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Graphical Abstract

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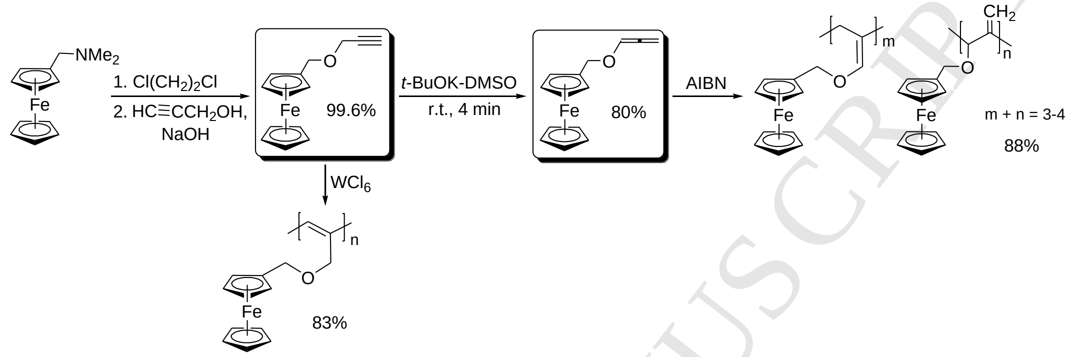

*Graphical abstract: synopsis (for review)

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Highlights

An efficient method for the synthesis of propargyloxymethylferrocene in almost quantitative yield has been elaborated. Previously unknown allenyloxymethylferrocene has been synthesized in 80% yield. Preliminary cationic and radical oligomerizations of both monomers have been studied and novel oligomers with the polyene chain and pendant ferrocenyl moieties synthesized in 83-88% yields. The oligomers exhibit semiconducting and paramagnetic properties and stable up to 300-340 ºC.

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A B S T R A C T

Propargyloxymethylferrocene has been synthesized by the modified reaction of available N,N-dimethylaminomethylferrocene with propargyl alcohol in the presence of dichloroethane and NaOH, the yield reaching 99.6%. The rapid prototropic isomerization of propargyloxymethylferrocene in the superbase system *t*-BuOK/DMSO (room temperature, 4 min) leads to previously unknown allenyloxymethylferrocene in 80% yield. Preliminary cationic and radical polymerization of both monomers have been studied and novel oligomers with the polyene chain and pendant ferrocenyl moieties containing soluble and insoluble fractions have been synthesized in 83-88% total yields. All the oligomers exhibit semiconducting and paramagnetic properties and stable up to 300-340 °C.

Keywords: propargyloxymethylferrocene, allenyloxymethylferrocene, synthesis, oligomerization, electroconductivity, paramagnetic properties

1. Introduction

Chemistry of the ferrocene-tailored compounds keeps rapidly developing due to the great diversity of their applications. The ferrocene derivatives are applied as biosensors [1,2], ligands of asymmetric synthesis catalysts [3,4], ionic liquids [5], components of the rocket propellants [6], starting materials for various carbon modifications [7]. They exhibit multi-facet biological activity including anti-malarial [8], anti-cancer [9-12], anti-microbial [13,14]. They possess electrochromic [15] and NLO properties [16], and prospective as electro-conductive materials [17].

Now, an ever-growing attention is attracted to ferrocene-containing polymers and oligomers as promising materials for advanced technologies. In this line, of a special interest are the polyenes with pendant ferrocenyl moieties. For instance, the polyene obtained from ethynylferrocene in the presence of rhodium catalysts, is considered as new cathode-active, charge-storage material for rechargeable batteries [18]. Oligomers and copolymers of the same monomer synthesized in the presence of molybdenum catalysts show NLO properties [19]. Recently, we have synthesized

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similar polyenes, having semi-conducting and paramagnetic features, oligomerization of phenylferrocenylacetylene in the presence of WCl_6 [20].

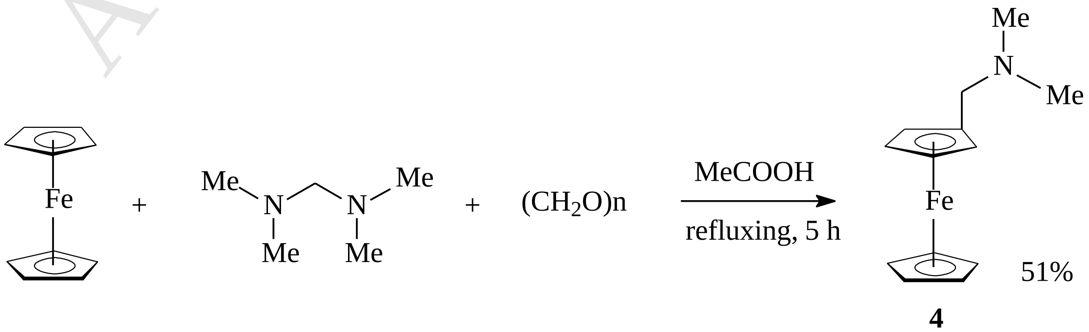
Here we report a new synthetic approach from ferrocene to propargyloxymethylferrocene (**1**) and allenyloxymethylferrocene (**2**) and their oligomers, reactive building blocks, monomers and macromonomers.

Ferrocene (**1**) has been recently synthesized (in 50% yield) by the reaction of ferrocenylmethanol with propargyl bromide in DMSO in the presence of NaOH [21]. The starting ferrocenylmethanol was prepared by reduction of ferocenylcarbaldehyde [22]. Ferrocene (**1**) has been employed for the synthesis of supramolecular structures [21], 4-(ferrocenylmethoxymethyl)-1-(1,2,3-triazolyl)benzylacetate [23] and ferrocene-glycine conjugate [24], the latter being applied as electrochemical receptor for selective detection of Hg^{+2} in water.

2. Results and discussion

The disadvantage of the known method for the preparation of propargyloxymethylferrocene (**1**) is application of expensive *t*-BuLi at the stage of ferrocene deprotonation.

Here for the synthesis of ferrocene (**1**) we have modified the synthesis of alkoxymethylferrocenes via quaternary ammonium salts of N,N-dimethylaminomethylferrocene (**3**) [25-27]. This method was previously used for the preparation of alkyl and allyl ethers of ferrocenylmethanol [25,26]. However, its suitability for the preparation of propargyl ethers remains obscure. Our modification of the synthesis of ferrocene (**1**) comprises the reaction between N,N-dimethylaminomethylferrocene (**4**) and propargyl alcohol in the presence of dichloroethane (90-96 ºC, 1.5 h) followed by the treatment with NaOH (54-103 ºC, 2 h). The yield of ferrocene (**1**) is almost quantitative (99.6% based on the aminomethylferrocene **4** consumed or 72% based on the ferrocene **4** taken), Scheme 1. Unreacted ferrocene **4** is easily isolated (as the salt) from the reaction mixture upon its acidification with 2% aqueous HCl.



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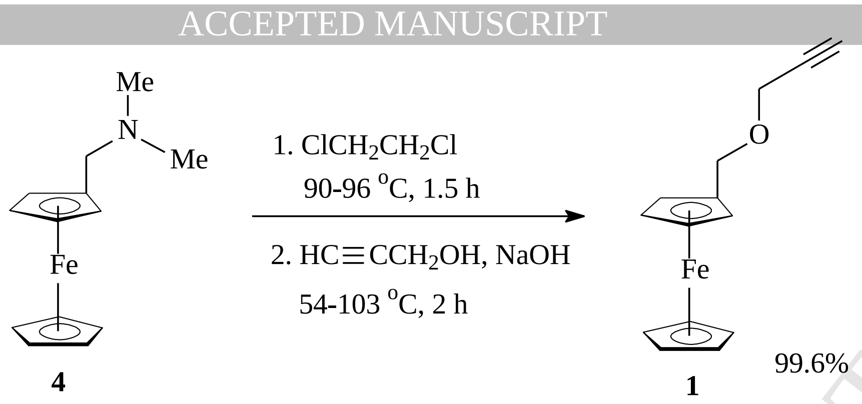
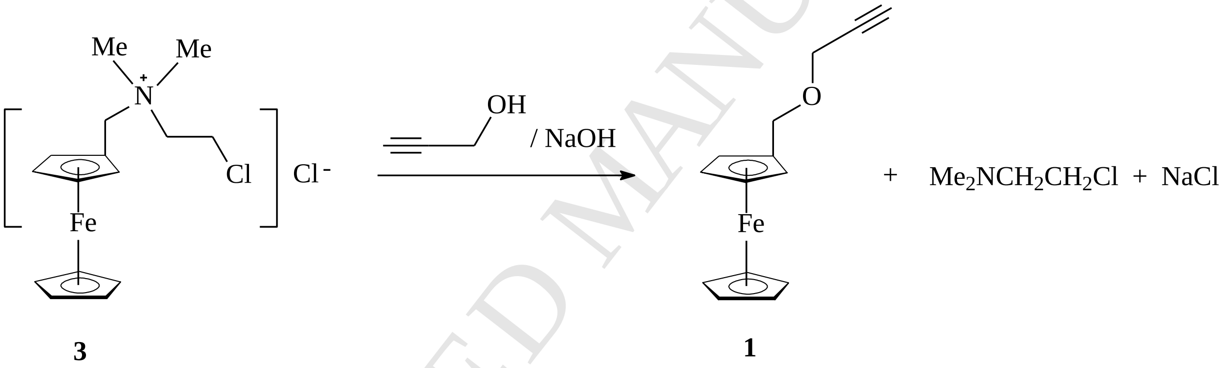


Scheme 1. Synthesis of propargyloxymethylferrocene from ferrocene.

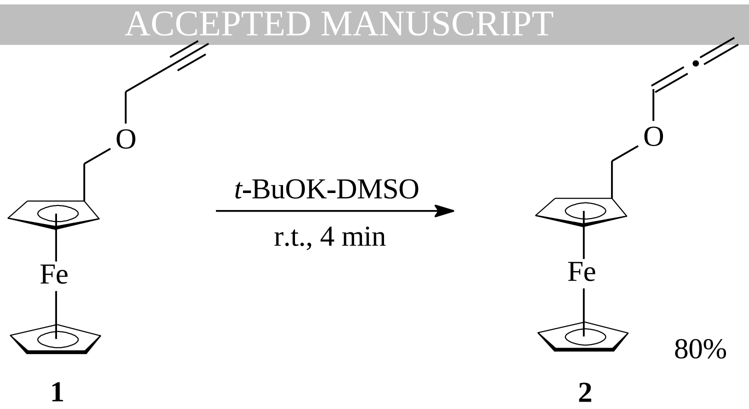
Apparently, the quaternary ammonium salt (**3**) undergoes the nucleophilic substitution by propargyloxy anion at the Fc<u>C</u>H$_2$ carbon to release (2-chloroethyl)dimethylamine hydrochloride, which further decomposes by NaOH (Scheme 2).



Scheme 2. Decomposition of quaternary ammonium salt (**3**) under the action of propargyl alcohol and NaOH.

The obvious advantages of the method developed (except for the quantitative yield of the target product) are its one-pot implementation, avoiding use of expensive *t*-BuLi and inert atmosphere which require for the synthesis of ferrocene carbaldehyde, an intermediate in the alternative method [22]. The starting N,N-dimethylaminomethylferrocene (**4**) is readily available by aminomethylation of ferrocene with N,N,N',N'-tetramethyldiaminomethane and paraform according to [28].

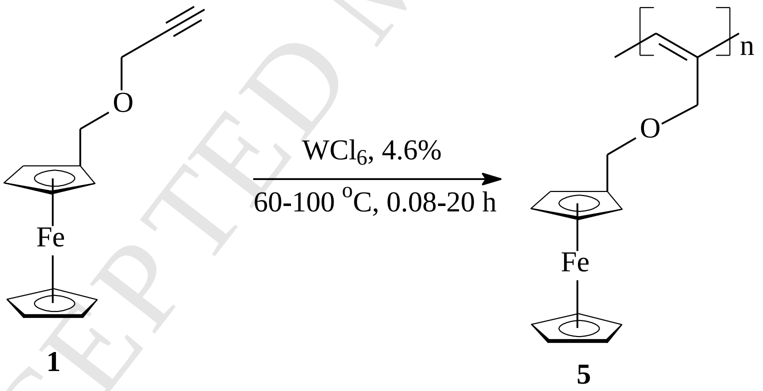
Previously unknown allenyloxymethylferrocene (**2**) has been synthesized by the instant prototropic isomerization of ferrocene **1** in the superbase system *t*-BuOK-DMSO (room temperature, 4 min), the yield being 80% and the conversion of ferrocene **1** reaching 96% (Scheme 3).



Scheme 3. Prototropic isomerization of ferrocene **1** to allenyloxymethylferrocene (**2**).

Thus, due to the methods elaborated, ferrocenes **1** and **2** are now becoming readily available ferrocene synthons and monomers for their further large-scale explorations, first of all, oligomerization.

Previously, we have carried out the cationic oligomerization of phenylferrocenylacetylene in the presence of WCl_6 (4.6%) [20]. Consequently, we have employed this catalyst for cationic oligomerization of ferrocene **1** to afford the expected polyene **5** with pendant ferrocenylmethyloxymethyl moieties (Scheme 4).



Scheme 4. Cationic oligomerization of propargyloxymethylferrocene.

Under the conditions shown in Table 1, oligomers **5** have been isolated as soluble (benzene, chlorobenzene and chloroform) and insoluble fractions in a total yield up to 83%, **5a**,**c**,**e** and **5b**,**d**,**f**, respectively. When oligomerization is performed in benzene (60 ºC), the yields of the soluble and insoluble fractions are 55% and 21%, correspondingly. Under the solvent-less conditions (100 ºC) the yield of the soluble fraction decreases to 33%, while the yield of insoluble increases to 50% (Table 1).

Table 1

Conditions of monomers **1**, **2** oligomerization

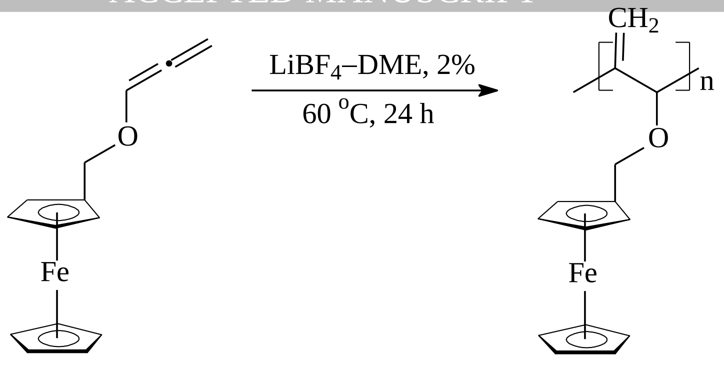
Monomer	Catalyst or initiator (wt %)[a]	T, ^{o}C	Time, h	Oligomer	Yield, %
1	WCl_6, 4.6	100	0.08	**5a**	33[b]
				5b	50[c]
1	WCl_6, 4.6	60[d]	20	**5c**	55[b]
				5d	21[c]
1	WCl_6, 4.6	60[d]	2	**5e**	20[b]
				5f	11[c]
2	$LiBF_4$, 2.0	60	24	**6**	10[b]
2	AIBN, 3.0	80	24	**7a**	88[b]
2	AIBN, 2.0	80	24	**7b**	79[b]
2	AIBN, 3.0	60	69	**7c**	81[b]
2	AIBN, 2.0	60	24	**7d**	44[b]

[a] Relative to monomer.
[b] Yield of the soluble fraction.
[c] Yield of the insoluble fraction.
[d] Polymerization in benzene (monomer:benzene = 1:3).

The IR spectra confirm that polyenes **5a**-**f** consist of the polyene chain with pendant ferrocenylmethyloxymethyl substituents. The spectra lack the absorption bands at 3222 (HC≡) and 2119 cm^{-1} (C≡C) which are present in monomer **1**. Absorption bands of the ferrocene nuclei (1730-1685 cm^{-1}), C–O–C (1037-1022 cm^{-1}) and OCH_2 (2886-2833 cm^{-1}) groups remain in the spectra and absorption band of the polyene chain appears at 1640-1630 cm^{-1}. As typical for oligomers, all the absorption bands are broaden.

The ^{1}H NMR spectrum of oligomers **5a**,**c**,**e** shows broad signals of the vinyl protons at 5.69-5.46 ppm, broad signals of ferrocene skeleton protons at 4.35-3.90 ppm, while a signal of the OCH_2 group protons (4.11-4.15 ppm) is observed in a region of ferrocene protons. Also, signals of the C–CH_2 group protons appear (3.31-3.39 ppm), and signals of the –C≡CH fragment are absent (in the monomer the signal of this fragment is at 2.43 ppm).

The cationic oligomerization of allenyloxymethylferrocene (**2**) has been carried out in the presence of catalytic system $LiBF_4$–dimethoxyethane (DME), especially efficient in the polymerization of vinyl ethers [29], the soluble oligomer **6** in 10% yield has been obtained (Table 1, Scheme 5).

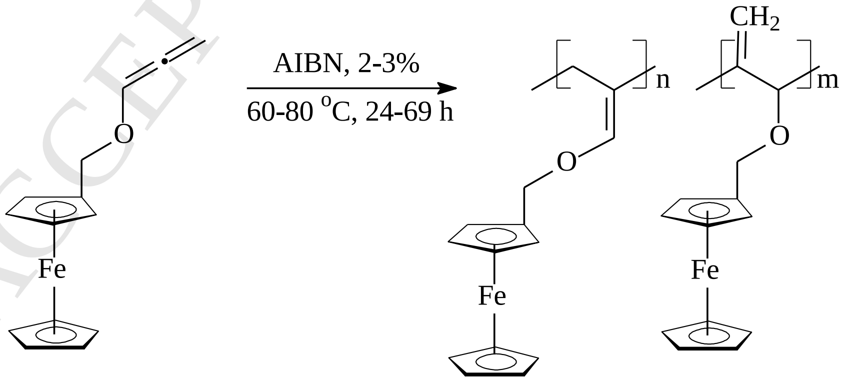


2 **6**

Scheme 5. Cationic oligomerization of allenyloxymethylferrocene.

According to the IR and ^{1}H NMR spectra, the oligomerization proceeds across the double bond adjustment to the oxygen atom to form the oligomer containing *exo*-methylene group in each oligomer unit that is in agreement with the literature data on polymerization of alkoxyallenes [30, 31]. In the IR spectrum of sample **6**, absorption bands assigned to the CH_2=C group are observed at 1642 cm^{-1}, and the absorption bands of the ferrocene skeleton (1715-1680 cm^{-1}) and the C–O–C (1040-1024) and OCH_2 (2886-2833) groups remain. In the ^{1}H NMR spectrum, one signals of the vinyl group protons is present at 4.93-4.98 ppm (CH_2=C), protons of the polymer chain –CH appear at 2.58-2.44 ppm, signals of the ferrocene fragment and the OCH_2 group are observed at 4.32-4.21 and 4.40-4.34 ppm, respectively.

Oligomerization of allenyloxymethylferrocene (**2**) has also been carried out under radical conditions in the presence of azobisisobutiric acid dinitrile (AIBN) (Scheme 6).



2

7 n + m = 8-9

Scheme 6. Radical oligomerization of allenyloxymethylferrocene.

Conditions of monomer **2** oligomerization and the oligomers yield are given in Table 1.

The experiments have shown that allenyloxymethylferrocene (**2**) is more reactive under the radical oligomerization as compared to the cationic ones. The soluble oligomers have been obtained in up to 88% yields (Table 1). The highest yield is achieved at 80 ºC in the presence of 3.0% AIBN. The decrease of temperature and AIBN concentration leads to the reduction of the oligomer yield. Molecular weight of oligomer **7a** is 2000 that corresponds to 8-9 elementary units.

The structure of oligomers **7a-d** has been proved by IR and ^{1}H NMR spectroscopy. In the IR spectra of compounds **7a-d**, absorption bands of the C=C=C bond are absent (in the monomer this band is observed at 1950 cm^{-1}). The bands of other groups and bonds were significantly broadened. The absorption bands of the ferrocene skeleton are present in the region 1730-1685 cm^{-1}. The absorption bands of the C=CH–O group appear at 1670-1660 cm^{-1}. Also, the absorption bands attributed to the CH_2=C *exo*-methylene fragments are shown at 1645-1636 cm^{-1}. The ^{1}H NMR spectrum contains broaden signals characteristic of the vinyl group protons at δ 5.31-5.09 ppm (CH_2=C) and δ 6.19-5.94 ppm (CH=C), the polymer chain protons –CH_2 (4.02-3.88 ppm) and –CH (2.62-2.46 ppm), the ferrocene moiety (4.28-4.11 ppm) and signals of the OCH_2 group at 4.42-4.38 ppm.

From the spectral data follows that under radical polymerization of allenyloxymethylferrocene (**2**), macromolecules **7a-d** are formed at the 1,2- and 2,3-positions of the allenyl group, as it is observed for alkoxyallenes [32-33], i.e. they have two types of structural blocks containing no polyene chains (Scheme 5).

Electroconducting and paramagnetic properties of oligomers **5a**,**b** and **7a** have been studied and their thermal behavior has been evaluated.

As expected, the oligomers exhibit properties of organic semiconductors (σ = 2.5×10^{-10} - 8.8×10^{-10} S/cm). When doped with iodine, their electroconductivity increases by 4-5 orders (σ = 4.3×10^{-6} - 1.7×10^{-5} S/cm) (Table 2).

Table 2
Electroconductivity and paramagnetic properties of the oligomers

Compounds	Iodine content (%)	σ, S/cm	Intensity of the main ESR signal, rel. un.[a]	ΔH, G	*g*-factor	Additional peaks in ESR spectra, *g*-factor
1	No	-	3.1	320	2.24	4.43; 3.26; 2.03; 1.96
5a	No	8.8×10^{-10}	10.0	220	2.01	4.39; 2.97; 2.22
5b	No	6.4×10^{-10}	7.6	250	2.01	4.39; 2.97
5b-I	68.79	1.7×10^{-5}	19.0	700	2.21	4.30; 2.50; 2.0052[b]

2	No	-	2.4	305	2.20	3.43; 1.97; 1.85
7a	No	2.5×10^{-10}	1.0	630	2.19	3.01; 1.99
7a-I	47.48	4.3×10^{-6}	6.7	520 170	2.17 2.03	4.30; 2.50; 2.0052[b]

[a] Relative to minimum, signal of compound **7a**.

[b] Narrow ($\Delta H \approx 10$ G) symmetric singlet, *g*-factor was measured in the range of 100 G.

The detail study of the ESR spectra of the starting compounds **1**, **2** and the oligomers synthesized (Table 2) have shown that all the solid compounds are paramagnetic at room temperature. The ESR spectra of the starting compounds **1** and **2** contain central broad bands of almost the same intensity with ΔH ~300 G. The bands are strongly low-field shifted (towards the increase of *g*-factor in comparison with this value for free electron). In addition, in the ESR spectra, some low-intensive absorption bands are present in the region of low and high fields of the both compounds. Also, in the spectra, the peaks with *g*-factors 4.43 and 3.43 for compounds **1** and **2** respectively, are observed (Table 2). The values of the *g*-factors allows one to conclude that iron in the compounds obtained is three-valent and mainly in low-spin state [34]. When sample **1** and **2** are dissolved in chloroform, all the ESR signals disappear.

The ESR spectra of soluble **5a** and insoluble **5b** fractions of poly(propargyloxymethylferrocene) considerably differ from those of the starting compound **1** and between each other (Table 2). But the signals character and *g*-factor values also correspond to three-valent iron in low-spin state.

The ESR spectrum of oligomer **7a** consists of broad (more than 600 G) asymmetric line with *g*-factor of approximately 2.2. In comparison with the starting compound **2,** central signal of the polymer becomes broader and is high-field shifted. This indicates the alteration of asymmetry of paramagnetic centers surrounding that leads to decrease of spin-orbitals contribution and shortening the relaxation time. A narrow signal with *g*-factor 1.99, which is often present in the ESR spectra of three-valent iron in low-spin state, appears.

The dopping of samples **5b** and **7a** with iodine gives almost the identical ESR spectra. Integral intensity of the spectra increases for oligomer **5b-I** by 2.5 times, and for compound **7a-I** – by the order. In the spectra of the dopped samples, all weak low-field absorption bands disappear and intensities of low-field bands sharply decrease. The main intensive band is split and in the region $g = 2.0052$ of sample **5b-I**, a narrow band of 10 G appears. In the spectrum of oligomer **7a-I**, this band is almost indiscernible, but it has been recorded in narrow range of field screening. This signal can be assigned to free radicals (polarons), formed during the dopping.

Since ferrocene itself is diamagnetic, the paramagnetism of the monomers and their oligomers can be rationalized by the stacking effect, both in the monomer crystals and the oligomer solids, transmitted through the ferrocene units with a participation of the multiple bonds.

The investigation of thermooxidative destruction of polymers **5a**, **5b** have revealed that they are stable to 330-340 ºC. Upon further heating up to 460-480 ºC, the weight loss is 50%. The DTA curves show one exothermic peak at 380 ºC and 400 ºC for **5b**, **5a** respectively (ΔT = 30 и 36 ºC). Total decomposition of the polymers is observed at 590-610 ºC.

Oligomer **7a** is slightly less stable than **5a** and **5b**. Its decomposition begins at 300 ºC. Further heating up to 420 ºC leads to 50% weight loss. One exothermic peak at 435 ºC (ΔT = 86 ºC) is detected on the DTA curve. Total decomposition of the polymers occurs at 510 ºC.

3. Conclusion

An efficient method for the synthesis of propargyloxymethylferrocene in almost quantitative yield has been elaborated. The synthesis is based on the modified reaction of available N,N-dimethylaminomethylferrocene with propargyl alcohols in the presence dichloroethane and NaOH. Previously unknown allenyloxymethylferrocene has been synthesized in 80% yield by rapid prototropic isomerization of propargyloxymethylferrocene in the superbase system *t*-BuOK–DMSO (room temperature, 4 min). Propargyloxymethylferrocene undergoes cationic polymerization in the presence of WCl_6 to afford polyenes with pendant ferrocenyl groups, consisting of soluble (20-55%) and insoluble (11-50%) fractions, in up to 83% total yield. Allenyloxymethylferrocene oligomerizes preferably radically (initiator AIBN) to soluble oligomers with *exo*-methylenic groups in up to 88% yield. All the oligomers possess semiconducting and paramagnetic properties and stable up to 300-340 ºC. The monomers and oligomers synthesized represent prospective building blocks and components for the design of advanced materials.

4. Experimental section

4.1. General remarks

IR spectra of propargyloxymethylferrocene (**1**), allenyloxymethylferrocene (**2**) and oligomers **5-7** 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 ^{13}C) using $CDCl_3$ solvent and HMDS as the internal standard. The microanalyses were performed on a Flash EA 1112 Series elemental analyzer. The electrical conductivity of polymers **5a**,**b** and **7a** 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 mode (frequency 9.7 GHz, high frequency modulation 100 KHz, amplitude modulation 10 G) at room temperature. The relative concentration of paramagnetic centers was calculated as double integral per gram and standardized per unit. The thermogravimetric analysis (TGA) of oligomers **5a-b**, **7a** was performed on a Q-1500D derivatograph (MOM, Hungary), maximal temperature 700 ºC, at heating rate of 5 ºC min^{-1}; the sensitivity for DTA was 1/10. To evaluate the molecular weight of oligomers **7a** 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 ºC.

N,N,N’,N’-Tetramethyldiaminomethane and N,N-dimethylaminomethylferrocene were synthesized by literature procedures [28].

Solvents (benzene, *n*-hexane) were purified according to the literature protocols [35]. AIBN was recrystallized twice from ethanol (m.p. 102 ºC).

4.2. Synthesis

*4.2.1. Propargyloxymethylferrocene (**1**)*

A mixture of $FcCH_2NMe_2$ (14.72 g, 0.06 mol) (**4**), propargylic alcohol (72.23 g, 1.29 mol) and dichloroethane (23.8 g, 0.24 mol) was heated at 90-96 °C for 1 h 30 min and cooled to 54 ºC. Then powdered NaOH (9.6 g, 0.24 mol) was added in one portion and the mixture was heated at 83-103 °C for 2 h. The unreacted alcohol (43 g) was distilled. Water (100 ml) was added to the residue and the products were extracted with ether (5 x 50 ml). The black extracts were washed with water (3 x 40 ml), 2% HCl (3 x 30 ml), and again with water (3 x 30 ml) and dried over K_2CO_3. After removal of ether under slight vacuum and vacuumizing the residue (1 Hg mm, ~50 °C, 20 min), 17.25 g of orange crystalline product was obtained. From the latter pure propargyloxymethylferrocene (**1**) (11 g, 72%) was isolated by chromatography with ether over small layer (3 cm) of Al_2O_3 (neutral) and repeated recrystallization from ether at –15 °C. Acidic aqueous solution of the amine **4** hydrochloride was neutralized with 20% solution of KOH until strongly alkaline reaction and extracted with ether (3 x 20 ml). The extracts were washed with water, dried over K_2CO_3 and after removal of the solvent 4.89 g of residue was obtained. From the latter, 4.15 g of N,N-dimethylaminomethylferrocene (**4**) was isolated, b.p. 125 ºC<1 Hg mm. The yield of propargyloxymethylferrocene (**1**) calculated by the consumed N,N-dimethylaminomethylferrocene was 99.6%, m.p. 95-96 ºC (amber plates from Et_2O). IR (KBr, cm^{-1}): 3223 s (ν ≡C–H), 3103 w, 3067 w, 2977 w, 2923 w, 2899 w, 2862 w, 2119 w (νC≡C), 1780-1600 (w, ferrocene skeleton), 1456 m, 1444 w, 1410 w, 1397 w, 1374 m, 1353 m, 1269 m, 1213 w, 1103 m, 1066 s, 1038 m, 994 m, 955 m, 926 w, 908 m, 877 m, 831 m, 808 m, 748 m, 704 m, 549 w, 494 m, 477 m. ^1H NMR ($CDCl_3$): δ 4.37 (s, 2H, CH_2O), 4.24 (t, 2H, $^3J_{\alpha\beta}$ = 1.83 Hz, H_α), 4.15 (t, 2H, $^3J_{\beta\alpha}$ = 1.83 Hz, H_β), 4.13 (s, 5H, C_5H_5), 4.10 (d, 2H, $^4J_{C\underline{H}2\text{-}C\equiv C\underline{H}}$ = 2.34 Hz, $C\underline{H}_2$–C≡CH), 2.43 (t, 1H, $^4J_{C\underline{H}2\text{-}C\equiv C\underline{H}}$ = 2.34

Hz, $\underline{H}C\equiv C{-}CH_2$). ^{13}C NMR ($CDCl_3$): δ 82.21 (C_i), 79.88 (–C≡), 74.31 (HC≡), 69.47 (C_α), 68.58 (C_β), 68.41 (C_5H_5), 67.56 (OCH_2), 56.39 ($\underline{C}H_2{-}C\equiv CH$). Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found: C, 66.20; H, 5.57; Fe, 21.92.

*4.2.2. Allenylyloxymethylferrocene (**2**)*

To a solution of *t*-BuOK (2.8 g, 25.0 mmol) in dry DMSO (90 ml, water content < 0.2%), was added propargyloxymethylferrocene (6.0 g, 23.6 mmol) (**1**). The reaction mixture was stirred for 4 min at room temperature (23 ºC), then diluted with cold water (~200 ml), extracted with ether (4 x 50 ml). The combined ether solution was washed with water to remove DMSO and dried over $MgSO_4$. After removal of ether under slight vacuum and vacuumizing the residue (1 Hg mm, 20 min), the product was purified by column chromatography on Al_2O_3 (eluent – petroleum ether–Et_2O, 15:1) to recover 0.24 g of propargyloxymethylferrocene (conversion 96%) and to give 4.8 g of allenyloxymethylferrocene (80% yield), m.p. 46-48 ºC (yellow crystals). IR (KBr, cm^{-1}): 3089 w, 3033 w, 2983 w, 2927 w, 2892 w, 2850 w, 1950 m (νC=C=C), 1729-1600 (w, ferrocene skeleton), 1476 w, 1461 m, 1408 w, 1397 w, 1381 m, 1359 w, 1248 m, 1243 m, 1188 s, 1104 m, 1030 s, 997 m, 967 w, 913 m, 893 m, 866 w, 850 w, 839 w, 827 m, 813 m, 781 w, 704 m, 652 w, 507 m, 496 m, 483 m. ^1H NMR ($CDCl_3$): δ 6.73 (t, 1H, $^4J_{\underline{CH}=C=C\underline{H2}}$ = 5.87 Hz, $C\underline{H}=C=CH_2$), 5.48 (d, 2H, $^4J_{C\underline{H}=C=C\underline{H}2}$ = 5.87 Hz, $CH=C=C\underline{H}_2$), 4.35 (s, 2H, CH_2O), 4.24 (t, 2H, $^3J_{\alpha\beta}$ = 1.71 Hz, H_α), 4.15 (t, 2H, $^3J_{\beta\alpha}$ = 1.71 Hz, H_β), 4.13 (s, 5H, C_5H_5). ^{13}C NMR ($CDCl_3$): δ 201.28 ($CH=\underline{C}=CH_2$), 121.37 ($\underline{C}H=C=CH_2$), 90.77 ($CH=C=\underline{C}H_2$), 82.49 (C_i), 69.23 (C_α), 68.56 (C_β), 68.45 (C_5H_5), 67.01 (OCH_2). Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found: C, 65.98; H, 5.52; Fe, 21.97.

4.3. Oligomerization

*4.3.1. Propargyloxymethylferrocene (**1**)*

Propargyloxymethylferrocene (3 g, 11.81 mmol) (**1**) and WCl_6 (0.14 g, 0.35 mmol) were placed in ampoule blown with argon. The ampoule was sealed, heated in thermostat at 100 ºC for 5 min, cooled and opened. The reaction mixture was dissolved in benzene (15 ml) and insoluble fraction was separated from soluble one by filtration. The insoluble fraction was washed with benzene. The soluble fraction was precipitated in *n*-hexane (50 ml) and washed with the precipitant (3×50 ml). Both fractions were dried in vacuum (1 Hg mm) to the constant weight to give 0.98 g (33%) of soluble oligomer **5a** and 1.50 g (50%) of insoluble oligomer **5b**. The soluble fraction **5a** is a brown powder (m.p. 196-198 ºC), soluble in benzene, chlorobenzene, chloroform. Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found: C, 66.04; H, 5.70, Fe 21.88. Insoluble fraction **5b** is a black powder unmelted up to 350 °C. Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found, %: C, 65.94; H, 5.78, Fe 21.76.

*4.3.2. Propargyloxymethylferrocene (**1**) (in benzene)*

Propargyloxymethylferrocene (3 g, 11.81 mmol) (**1**) and WCl_6 (0.14 g, 0.35 mmol) dissolved in benzene (10 ml) were placed in ampoule filled with argon. The ampoule was sealed and heated in thermostat at 60 ºC for 20 h. After the reaction completion, the ampoule cooled and opened and insoluble fraction was separated from soluble one by filtration. The insoluble fraction was washed with benzene. The soluble fraction was precipitated in *n*-hexane (50 ml) and washed with the precipitant (3×50 ml). Both fractions were dried in vacuum (1 Hg mm) to the constant weight to give 1.64 g (55%) of soluble oligomer **5c** and 0.64 g (21%) of insoluble oligomer **5d**. The soluble fraction **5c** is a brown powder (m.p. 193-196 ºC), soluble in benzene, chlorobenzene, chloroform. Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found, %: C, 66.08; H, 5.69, Fe 21.78. Insoluble fraction **5d** is a black powder unmelted up to 350 °C. Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found, %: C, 66.02; H, 5.71, Fe 21.82.

*4.3.3. Allenyloxymethylferrocene (**2**) ($LiBF_4$–DME)*

Catalytic complex $LiBF_4$–DME was prepared by the dissolution of the above salt (0.35 g) in dimethoxyethane (1.0 g).

To allenylnyloxymethylferrocene (2.0 g, 7.87 mmol) (**2**) was added 0.15 g of catalytic complex $LiBF_4$–DME (2 wt % calculated by $LiBF_4$) on stirring in argon flow. The polymerization was carried out in a sealed ampoule at 60 ^{o}C for 24 h. The ampoule was cooled and opened, the catalyst was neutralized by gaseous NH_3, and the reaction mixture was filtered. The oligomer was dissolved in benzene (5 ml), precipitated to *n*-hexane (50 ml), filtered off, washed with *n*-hexane (3×20 ml) and dried in vacuum (1 Hg mm) to the constant weight to give 0.2 g (10% yield, m.p. 94-97 ^{o}C) of oligomer **6**. Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found, %: C, 66.21; H, 5.60, Fe 21.78.

*4.3.4. Allenyloxymethylferrocene (**2**) (AIBN)*

Allenyloxymethylferrocene (4.0 g, 15.74 mmol) (**2**) and AIBN (0.08 g, 0.49 mmol) were placed into an ampoule filled with argon. The ampoule was sealed and heated in thermostat at 80 ºC for 24 h, then cooled and opened. The polymeric product was recovered and purified by re-precipitation from benzene into hexane, washed with hexane and dried to constant weight to give 3.54 g of poly(allenyloxymethylferrocene) **7a** (88% yield, m.p. 98-100 ºC). Anal. Calc. for $C_{14}H_{14}FeO$ (254.10): C, 66.17; H, 5.55; Fe, 21.98. Found, %: C, 66.14; H, 5.61, Fe 21.70.

Acknowledgement

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Dear Professor Herrmann,

We are submitting herewith the manuscript entitled “Propargyloxy- and allenyloxymethylferrocenes: synthesis and oligomerization” by Olga A. Tarasova et al. revised according to the referess’ critics and suggestions.

First of all, please thank both the referees on our behalf for the fair and genuine work with our manuscript and very useful remarks which we have addressed in the revised paper.

The following alterations have been made in the manuscript.

Referee 2 wrote: “It is claimed page 5 that the mixture Li BF4-dimethoxyethane is a cationically polymerizing system. This is rather doubtful because this system is lacking of a powerful electron deficient site. Whatsoever, oligomerization of allenyloxymethylferrocene was observed by authors”.

The following paragraphs have been included in the text:

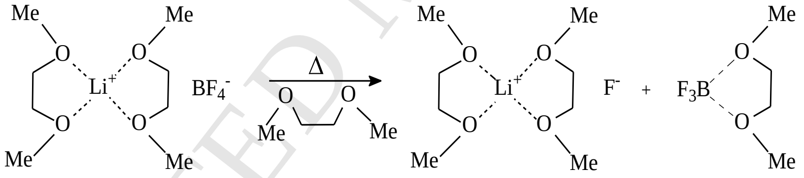
As discovered a while ago [29, 30], the complexes of $LiBF_4$ with dimethoxyethane and some other ethers of ethylene- and polyethylene glycol are latent cationic catalysts which effectively catalyze the cationic polymerization of vinyl ethers.

Mechanism of catalysis by these systems involves thermal dissociation of $LiBF_4$ to release minor concentration of BF_3, a well-known catalyst for cationic polymerization [32, 33]:

$$LiBF_4 \rightleftarrows LiF + BF_3$$

At ambient temperature this dissociation is negligible, while upon heating it starts producing BF_3 in amounts enough for polymerization.

Dimethoxyethane transforms the salt $LiBF_4$ to the complex of the separated ion pair type in which the above dissociation is facilitated:



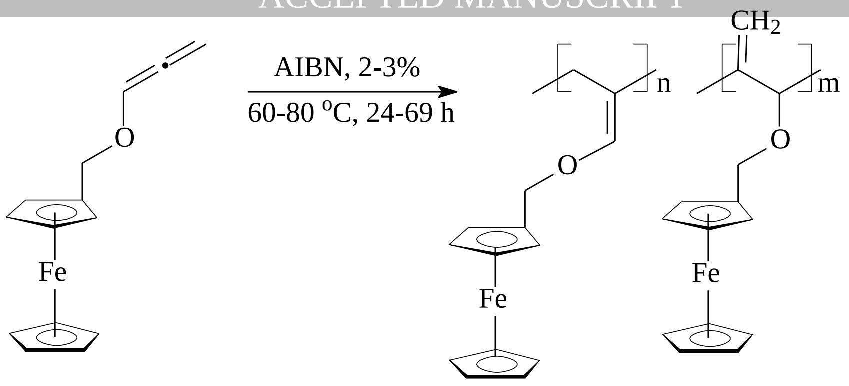
Referee 2 wrote: “Indeed, oligomerization described page 6 can probably better be assigned to the experimental conditions (60°C, 24 h) inducing a slow radical induced thermal oligomerization”.

We have checked this suggestion and the following sentence has been included into the text:

The special experiment has confirmed that thermal oligomerization of monomer **2** at 60°C for 24 h was much slower (the yield of the oligomer did not exceed 3%).

Referee 2 wrote: “About average number molar masses, authors must indicate what were the standards used in the SEC determinations, because the hydrodynamic volumes of polystyrene and of polyallenyoxymethylferrocene of the same molar mass must be very different, and the value given to the polymerization degree could be subject to large overestimation”.

Indeed, according to the mass spectrometry data (Bruker Ultraflextreme TOF/TOF (Bruker Daltonics GmbH)), oligomer **7a** consists of molecules with molecular masses 762 and 1016 that corresponds to trimer and tetramer, probable of cyclic structure. From the spectral data (see below) follows that the oligomer may be represented by combination of two different structures:



2

7 n + m = 3-4

Therefore, the molecular mass data based on GPC given in the first version of the manuscript are excluded from the text as actually overestimated as the referee suggested.

Referee 2 wrote: “Authors should give ^{13}C NMR spectrum of the soluble fraction and compare with the spectrum of the monomer”.

In the Results and Discussion, the data of ^{13}C NMR for synthesized oligomers have been added (pages 5,7,9). Also, original spectrum information concerning these spectrum have been give in Supporting information as a separate file.

Now, we hope that after all the above amendments the manuscript has been improved to the state suitable for publication.

Best regards,

Boris Trofimov