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NEW FERROCENE POLYMERS: POLYFERROCENYLENIMINOIMIDES

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Summary

The influence of the reaction conditions in the polycondensation of 1,1′-diacetylferrocene and 1,1′-bis[β-(2-furyl)acryloyl]ferrocene with biuret is studied and the optimum parameters for obtaining new ferrocene polymers, polyferrocenyleniminoimides, determined. The synthesized polymers are stable up to 225°C and show semiconducting properties.

Homo- and heterochain polymers containing a ferrocene nucleus either in the main chain or as a substituent have been prepared by all the reaction types known in macromolecular chemistry.

The polyferrocenylacetylenes have been obtained recently by the polymerisation of ferrocenylalkinic derivatives in the presence of benzoyl peroxide, lauroyl peroxide, triisopropylboron and complex catalysts of triphenylphosphine [1—4], AIBN [5], Ziegler catalysts [6,7], as well as by the polycondensation of acetyl- and diacetylferrocene [5,6,8—12].

Due to the possibly complex structures produced by the polycondensation of the carbonylic ferrocene derivatives with different diaminic components, these reactions have been scarcerly studied. Polyazines [13,14], Schiff polybases [14], polycyclotrimers [15,16] and products of the polycondensation of acetylferrocene with carbamide [17] have been synthesised.

In the present paper the synthesis and properties of new ferrocene polymers, namely polyferrocenyleniminoimides, are reported.

Experimental

Diacetylferrocene (DiAcFc)

Diacetylferrocene was obtained by Friedel-Crafts acylation [18—21] of ferrocene. After recrystallization (water), the pure product was obtained as red-orange needles melting at 124—125°C.

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1,1′-Bis[β-(2-furyl)acryloyl]ferrocene (DiAcFcF)

A solution of 1.35 g (5 mmol) diacetylferrocene and 0.96 (10 mmol) furfurol in 15—20 ml ethanol was added under stirring to 0.5 g NaOH in 4.1 ml water and 2 ml ethanol cooled below 0° C. The reaction mixture was then stirred under cooling for an hour. The product obtained was filtered and washed with 15 ml of an alcoholic solution (ethanol/water 2/1). After purification from an acetic acid/water mixture a brick red-coloured product melting at 162° C was obtained. This product was soluble in benzene, dioxan, acetone, acetic acid, methylene chloride, chloroform, methanol and ethanol and is insoluble in water.

Biuret was obtained from Schuchard (München).

Polycondensation of DiAcFc and DiAcFcF with biuret

The polycondensation was carried out in an inert medium by using either dioxan and dimethylsulphoxide (solvent) and $ZnCl_2$ as dehydrating reagent or acetic acid as solvent and catalyst; 25 ml solvent and 1 g $ZnCl_2$ were used for 5 mmol of dicarbonylic component. The insoluble polymer was separated by filtration and the soluble one extracted by adding methanol or water to the filtrate. After repeated washings with acetone, methanol or ethanol and water, the polyferrocenyleniminoimides (PFcImImd) were obtained as brown to black coloured products, insoluble in the common organic solvents and in sulphuric acid. The melting points are above the decomposition temperatures.

The IR, NMR and ESR spectra were recorded on Specord 71, Jeol and ART-5 apparatus, respectively. The thermodifferential analysis was performed on a J. Paulik-F. Paulik-L. Erdey MOM Budapest apparatus. The runs were made in air, within the 20—900° C temperature range, at a heating rate of 10°/min.

Results and discussion

Since the literature data on the reaction of diacetylferrocene with furfurol are rather contradictory [22], the 1,1′-bis[β-(2-furyl)acryloyl]ferrocene was synthesized according to the method described for acetylferrocene [23,24].

The DiAcFcF was characterised by means of elemental and thermogravimetric analyses as well as by IR and NMR spectral measurements.

The IR spectrum shows the bands characteristics of the ferrocene nucleus (830—855, 1090, 1190, 1380, 1450, 1545 cm^{-1}), the carbonyl group (1650 cm^{-1}), the newly created C=C double bond (1590 cm^{-1}) and the fundamental frequencies of furan (680, 735—745, 1010—1030, 1140, 1240—1290 cm^{-1}).

The NMR spectrum recorded in $CDCl_3$ solution, confirms DiAcFcF structure (Fig. 1). The spectrum shows the chemical shifts belonging to the ferrocene nucleus (4 H_a δ 4.92 ppm, 4 H_b δ 4.50 ppm) [12], furan ring (2 H_e δ 6.63 ppm, 2 H_f δ 6.42 ppm, 2 Hg δ 7.35 ppm) [24,25] and the disubstituted double bond (2 H_c δ 7.45 ppm and 2 H_d δ 6.87 ppm) [26,27].

The thermal stability of DiAcFcF was studied in comparison to that of DiAcFc. The former was found to be more stable than the latter by about 75° C, probably due to the extension of the conjugation. The data obtained are listed in Table 1.

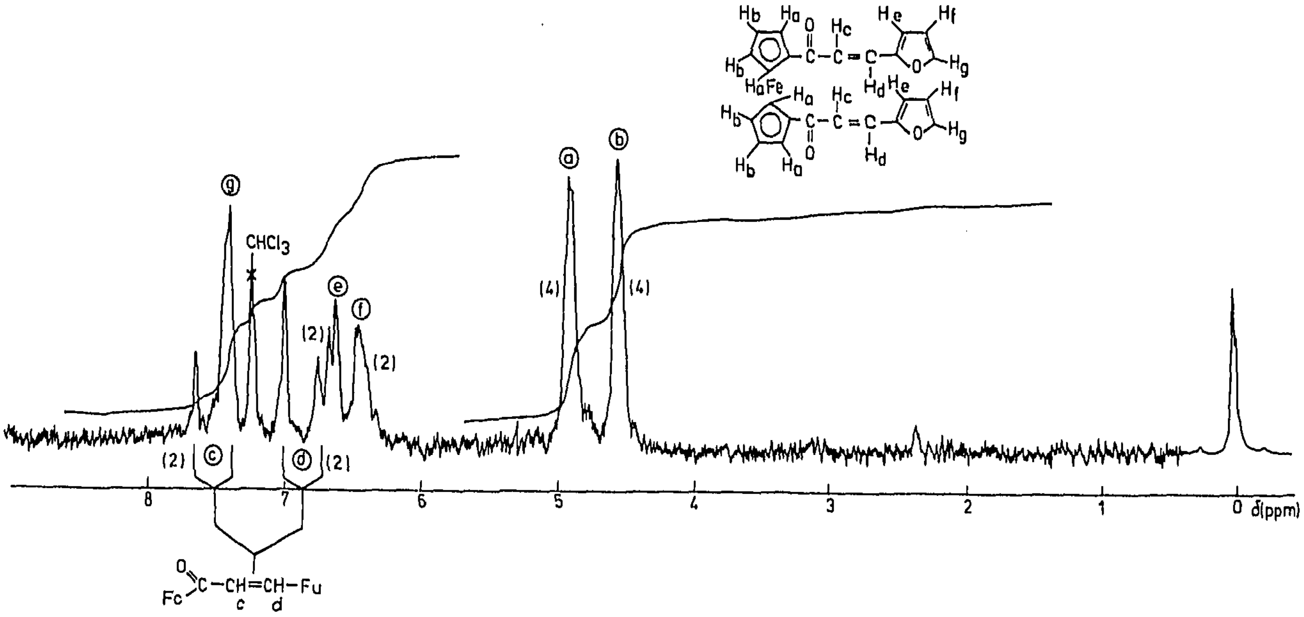

Fig. 1. The NMR spectrum of 1,1′-bis[β-(2-furyl)acryloyl]ferrocene.

TABLE 1

THERMAL BEHAVIOUR OF DiAcFc AND DiAcFcF [a]

Diketonic component	T_d (°C)	Decomposition stage	T_{max} (°C)	Weight losses (%)	E_a (kcal/mol)	Reaction order
DiAcFc	155	I 155—262	230	22.85	16.1	0.20
		II 262—450	330	52.85	25.5	2.10
DiAcFcF	230	230—660	350	84.00	7.4	0.20

[a] T_d = temperature at which the sample degradation begins, T_{max} = temperature corresponding to the maximum decomposition rate, E_a = the activation energy.

The polycondensation of DiAcFc and DiAcFcF with biuret were carried out under different conditions and the influence of solvent, temperature and catalyst on the conversion were studied. The reaction parameters are given in Table 2.

The solvent influence may be discussed by taking into account the data for the samples 3 and 5 as presented in Table 2. It can be seen that DMSO promotes the polycondensation compared to dioxan, probably due to the molecular polarity.

The catalyst nature also influences the conversion. The zinc chloride acts as both dehydrating reagent and activator of the $>C{=}O$ group [28], leading to higher conversions than with acetic acid. Acetic acid might decrease the nucleophilicity of the NH_2 group towards biuret by protonation; the acylation of this group would also be possible under the reaction conditions.

As regards the dicarbonylic component, the higher reactivity of DiAcFcF towards DiAcFc causes higher amounts of soluble oligomers to be formed.

The temperature also influences the conversion, promoting the formation of insoluble products (samples 5 and 6, Table 2).

The molecular structure of the polymers was investigated by elemental analysis and IR spectra. The IR spectra of all soluble and insoluble compounds are identical, therefore molecular structure is not influenced significantly by the variation of reaction parameters. All spectra show the characteristic bands for the ferrocene and furanic nuclei (when DiAcFcF is the dicarbonylic component), functional end groups $\nu(NH_2)$ 3200—3400 cm^{-1} and $\nu(CO)$ 1690—1730 cm^{-1}, $\nu(CH_{sat})$ 2900 cm^{-1} as well as the frequencies attributable to the newly

TABLE 2

POLYCONDENSATION OF DiAcFc AND DiAcFcF WITH BIURET [a]

No.	Dicarbonylic 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] Dicarbonylic component/biuret mole ratio = 1/1; reaction duration 20 hours.

TABLE 3

THERMAL STABILITY OF PFcImImd [a]

No.	Dicarbonylic component	Reaction conditions		Destruction temperature (°C)					Weight losses (%)				
		Temperature (°C)	Solvent	T_i	I	II	III	T_f	T_i	I	II	III	T_f
1	DIAcFc	120	Dioxan	186	230	300	—	390	1.8	24.6	56.5	—	81.1
2	DIAcFc	120	DMSO	198	232	320	363	438	3.5	17.8	44.5	13.3	75.6
3	DIAcFc	90	DMSO	186	225	304	370	421	5.2	15.8	57.6	10.5	83.9
4	DIAcFcF	90	DMSO	176	240	316	383	481	5.0	17.3	50.4	20.3	88.0
5	DIAcFcF	90	DMSO	205	270	360	—	435	4.5	8.9	46.3	—	59.7

[a] $T_i = T_{\text{initial}}$, $T_f = T_{\text{final}}$.

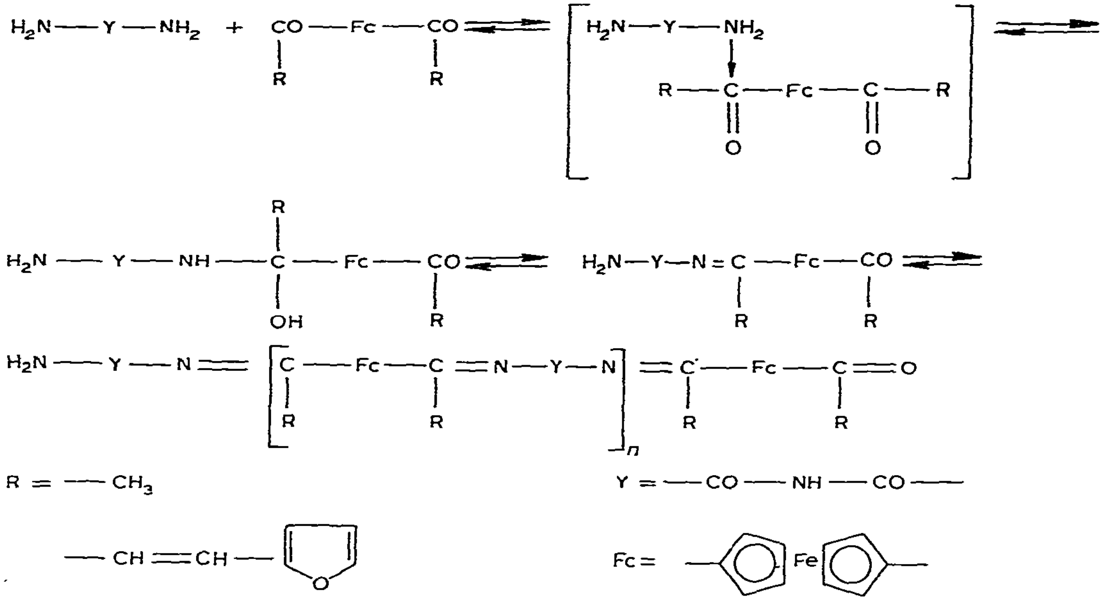

Fig. 2. The polycondensation reaction mechanism.

formed bonds ($\nu(>C=N-)$ 1650 cm^{-1}, $\nu(>C=C<)$ 1590—1600 cm^{-1}).

The polycondensation involves a nucleophilic addition followed by elimination [29] (Fig. 2). A set of competitive reactions may proceed under our experimental conditions, such as the conversion of DiAcFc into polyferrocenylninylenes [8—11] and triferrocenylbenzenes [15,16]. The hydrogen chloride generated by the HOH/$ZnCl_2$ system may protonate ferrocene, eliminating cyclopentadienyl [30—33] which is an alkylating reagent towards other ferrocene nuclei.

Based on the elemental analysis data and IR spectra it may be assumed that only insoluble PFcImImd show a three-dimensional structure with units of a, b, c, d types (Fig. 3). Due to protonation some ferrocene nuclei contain Fe^{III}.

PFcImImd were characterized by determining the thermal stability and testing the electrical conductivity and paramagnetism. The results are listed in Tables 3 and 4. The thermodifferential and thermogravimetrical analyses indicate a good thermal stability of the polymers up to 225°C. The greatest weight

TABLE 4

ELECTROPHYSICAL CHARACTERISTICS OF PFcImImd

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	1.475×10^{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}

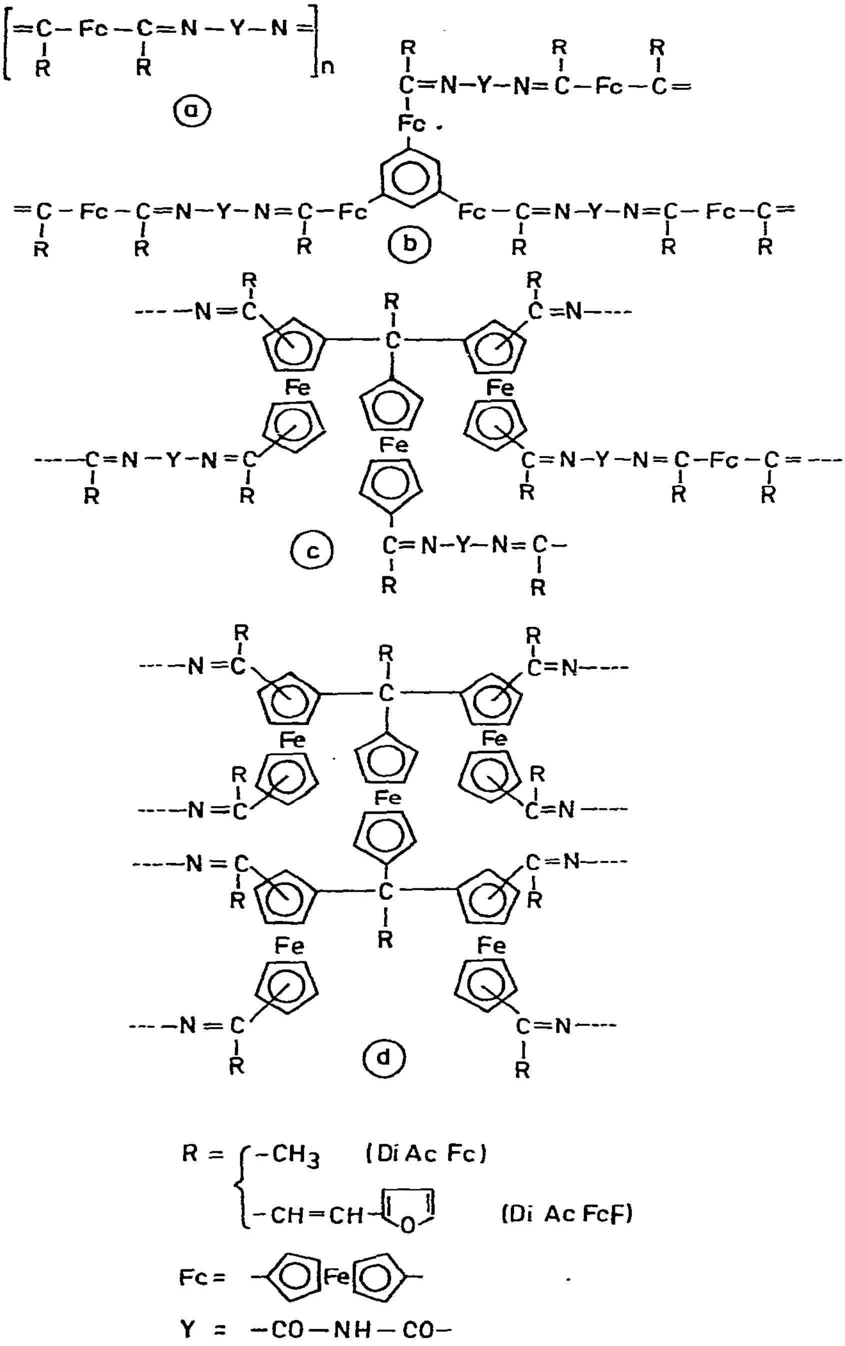

Fig. 3. The molecular structure of polyferrocenyleniminoimides.

losses are noticed during the second decomposition stage (300—400° C), probably due to the volatilization of small molecules of the ferrocenophanic type which are formed during polycondensation and included in the polymer [13]. The values of the electrical conductivity, of the 10^{-12} ohm^{-1} cm^{-1} order, and the paramagnetism (10^{20}—10^{22} spin/g) place PFcImImd among the organic semiconductors.

Conclusions

By polycondensation of DiAcFc and DiAcFcF with biuret a series of new ferrocene polymers, namely polyferrocenyleniminoimides, have been synthesized. The influence of temperature, reaction duration and solvent nature on the conversion has been studied.

Based on the elemental analysis data and IR spectra a complex three-dimensional structure of the insoluble PFcImImd is proposed. PFcImImd show a good thermal stability up to 225° C. The values of electrophysical constants attest to the semiconducting properties of these polymers.

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