

We synthesized poly-*p*-ferrocenylphenylacetylenes by *p*-ferrocenylacetophenone polycondensation in the presence of metallic halides, using a molar ratio ketone/catalyst 1/0.1 for a period of 9 hours. The study of the catalytic effect upon the conversion for ten metallic halides showed a decrease of the catalytic power in the following order: $HgCl_2 \geqslant SnCl_2 \geqslant AlCl_3 > FeCl_3 > CuCl_2 \geqslant MgCl_2 > CoCl_2 \geqslant NiCl_2 > ZnCl_2 > CdCl_2$. The metallic salt increases, on the one hand, the reactivity and, on the other, labilizes the hydrogen atom from the α position through intermediate formation of coordination complexes [43,44].

B. Polyferrocenyleniminoimides. Polyferrocenyleniminoimides (PFcImImd) were obtained by the polycondensation of diacetylferrocene and 1,1′-bis[β-(2-furyl)-acryloyl]ferrocene with biuret. The reaction was carried out in dioxane or DMSO under argon in the presence of anhydrous $ZnCl_2$ as a dehydrating agent or in glacial acetic acid, which acted both as solvent and dehydrating agent. Products soluble and insoluble in the reaction medium were obtained. The reaction conditions are listed in Table 5.

The polycondensation is affected by the solvent polarity, catalyst nature,

TABLE 5

POLYCONDENSATION OF DiAcFc AND DiAcFcF WITH BIURET [a]

No.	Dicarbonilic component	Reaction temperature (°C)	Solvent	Conversion (%)		
				Soluble	Insoluble	Total
1	DiAcFc	140	CH_3COOH	—	8.1	8.1
2	DiAcFcF	140	CH_3COOH	—	77.9	77.9
3	DiAcFc	120	Dioxan	—	24.3	24.3
4	DiAcFcF	120	Dioxan	52.4	26.0	78.4
5	DiAcFc	120	DMSO	—	78.8	78.8
6	DiAcFc	90	DMSO	39.4	2.7	42.1
7	DiAcFcF	90	DMSO	70.3	8.3	78.6

[a] DiAcFc = 1,1′-diacetylferrocene, DiAcFcF = 1,1′-bis[β-(2-furyl)acryloyl]ferrocene, Dicarbonylic component/biuret mole ratio = 1/1. Reaction duration 20 hours.

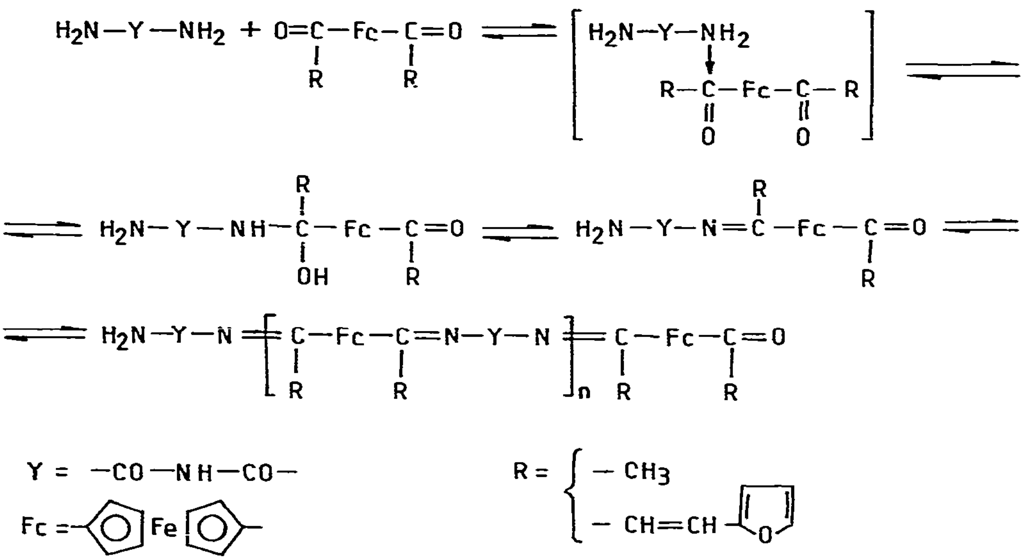
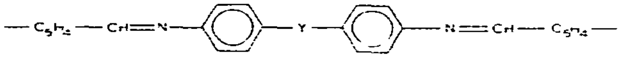


Fig. 4. The polycondensation reaction mechanism.

temperature and reactivity of dicarbonylic component. Higher conversions were obtained in DMSO than in dioxane, due to the increased polarity of the former solvent. $ZnCl_2$, which besides the dehydrating action has also an activating role for the $>$C=O group [44], proved to be a more efficient catalyst than acetic acid which protonates the $-NH_2$ group, diminishing thus its nucleophilicity. The temperature promotes the formation of insoluble products of three-dimensional structures. 1,1′-Bis[β-(2-furyl)-acryloyl]ferrocene, being more reactive than diacetylferrocene, gives a larger amount of oligomers which are soluble in the reaction medium. The polycondensation presumably involves a nucleophilic addition-elimination step [45] (Fig. 4.).

C. Polyazomethines. Starting from the scarcely cited data in the literature referring to ferrocene-containing polyazines [41,42,46,47] and polyazomethines [42,48—50] and from the fact that the ferrocene does not transmit the resonance effect through the central iron atom (the extension of the conjugation being limited to the length of the system



[51] the polycondensations of DiAcFc and DiAcFcF were performed with aromatic diamines of benzidine type, where Y is either absent or is an oxygen, sulphur or disulphydic bridge. The influence of Y on the yield and the polymer properties was also investigated.

The polycondensation was carried out either in solvent (dioxane) or in melt under nitrogen. $ZnCl_2$ or p-toluene sulphonic acid was used as dehydrating agents. Reaction conditions and some characteristics of the obtained products are presented in Table 6. In the melt only an insoluble material was formed. The long reaction time and the high temperature favour the formation of three-

TABLE 6

POLYCONDENSATION OF DiAcFc AND DiAcFcF WITH AROMATIC DIAMINES. DICARBONYLIC COMPONENT/DIAMINIC COMPONENT MOLE RATIO 1/1; CATALYST $ZnCl_2$ [a]

No.	Type of polymer	Reaction conditions		Conversion (%)		
		Temp. (°C)	Time (h)	Soluble	Insoluble	Total
1	A_1	120	20	17.40	15.20	32.60
2	A_1 [b]	150	21	—	52.60	52.60
3	A_2 [b]	150	21	—	88.00	88.00
4	B_1	120	10	6.38	50.21	56.59
5	B_1 [c]	120	10	14.80	4.60	19.40
6	B_2	120	10	14.50	18.10	32.60
7	C_1	120	10	14.50	9.16	23.66
8	D_1	120	10	13.70	24.50	38.20
9	D_1 [c]	120	10	4.08	41.60	45.68
10	D_1 [d]	120	10	2.60	23.70	26.30
11	D_1	120	20	—	41.60	41.60
12	D_1	120	35	—	68.80	68.80
13	D_1 [b]	150	23	—	90.16	90.16
14	D_2	120	10	22.21	48.80	71.01
15	D_2	120	20	—	69.10	69.10
16	D_2	120	35	—	85.30	85.30
17	D_2 [b]	200	20	—	51.00	51.00

[a] A_1 = DiAcFc + benzidine, A_2 = DiAcFcF + benzidine, B_1 = DiAcFc + 4,4′-diaminophenylether, B_2 = DiAcFcF + 4,4′-diaminodiphenylether, C_1 = DiAcFc + 4,4′-diaminodiphenylsulphide, D_1 = DiAcFc + 4,4′-diamino-2,2′-dinitrodiphenyldisulphide, D_2 = DiAcFcF + 4,4′-diamino-2,2′-dinitrodiphenyldisulphide. [b] Reaction in melt. [c] *p*-Toluenesulphonic acid as catalyst. [d] Dicarbonylic component/diaminic component mole ratio 1/2.

dimensional insoluble compounds. DiAcFcF is more reactive than DiAcFc, and yields a larger amount of oligomers which are soluble in the reaction medium. The excess of the diaminic component influence neither the conversion nor the properties of the polymers.

3. *Molecular structure of polymers*

The molecular structures of polymers was elucidated based on the IR measurements and elemental analysis data.

Benzene-soluble polyferrocenylacetylenes have linear structures (I, II) while the insoluble ones have three-dimensional structures (III, IV) (Fig. 5). The three-dimensional structure may be correlated with the broadening of IR bands in the case of insoluble polymers as compared with the IR spectra of soluble ones.

For poly-*p*-ferrocenylacetylenes obtained by polymerization and for the copolymers obtained by the thermal polymerization of α-chloro-β-formyl-*p*-ferrocenylstyrene the three-dimensional structures V and VI were assumed. These structures may be formed either by the cleavage of some double bonds from the main chain or by the insertion of some ferrocene groups (Fig. 6). The structure VI is also confirmed by the fact that the reaction is accompanied by monomer (polymer) dehydrohalogenation or dehaloformylation. Type VI copolymers were also obtained by Paushkin [53] and Korshak [54] by polymerization of α-chloro-β-formylvinylferrocene.

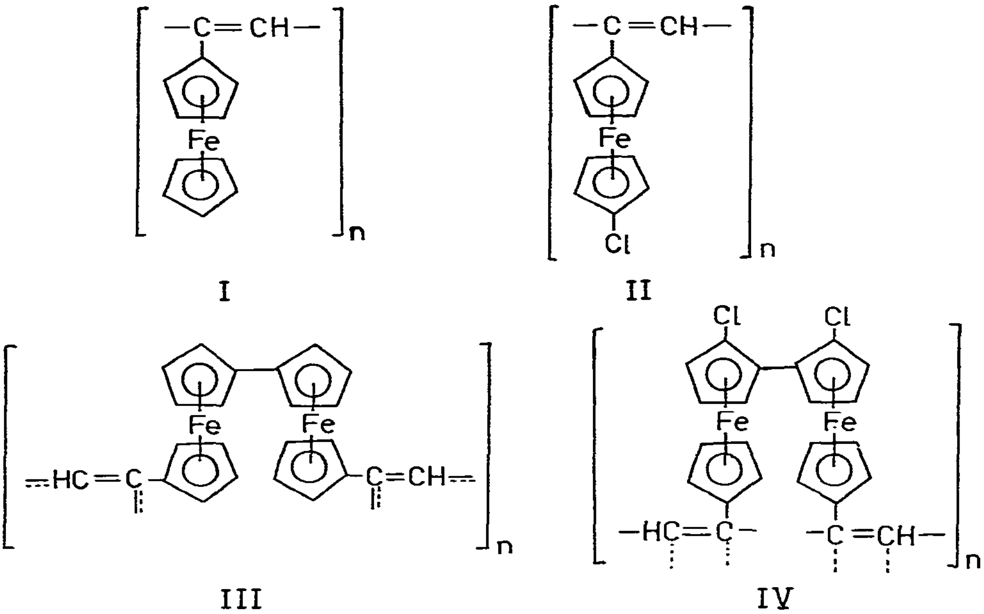
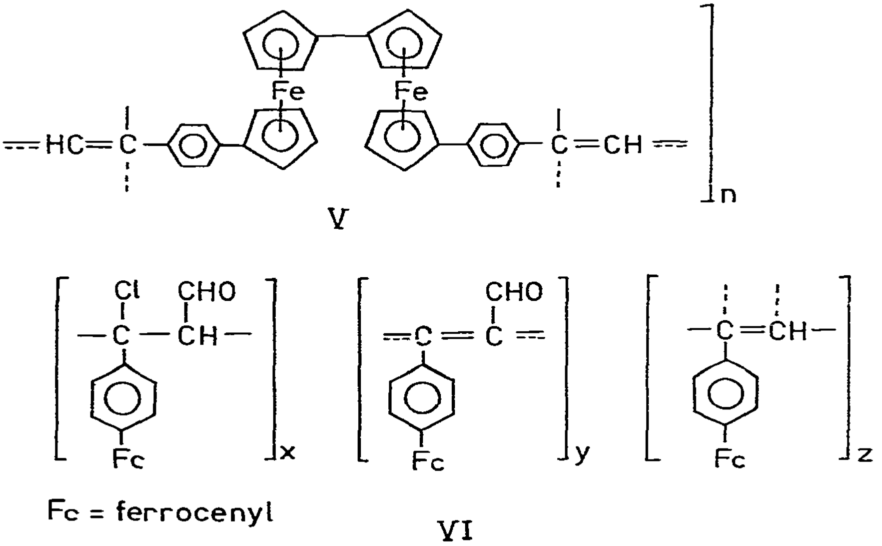


Fig. 5. The structure of polymers obtained by polymerization.

Poly-*p*-ferrocenylphenylacetylenes obtained by polycondensation are three-dimensional polymers containing polyene units (a) as well segments of the same type as those obtained by the reaction of ferrocene with ketones in the presence of Lewis acids (b, c) [51] (Fig. 7). Under our experimental conditions the formation of the cyclic trimer is also possible. Since the polymers were insoluble, additional analyses for structure were not possible.



Fc = ferrocenyl

Fig. 6. The structure of polymers obtained by polymerization.

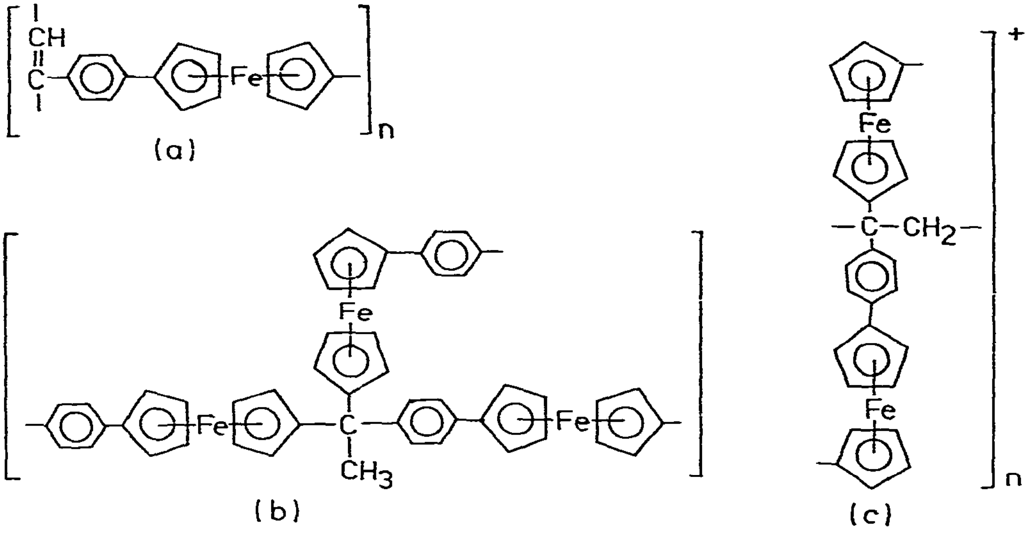


Fig. 7. The poly-p-ferrocenylphenylacetylene obtained by polycondensation.

Polyferrocenyleneiminoimides and polyferrocenyleneazomethines show a complex three-dimensional structure, perhaps due to some competitive reactions.

DiAcFc might react with itself leading to polyferrocenylenvinylenes [37—39] or triferrocenylbenzenes (1590—1600 cm^{-1} in IR spectra). As long as the dehydration reaction occurs in the system HOH—$ZnCl_2$—HCl, which is strongly acid, the protonated ferrocene splits the cyclopentadienyl ion which alkylates inter- or intra-molecularly the ferrocene groups [29]. This might explain the increased content of carbon and the lower content of iron of these polyenes. For the insoluble compounds the three-dimensional structure containing a, b, c, d units was assumed (Fig. 8).

With the idea of promoting the one-way polycondensation and to accomplish a non-catalyzed reaction (the catalysts might favour the formation of a more complicate structure of the macromolecule), we synthesized *N,N'*-disulphynyl-bis(4-amino-2-nitrophenyl) disulphide following Westphal and Henklein's method for aromatic diamines [55]. The polycondensation of DiAcFc and DiAcFcF with *N,N'*-disulphynyl-bis(4-amino-2-nitrophenyl) disulphide was carried out in nonpolar solvents (benzene) using pyridine as catalyst.

According to Hörhold [56], pyridine forms an adduct with the disulphynylic compound, involving the —N=S=O group which has a strong nucleophilic character. The condensation takes place through the formation of an intermediate with an open or cyclic structure. It eliminates the catalyst and SO_2, generating the Schiff polybase with a linear structure (Fig. 9). The reaction duration and the reactivity of dicarbonylic component have the same influence upon the conversion as in the polycondensation of DiAcFc and DiAcFcF with 4,4'-diamino-2,2'-dinitrodiphenyldisulphide in the presence of $ZnCl_2$.

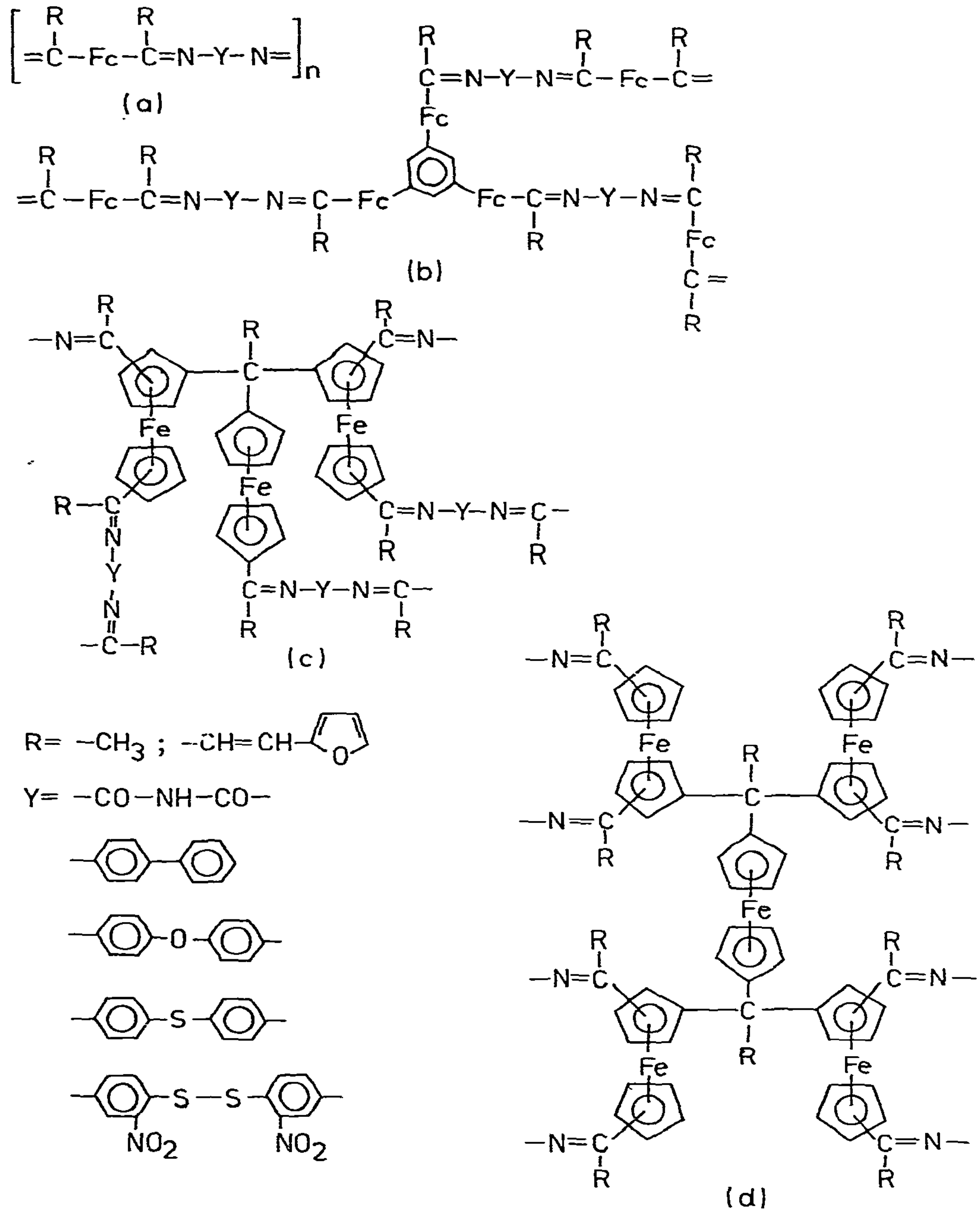


Fig. 8. The structure of polyferrocenyleneiminoimides and polyferrocenyleneazomethines.

4. Properties of the polymers

The conjugation, on the one hand, and the ferrocenyl residue on the other, induce some properties of the polymers, e.g. thermal stability, electrical conductivity and magnetic properties.

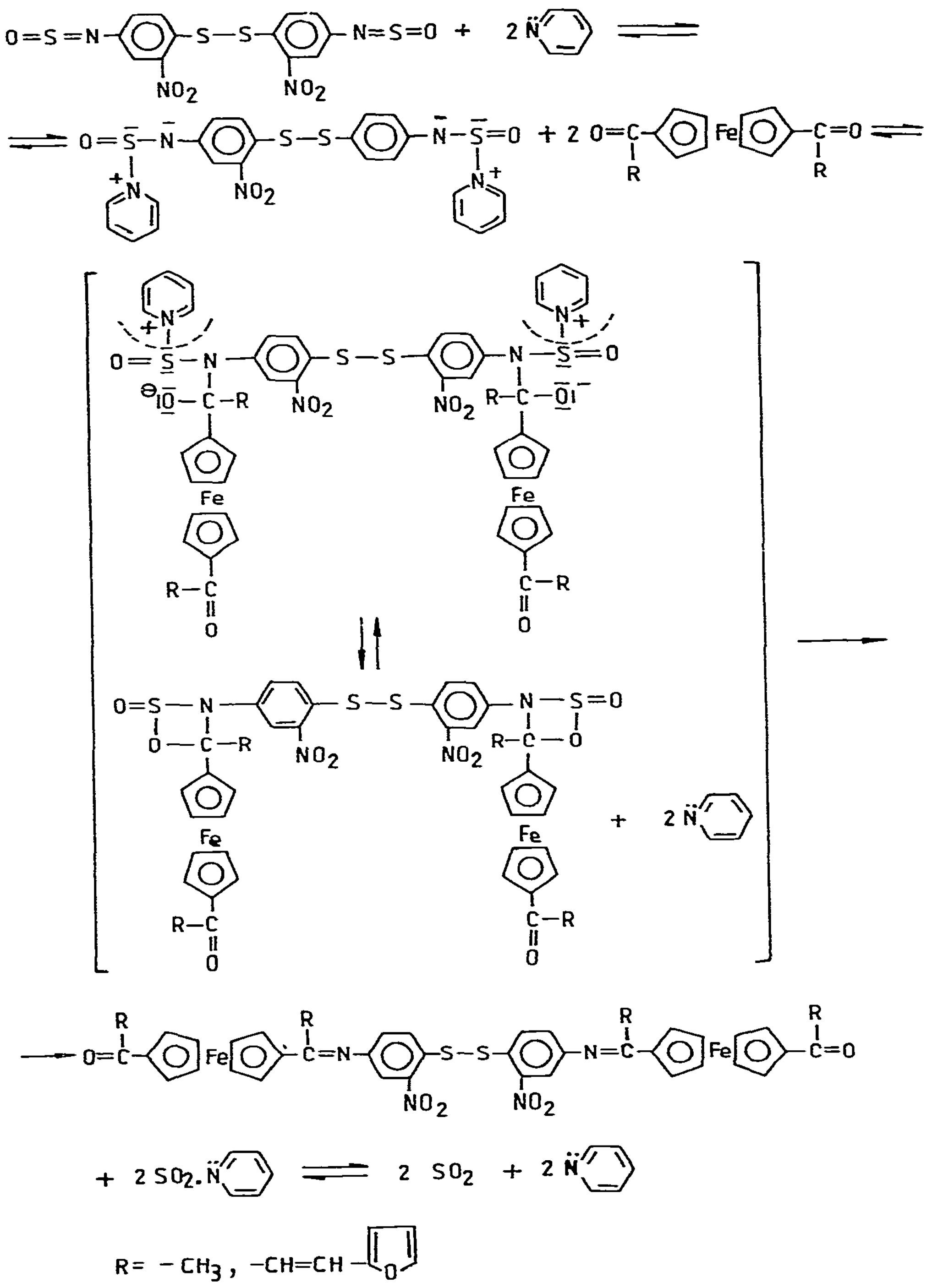


Fig. 9. Polycondensation mechanism of DiAcFc and DiAcFcF with *N*,*N*′-disulphynyl-bis-(4-amino-2-nitr phenyl)disulphide.

4.1. Thermal stability

Although ferrocene is very thermostable, the ferrocenyl groups introduced into the polymer structure do not improve its thermal stability. Most of the polyenes synthesized are stable up to 200—300°C.

Polyferrocenylacetylenes obtained by radical polymerization of ethynylferrocene in the presence of benzoyl peroxide, lauroyl peroxide and trisisopropylboron are stable up to 220—230°C. The polymers derived from ferrocenylacetylene in the presence of the complex catalyst $[P(C_6H_5)_3]_2 \cdot NiX_2$ begin to loose weight at lower temperatures, i.e. 170—180°C. The degradation is strong exothermal and continues up to 500°C.

Polychloroferrocenylacetylenes are stable up to 190—200°C, and the weight losses amount to 60% at 580°C. The presence of chlorine diminishes the thermal stability of polymers.

Poly-*p*-ferrocenylphenylacetylenes are stable up to 300°C.

The thermal behaviour of polyferrocenyleneiminoimides and polyferrocenyleneazomethines was studied in comparison with those of the dicarbonylic and diaminic components used. The degradation temperature (T_d) of PFcImImd is not influenced by the nature of dicarbonylic component (T_d = 186—196°C for DiAcFc and T_d = 184—198°C for DiAcFcF). The thermal stability of PFcImImd is enhanced by 60—80°C as compared with that of biuret (T_d = 120°C), T_d values being 30—40°C higher than that corresponding to DiAcFc (155°C) and 30—50°C below that for DiAcFcF degradation (230°C).

In the first stage of PFcImImd degradation decomposition processes occur, affecting the diaminic component. They are similar to those taking place in the thermal degradation of biuret in the case of Schiff polybases derived from 4,4′-diaminodiphenyl thioether, the first degradation step is attributed to the diaminic component.

The diaminic component is responsible also for the first two steps, in the degradation of PFcAzm derived from 4,4′-diamino-2,2′-dinitrodiphenyl disulphide. An explosive decomposition of nitro groups takes place in this case in the first step. Schiff polybases having DiAcFc as diketonic component start to lose weight at temperatures 30—50°C higher than for DiAcFc, while PFcAzm derived from FiAcFcF have T_d values 10—20°C below that of DiAcFcF.

The same correlation between T_d of polycondensation products and that of dicarbonylic components was observed also in the case of PFcImImd.

Polyferrocenyleneazomethines proved to be more stable than polyferrocenyleneiminoimides, the T_d values ranging between 200°C and 280°C for PFcAzm and 184—198°C for PFcImImd.

The thermal behaviour of PFcAzm synthesised by us, which shows a major weight loss in the range of 300—400°C (in air), is similar to that of polyferrocenyleneazomethines obtained by Neuse et al. [49] by polycondensation of 1,1′-diformylferrocene with *p*-phenylenediamine (a rapid weight loss was reported at 450—500°C in argon).

4.2. Electrophysical characteristics

All polymers synthesised are paramagnetic (ESR signal) and exhibit electrical conductivity. The electrophysical properties of polyferrocenylacetylenes, poly-

TABLE 7

ELECTROPHYSICAL CHARACTERISTICS OF POLYFERROCENYLACETYLENES [a]

No.	Polymer type	Initiator Catalyst	Electrical conductivity, σ_{50} (ohm^{-1} cm^{-1})	Energy of activation E_a (eV)	Concentration of unpaired electrons, (spin/g)
1	PEFc	$ZnCl_2$ (200° C)	10^{-10}		
2	PEFc	PB	10^{-11}—10^{-10}	2.01—1.39	10^{18}—10^{19}
3	PEFc	$B(i\text{-}C_3H_7)_3$	10^{-11}—10^{-10}	1.23—0.81	
4	PEFc	$[P(C_6H_5)_3]_2 \cdot NiX_2$	10^{-12}—10^{-10}	2.29—1.72	
5	P-ClEFc	PB	10^{-15}	1.44	2.55×10^{17}
6	P-ClEFc	PL	10^{-14}	0.78	2.14×10^{17}
7	P-*p*-FcFAc	MeX_n	10^{-18}—10^{-11}	0.20—1.43	10^{17}—10^{18}

[a] PEFc = polyethynylferrocene, P-ClEFc = polychloroethynylferrocene, P-*p*-FcFAc = poly-*p*-ferrocenylphenylacetylene, PB = benzoyl peroxide, PL = lauroyl peroxide, MeX_n = metallic halide.

ferrocenyleneiminoimides and polyferrocenyleneazomethines are listed in Tables 7, 8 and 9.

For polyferrocenylacetylenes obtained by polycondensation and heterochain polymers the electrical conductivity may be due to traces of catalyst included in the polymer and/or the mixed valence states of iron (Fe^{II}, Fe^{III}) [57]; in the case of the polyferrocenylacetylenes obtained by polymerization, this feature might be caused by the extended conjugated system only.

The introduction of oxygen or sulphur atoms, as etheric (—O—), thioetheric (—S—) or disulphide (—S—S—) bridges does not affect significantly the thermal stability and electrophysical properties of polymers. This fact may be explained by the contribution of non-participating electrons of oxygen and sulphur atoms to the resonance hybrids (pseudoconjugated polymers) [58]. On the other hand, the fact that the thermal stability and the electrical conductivity are comparable to those of benzidine polymers might be due to the three-dimensional structures [59] or to possible increase in crystallinity compensating the lack of conjugation determined by the introduction of oxygen and sulphur atoms [60].

The values of the electrical conductivity (10^{-12}—10^{-10} ohm^{-1} cm^{-1}), as well as the concentrations of paramagnetic particles (10^{17}—10^{22} spin/g) place these polymers among the organic semiconductors.

TABLE 8

ELECTROPHYSICAL CHARACTERISTICS OF POLYFERROCENYLENIMINOIMIDES

No.	Dicarbonylic component	Reaction conditions		Electrical conductivity σ_{55} (ohm^{-1} cm^{-1})	Energy of activation E_a (eV)	Concentration of unpaired electrons (spin/g)
		Temperature (°C)	Solvent			
1	DiAcFc	140	CH_3COOH	1.74×10^{-12}	0.9176	2.27×10^{22}
2	DiAcFcF	140	CH_3COOH	9.98×10^{-12}	0.467	1.47×10^{21}
3	DiAcFc	120	Dioxan	2.40×10^{-12}	1.037	—
4	DiAcFcF	120	Dioxan	7.70×10^{-13}	1.500	8.00×10^{20}
5	DiAcFc	90	DMSO	—	—	3.34×10^{21}

TABLE 9

ELECTROPHYSICAL CHARACTERISTICS OF POLYFERROCENYLENAZOMETHINES [a]

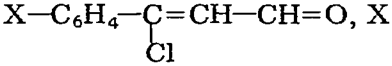
No.	Polymer type	Reaction conditions				Electrical conductivity, σ_{SS} (ohm^{-1} cm^{-1})	Energy of activation, E_a (eV)	Concentration of unpaired electrons, (spin/g)
		Temp. (°C)	Time (h)	Solvent	Catalyst			
1	A_2 [b]	150	21	Melt	$ZnCl_2$	6.599×10^{-12}	0.603	—
2	B_1 [c]	120	10	Dx	AcPTS	—	—	5.124×10^{22} (sol)
3	B_2	120	10	Dx	$ZnCl_2$	—	—	1.975×10^{23} (ins)
4	C_1	120	10	Dx	$ZnCl_2$	—	—	4.409×10^{22} (sol)
5	D_1	120	10	Dx	$ZnCl_2$	1.394×10^{-11} (sol)	0.476	3.000×10^{20} (sol)
						—	—	1.560×10^{21} (ins)
6	D_1	120	20	Dx	$ZnCl_2$	9.360×10^{-12} (ins)	0.169	3.940×10^{22} (ins)
7	D_1	120	35	Dx	$ZnCl_2$	—	—	6.480×10^{21} (ins)
8	D_1 [b]	150	23	Melt	$ZnCl_2$	1.113×10^{-11} (ins)	0.661	—
9	D_1 [c]	120	10	Dx	AcPTS	—	—	1.765×10^{23} (sol)
10	D_1 [d]	120	10	Dx	$ZnCl_2$	—	—	1.477×10^{20} (sol)
11	D_2	120	10	Dx	$ZnCl_2$	—	—	4.380×10^{20} (sol)
						—	—	6.180×10^{21} (ins)
12	D_2	120	35	Dx	$ZnCl_2$	—	—	2.320×10^{22} (ins)

[a] Dx = dioxane, AcPTS = *p*-toluene sulphonic acid. [b] Reaction in melt. [c] *p*-Toluenesulphonic acid as catalyst. [d] Dicarbonylic component/diaminic component in the ratio 1/2.

5. *Catalytic activity*

The reversible conversion of ferrocene into ferricinium ion recommends the ferrocene polymers as catalysts in reactions proceeding with electron exchange between substrate and catalyst.

The catalytic action of ferrocene polymers has been investigated mainly for dehydration and dehydrogenation reactions of alcohols [53,61]. The dehydration reaction of cyclohexanol to cyclohexene was carried out in the presence of polymers containing *p*-ferrocenylphenylacetylene, *p*-ferrocenylacetophenone and α-chloro-β-formyl-*p*-ferrocenylstyrene (heterogenous catalysis). The influence of reaction duration and temperature upon the yield of dehydrated product was established. The catalytic activity of the polymers decreases in time and after 4—5 hours vanishes. They may be reactivated by heating at 150°C in air [62].

The catalytic effect of ferrocene and related derivatives in polymerization of vinylic compounds being known [63,64], we tested the action of polymers containing *p*-ferrocenylphenylacetylene and α-chloro-β-formyl-*p*-ferrocenylstyrene in the polymerization of some *p*-substituted chloroformylated vinylic compounds, i.e.  $X{-}C_6H_4{-}\underset{Cl}{\underset{|}{C}}{=}CH{-}CH{=}O$, X = Cl, Br, CH_3, C_2H_5. The catalysts showed their efficiency at rather low temperatures, at which thermal polymerization did not succeed, especially in the case of less reactive monomers. Because these catalysts did not influence the polymerization of styrene and methylmethacrylate, we consider that they are specific to chloroformylated vinylic monomers [65,66].

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