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Synthesis and Characteristics of Acetylenedicarboxylic Acid Salts as Precursors for Obtaining of Nanocomposites

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Summary: acetylenedicarboxylic acid salts were used as precursors for further polymerization and thermal degradation to obtain nanocomposites. Monomers and composites structure was investigated with different methods including IR spectroscopy, thermal analysis and electron microscopy.

Keywords: acetylenedicarboxylic acid salts; magnetic polymers; metal-polymer; monomers; nanocomposites; TEM

Introduction

Interest in carboxylates with unsaturated ligands of acetylene type depends on their solid state polymerization capacity that is determined by the short distances between reaction centers and occurrence of short acetylene-acetylene contacts. In general-dicarboxylic acids complexes with bidentate carboxylic bridges between paramagnetic centers are efficient magneto-concentratedsystems.[1]

We decided to consider different ligands of acetylene type depending on their functional groups and number of C-atoms between multiple bonds in order to obtain metal-containing monomers, polymers and nanocomposites on their base. There is a great variety of structures including monomeric salts, linear and three-dimensional coordinating polymers depending on metal type. First we took acetylenedicarboxylic acid as it was the simplest of acetylene typedicarboxylic acids, moreover it was interesting because of probable conjugation of C=C and C=O bonds in polymeric compounds.

Some authors show interest to the synthesis and structure of different acetylenedicarboxylic acid salts.There is information aboutcobalt, nickel,[2] calcium, magnesium,[3] lead[4] and other acetylenedicarboxylic acid salts. Also there are studies on solid state polymerization of acetylenedicarboxylic acid,[5] its cadmium[6] and potassium[7] salts. The polymers and polymerization are learned much less than monomers.

In addition, acetylenecarboxylic acids salts can be used for nanocomposite materials obtaining.[8] Having such conjugated systems on the stage of polymerization acetylenedicarboxylates-based nanocomposites could reveal interesting magnetic properties.In this paper we considered transition metals salts, namely cobalt, copper and iron acetylenedicarboxylates.

Experimental Part

The needed copper and cobalt salts were obtained from acetylenedicarboxylic acid and appropriate metal carbonate, iron(III)-hydroxide was taken in the case of iron(III) salt. The all reactions were carried out in

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solutions. The literary data[9,10] was used for copper and cobalt salts to estimate quantities of reagents, the molar ratio of acid and metal carbonate was equal to one.In the case of iron there was no data, sothe solution of acetylenedicarboxylic acid was added to the freshly made iron hydroxideby small portionswhilestirringtill complete dissolving.The molar quantity of acetylenedicarboxylic acid was three times larger thanthat of iron hydroxide.

Copper Acetylenedicarboxylate

Water solution of acetylenedicarboxylic acid (0.5 g, 4.4 mmol) was added while stirring to copper(II) carbonate (0.45 g, 4.4 mmol) at room temperature.Copper carbonate powder was completely dissolved in an hour with formation of blue solution. After that blue precipitate appeared. Copper acetylenedicarboxylate is known to be unstable in air,[9] that's why it was isolated and washed with alcohol in inert atmosphere, and then dried in vacuum.Elemental analysis: carbon – 19.2%, hydrogen – 3.0%, metal – 25.8%.Yield was 0.77 g (71%).

Cobalt Acetylenedicarboxylate

Water solution of acetylenedicarboxylic acid (2.05 g, 18 mmol) was added while stirring to cobalt(II) carbonate (2.14 g, 18 mmol) at room temperature. Cobalt carbonate powder was completely dissolved with formation of red solution. Cobalt acetylenedicarboxylate was precipitated by addition of alcohol excess (ratio ≈10:1), washed and dried in vacuum.Elemental analysis: carbon – 24.0%, hydrogen – 2.2%, metal – 25.9%. Yield was 3,5 g (68%).

Iron Acetylenedicarboxylate

Water solution of acetylenedicarboxylic acid (4 g, 35.1 mmol) was added while steering to freshly obtained iron(III) hydroxide (1.25 g, 11.7 mmol) at room temperature. After several hours dissolving was completed with formation of dark brown solution. Precipitation with alcohol or ether didn't give acceptable result so water was removed in vacuum with the usage of freezingtrap and liquid nitrogen. Obtained dark brown powder was washed with acetone and dried in vacuum.Elemental analysis: carbon – 31.7%, hydrogen – 4.5%, metal – 18.5%. Yield was 1.5 g.

Nanocomposites

Nanocomposites were obtained from appropriate acetylenedicarboxylate by thermolysis(at 400 °C).The process was started in inert atmosphere, after reaching 200 °C it was carried out in vacuum and lasted for one hour.

Characterization

Infrared spectra were taken on KBr pellets with a FT-IR spectrometer Perkin-Elmer spectrum 100. Combinational scattering (Raman) spectra were obtained with Nicolet NXR FT-Raman 9610.DSC analysis and termogravimetric measurements were performed on thermal analyserSTA 409C Luxxinterconnected with quadrupole mass spectrometer QMS 403C Aeolos.

Microstructure was observed by Scanning Electron Microscope (SEM Hitachi S-3500N) and analyzed using High Resolution Electron Microscope (JEOL JEM 1200 EX).

Hysteresis loops were recorded at room temperature, and separately in the temperature range from 90 K to 300 K in a magnetic field ±1600 kA/m (~2T), using a Vibrating Sample Magnetometer (VSM, Lake Shore 7410).

To measure the zero-field-cooled (ZFC) and field-cooled (FC) curves the Physical Property Measurement System (PPMS) equipped with Vibrating Sample Magnetometer Option (VSM), was applied. The FC curve was assigned in a magnetic field of 8 kA/m (100Oe) at a temperature ranging from 5 K to 300 K. In the FC regime, the specimens were cooled to 5 K in a field of 8 kA/m and subsequently heated in the same field to room temperature. In the ZFC regime, cooling was performed without the magnetic field.

To determine a dependence χ versus T several M vs H curves were recorded at different temperature (100, 150, 200, 250, 300 K).

Results and Discussion

IR spectra of obtained salts (monomers) were compared with that of acetylenedicarboxylic acid (ADC)(Figure 1). In the case of acid there is a characteristic peak at 1702 cm^{-1}that is referred to a dimer between two carboxylic groups of the ADC.Spectra of acetylenedicarboxylic acid saltscan help to indicate the coordination between metal and carboxylate anion.[8] The difference between frequencies of asymmetric and symmetric vibration modes of the carboxylate anion for CuADC, FeADC and CoADC is more, than 200 cm^{-1}(217 and 212 cm^{-1} respectively), that shows the pseudo-monodentate coordination of anion.

IR spectra can't show the triple bond presence in our compounds, because its vibration isn't attended by changing of dipole moment. But control of triple bond presence may be very important for the polymerization. So we applied Combinational scattering (Raman) spectroscopy. Figure 2 shows combinational scattering spectra of ADC and CoADC. CoADC spectrum contains only two peaks and first of them (2230 cm^{-1}) is assigned to triple bond C–C, so it's moved to low-frequency region in comparison with that of ADC (2238 cm^{-1}). The presence of 1397 cm^{-1} peak lets hope to earn an internal standard for polymerization control.

The crystal structure of copper salt shown in Figure 3 was investigated with X-ray analysis and obtained data was similar to described in literature.[9] It's known that CoADC has two crystal structures: with 4 or 6 molecules of water.[10] On the basis of elemental, thermal analysis and reaction conditions we suppose our sample to have such composition:

$$[Co(C_2(COO)_2)(H_2O)_4]2H_2O.$$

Thermal Analysis

To predict solid-statepolymerization conditions thermal analysis methods were applied: differential scanning calorimetry (DSC), differential thermal analysis (DTA) and thermogravimetric analysis (TGA). CoADCwas most studied because of its stability (FeADC appeared to be unstable

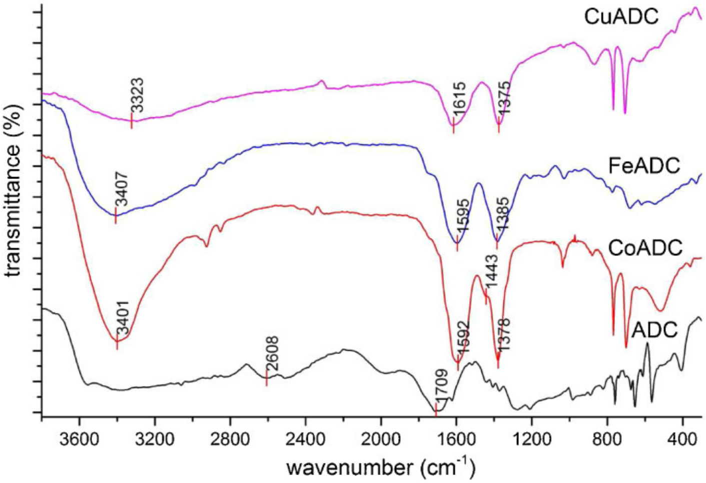

Figure 1.

IR spectraof acetylenedicarboxylic acid (ADC), cobalt acetylenedicarboxylate (CoADC) and iron acetylenedicarboxylate (FeADC).

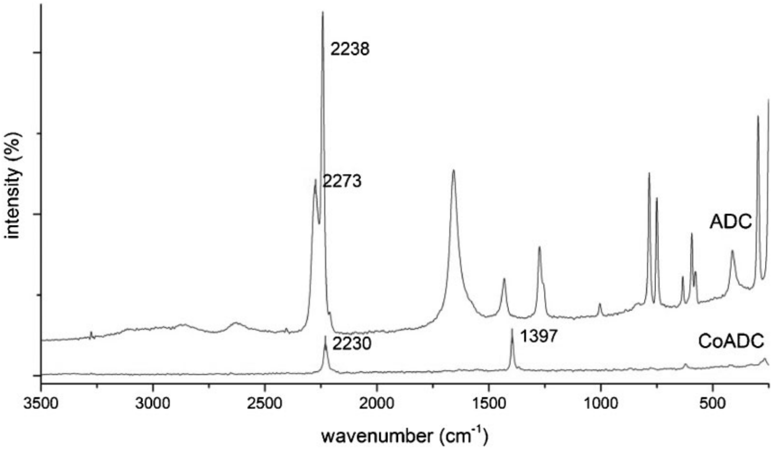

Figure 2.
Combinational scattering spectra of acetylenedicarboxylic acid (ADC), cobalt acetylenedicarboxylate (CoADC) and iron acetylenedicarboxylate (FeADC).

as well as CuADC). Figure 4 and Figure 5 show DSC and TGA spectra for CoADC in inert atmosphere (argon). Mass spectra show that lose of water and carbon dioxide are highest at the range of 160–220 °C.

It seems that the peak at 193.9 °C on DSC spectrum corresponds to polymerization. TGA diagram shows that at this temperature mass loss is about 30% that may be referred to 4–5 molecules of water. DSC peak width indicates that polymer must contain some molecules of water. Further mass loss of the sample reveals degradation of polymer at temperatures above 300 °C and at about 400 °C sample mass becomes almost stable.

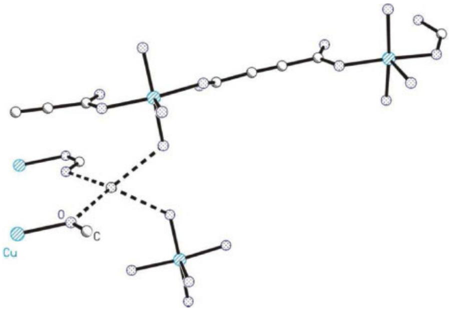

Figure 3.
CuADC crystal structure.

Microstructure of Nanocomposites

Size and shape of nanoparticles were characterized with scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The images are given in the Figure 6. TEM dataallows to determine nanoparticles size. For Co particles it’s in the range of 10–20 nm and for Fe nanoparticles – less than 10 nm.

Magnetic Properties of Nanocomposites

Magnetochemistry methods were applied to study magnetic properties of initial salts and obtained nanocomposites. Given Figure 8 shows dependence of magnetization on temperature which was measured with applied magnetic field (FC – field cooled) or without that (ZFC – zero field cooled). Figure 9 indicates dependence of magnetization on applied field at constant temperatures (hysteresis loops).

The character of hysteresis loops shows pronounced ferromagnetic properties for the products of thermolysisof CoADC and much weaker properties for iron nanocmposite. The size of the particles is probably one of the reasons of that. Besides the bend on ironnanocomposite thermomagnetic curve could be referred to the contribution of superparamagneticphase.

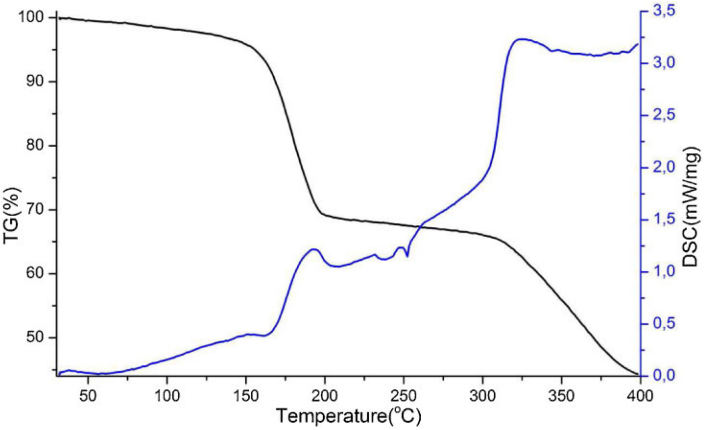

Figure 4.
DSC and TGA for cobalt acetylenedicarboxylate.

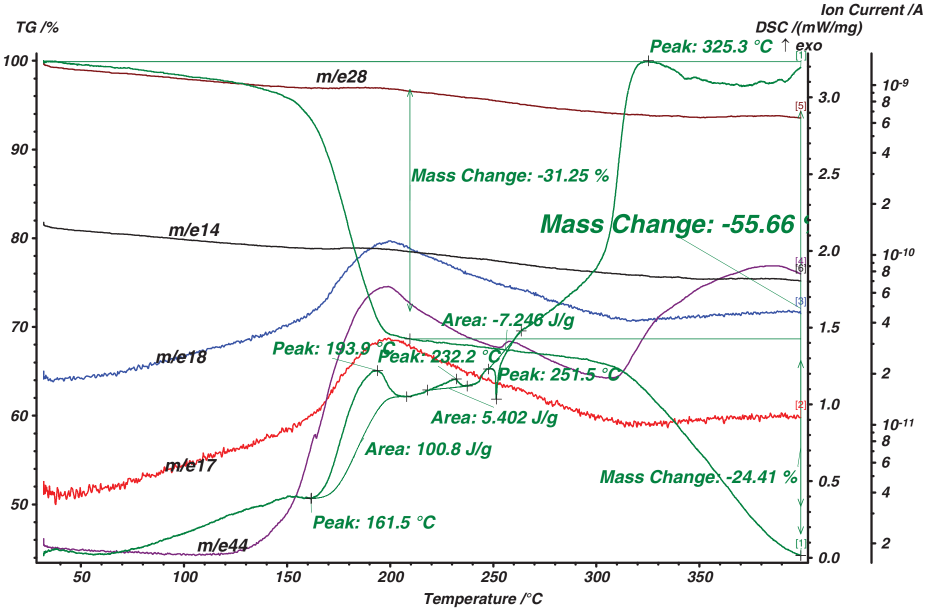

Figure 5.
TGA, DSCand mass spectra for cobalt acetylenedicarboxylic acidsalt.

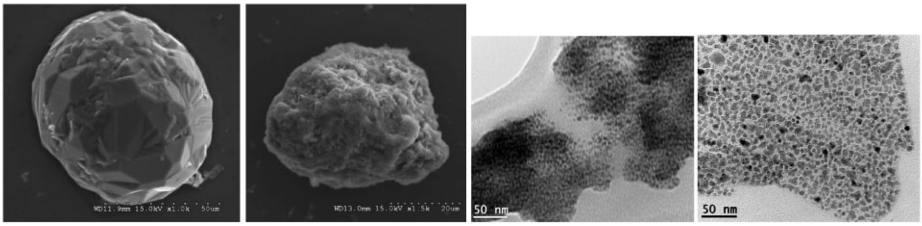

Figure 6.
SEM and TEM for Co (left) and Fe (right) nanocompositesobtained by thermolysis of CoADC and FeADC at 400 °C.

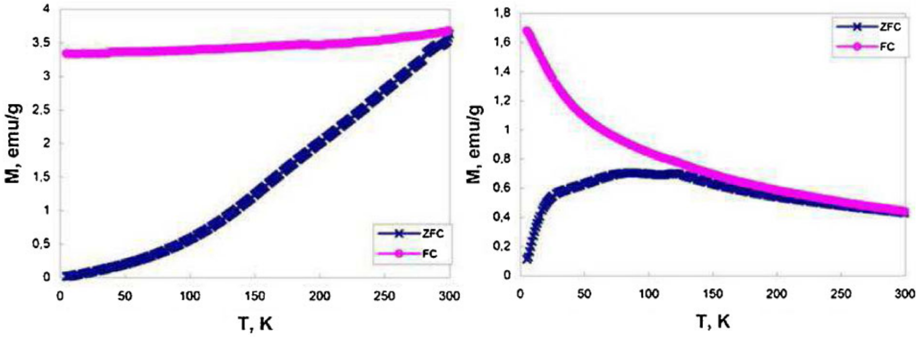

Figure 7.
FC and ZFC curves for Co (left) and Fe (right) nanocomposites obtained by thermolysis of CoADC and FeADC at 400 °C.

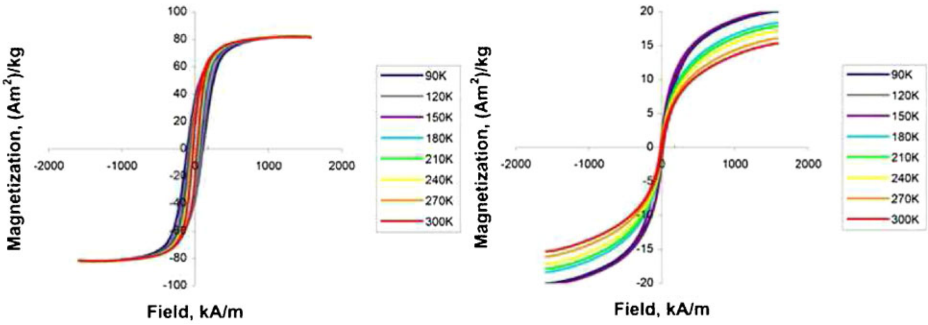

Figure 8.
Hysteresis loops at various temperatures for Co (left) and Fe (right) nanocomposites obtained by thermolysis of CoADC and FeADC at 400 °C.

Table 1.
Magnetic parameters for Co and Fe nanocomposites assessed at room temperature. ${}_{J}H_C$ – the coersive force, M_R – the remanent magnetization, M_S – the saturation magnetization.

Sample	${}_{J}H_C$, $\frac{kA}{m}$	M_R, $\frac{Am^2}{kg}$	M_S, $\frac{Am^2}{kg}$
Co nanocomposite	28.6	17.28	75.3
Fe nanocomposite	13.4	0.96	16.22

Conclusion

The study of monomers based on acetylenedicarboxylic acid salts allowed to learn the structure and properties of monomers and nanocomposites.Also it has been shown that the process of polymerization is conjugated with decarboxylation that leads to nanocomposite formation.The microstructure of obtained nanocompositesrepresents metal-containing nanoparticles (10–20 nm) distributed gomogeniously in pyrolized polymer matrix.They were studied with magnetochemistry methods, and revealedferromagnetic and superparamagnetic properties that would be subject of further investigation as well as the polymerization of acetylenedicarboxylic acid salts.

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