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FERROCENE POLYMERS. SYNTHESIS AND THERMAL POLYMERIZATION OF α-CHLORO-β-FORMYL-p-FERROCENYLSTYRENE

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Summary

The synthesis and thermal polymerization of a new chloroformylated vinyl derivative containing a ferrocenyl residue are reported.

The reactivity of α-chloro-β-formyl-p-ferrocenylstyrene in the polymerization reaction is discussed in the light of the experimental results and data obtained from molecular orbital calculations using the Hückel approximation.

Introduction

Having obtained p-substituted phenylacetylene copolymers by the thermal polymerization of various chloroformylated vinyl derivatives [1,2], and having synthesized some ferrocenylacetylenes by the polymerization of α-chloro-β-formylvinylferrocene [3,4], we decided to synthesize p-ferrocenylphenylacetylene copolymers.

Simionescu et al. have already obtained poly-p-ferrocenylacetylenes by polycondensation of p-ferrocenylacetophenone in the presence of metallic halides [5].

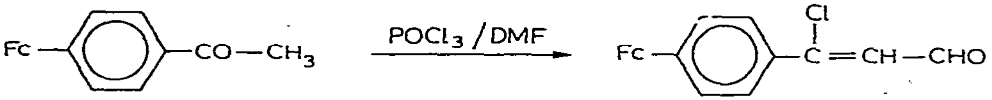
In the present paper the influence is studied of the ferrocenyl residue on both the α-chloro-β-formylstyrene reactivity and the properties of the synthesized copolymers.

Experimental

Synthesis of the monomer

By applying methods described in the literature for the synthesis of chloroformylated vinyl derivatives [6-10], α-chloro-β-formyl-p-ferrocenylstyrene was obtained by treating p-ferrocenylacetophenone with Vielsmeier complex (DMF/

$POCl_3$), according to eqn. 1.



(1)

The Vielsmeier complex, prepared from $POCl_3$ (6.1 ml, 60 mmol) in DMF (20 ml) at 0°C, was added with stirring to a cooled solution of ketone (6.08 g, 20 mmol) in DMF (30 ml). The reaction mixture was maintained at 0°C for 15 min and then at 60°C for 2 h; 150 ml of 20% sodium acetate was then added. After extracting with methylene chloride and removal of the solvent, chromatography on aluminium oxide gave a cherry-red product. Recrystallization from a 1/1 acetone—water mixture gave the pure product with a melting point of 98°C. α-Chloro-β-formyl-*p*-ferrocenylstyrene is soluble in dioxane, dimethyl formamide and acetone, partially soluble in benzene, methanol and ethanol, and insoluble in n-hexane and n-heptane (Analyses found: C, 65.19, 65.23; H, 3.55, 3.62; Fe, 17.07, 17.56. Calcd.: C, 65.07; H, 4.28; Fe, 15.6%. Mol. wt. 350.35.)

Synthesis of the polymers

The polymerization was carried out by a bulk polymerization technique in an inert medium using sealed glass phials. The polymers obtained were insoluble in the usual organic solvents. Unreacted monomer was removed by repeated washing with acetone.

IR spectra were recorded on a UR-20 spectrophotometer and NMR spectra on a Jeol type apparatus, using $CDCl_3$ as solvent and TMS as internal reference.

The thermal stabilities of the synthesized products were estimated by means of differential thermal analysis data obtained on a Paulik—Paulik—Erdey MOM - Budapest apparatus.

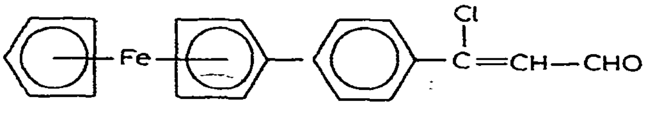
For the α-chloro-β-formyl-*p*-ferrocenylstyrene molecule, the MO Hückel calculations were performed with an IRIS-50 electronic calculator.

Results and discussion

Structure and reactivity of the monomer

The structure of the new vinyl monomer was elucidated by means of IR and NMR spectral measurements and elemental analysis. The IR spectrum shows absorption bands characteristic of an aromatic ring [ν(C—C) 1600 cm^{-1}], a ferrocenecyclopentadienyl ring (830, 1130, 1190 cm^{-1}) [11] and a carbonyl group (1680 cm^{-1}). The absorption band at 720 cm^{-1} may be attributed to the chlorine atom as it does not exist in the spectrum of the original ketone. This band is shifted slightly with respect to that of the chlorine atom in vinyl chloride, at 724 cm^{-1} [12].

The NMR spectral values: δH(aromatic) 7.19 and 7.48, δH(olefinic) 6.65, δH(cyclopentadienyl) 4.5, and δH(aldehydic) 10.30 ppm, also confirm the structure of the monomer to be α-chloro-β-formyl-*p*-ferrocenylstyrene:



In order to investigate the influence of the ferrocenyl residue on the reactivity of α-chloro-β-formyl-*p*-ferrocenylstyrene certain molecular characteristics were calculated, e.g. charge distribution, free valence indices, resonance energy and bond orders for α-chloro-β-formylvinylferrocene, α-chloro-β-formyl-*p*-ferrocenylstyrene and α-chloro-β-formylstyrene, from MO calculations using the Hückel approximation.

The parameters α(coulomb integral) and β(resonance integral) were selected according to literature methods [13-16]. The values obtained are listed in Table 1. As regards the values of the resonance energies and free valence indices at the olefinic carbon atoms, the reactivity decreases in the order: α-chloro-β-formylvinylferrocene > α-chloro-β-formyl-*p*-ferrocenylstyrene >α-chloro-β- formylstyrene, which is in good agreement with the experimental results obtained by thermal polymerization [1-4]. When other *p*-substituted derivatives of α-chloro-β-formylstyrene are included the reactivity scale may be enlarged to: 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 > α-chloro-β-formyl-*p*-methylstyrene. The high reactivity of α-chloro-β-formylvinylferrocene is due to the strongly electron donating character of the ferrocenyl residue directly attached at the vinyl residue.

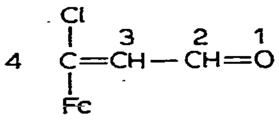
The copolymerization constants which were calculated also shed some light on the monomer reactivities. The copolymerization constants were determined by means of eqn. 2 where $(\Delta E_{rs})_1$ and $(\Delta E_{rs})_2$ denote the resonance stabilization energies of the transition states between the radical and its monomer and between the same radical and comonomer, respectively. The (ΔE_{rs}) values were calculated according to the literature methods [18] and expressed in $-(\Delta\beta^2/\beta)$ units. The indices r and s in the expression ΔE_{rs} refer to the atoms in the monomer and radical, respectively, interacting in the transition state. In the present case, monomers I, II, III and IV interact in the transition state with atom 3, while the styrene interacts with atom 1 (the electron densities on the outer orbitals being greatest at these positions). In all cases carbon atom 4 is a radical.

$$-RT \ln r = (\Delta E_{rs})_1 - (\Delta E_{rs})_2 \qquad (2)$$

TABLE 1

MOLECULAR CHARACTERISTICS OF SOME *p*-SUBSTITUTED CHLOROFORMYLATED VINYL DERIVATIVES

Monomer	Total energy (β)	Resonance energy (β)	Free valence indices	π-Electronic bond order	Ref.
α-Chloro-β-formylstyrene	19.5636	9.5634	0.3977	0.7941	1, 2
α-Chloro-β-formyl-*p*-chlorostyrene	24.6642	12.1642	0.3968	0.7911	1
α-Chloro-β-formyl-*p*-bromostyrene	24.3663	9.4663	0.4477	0.7940	1
α-Chloro-β-formyl-*p*-methylstyrene	23.5436	12.2436	0.3944	0.7850	2
α-Chloro-β-formyl-*p*-nitrostyrene	24.7919	10.7919	0.4125	0.7903	2
α-Chloro-β-formylvinylferrocene	40.1824	5.1824	0.3936	0.7498	This work
α-Chloro-β-formyl-*p*-ferrocenylstyrene	48.5490	7.5490	0.3985	0.7828	This work



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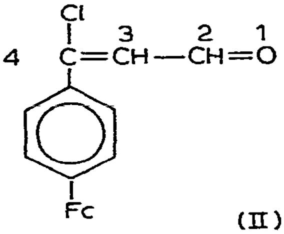

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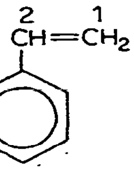

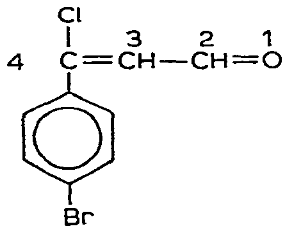

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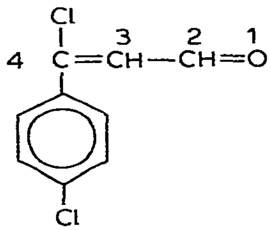


(IV)

Table 2 lists the values of copolymerization constants, r, calculated at 60°C (333 K) for the copolymerization of I and II with styrene, and at 200°C for copolymerization of I with III and IV.

For cases a and b in Table 2 the proportion of the two monomers is not important since if the copolymer has a higher styrene content, the monomers I and II will eventually polymerize by themselves.

Thermal copolymerizations of monomers I with III and I with IV were carried out at 200°C, a mixture of homopolymers being thus obtained. The same result was obtained by theoretical calculations.

TABLE 2

COPOLYMERIZATION CONSTANTS

Type	Radical	Monomer	ΔE_{rs} —$(\Delta\beta^2/\beta)$	Difference ΔE_{rs} —$(\Delta\beta^2/\beta)$	$r_{calc.}$
a	I	I	0.6768	0.0046	0.983
	I	Styrene	0.6614		
	Styrene	Styrene	0.9323	—0.2116	2.180
	Styrene	I	0.7207		
b	II	II	0.7011	0.0652	0.786
	II	Styrene	0.7663		
	Styrene	Styrene	0.9323	—0.2305	2.34
	Styrene	II	0.7018		
c	I	I	0.6768	—0.0893	1.261
	I	III	0.5875		
	III	III	0.7188	—0.0905	1.265
	III	I	0.6283		
d	I	I	0.6768	—0.0710	1.20
	I	IV	0.6058		
	IV	IV	0.7148	—0.0998	1.29
	IV	I	0.6150		

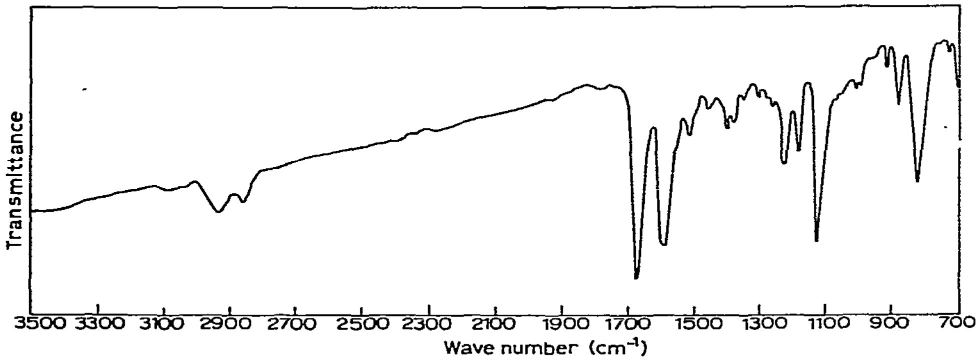


Fig. 1. Infrared spectrum of α-chloro-β-formyl-*p*-ferrocenylstyrene.

Theoretical studies of the copolymerization reaction are seen to be experimentally confirmed, which indicates that the parameters used in calculations in our previous papers [1,2,5,16] are valid.

Thermal polymerization of α-chloro-β-formyl-p-ferrocenylstyrene

The influence of temperature on the percentage conversion at a constant reaction time of 10 h was investigated. The results obtained are listed in Table 3.

It may be noticed that for any temperature the highest conversions are reached with α-chloro-β-formyl-*p*-ferrocenylstyrene, which is in fairly good agreement with the results on monomer reactivities obtained from calculations.

All polymers which were synthesized were obtained as black, insoluble powders, infusible up to 350°C.

Molecular structures and characterization of the polymers

Structures of the polymers were elucidated by IR spectral measurements and elemental and differential thermal analyses.

The IR spectra of polymers synthesized at 180 and 200°C show absorption bands characteristic of the functional groups in the molecule but much flattened. Polymers prepared at higher temperatures (230 and 300°C) show a very large fundamental absorption, and pronounced bands at 1400 and 1600 cm^{-1} (for the

TABLE 3

COMPARATIVE DATA ON THE THERMAL POLYMERIZATION OF SOME *p*-SUBSTITUTED CHLOROFORMYLATED VINYL DERIVATIVES AT DIFFERENT TEMPERATURES

X	180°C		200°C		230°C		300°C		Ref.
	Conversion (%)	M.p. (°C)	Conversion (%)	M.p. (°C)	Conversion (%)	M.p. (°C)	Conversion (%)	M.p. (°C)	
Br	35.08	230	43.79	250	43.98	266	51.72	294	1
Cl	6.98	204	8.03	218	18.10	195	35.82	249	1
CH_3	18.50	256	27.80	210	31.80	256	44.50		2
NO_2	68.30	185	79.00	>350	76.40	>350	59.60	>350	2
Fc[a]	94.70	>350	95.00	>350	95.20	>350	91.80	>350	This work

[a] Fc = ferrocenyl

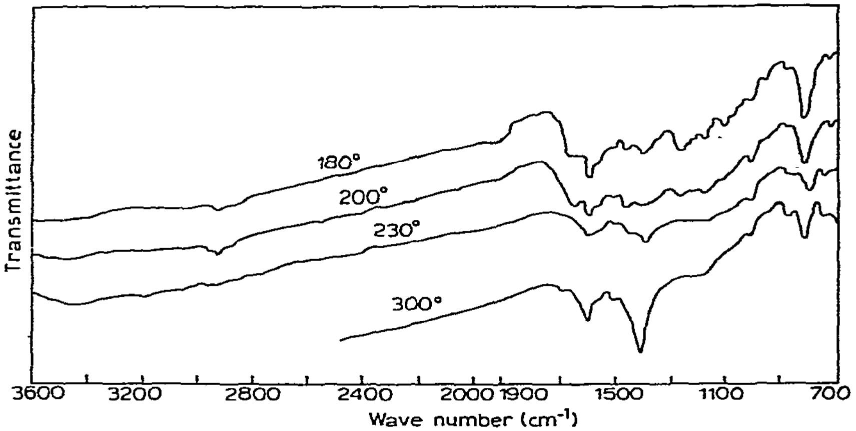
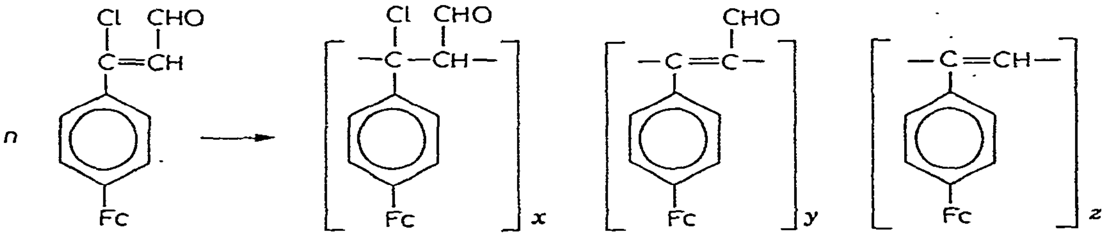


Fig. 2. Infrared spectra of the polymers synthesized at different temperatures.

polymer obtained at 300°), which are attributable to the conjugated systems formed in the chain. The bands characteristic of the carbonyl group (1680 cm^{-1}) and the halogen (720 cm^{-1}) become weaker with increasing reaction temperature, disappearing altogether in the spectra of polymers obtained at 230 and 300°C.

Taking this observation into account together with the elemental analysis data it might be assumed that a dehaloformylating and dehydrohalogenating process of either the monomer or the polymer is taking place. Reactions of this type have been reported elsewhere for chloroformylated vinyl derivatives [6] and halogenated polymers [19]. The reaction mechanism is similar to that described in our previous papers for other chloroformylated vinyl derivatives [1,2].



Poly-*p*-ferrocenylacetylenes are obtained with cross-linked structures as a result of either ferrocene ring chaining or double bond cleavage in certain positions on the macromolecular chain.

The assumption of cross-linked structures is supported both by the fact that the polymers are insoluble and infusible, and by their IR spectra which show flattened absorption bands and a significant fundamental absorption. For the polymers synthesized at 230 and 300°C, the z type structure predominates.

Our results are in agreement with those of Korshak and Paushkin in the polymerization of α-chloro-β-formylvinylferrocene [3,4].

The occurrence of double bonds on the macromolecular chain as a result

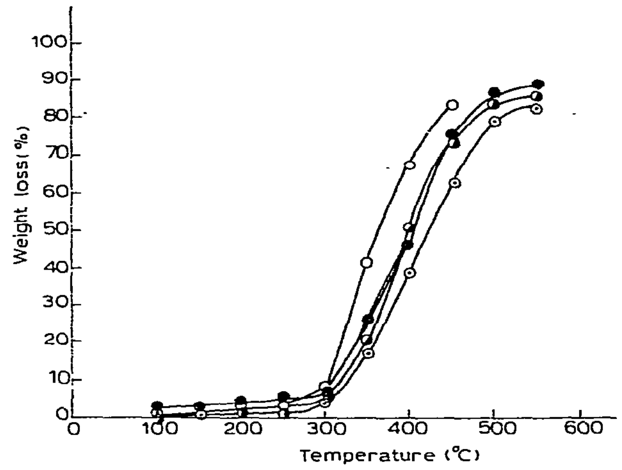


Fig. 3. Weight losses vs. temperature for polymers obtained from α-chloro-β-formyl-*p*-ferrocenylstyrene at 180 (◑——◑), 200 (○——○), 230 (⊙——⊙) and 300°C (●——●).

of dehydrohalogenation and dehaloformylation should accompany semiconducting properties, as has been noticed in similar cases [1-4], but these were not observed. The absence of semiconducting properties may be explained by taking the steric effects into account; the bulky substituents distort the planarity of the molecule and hence the extension of the conjugation.

The thermal stability of the polymers was investigated by differential thermal analysis carried out over a temperature range of 40 to 550°C, at a heating rate of 10°C/min, in air. The weight losses are given as a function of temperature in Fig. 3. The polymers are found to be stable up to 300°C, the weight losses then increasing gradually up to 550°C.

The polymers which we synthesized show catalytic activity in polymerization reactions of vinyl derivatives. For instance, α-chloro-β-formyl-*p*-chlorostyrene does not polymerize thermally at 140°C, but in the presence of these polymers (in catalytic amounts), at the same temperature, polymerization takes place with 25% conversion.

Conclusions

In the present paper the synthesis of a new ferrocene derivative is reported together with preliminary investigations into its thermal polymerization.

α-Chloro-β-formyl-*p*-ferrocenylstyrene was synthesized and its reaction parameters determined. The monomer was characterized by means of chemical analysis and spectral measurements. By applying the Hückel LCAO-MO method some discussion has been made on both the monomer reactivity and the influence of the ferrocenyl substituent in the aromatic ring, and on the polymerization and copolymerization reactions of the vinyl monomers.

Thermal polymerization of α-chloro-β-formyl-*p*-ferrocenylstyrene resulted in cross-linked, insoluble polymers whose structures have been elucidated by spectral and elemental analyses.

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