Polymeric nanomaterials based on iron (III) tris-acetylacetonate: synthesis, structure and properties

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Abstract. The formation of iron (III) polychelates under different conditions has been investigated: at mechanochemical activation of iron (III) tris-acetylacetonate with subsequent condensation in boiling toluene (method 1) and through chelate heating in air at 100, 150, and 200°C (method 2). The obtained compounds have been studied by the methods of gel permeation chromatography, diffractometry and infrared spectrometry, scanning electron microscopy, and gamma resonance spectroscopy. Based on the obtained data, the maximal particle size has been calculated. The fractal structure of spherical particles was presented.

1. Introduction

Dielectric paramagnetic films based on metal acetylacetonates keep finding an extensive application in electronics [1]. They are used in surface passivation of semiconductor devices parameters stabilization, as shielding coatings, and in creation of film condensers and insulators in multilayer structures [1, 2]. Oxides in the form of homogeneous solid films are deposited from the vapor phase through decomposition of metal acetylacetonates [1, 2]. To obtain polymeric nanocomplexes of metals we used the interaction of magnesium acetylacetonate containing the hydronate water in synthesis of polymetalorganosiloxanes, a low yield of the target product is caused by the formation of magnesium polyacetylacetonate upon heating [3]. Similarly, at the interaction of vanadylacetylacetonate with polyphenylsiloxane [4] with boiling in toluene, a low yield of the final product is observed as well. It depends on the formation of vanadylpolyacetylacetonate ([(Acac)\textsubscript{3}VO\textsubscript{n}]) participating in the reaction only under strict conditions.

To sum up, there arises the necessity to study the behavior of metal acetylacetonates under different conditions: heating in air, mechanochemical impact, and boiling in solvent.

2. Results and Discussion

Iron (III) tris-acetylacetonate polymerization was carried out by two methods. In the first one, the initial chelate was treated mechanochemically, dissolved in toluene, boiled until complete solvent evaporation, and heated in vacuum up to 80°C (10 mm Hg – synthesis 1). In the second one, the chelate was heated in air at 100, 150, and 200°C (syntheses 2, 3, and 4, respectively).

The data of element analysis and gel permeation chromatography (GPC) are shown in Table 1. One observes essential differences in iron polyacetylacetonates (IPA) treated mechanochemically with isolation from solution and by heating in air. Here, from the GPC data, the mass of soluble trimers and tetramers somewhat increases at heating up to 100°C for 1 h (Fig. 1c). Further heating up
to 150°C under similar conditions results in producing an insoluble fraction with an output of 30%, in which 1.5 of acetylacetonate group and 0.5 of oxygen atom are per 1 iron atom.

Table 1. Element analysis and gel permeation chromatography data for the obtained materials.

| Synthesis                  | Found C  | Found M | Calculated C | Calculated M | Molecularweight | General formula |
|----------------------------|----------|---------|--------------|--------------|-----------------|----------------|
| Initial chelate            |          |         |              |              |                 |                |
| №1: mechanochemistry, solution | 51.2     | 16.1    | 50.9         | 15.8         | ≈1090 – 700     | (C₅H₇O₂)₃Fe     |
|                            | 43.5     | 20.9    | 44.4         | 20.7         | mixture         | a Fe(C₅H₇O₂)₂OH  |
| №2: 1 h, 100°C             |          |         |              |              | mixture         | b                |
|                            | 51.7     | 14.9    | 50.9         | 15.8         | ≈ 4000 – 12%    | [Fe(C₅H₇O₂)₃Fe] |
|                            |          |         |              |              | ≈ 2100 – 64%    | c                |
| №3 1 h, 150°C              |          |         |              |              | mixture         | d                |
|                            | 51.3     | 14.8    | 51.0         | 15.0         | ≈ 1500 – 55%    | [Fe(C₅H₇O₂)₃Fe] |
|                            |          |         |              |              | ≈ 1000 – 38%    | e                |
| №4 1 h, 200°C              |          |         |              |              | insoluble fraction, output 30% | [Fe(C₅H₇O₂)₃Fe] |
|                            | 42.3     | 25.8    | 42.5         | 24.5         | mixture         | f                |
|                            |          |         |              |              | ≈ 700 – 55%     | [Fe(C₅H₇O₂)₃Fe] |
|                            |          |         |              |              | ≈ 1000 – 38%    | [Fe(C₅H₇O₂)₃Fe] |
|                            | 36.1     | 29.6    | 35.3         | 29.3         | insoluble fraction, output 57% | [Fe(C₅H₇O₂)₃Fe] |

The data of gel permeation chromatography for oligomers from the synthesis 1 are shown in Figure 1b.

Figure 1. Gel permeation chromatograms: a – initial chelate; b – synthesis 1; c – synthesis 2; d – synthesis 4.
Heating up to 200°C (synthesis 4) under similar conditions results in the increase of the quantity of the insoluble fraction up to 57%, where 1 iron atom corresponds to 1 acetylacetonate group and 1 oxygen atom. There are also end groups: hydroxyl groups or water molecules. The soluble part (synthesis 4) comprises a mixture of trimers, dimers, and oligomers with n of 9–10 (Fig. 1d).

The IR spectroscopy data corroborate the suggested general formulas. All the spectra contain absorption bands at 1570–1571 cm\(^{-1}\) and 1524–1526 cm\(^{-1}\) corresponding to C=O and C=C bonds vibrations in the acetylacetonate ring, respectively. The absorption bands at 2922–2924 cm\(^{-1}\) correspond to stretching vibrations of the C–H bond of the methyl group. The most informative is the band at 435–436 cm\(^{-1}\) corresponding to stretching vibrations of the Fe–O bond [5].

The absorption band corresponding to vibrations of the Fe–O bond in the initial chelate is at 435 cm\(^{-1}\), while in the course of polymerization it shifts to higher frequencies, for the oligomer (synthesis 1) it is at 435 cm\(^{-1}\), and for insoluble fractions – at 441 cm\(^{-1}\).

The obtained oligomers were studied by X-ray diffraction analysis (Figure 2).

![Figure 2](image)

**Figure 2.** Diffractograms of: a – iron tris-acetylacetonate; b – oligomers obtained in solution (synthesis 1); c – product of the synthesis 2; d – soluble fraction of the synthesis 3; e – insoluble fraction of the synthesis 3; f – soluble fraction of the synthesis 4; g – insoluble fraction of the synthesis 4.

The diffractograms of the oligomer from the synthesis 1 (Fig. 2b) corresponds to the structure of a mesomorphous polymer. The soluble fractions of the syntheses 2–4 comprise mixtures of crystalline forms of dimers, trimers, and tetramers of iron acetylacetonates (Figs. 2d, f). The diffractograms of the insoluble fractions of the syntheses 3 and 4 (Figs. 2e, g) correspond to amorphous products. The diffractogram of the soluble polychelate at 200°C in air corresponds to the structure of a mesomorphous polymer.

According to [6,7], in case of mesomorphous polymers, the first reflection corresponds to the distance between adjacent chains. Using the calculation methods suggested in [7], the volumes of coherent scattering regions (CSR) and the cross-section areas were calculated on the Selyakov–Shearer formula[8]. The calculated data are shown in Table 2.

**Table 2.** Calculated physical-chemical characteristics from the data of X-ray diffraction analysis.

| Compounds                      | d, 100 Å   | L\(_{\text{CSR}}\), Å | S, Å\(^2\) | V\(_{\text{CSR}}\), Å\(^3\) |
|--------------------------------|------------|------------------------|------------|-----------------------------|
| Initial chelate               | 8.31       | 1150.0                 | 58.8       | 67620.0                     |
| Oligomer, synthesis 1         | 8.48       | 10.9                   | 60.9       | 663.8                       |
| Oligomer, synthesis 4         | 9.26       | 13.25                  | 70.5       | 930.6                       |
The coherent scattering region size for the initial crystalline chelate is two orders of magnitude larger than that for the oligomer with \(n = 8–9\). One can assume that in the case of the chelate crystalline form the CSR size is that of the crystallite (0.12 µm).

To obtain more accurate notions on the structure of polymeric forms of \([\text{Fe(C}_5\text{H}_7\text{O}_2)_x\text{Fe}]_n\), geometric parameters and theoretical cross-section areas of its tris-chelate and polychelate were calculated.

The theoretical calculations were carried out using the FireGly 8.1.0 software package [9] partially based on the initial GAMESS code (US) [10]. Calculations were carried out by the method of density functional theory (DFT), whereas to describe the electron interaction the hybrid exchange-correlation B3LYP5 functional was used (basis 6-31G) [11]. The initial complexes geometries were taken from the experimental data, prior to the optimization procedure.

The spectra were processed using the CASA XPS program. The energy scale was calibrated according to the internal standard technique – the C1s level was selected (285.0 eV).

In comparison with \(\text{Fe(C}_5\text{H}_7\text{O}_2)_2\), in the \([\text{Fe(C}_5\text{H}_7\text{O}_2)_x\text{Fe}]_n\) complex, one observes the increase of interatom distances and angles. The largest cross-section area of the initial \(\text{Fe(C}_5\text{H}_7\text{O}_2)_2\) complex is 57.93 Å², while that of the \(\text{Fe(C}_5\text{H}_7\text{O}_2)_2^+\) complex – 56.6 Å, according Figure 3.

![Figure 3. The structures: a) \(\text{Fe(C}_5\text{H}_7\text{O}_2)_2\); b) \([\text{Fe(C}_5\text{H}_7\text{O}_2)_x\text{Fe}]_n\) complex.](image)

Based on the element analysis (Table 1), GPC, diffractometry, and calculated data (Table 2), the structure of the \([\text{Fe(C}_5\text{H}_7\text{O}_2)_x\text{Fe}_8^*2\text{OH}]_n\) oligomer with MW 2100–2200 Da was revealed (Figure 4).

![Figure 4. Oligomer structure (synthesis 1).](image)

The oligomer with the molecular weight of 2066 (calculated data) and 2100 (found value) is well soluble in organic solvents. Unlike the polychelate obtained through heating in air, in which a significant loss of acetylacetonate groups takes place, in the former case, the iron chelate transforms into a spatial insoluble polymer due to formation of oxygen bridges (150-200 °C).

Upon heating up to 200°C, further loss of acetylacetonate groups takes place and the number of oxygen bridges increases dramatically. The element analysis confirms the formula \([\text{Fe}_8(\text{C}_5\text{H}_7\text{O}_2)_3\text{O}_{18}]_n\).

Since the structure of solid-state samples of iron polychelates is of practical importance for their further application as magnetic materials, to study magnetic properties, the following samples were
taken: initial chelate, polychelate obtained in solution (sample 1, Table 1), polychelate obtained at heating up to 200°C in air (sample 4). Samples were studied using an American vibrating type magnetometer LakeShore VSM 7410.

![Graphs](image_url)

**Figure 5.** a) Dependence of the sample inductive magnetic moment on the induction of the applied magnetic field of the sample 1 in the initial state; b) Dependence of the saturation magnetic moment on temperature for the sample 1 (→ heating, ← cooling); c) Dependence of the inductive moment on induction of the applied field for the sample 4 ([Fe(C₅H₇O₂)x]n); d) Dependence of the inductive moment of [Fe(C₅H₇O₂)x]n (sample 4) in the field of 100 mT on temperature.

The curve is characteristic of ferrimagnetics (Figure 5 a-d): at low field intensities – the area of fast moment changes related to shifting boundaries between domains; at high intensities (from 40 to 100 mT) – slow changes in the magnetic moment related to rotation of spin moments of iron atoms, closeness to saturation. From the moment close to saturation, one can estimate the magnetic moment per iron atom: at the iron content of 21.0 % and the density of 1.46 g/cm³. The decrease of the Bohr magneton number for the samples 1 and 4 (Table 3) is determined by the polymeric structure – formation of oxygen bridges, whose role belongs to oxygen atoms of the polyacetylacetonate group. The authors of [12] observed similar changes in the magnetic moment for bridge groups of the type below.

| Table 3. Magnetic studies data. |
|---------------------------------|
| Substance, sample no. | Initial chelate | Iron polyacetylacetonate (sample 1) | Iron polyacetylacetonate (sample 4) |
| Bohr magneton number | 6.0 | 4.32 | 0.33 |

The data of Table 4 were obtained from the Mössbauer spectra of the initial chelate and the samples 1 and 4.
Table 4. Physico-chemical characteristics of polymers calculated using with the help of Mössbauer spectra.

| Substance      | δ    | ΔЕ, mm/s |
|----------------|------|---------|
| Initial chelate| 0.36 | 0.365   |
| Sample 1       | 0.40 | 0.395   |
| Sample 4       | 0.44 | 0.55    |
|                | 1.38 | 2.77    |

The data of GR spectroscopy (Table 4) show that polyacetylacetonate obtained in solution (sample 1) is characterized with smaller isomeric shift and lower ΔЕ value in comparison with the sample 4 heated in air up to 200°C. Moreover, for the sample 4, there emerges a doublet corresponding to the divalent iron atom with the isomeric shift of 1.38. Thus, according to the above data (Table 4), an oligomer of more regular structure is formed in the solution.

The sample 1 morphology was studied by the method of electron microscopy (Figure 6).

![Figure 6. Scanning electron microscopy images of polychelate (sample 1).](image)

Iron polyacetylacetonate (sample 1) in solid phase comprises a pack of spherical particles of various diameters – sizes vary from 200 to 800 nm.

Physical-chemical characteristics of polyacetylacetonates (samples 1, 4) (S\(_{\text{spec}}\), V\(_{\text{spec}}\)) were determined from low-temperature adsorption. The obtained data are shown in Table 5.

Table 5. Physical-chemical characteristics of polyacetylacetonates.

| Sample № | S\(_{\text{spec}}\), m\(^2\)/g | V\(_{\text{spec}}\), cm\(^3\)/g | D\(_{\text{pore}}\), nm | ρ, g/cm\(^3\) |
|----------|------------------------------|-------------------------------|----------------------|--------------|
| 1        | 0.92                         | 0.003                         | 3.0–4.0              | 1.46         |
| 4        | 1.25                         | 0.0022                        | 3.0–4.0              | 1.32         |

The found values of density and specific surface area (Table 5) allow determination of the layer of oligomer spherical particles (sample 1) by method [13].

First, the substance specific volume is calculated, then the obtained value is divided to the specific surface area:

\[
L(\text{layer}) = \frac{1/\rho}{S}
\]

where: \(L_{\text{layer}}\) – the layer thickness (nm, Å); \(\rho\) – the substance density (g/cm\(^3\)); \(S\) – the specific surface area measured on nitrogen (nm).

The layer thicknesses calculated in this way are equal to 740 nm (sample 1), 600 nm (sample 4). The found values are in agreement with the scanning electron microscopy data (Fig. 6).
The values $L_{layer} = 740$ nm (sample 1) and 600 nm (sample 4) correspond to the maximal size of a spherical particles (Fig. 6) while, as can been at sufficient magnification, these large particles consist of those of smaller sizes. The final smallest size of spheres corresponds to a chain of the oligomer formed by three CSR volumes linked to each other, analogy in work [14] this is fractal structure.

3. Conclusions
Nanomaterials based on iron (III) tris-acetylacetonate have been fabricated by two methods. The first one included mechanochemistry and condensation in boiling toluene solution, the second one – heating up to 200°C. The difference between them consisting in more ordered structure of the oligomer obtained in solution (method 1) was demonstrated by the methods of XRD, gel permeation chromatography and gamma resonance spectroscopy. The cross-section values for oligomer molecules were found from the XRD data (60 Å), calculated from the X-ray structural analysis data (59 Å). The volume CSR data for the initial chelate found from the XRD (67620) data enabled us to conclude that the suggested approach to studies of solid oligomeric iron oxides was rather efficient. The first method is more promising in deposition of iron (III) oxides on the substrate surface.

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