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# FERROCENE POLYMERS

# THE POLYCONDENSATION OF *p*-FERROCENYLACETOPHENONE*

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## Summary

The polycondensation of *p*-ferrocenylacetophenone in the presence of some metallic salts has been studied, and a scale of the catalytic activity of the metallic salts has been determined. The influence of the ferrocenyl residue on the carbonyl group in *p*-ferrocenylacetophenone and on the electrophysical properties is considered by applying Hückel MO calculations. The monomers synthesised show semiconducting properties.

## Introduction

In recent years an increasing number of investigators turned their attention to the effects of substituents in polyphenylacetylene syntheses as well as to their influence upon the properties of the polymers formed. Thus, for the polyphenylacetylenes obtained both by condensation and by polymerization the effects have been studied of *ortho*-, *meta*- and *para*-directing substituents introduced either by synthetic reactions of polymers [1] or by polymerization of the previously substituted monomers [2, 3].

Polyferrocenylacetylenes showing good electrophysical properties have been synthesised either by polymerization [4—6] or by polycondensation [7—9] of some substituted ferrocene derivatives.

The improvement of semiconducting properties achieved by introduction of the ferrocene ring into the macromolecular chain of polyphenylacetylene suggested that we should synthesize *p*-ferrocenyl substituted polyphenylacetylenes. In the present paper the syntheses and the properties of the poly-*p*-ferrocenylphenylacetylenes are reported.

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## Experimental

Attempts to prepare the $p$-ferrocenylacetophenone by means of Broadhead and Pauson's method [10] resulted in very small yields [11, 12]. By applying Nesmeyanov and co-worker's method, reported for the $p$-tolylferrocene synthesis [13], we prepared $p$-ferrocenylacetophenone in a 63% yield, starting from diazotised $p$-aminoacetophenone and ferrocene.

The values of physical constants of the obtained monomer are identical with those in the literature [11].

The bulk polycondensation was carried out in sealed glass ampoules, under inert atmosphere, in the presence of previously dehydrated metallic halides [14—18] as dehydrating catalysts.

The IR spectra were recorded on a Unicam SP 200 spectrophotometer. The thermodifferential analyses were performed by using a Paulik, Paulik and Erdey M.O.M.-Budapest apparatus. The monomer reactivity was estimated by means of calculations carried out with the aid of an Iris 50 type electronic computer.

## Results and discussion

### *Characterization of the monomer*

The $p$-ferrocenylacetophenone was characterized by elementary analysis, infrared absorption, and thermodifferential analysis. The IR spectrum (Fig. 1) shows all the absorption bands characteristic of aromatic and ferrocene rings at 1067 $cm^{-1}$ and 840, 1020 and 1110 $cm^{-1}$, respectively. The carbonyl absorption band at 1685 $cm^{-1}$ is very strong.

Since the reaction of the diazonium salt of the $p$-aminoacetophenone with ferrocene is carried out in acidic medium the ferrocene nucleus may protonate (iron is oxidised) leading to a cation as shown by Rosenblum [19]. The sulphur present in the counter ion was identified by elemental analysis.

In the NMR spectrum, in addition to the chemical shifts characteristic of the ferrocene nucleus $\delta$ 4-5 ppm, benzene ring 7.95 ppm and of the $CH_3$ group $\delta$ 2.7 ppm and 7.55 ppm, offset signals occur ($\delta$ 11.8-13.2 ppm) which may be probably attributed to the proton in the counter ion.

The monomer thermostability was determined from thermodifferential analysis data. The thermal decomposition takes place in several stages which

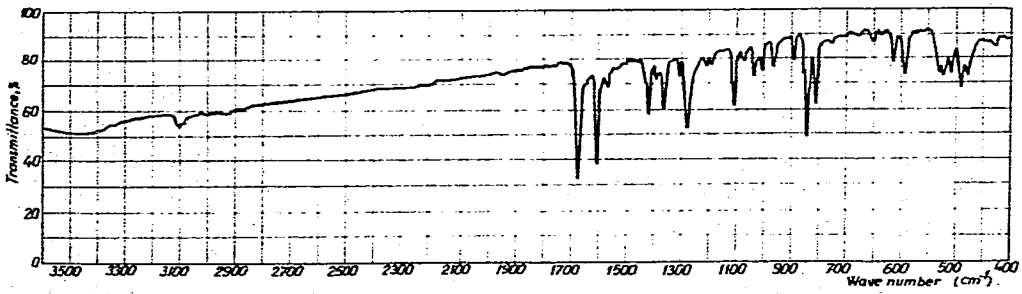


Fig. 1. Infrared spectrum of $p$-ferrocenylacetophenone.

TABLE 1

THERMAL DEGRADATION OF THE *p*-FERROCENYLACETOPHENONE

| Compound | Temperature range (°C) | Time interval (min.) | Weight loss (%) |
|---|---|---|---|
| *p*-Ferrocenylacetophenone | 155—400 | 15—40 | 32.90 |
| *p*-Ferrocenylacetophenone | 400—600 | 40—60 | 72.86 |

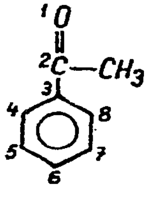
superimpose on one another, two processes being more distinct. The thermodestruction, as a function of temperature and time, is given in Table 1.

To appreciate the influence of ferrocenyl substituent on the reactivity of the carbonyl group some characteristics of the molecule were determined, such as the total energy, the resonance energy and the charge distribution, by Hückel molecular orbital calculation.

The parameters used in calculations, $\alpha$ (coulomb integral) and $\beta$ (resonance integral) were chosen according to the indications given in literature [19—22] (see Fig. 2).

Table 2 lists the values of total energy, resonance energy and electric charges on the atoms 1 and 2 in acetophenone as well as in *p*-ferrocenylacetophenone.

As can be seen from Table 2 the electric charges on the C and O atoms in the C=O group are larger for the *p*-ferrocenylacetophenone. This supports the assumption of a transmission of the ferrocene (electron donating) character to the carbonyl group through the benzene ring. The increased electron density at the carbonyl carbon atom results in a decreased reactivity of this group, as compared to that of the carbonyl group in acetophenone. This fact is also indicated by the values of resonance energies which are indicative of the greater reactivity of the unsubstituted monomer.



$\alpha_1 = \alpha + \beta$

$\alpha_2 = \alpha_3 = \alpha_{12} = \alpha_{18} = .......... = \alpha_{22} = \alpha$

$\alpha_{14} = ... = \alpha_{17} = \alpha + 2\beta$

$\beta_{1-2} = 1.1\ \beta$

$\beta_{2-3} = 0.9\ \beta$

$\beta_{14-9} = \beta_{14-18} = .... = 0.1\ \beta$

$\beta_{15-9} = \beta_{15-18} = .... = 0.2\ \beta$

$\beta_{16-9} = \beta_{16-18} = .... = 0.15\ \beta$

$\beta_{17-9} = \beta_{17-18} = .... = 0.5\ \beta$

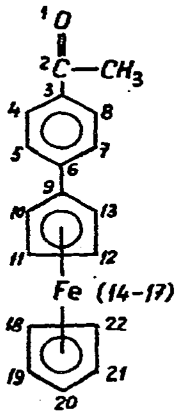


Fig. 2. Values of the parameters α and β.

TABLE 2

MOLECULAR CHARACTERISTICS OF THE MONOMER

| Monomer | Total energy (β) | Resonance energy (β) | Electric charge | |
|---|---|---|---|---|
| | | | O in C=O | C in C=O |
| Acetophenone | 11.7780 | 3.7780 | 1.4630 | 0.6533 |
| *p*-Ferrocenylacetophenone | 40.7600 | 14.7600 | 1.4727 | 0.6654 |

## *Polycondensation of p-ferrocenylacetophenone*

In the published literature rather few reports are to be found concerning the preparation of conjugated polyenes by poly- and copoly-condensation reactions [7—9, 24—27], although these reactions lead to polymers having uniform structures and higher molecular weights than those of polymers obtained by polymerization [25—27].

We synthesized poly-*p*-ferrocenylacetylene by condensation of *p*-ferroceny acetophenone in the presence of ten metallic halides. Dark-brown polymers were obtained that were insoluble in common solvents and burned without melting. The monomer was removed by extraction with acetone and the catalyst was removed by repeated washings with water, ammonia or alcohol.

The catalytic activity of the metallic halides was determined from the conversion values and is given in Table 3. As is obvious from Table 3 the catalytic activity of the metal halides decreases in the following order: $HgCl_2 \geqslant SnCl_2 \geqslant AlCl_3 > FeCl_3 > CuCl_2 \geqslant MgCl_2 > CoCl_2 \geqslant NiCl_2 > ZnCl_2 > CdCl_2$.

In the case of polycondensation reaction of phenylacetaldehyde the above catalysts were found to lie on another reactivity scale [27]. This is probably due to the nature of the carbonyl group, on one hand, and to the influence of the strong electron-donating ferrocenyl residue, on the other hand. The higher polymer yields obtained by Paushkin and co-workers on polycondensation of acetyl- and diacetyl-ferrocene, in the presence of $ZnCl_2$, as well as on copolycondensation with acetone and acetophenone [7—9], support the assumption that extension of the π—π conjugating effect in the case of our monomer results in a decrease of the ketonic group reactivity. Under our experimental conditions (catalyst/monomer mole ratio = 1/10) splitting of the ferrocene molecule did not occur.

TABLE 3

POLYCONDENSATION OF *p*-FERROCENYLACETOPHENONE IN THE PRESENCE OF METAL CHLORIDES

*Catalyst concn. (moles of catalyst/mole of monomer) = 0.1. Time of reaction 9 h.*

| Catalyst | Conversion (%) | Aspect of the polymer |
|---|---|---|
| $HgCl_2$ | 88.86 | brown-black powder |
| $SnCl_2$ | 87.86 | brown-black powder |
| $AlCl_3$ | 86.12 | bright black powder |
| $FeCl_3$ | 73.95 | bright brown powder |
| $CuCl_2$ | 67.53 | brown-black powder |
| $MgCl_2$ | 66.64 | brown-black powder |
| $COCl_2$ | 59.10 | brown-black powder |
| $NiCl_2$ | 58.60 | brown-black powder |
| $ZnCl_2$ | 52.63 | brown-black powder |
| $CdCl_2$ | 39.29 | brown-black powder |

### *The molecular structure and the properties of poly-p-ferrocenylacetylenes*

*(a). The molecular structure of the polymers* was deduced from IR spectra (see Fig. 3) and elemental analytical data. The spectra of the polymers synthesized in the presence of different metallic halides are identical. This fact is strong evidence for the fact that the catalyst nature does not influence the structure of the polymers obtained. The spectra show absorption bands characteristic of the benzene ring (at 1600—1610 $cm^{-1}$) and of the ferrocene ring (at 830—840 $cm^{-1}$, 1018—1020 $cm^{-1}$, 1090—1120 $cm^{-1}$). The absorption band $\nu(C=O)$, characteristic of the carbonyl group at the end of macromolecular chain, can also be found at 1675—1692 $cm^{-1}$.

Following the mechanism of Simionescu and co-workers [25, 27] for the polycondensation reaction carried out in the presence of metallic halides, in which the intermediate occurrence of some coordinate complexes is implied, the metallic halides are considered to increase the carbonyl group reactivities and to labilise the hydrogen at $C_\alpha$. Polyene units could be formed as shown in Fig. 4. Polymers of analogous structure, but with saturated main chain, have been obtained by synthetic reactions of polystyrene [28].

The possibility of a cross-linked structure is suggested by the insolubilities of the polymers as well as their decomposition without melting.

The reaction of ferrocene with ketones, in the presence of Lewis acids, leading to substitution products [29] suggests the formation of some segments of the type shown in Fig. 5, which contain ferrocenyl residues fixed heteroannularly.

As the acetylferrocene [30] can easily trimerize, cyclic trimer formation is also expected. Under our experimental conditions all these reactions are, undoubtedly, competitive and the synthesised polymers have three-dimensional structures.

The structures attributed to the polymers on the basis of only IR spectral measurements are inconclusive because of the superposition of the absorption of the ethylenic links on that of the aromatic ring, existing in the monomer molecule. In this connection the NMR spectra would have been of interest, but they could not be recorded because of the insolubilities of the polymers.

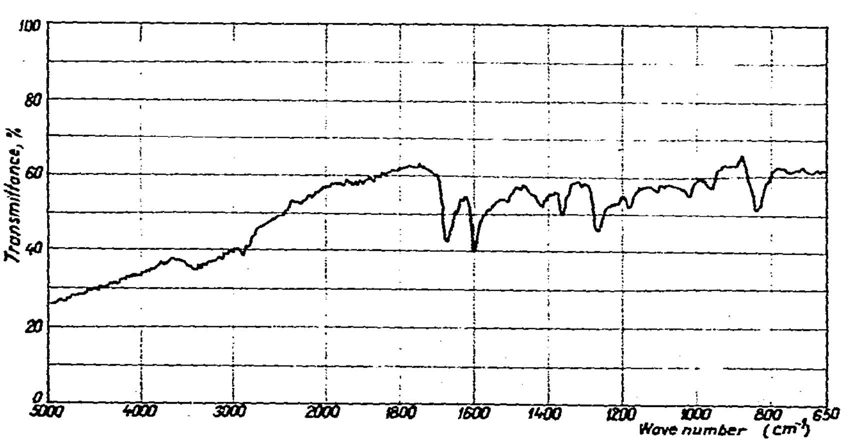
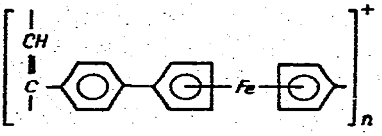


Fig. 3. Infrared spectra of polymers.



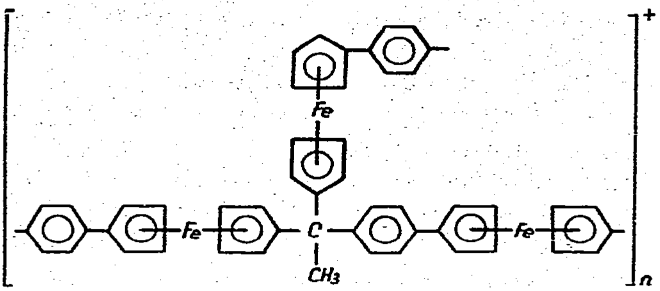


Fig. 4. Polyene units in the structures of the polymers.

Fig. 5. The assumed structure of the polymers.

*(b). Thermogravimetric analysis.* The thermostability was determined by thermodifferential analysis carried out between 20 and 900° at a heating rate of 9.8°/min in air. Table 4 shows the weight losses at different temperatures and time intervals. The thermal stability of the polymers up to 220—240° is good, thereafter losses begin. The thermal behaviour is analogous with that of condensation polyphenylacetylenes.

*(c). Electrophysical properties.* The electroconductivity and the paramagnetism (Table 5) are discussed as a function of the catalyst nature. The polymers showing the best electrophysical properties were found to be those synthesized in the presence of $NiCl_2$ and $CoCl_2$ which exhibit a lower catalytic activity. When using these catalysts the structure containing conjugate units predominates.

Table 6 compares the influences of the ferrocenyl residue and other substituents on the electrophysical properties of substituted polyphenylacetylenes and of polyferrocenylacetylenes obtained by several authors. The values of the electroconductivity and of the paramgnetic particle concentrations of poly-

TABLE 4

THERMAL DESTRUCTION OF POLY-*p*-FERROCENYLPHENYLACETYLENES

| Catalyst | Temperature range (°C) | Time (min.) | Weight loss (%) |
|---|---|---|---|
| $HgCl_2$ | 20—240 | 2—24 | 5 |
| | 240—725 | 24—72 | 71.70 |
| $SnCl_2$ | 20—225 | 2—22.5 | 2.5 |
| | 225—710 | 22.5—71 | 71 |
| $AlCl_3$ | 235—605 | 23—60 | 39.5 |
| | 605—900 | 60—90 | 73 |
| $FeCl_3$ | 235—660 | 23—66 | 48.46 |
| | 660—900 | 66—90 | 77.55 |
| $MgCl_2$ | 20—235 | 2—23.5 | 2.5 |
| | 235—760 | 23.5—76 | 81 |
| $CoCl_2$ | 20—240 | 2—24 | 4 |
| | 240—725 | 24—72.5 | 77 |
| $NiCl_2$ | 10—220 | 1—22 | 2 |
| | 220—735 | 22—73.5 | 78 |
| $ZnCl_2$ | 245—540 | 24.5—54 | 71 |
| $CdCl_2$ | 20—230 | 2—23 | 1 |
| | 230—760 | 23—76 | 77.27 |

TABLE 5

ELECTROPHYSICAL PROPERTIES OF THE POLYMERS AS A FUNCTION OF THE CATALYST

| Catalyst | Electroconductivity, $\Omega^{-1}$ ($cm^{-1}$) | $E_A$ (eV) | Unpaired electron concn. (spin/g) |
|---|---|---|---|
| $HgCl_2$ | 1.13 $10^{-11}$ | 0.207 | |
| $SnCl_2$ | 2.60 $10^{-12}$ | 0.445 | 6.5 $10^{17}$ |
| $AlCl_3$ | 2.10 $10^{-18}$ | 0.907 | |
| $FeCl_3$ | 1.86 $10^{-18}$ | 0.234<br>1.436<br>0.0229 | 1.9 $10^{18}$ |
| $CuCl_2$ | 6.20 $10^{-13}$ | 0.318 | 1.06 $10^{18}$ |
| $MgCl_2$ | 2.9 $10^{-13}$ | 0.345 | |
| $CoCl_2$ | 2.34 $10^{-12}$ | 0.283 | 6.09 $10^{17}$ |
| $NiCl_2$ | 4.13 $10^{-12}$ | 0.524 | 1.19 $10^{18}$ |
| $ZnCl_2$ | 2.5 $10^{-18}$ | 1.03 | 2.35 $10^{18}$ |

*p*-ferrocenylacetylenes are comparable with those of the other *p*-substituted polyphenylacetylenes, which places these polymers among the organic semiconductors. The poly-*p*-ferrocenylphenylacetylenes would be expected to possess higher semiconducting properties owing to the strong electron donating properties of the ferrocenyl as a substituent in aromatic ring [31, 32]. However, this was not so, probably because of steric hindrance, on one hand, and the three dimensional structure with a sufficiently small weight of the polyenic chain, on the other hand. The iron in the polymer is $Fe^{III}$ but on reduction it may change to $Fe^{II}$.

$$\text{P-}p\text{-FcFA} \rightleftharpoons \text{P-}p\text{-FcFA}^{n+} + ne^-$$

As this process is reversible the polymer might be used in redox systems.

## Conclusion

In order to obtain polymers with good semiconducting properties, the polycondensation of the *p*-ferrocenylacetophenone was studied. 1, The *p*-ferrocenylacetophenone was synthesized and characterized by means of elemental analysis, infrared absorption and thermodifferential analysis; 2, The influence of the ferro-

TABLE 6

VALUES OF THE ELECTROPHYSICAL CONSTANTS OF THE POLYMERS AS A FUNCTION OF THE *p*-SUBSTITUENT NATURE

| Polymer | Catalyst | Electroconductivity, $\Omega^{-1}$ ($cm^{-1}$) | Energy of activation (eV) | Paramagnetic particle concn. (spin/g) | Ref. |
|---|---|---|---|---|---|
| PFA [a] | $ZnCl_2$ | 1.4 $10^{-13}$ | 1.41 | 6.8 $10^{19}$ | 25 |
| $NO_2$-PFA | | 2.0 $10^{-14}$ | 1.43 | 4.42 $10^{17}$ | |
| $NH_2$-PFA | | 1.67 $10^{-13}$ | 0.96 | 5.38 $10^{18}$ | |
| Cl-PFA | | 6.10 $10^{-13}$ | 0.70 | 6.7 $10^{19}$ | 3 |
| PFcA [b] | $ZnCl_2$ | $10^{-10}$ | | | 9 |
| PFcA | $B(i\text{-}C_3H_7)_3$ | $10^{-12}$ to $10^{-10}$ | 1.12 to 0.96 | $10^{18}$ to $10^{19}$ | 5 |
| P-*p*-FcFA [c] | MeX | $10^{-18}$ to $10^{-11}$ | 0.20 to 1.43 | $10^{17}$ to $10^{18}$ | |

[a] PFA = polyphenylacetylene. [b] PFcA = polyferrocenylacetylene. [c] P-*p*-FcFA = poly-*p*-ferrocenylphenylacetylene.

cenyl residue on the $C=O$ group reactivity in acetophenone was elucidated by Hückel molecular orbital calculations; 3, The catalytic activity of ten metallic halides in these polycondensation reactions was determined; 4, The influence of the ferrocenyl residue on the electrophysical properties of the polymers is discussed in comparison with that of other substituents; 5, The influence of steric factors on the values of the paramagnetic particle concentrations and of the electroconductivity was determined; 6, It is suggested that these polymers may be used in redox systems.

## References

1 Cr. Simionescu and S. Vasiliu, Acta. Chim. Acad. Sci. Hung., in print.
2 T. Lixandru, S. Dumitrescu, F. Deneş, B. Simionescu and M. Vâţă, R.C.G.P., 48, 2 (1971) 193.
3 Cr. Simionescu, S. Dumitrescu, T. Lixandru, M. Dărîngă, B. Simionescu and M. Vâţă, Eur. Polym. J., 8 (1972) 719.
4 Cr. Simionescu, T. Lixandru, I. Mazilu and L. Tătaru, Makromol. Chem., 147 (1971) 69.
5 Cr. Simionescu, T. Lixandru, I. Negulescu, I. Mazilu and L. Tătaru, Makromol. Chem., 163 (1973) 59.
6 T. Nakashima, T. Kuitake and C. Aso, Makromol. Chem., 157 (1972) 73.
7 Ya.M. Paushkin, T.P. Vishnjakova, P.I. Patalah, T.A. Sokolinskaja and F.F. Macius, Dokl. Akad. Nauk SSSR, 149 (1963) 856.
8 Ya.M. Paushkin, T.P. Vishnjakova, J.A. Golubeva, T.A. Sokolinskaja and F.F. Macius, J. Polymer Sci., Part C, 16 (1969) 4297.
9 Ya.M. Paushkin, T.P. Vishjakova, L.S. Polak, I.I. Patalah, F.F. Macius and T.A. Sokolinskaja, Vîsokomol. Soed., 6 (1964) 545; J. Polymer Sci., Part C, 4 (1964) 1481.
10 G.D. Broadhead and P.L. Pauson, J. Chem. Soc., (1955) 367.
11 M. Rosenblum, W.G. Howells, A.K. Banerjee and C. Bennet, J. Amer. Chem. Soc., 84 (1962) 2726.
12 M. Rosenblum, J. Amer. Chem. Soc., 81 (1959) 4530.
13 A.N. Nesmeyanov, E.G. Perevalova, N.A. Simucova, T.V. Nikitina and P.D. Reşetova, Izv. Akad. Nauk SSSR, 77 (1961).
14 T. Zürrer, Helv. Chim. Acta, 15 (1932) 1276.
15 P. Pascal, Traité de Chimie Minérale, 1932, vol. 7, p. 257.
16 P. Pascal, Nouveau Traité de Chimie Minérale, 1963, vol. 8, p. 361.
17 B. Khundkar, J. Ind. Chem. Soc. Ind. News, 14 (1951) 39.
18 P. Pascal, Nouveau Traité de Chimie Minérale 1963, vol. 17, 216.
19 T.J. Curphey, J.O. Santer, M. Rosenblum and J.H. Richards, J. Amer. Chem. Soc., 82 (1960) 5249.
20 W.P. Purcele and J.A. Singer, J. Chem. Eng. Data, 12 (1967) 235.
21 A. Streitwieser, Jr., Molecular Orbital Theory for Organic Chemistry, Russian edition, 1965.
22 K. Higasi, H. Baba and A. Rembaum, Quantum Organic Chemistry, Russian edition, 1967.
23 J.P. Dahl and C.J. Ballhausen, Mat. Fys. Medd. Dan. Vid. Selsk., 33 (1961) 1.
24 V.A. Kargin, V.A. Kabanov, V.P. Zubov, I.M. Papisov and G.I. Kurocikina, Dokl. Akad. Nauk, SSSR, 140 (1961) 122.
25 Cr. Simionescu and S. Vasiliu, Plaste und Kautschuk, 18, (1971) 260.
26 S. Vasiliu, T. Istrati and A. Bilanici, Materiale plastice, 10 (1973) 305.
27 Cr. Simionescu and S. Vasiliu, Acta Chim. Acad. Sci. Hung., 74 (1972) 461.
28 B. Sansoni and O. Sigmund, Angew. Chem., 73 (1961) 299.
29 E.W. Neuse and H. Rosenberg, J. Makromol. Sci., 4 (1970) 1.
30 K. Schlögl and H. Soukup, M., 99 (1968) 927.
31 E.G. Perevalova, K.I. Grandberg, N.A. Jarikova, S.P. Gubin and A.N. Nesmeyanov, Izv. Akad. Nauk SSSR, Ser. Khim., (1966) 832.
32 A.N. Nesmeyanov, E.G. Perevalova and R.V. Golovnja, Dokl. Akad. Nauk SSSR, 103 (1955) 81.