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FERROCENE POLYMERS. SYNTHESIS AND POLYMERIZATION OF *p*-FERROCENYLPHENYLACETYLENE

CR. SIMIONESCU *, TATIANA LIXANDRU, I. MAZILU and LUCIA TĂTARU

Department of Organic Chemistry, Polytechnic Institute of Jassy, Str. 23 August, Nr. 11, Jassy (Romania)

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Summary

To investigate the influence of the ferrocenyl residue on the reactivity of phenylacetylene towards polymerization and on the properties of polyphenylacetylene, *p*-ferrocenylphenylacetylene has been synthesised and then polymerized with initiation by free radicals. Theoretical studies on the reactivity of *p*-ferrocenylphenylacetylene showed good agreement with the observation that the reactivity of this monomer is lower when compared to that of ferrocenylacetylene. The polymers synthesised showed good thermal stability.

Introduction

In previous papers [1—5] the influence of the electron-withdrawing and electron-donating substituents on the properties of polycondensed and polymerized polyphenylacetylenes has been studied.

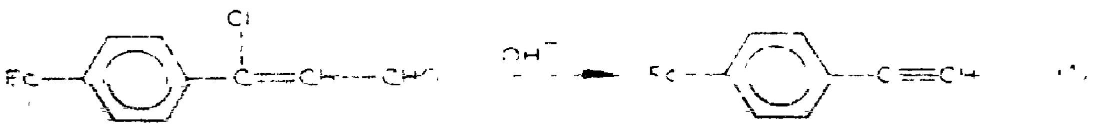
Since the polyferrocenylacetylenes show better properties than the polyphenylacetylenes [6—14] the influence of the ferrocenyl residue on the synthesis and properties of polyphenylacetylenes was investigated [15].

In the present paper the synthesis and polymerization of *p*-ferrocenylphenylacetylene, in the presence of initiators, are discussed.

Experimental

Monomer synthesis

p-Ferrocenylphenylacetylene was prepared according to the literature method [16,17] for obtaining acetylene derivative starting from chloroformaldehyde compounds, by treating α-chloro-β-formyl-*p*-ferrocenylstyrene with alkali (eq. 1).



An aqueous solution of 0.5% NaOH (20 ml) was added to a refluxing solution of α-chloro-β-formyl-p-ferrocenylstyrene (1.2 g, 3.42 mmol) in 30 ml of dioxan and refluxed for another 5 min. The reaction mixture was poured onto 125 ml of cold water and extracted with diethyl ether. The ethereal solution was chromatographed on alumina. After removal of the solvent a red-brown viscous product was obtained which was soluble in most common solvents. (Found: C, 74.20, 76.30; H, 6.26, 6.86; Fe, 19.50; calcd.: C, 75.57; H, 4.89; Fe, 19.18%. Mol. wt. 285.84.)

Polymerization of p-ferrocenylphenylacetylene

p-Ferrocenylphenylacetylene was polymerized in a selaed glass ampoule, in the absence of air, by bulk procedure.

The IR spectra were recorded on a UR-20 spectrophotometer. The thermodifferential analysis was carried out on a J. Paulik—F. Paulik—L. Erdey MOM Budapest apparatus. The MO Hückel calculations for characterizing the molecule were run on a IRIS 50 computer.

Results and discussion

The structure and reactivity of p-ferrocenylphenylacetylene

The structure of *p*-ferrocenylphenylacetylene was elucidated on the basis of elemental analysis and IR spectral measurements. In the IR spectrum are found absorption bands characteristic of a benzene ring [1610 $\mathrm{cm^{-1}}$ ν(C—C), 2930, 2970 $\mathrm{cm^{-1}}$ ν(CH)], cyclopentadienyl residue in ferrocene (840, 890, 1110, 1415 $\mathrm{cm^{-1}}$), a triple bond (ν(C≡C), 2115 $\mathrm{cm^{-1}}$) and acetylene bond ν(CH) at 3300 $\mathrm{cm^{-1}}$.

p-Ferrocenylphenylacetylene changes in time to a brown powder, insoluble in ether; its IR spectrum does not show absorption bands characteristic of a triple bond (2115 $\mathrm{cm^{-1}}$ and 3300 $\mathrm{cm^{-1}}$). The large fundamental absorption and the weakness of the other bands in the spectrum suggest the polymer has a three-dimensional structure.

To estimate the *p*-ferrocenylphenylacetylene reactivity in polymerization reactions, some molecular characteristics have been calculated by using the MO Hückel approximation. The α (Coulomb integral) and β (resonance integral) parameters were selected according to indications in the literature [18—20]. The data given in Table 1 permit an appreciation of the influence of the ferrocenyl residue on the phenylacetylene reactivity.

The values of both resonance energy and free valence index are indicative of a high reactivity of ferrocenylacetylene, due to the strong electron-donating character of the ferrocenyl residue. These indices indicate a lower reactivity for *p*-ferrocenylphenylacetylene. The reactivities of the three monomers decrease in the following order: ferrocenylacetylene > phenylacetylene > *p*-ferrocenylphenylacetylene.

TABLE 1

MOLECULAR CHARACTERISTICS OF SOME ACETYLENE MONOMERS

Monomer	Total energy (β)	Resonance energy (β)	F [a]	p [b]
Phenylacetylene		2.4242	0.6176	0.9334
Ferrocenylacetylene	31.1949	1.6519	0.6323	0.8791
p-Ferrocenylphenylacetylene	40.3257	4.3257	0.6232	0.9339

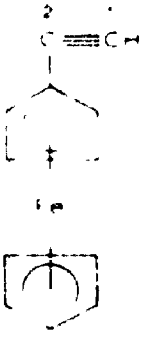
[a] F = free valence index. [b] p = electronic bond order.

The calculated copolymerization constants also gave some indications of the reactivities of the monomers. The copolymerization constants have been estimated by means of the relationship [21]:

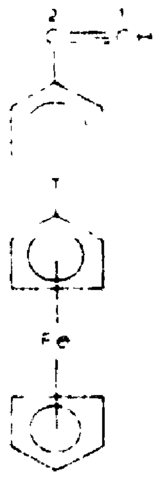
$$-RT \ln r = (\Delta E_{rs})^1 - (\Delta E_{rs})^2$$

where $(\Delta E_{rs})^1$ and $(\Delta E_{rs})^2$ are 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 have been calculated according to literature methods [22] and are expressed in $-\beta^2/\beta$ units. The r and s indices in ΔE_{rs} refer to the atoms in monomer and radical, respectively, participating in the transition state.

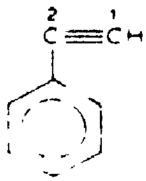
The copolymerization constants have been calculated for copolymerization of ferrocenylacetylene and p-ferrocenylacetylene with phenylacetylene.



(I)



(II)



(III)

The monomers I, II and III participate in the transition state with the atom 1 (the electronic density on the boundary orbitals being a maximum for these positions). In any case the carbon 2 is radicalic. Table 2 lists the copolymerization constants (r) calculated for 200°C (473 K) temperature. In both cases, regardless of the ratios of the two monomers, the copolymer would have a

TABLE 2

COPOLYMERIZATION CONSTANTS

	Radical	Monomer	ΔE_{rs} $-\beta^2/\beta$	Difference ΔE_{rs} $-\beta^2/\beta$	r_c
a	I	I	0.7978	−0.2260	2.30
	I	III	0.5718		
	III	III	0.6650	0.0125	0.95
	III	I	0.6775		
b	II	II	0.5992	0.0252	0.91
	II	III	0.6244		
	III	III	0.6650	−0.0533	1.21
	III	II	0.6117		

greater content of ferrocenylacetylene in case *a* and of phenylacetylene in case *b*. Finally, the monomers II and III would polymerize by themselves. The copolymerization constants indicate the same reactivity sequence for the monomers under consideration: I > III > II.

The polymerization of p-ferrocenylphenylacetylene

The polymerization was carried out in the presence of benzoyl and lauroyl peroxides. The results are given in Table 3. The conversion was found to increase with increasing reaction temperature, the results obtained using the two peroxides being practically the same. In contrast to the polyferrocenylacetylenes, obtained under the same conditions, which are soluble in benzene [7], the poly-*p*-ferrocenylphenylacetylenes are insoluble in common organic solvents and do not melt up to 350°C. The conversion value in the absence of initiator is much higher than in their presence, at 200°C, which indicates that the initiators are favourable to the formation of a great amount of soluble oligomers which have been removed by solvent washings.

The molecular structure and characterization of poly-p-ferrocenylphenylacetylenes

The polymeric structures were elucidated by means of elemental analyses and IR spectral measurements. The IR spectra of the polymers obtained either with

TABLE 3

THE BULK POLYMERIZATION OF *p*-FERROCENYLPHENYLACETYLENE (reaction time 10 h)

Monomer	Initiator [a]	Temperature (°C)	Conversion (%)
p-Ferrocenylphenylacetylene	PB	140	16
p-Ferrocenylphenylacetylene	PL	140	17.9
p-Ferrocenylphenylacetylene	PB	200	19.9
p-Ferrocenylphenylacetylene	PL	200	24
p-Ferrocenylphenylacetylene	thermic	200	63.5

[a] PB = benzoyl peroxide, PL = lauroyl peroxide.

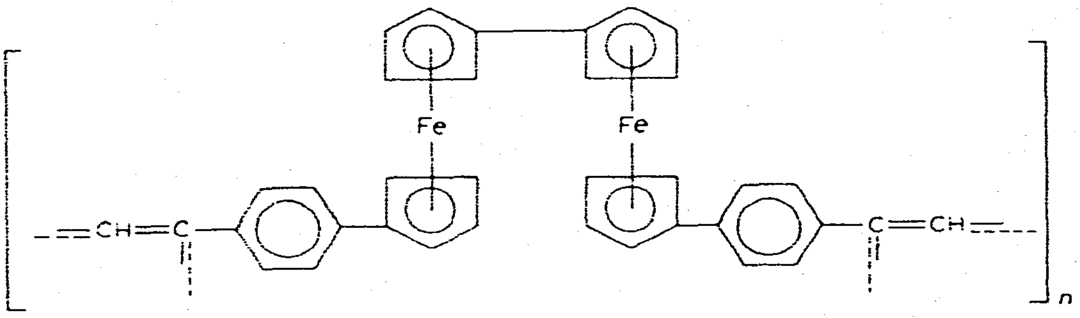
TABLE 4

THERMAL STABILITY ON THE POLYMERS

Polymer	Initiator [a]	Reaction temperature (°C)	Decomposition temperature (°C)	Weight losses (%)
Poly-*p*-ferrocenyl-phenylacetylene	PB	140	250—300	0—2
			300—400	2—30
			400—500	3—61
Poly-*p*-ferrocenyl-phenylacetylene	PL	140	200—300	0—8
			300—500	8—40
Poly-*p*-ferrocenyl-phenylacetylene	PB	200	200—300	0—2
			300—400	2—42
			400—550	42—80
Poly-*p*-ferrocenyl-phenylacetylene	PL	200	100—300	0—2
			300—400	4—8
			400—550	8—40

[a] PB = benzoyl peroxide, PL = lauroyl peroxide.

initiator or thermally are identical. Absorption bands characteristic of the aromatic ring (1610 cm^{-1}, ν(CH) 1930 cm^{-1}) and of the cyclopentadienyl ring in ferrocene (830, 890, 1110, 1190, 1415 cm^{-1}) are found. The absorption features of the triple bond (ν(C≡C), 2115 cm^{-1}) and acetylene (ν(CH), 3300 cm^{-1}) bond in the spectrum of the monomer are absent in the spectrum of the polymer due to the polymerization. The absorption bands of the polymers, less intensive than those of the monomer, are identical with those in the IR spectrum of the product separated in time from the monomer ethereal solution. The lemental analysis data, spectral measurements and the insolubility and infusibility up to 350°C suggest a three-dimensional structure IV.



(IV)

Polymers with similar structure but without conjugated units have been obtained by synthetic reactions of polystyrene [23]. Under our experimental conditions the formation of the cyclic trimer is also possible [24]. At 200°C, in the absence of initiators, this trimer is supposed to be formed predominantly. This fact could account for the higher conversion than that obtained at the same temperature with initiators. Additional investigations of the cyclic trimer could not be accomplished due to the insolubility of the polymer.

The thermal stability of the polymers have been determined by thermodifferential analysis, carried out between 20 and 550°C at a heating rate of 10°/min in air. The weight losses at different temperatures are given in Table 4. The polymers show high stabilities at temperatures up to 300°C.

The electroconductivity and paramagnetic measurements showed that these polymers had no semiconducting properties. This fact could be explained by the sterical hindrance of the bulky substituents which hinder the conjugation extension.

Conclusions

The influence of the ferrocenyl residue on the phenylacetylene reactivity in polymerization reactions and on the properties of polyphenylacetylene has been investigated. A new acetylenic derivative, *p*-ferrocenylphenylacetylene, was synthesized and the structure elucidated by means of chemical analysis and spectral measurements. By applying the Hückel approximation of the MO calculation the *p*-ferrocenylphenylacetylene was found to be less reactive than ferrocenylacetylene, a fact also confirmed experimentally. The polymerization of *p*-ferrocenylphenylacetylene was carried out in the presence of peroxides and the polymer structures determined by elemental and spectral analyses. The synthesized polymers showed good thermal stability.

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