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Oligomerization of phenylferrocenylacetylene under the action of WCl₆

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ABSTRACT

Phenylferrocenylacetylene was found to be capable of oligomerizing in the presence of WCl₆ (130 °C, 24 h) to afford short polyenes (with about 5 monomer units in the macromolecule) in up to \sim 30% yield. The polyenes synthesized are promising reactive macromonomers and building blocks for high-tech materials.

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1. Introduction

The last decades have witnessed an immense research interest in ferrocene-containing polymers and oligomers due to the quest for novel high-tech materials including those employed in living systems and processes of transmission and storage of information [1,2]. For example, ferrocene-containing pyrrole was polymerized with glucoxidaze on the electrode surface to study the charge transfer from the enzyme to electrode [3]. As mediators between oxidases and electrode, ferrocene-containing polysiloxanes were used. Electrochemical properties of ferrocene-containing oligomers of polyethylene oxides were studied. The structure of these oligomers was close to that of natural compound, glycerol oligoethers, where a ferrocene moiety was bonded with the main chain by the sulfide bridge [3]. It is known that the incorporation of the ferrocene fragment into diverse polymeric architectures imparts them valuable redox, electric, magnetic, preceramic, catalytic and optical properties [2,4].

Synthesis of polyenes bearing pendant ferrocene substituents is one of the priority areas in this research. The insertion of ferrocene units into the polyene backbone attracts a special attention owing to the electronic donating ability, reversible of redox chemistry, peculiar steric properties and ready functionalization of these fragments [5]. As followed from the review, the most logical way to obtain polyenes with pendant ferrocene substituents was polymerization or oligomerization of ferrocenylacetylenes [5]. Numerous applications of such an approach were summarized in reviews and monographs [5]. However, it was reported [5] that many early attempts to polymerize ethynylferrocene produced poorly characterized oligomers [6,7]. Only decades later [8], the Schrock metathesis catalyst, $Mo(N-2,6-Me_2C_6H_3)(CHCMe_2Ph)$ [OCMe(CF₃)₂]₂, has been employed in ethynylferrocene polymerization to furnish well soluble polyene polymers with up 50 double bonds. Polymerization of N-(4-propynyloxy)-2-aza- [3]-ferrocenophane, catalyzed by the Rh(I) complex, produced polyenes with pendant ferrocenophane [9]. The polymerization of diphenylacetylenes containing the ferrocenyl group in para- or meta-positions was accomplished in the presence of catalytic system TaCl₅-n-Bu₄Sn [10]. Recently [11], dipolar second-order nonlinear optical chromophores containing ferrocene donor entity and 3dicyanomethylidene-1-indanone acceptor group bridged by the polyene chain of different length were synthesized.

The above short literature excursus clearly shows that the polymerization of acetylenes with ferrocene-containing substituents meets with success only in the case of application of sophisticated, inaccessible and expensive metal-complex catalysts.

The present work deals with the development of a facile and convenient method for the synthesis of polyene oligomers containing pendant ferrocene and benzene substituents *via* the oligomerization of phenylferrocenylacetylene (**1**) in the presence of cheaper and available catalyst WCl₆. Novelty and challenge of this research was that, unlike most known examples related to terminal



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ferrocenylacetylenes, here, an internal acetylene, namely ferrocenylacetylene bearing phenyl substituent at the acetylenic carbon, was subjected to oligomerization. Polymerization of such acetylenes is known to be substantially hampered due to steric hindrances toward the growth of polymer chain imposed by the phenyl substituents. It is not occasionally that the polymers of internal acetylenes with ferrocene substituents are virtually unknown, the only exception being likely the above-cited work [11]. Meanwhile, the introduction of extra benzene substituent into every unit of the polyene increases conjugation degree and ability of the polyconjugated chain to electron transfer. Besides, this creates additional opportunities for chemical modification of the oligomer through the reactions of the benzene ring.

2. Results and discussion

2.1. Synthesis of phenylferrocenylacetylene (1)

The starting monomer (phenylferrocenylacetylene) **1** was synthesized by the method representing a combination of the following four steps: (1) the synthesis of copper phenylacetylenide [12], (2) synthesis of chloromercuroferrocene [13], (3) synthesis of iodoferrocene [14] and (4) non-catalytic cross-coupling of the latter with copper phenylacetylenide [15] (Scheme 1).

When reproducing the protocols [12–15], at the first three steps we frustrated to reach the yields of the target compounds indicated in the above-cited works (Scheme 1). Only at the last step the yield of the target product (relative to the original protocol) was augmented noticeably due to the increase of the reaction duration.

2.2. Oligomerization of phenylferrocenylacetylene (1)

Oligomerization of phenylferrocenylacetylene (1) was carried out in the presence of WCl₆ (Scheme 2). The catalytic system WCl₆—Ph₄Sn, commonly employed for the polymerization of diverse acetylenic monomers [16], was used for the comparison. The efficacy of radical initiation by dinitrile of azoisobutyric acid (AIBN) and UV-irradiation was also checked. The oligomerization conditions and oligomers yields are shown in Table 1.

Under these conditions the oligomers of phenylferrocenylacetylene **2** were obtained in up to 29% overall yield. The oligomers consisted of soluble (chlorobenzene, nitrobenzene, chloroform, tetrahydrofuran) and insoluble (in some cases) fractions. Molecular weight of soluble oligomer prepared by WCl₆ catalysis (130 °C, 24 h, Table 1) was 1700 that corresponded to five elementary units.

The reactivity of disubstituted acetylenes in the WCl_6 or WCl_6 –Ph₄Sn-catalyzed polymerization is known to be many-fold lower (by 4–5 times) than that of the terminal acetylenes [16]. In

$$I. \qquad \bigoplus_{EiOH-H_2O, 20 °C, 15 min} \qquad \bigoplus_{GO\% (77\% [12])} Cu$$

$$I. \qquad \bigoplus_{GO\% (77\% [12])} Hg(CH_3COO) \qquad \bigoplus_{Fe} Hg(CH_3$$



93% (84% [15])

Scheme 1. Synthesis of phenylferrocenylacetylene.



n = 5 (for soluble oligomer obtained in the presence of WCl₆ (130 °C, 24 h))

Scheme 2. Polymerization of phenylferrocenylacetylene.

our case, the observed low proneness of phenylferrocenylacetylene to polymerization is in good agreement with these literature data. The comparison of oligomer yields obtained in the presence of WCl₆ and the system WCl₆—Ph₄Sn (Table 1) show that these catalysts possess almost similar reactivity.

Radical initiation of phenylferrocenylacetylene polymerization (AIBN, UV-irradiation or both) afforded the oligomers in negligible yields (not exceeding 5%), the final products being completely insoluble (Table 1).

According to the IR spectroscopy data, oligomers **2** have polyene main chain with pendant ferrocenyl and phenyl substituents (Scheme 2).

The spectra of the oligomers contained no absorption bands of the C=C bond (in the monomer, these bands were observed at 2208 and 2223 cm⁻¹). Bands of other groups and bonds were significantly broadened that was typical for oligomers. The absorption bands of the ferrocene skeleton and benzene ring remained at 1685–1780 cm⁻¹ and 693–700, 756–765, 1600, 1630–1638, 3057–3065 cm⁻¹, respectively. The absorption bands of the C=C bond appeared in the region 1640–1650 cm⁻¹.

Electroconductivity and paramagnetism of the soluble fraction of oligomers **2** were measured and its thermal stability was evaluated.

As expected, oligomers **2** showed semi-conducting properties ($\sigma = 1.0 \ 10^{-9} \ S \ cm^{-1}$). Doping of the oligomers with iodine increased their electroconductivity by 3 orders ($\sigma = 1.0 \ 10^{-6} \ S \ cm^{-1}$).

Oligomers **2** were paramagnetic. In their ESR spectra, a singlet on the background of very broad line of Fe³⁺ ($N = 6.7 \ 10^{17} \ \text{spin g}^{-1}$; $\Delta H = 9.2 \ \text{G}$; g = 2.0029) was registered.

Table 1	
Oligomerization conditions and yield of oligophenylferrocenylacetylene.	

Catalyst (wt %) ^a or initiator (wt %) ^a or initiation	Solvent	Monomer concentration, wt %	T, °C	Time, h	Yield ^b , %
WCl ₆ , 4.6	No solvent	100	130	64	29 (15 ^c)
	No solvent	100	130	24	15 (15 ^c)
	Chlorobenzene	30	90	24	14 (4 ^c)
	Chlorobenzene	10	90	24	11 (11 ^c)
WCl6-Ph4Sn, 14	Benzene	30	80	24	12 (9 ^c)
	Benzene	10	80	24	6 (6 ^c)
AIBN, 4.0	Benzene	35	90	48	4 (0 ^c)
AIBN + UV, 2.0	Benzene	35	85	48	5 (0 ^c)
UV	Benzene	35	85	48	5 (0 ^c)
WCl ₆ -Ph ₄ Sn, 14 AIBN, 4.0 AIBN + UV, 2.0 UV	Chlorobenzene Benzene Benzene Benzene Benzene Benzene Benzene	10 30 10 35 35 35	90 90 80 80 90 85 85	24 24 24 24 48 48 48	$ \begin{array}{c} 14 (4') \\ 11 (11^{c}) \\ 12 (9^{c}) \\ 6 (6^{c}) \\ 4 (0^{c}) \\ 5 (0^{c}) \\ 5 (0^{c}) \end{array} $

^a Relative to monomer.

^b Overall yield of oligomer.

^c Yield of soluble fraction.

The study of thermal oxidative destruction of a sample (obtained with 4.6 wt % WCl₆, 130 °C, 24 h, Table 1) of oligomers **2** demonstrated that it lost 10 wt % of weight upon heating up to 250 °C. Further heating (up to 400 °C) resulted in 50 wt % weight loss. The DTA curve showed one exothermic peak at 275 °C ($\Delta T = 118$ °C). Total destruction of the oligomer occurred at 540 °C.

3. Conclusion

In conclusion, for the first time, WCl₆ was shown to be active for the oligomerization of internal ferrocenylacetylenes to afford short polyenes with pendant ferrocene and benzene substituents in moderate yields. Such polyenes are promising reactive macromonomers and building blocks for the design of high-tech polymer materials including those possessing improved redox, electric, magnetic, preceramic, catalytic and optical properties.

4. Experimental

4.1. Materials

Solvents (chlorobenzene, toluene, *n*-hexane) were purified according to the literature protocols [17]. AIBN was recrystallized twice from ethanol (m.p. 102 $^{\circ}$ C).

Phenylferrocenylacetylene (1) was synthesized by the procedures [12–15]. Before polymerization, monomeric phenylferrocenylacetylene (1) was purified by recrystallization from ethanol, constants of the monomer corresponded to literature data [15], purity of the monomer was controlled by IR, NMR and chromatomass-spectrometry techniques.

4.2. Physical measurements

IR spectra of phenylferrocenylacetylene (1) and oligomers 2 were registered in the region 400–4000 cm⁻¹ with a FT IR Spectrometer Vertex-70 instrument as KBr pellets. NMR spectra were recorded at room temperature on a Bruker DPX 400 (400.13 MHz for ¹H and 100.6 MHz for ¹³C) using CDCl₃ solvent and HMDS as the internal standard.

The electrical conductivity of oligomers **2** was measured with an E6-13A teraohmmeter. The studied samples were prepared as pellets by molding under a pressure of 700 kg cm⁻². The oligomers were doped with iodine using diffusion technique from gas phase for 24 h.

The ESR spectra were measured with an ELEXSYS E580 Bruker spectrometer in CW or pulse mode at room temperature. The concentration of paramagnetic centers was calculated by the method of double integration using the calibrated diphenylpycrylhydrazyl as standard.

The mass spectra (electron impact, 70 eV) were recorded on a Shimadzu GCMS-QP5050A instrument. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer.

The thermogravimetric analysis (TGA) of oligomers **2** was performed on a Q-1500D derivatograph (MOM, Hungary), maximal temperature 700 °C, at heating rate of 5 °C min⁻¹; the sensitivity for DTA was 1/10.

Oligomerization of phenylferrocenylacetylene under UVirradiation was performed in a quartz ampoule using a 222 W Hg lamp.

To evaluate the molecular weight of oligomers **2** size exclusion chromatography (SEC) in THF (0.2% solution) was conducted at an elution rate of 1.1 mL min⁻¹ using Waters gel columns: 250, 500, and 1000Å at 25 °C.

4.3. Synthesis

4.3.1. Phenylferrocenylacetylene

M.p. 126-128 °C. IR (KBr, cm⁻¹): 3097 w, 3064 w, 3023 w, 2922 m, 2851 w, 2223 and 2208 ($v_{C}\equiv_{C}$), 1955 w, 1885 w, 1767–1644 (w, ferrocene skeleton), 1596 w, 1570 w, 1492 m, 1439 m, 1408 w, 1386 w, 1350 w, 1331 w, 1292 w, 1275 w, 1254 w, 1204 m, 1165 w, 1154 w, 1102 m, 1069 m, 1051 w, 1024 m, 999 m, 922 m, 864 w, 822 s, 813 m, 785 w, 693 s, 669 w, 544 m, 515 m, 496 s, 483 s, 468 m. ¹H NMR (CDCl₃): δ 7.47 (m, 2H, H_o), 7.29 (m, 3H, H_{m.p.}), 4.48 (t, 2H, ³J_{\alpha,\beta} = 1.9 Hz, H_{\alpha}), 4.22 (s, 5H, C₅H₅), 4.21 (t, 2H, ³J_{\beta,\alpha} = 1.9 Hz, H_{\beta}). ¹³C NMR (CDCl₃): δ 131.37 (C₀), 128.25 (C_m), 127.62 (C_p), 123.92 (C_i of the benzene ring), 88.27 (Fc–C=C), 85.70 (C=C–Ph) 71.38 (2Ca), 69.94 (C₅H₅), 68.78 (2C_{\beta}), 65.24 (C_i of the ferrocene ring). The assignment of carbon and proton signals was made using 2D HMBC technique. MS (*m*/*z*): 286 (*M*⁺, 100), 228 (9), 215 (2), 202 (3), 165 (17), 152 (6), 143 (11), 139 (5), 121 (18), 105 (1), 95 (2), 94 (2), 81 (3), 63 (3), 56 (28), 39 (7). Anal. Calc for C₁₈H₁₄Fe (286.16): C, 75.55; H, 4.93; Fe, 19.52. Found: C, 75.44; H, 5.08; Fe, 19.49.

4.3.2. Oligomerization of phenylferrocenylacetylene (typical procedure)

Phenylferrocenylacetylene (8.78 g, 30.68 mmol) and WCl₆ (0.404 g, 1.02 mmol) was placed in an ampoule blown with argon. The ampoule was sealed and thermostated at 130 °C for 24 h. The reaction mixture was dissolved in benzene (20 ml), the insoluble fraction was separated from soluble one by filtration. The insoluble fraction was washed with benzene. The soluble fraction was precipitated in *n*-hexane (100 ml) and washed with the precipitator (3 × 50 ml). Both fractions were dried in vacuum (1 Hg mm) until the constant weight to give 2.55 g of oligophenylferrocenylacetylene in 29% overall yield. The yield of soluble fraction was 15% (1.32 g). Both fractions of oligophenylferrocenylacetylene are dark-

brown powders, infusible on heating up to 350 °C, insoluble in *n*-hexane, ethanol, acetone, acetonitrile. Anal. Calc. for $C_{18}H_{14}Fe$ (286.16): C, 75.55; H, 4.93; Fe, 19.52. Found for soluble fraction: C, 74.97; H, 5.08; Fe, 19.10.

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