Polymer-Assisted Synthesis, Structure and Properties of Metal Nanocomposites

G.I. Dzhardimalieva*, A.D. Pomogailo

*Institute of Problems of Chemical Physics Russian Academy of Sciences,
1, acad. Semenov av., 142432 Chernogolovka, Moscow Region, Russia*

We have elaborated methods for synthesis of macromolecular metal complexes via homo- and copolymerization of metal-containing monomers (unsaturated metal carboxylates, metal nitrates acrylamide complexes. Thermal transformations of such compounds possess the unique way for preparation of nanocomposite materials when metal (or their oxides and carbides) nanoparticles and a stabilizing polymer matrix are formed simultaneously in situ. Molecular and supramolecular organization of nanocomposites obtained can be controlled during the thermal transformation of such monomers in inert or self-generated atmosphere. The process includes three macrostages: dehydration, solid-phase polymerization, and pyrolysis of the polymer products formed. The approach makes it possible to adjust the mean particle size in a given range by just choosing the appropriate reaction conditions. The composition of metal nanoparticles, their size and distribution on the size as well as the type and thickness of polymer shell can be controlled on the stage of nanocomposite formation. The nanocomposites obtained reveal ferromagnetic behaviour at room temperature with high coercive force and magnetic anisotropy. With aim to control the composition and structure (for example, core-shell type) of ferromagnetic nanomaterials obtained as well as their properties, the reaction conditions such as temperature, ratio of starting compounds, the type of polymer matrix can be varied.

Keywords: Nanocomposites, Thermolysis, Solid-phase polymerization, Metal nanoparticles, Core-shell structure.

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1. INTRODUCTION

The interest in metallopolymer nanocomposites is due to the unique combination of properties of metal-containing nanoparticles with mechanical, film-forming and other polymer characteristics, which allows these materials to be used as magnetic devices for data recording and storage, catalysts, sensors and for various purposes in medicine and biology [1,2].

The search and investigation of the self-regulated systems, in which both the synthesis of polymeric matrix and generation and growth of nanoparticles proceed simultaneously can be useful for the solution of nanoparticle stabilization problems. One of the perspective obtaining methods of metal-containing nanoparticles and their polymeric composites are thermal conversions of metal-containing monomers. It is possible to combine in situ formation of superfine metal particles and a stabilizing them polymeric matrix during these thermal conversions [3, 4]. For synthesis of matrix-stabilized nanoparticles the thermal transformations of corresponding metal-containing monomers in the solid phase are of great interest. The main advantage of the synthesis of composites by thermal transformation of metal-containing precursors is in the possibility of formation of nanocomposites with a relatively high concentration of metal phase. Another advantage deals with technological simplicity and the ease to control the processes and the properties of material obtained.

2. THE MACROSTAGES AND KINETIC PECULIARITIES OF THERMAL TRANSFORMATIONS OF METAL-CONTAINING MONOMERS

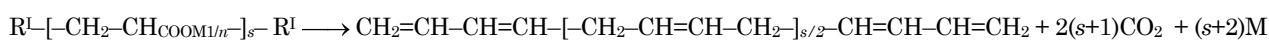Thermal transformations go through three main macrostages with different temperatures:

(1) Initial monomer dehydration (desolvation) at $303-473$ K; (2) The stage of solid-state homo-and copolymerization of the dehydrated monomer (at $473-573$ K); (3) The produced polymer decarboxylation to a metal-containing phase and oxygen-free polymer matrix at T ex >523 K with an intense gas emission. The analysis of the thermal transformation of the gaseous products and the composition of the solid product (decarboxylated polymer, including metal or its oxide) allows determining a general scheme of metal acrylate thermal transformations: Initiation

$$M(CH_2=CHCOO)_n \rightarrow M(CH_2=CHCOO)_{n-1} + CH_2=CHCOO^{\bullet}\ (R^I)$$
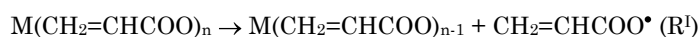
The formed R^I initiates the polymerization to produce the linear or networked polymers. Polymerization

$$R^I + s[CH_2=CHCOO]M^{n+}{}_{1/n} \rightarrow R^I{-}[{-}CH_2{-}CH_{COOM1/n}{-}]_s{-}\ R^I$$
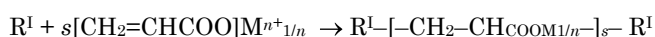
With temperature the metal-containing fragments of formed polymers decompose to produce a metal (or its oxide) and CO_2. Decarboxylation

$$R^I{-}[{-}CH_2{-}CH_{COOM1/n}{-}]_s{-}\ R^I \longrightarrow CH_2=CH{-}CH=CH{-}[{-}CH_2{-}CH=CH{-}CH_2{-}]_{s/2}{-}CH=CH{-}CH=CH_2 + 2(s+1)CO_2 + (s+2)M$$

The polymers resulted in the decarboxylation reaction can be additionally thermo-polymerized to form the net structure with conjugated multiple bonds.
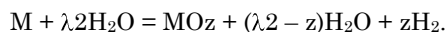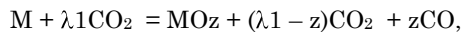
In general, the composition of solid phase products of thermolysis can be represent as a sum of the C-H-O-

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* adpomog@icp.ac.ru

fragment fractions:

$$MO_z(CH2CHCOO)_{p-x}(CHCHCOO)_{q-y}(CH_2CH)_x(CHCH)_n,$$

The metal oxides can be formed by the following oxidation reactions:

$$M + \lambda 1 CO_2 = MO_z + (\lambda 1 - z)CO_2 + zCO,$$

$$M + \lambda 2 H_2O = MO_z + (\lambda 2 - z)H_2O + zH_2.$$

One of the main transformations is the origin of the acrylic $CH2=CHCOO$ radical in the primary decomposition act that initiates metal-containing monomer polymerization with a consequent decarboxylation of metal-containing units. The process temperature has an impact on the product yield and their composition. At high temperatures the decarboxylation is accompanied by practically complete removal of the oxygen-containing units from the polymer matrix.

The thermal transformations of a series of unsaturated metal carboxylates (transition metal acrylates: $Cu(OCOCH=CH2)_2$ (CuAcr2), $Co(OCOCH=CH2)_2 \cdot H_2O$ (CoAcr2), $Ni(OCOCH=CH2)_2 \cdot H_2O$ (NiAcr2); cluster acrylate $[Fe_3O(OCOCH=CH2)_6 \cdot 3H_2O]OH$ (FeAcr3); monomer cocrystallites CoAcr2 or NiAcr2 - FeAcr3 with Fe:Co atomic ratio of 1:0.8 and 2:1 and Fe:Ni = 2:1; cobalt and iron maleates: $Co[OOCCH=CHCOO] \cdot 2H_2O$, $Fe_3O(OH)[OOCCH=CHCOOH]_6 \cdot 3H_2O$ maleates), and acrylamide complexes of metal nitrates (CoAAm, FeAAm) have been studied. Thermolysis of monomers under study is accompanied by the gas evolution and the mass loss due to the dehydration followed by thermal transformation of dehydrated specimens. The process stages proceed sequentially in different temperature ranges.

The kinetic peculiarities of this process were studied under isothermal SGA-conditions for CuAcr2 ($<T_{term}>$ = 363–513 K), CoAcr2 (623–663 K), NiAcr2 (573–633 K), FeAcr3 (473–643 K), FeCoAcr (613–633K), Fe2CoAcr (613–633 K), Fe2NiAcr (603–643 K), CoMal (613–643 K)**,** FeMal (573–643 K), CoAAm (463-503 K). The rate of gas evolution, $W = d\eta/dt$, decreases monotonically with the degree of conversion, $\eta = \Delta\alpha_{\Sigma, t}/\Delta\alpha_{\Sigma, f}$, where $\Delta\alpha_{\Sigma, t} = \alpha_{\Sigma, t} - \alpha_{\Sigma, 0}$, $\Delta\alpha_{\Sigma, f} = \alpha_{\Sigma, f} - \alpha_{\Sigma, 0}$, $\alpha_{\Sigma, f}$, $\alpha_{\Sigma, t}$ and $\alpha_{\Sigma, 0}$ are the final, current (corresponding to time t) and the initial number of moles of gaseous products released per mole of the starting substance at T_{room}, respectively. The kinetics of gas evolution $\eta(\tau)$ in the general case (up to $\eta \leq 0.95$) is satisfactorily approximated by the equation for two parallel reactions:

$$\eta(\tau) = \eta_{1f}[1 - \exp(- k_1\tau)] + (1 - \eta_{1f})[1 - \exp(- k_2\tau)], \quad (1)$$

where $\tau = t - t_0$ (t_0 is the time of heating); $\eta_{1f} = \eta(\tau)|_{k2t \to 0, k1t \to \infty}$, k_1, k_2 are the effective rate constants. The k_1, k_2, η_{1f}, and $\Delta\alpha_{\Sigma, f}$ parameters depend on T_{term} as follows:

$$\eta_{1f}, \Delta\alpha_{\Sigma, f} = A\exp[- E_{a,eff}/(RT_{term})],$$

$$k_{eff} = k_{0,eff}\exp[- E_{a,eff}/(RT_{term})],$$

where A, $k_{0,eff}$ is the pre-exponential coefficient [sec^{-1}], $E_{a,eff}$ is the activation energy [kJ/mol].

3. THE COMPOSITION AND STRUCTURE OF METALLOPOLYMER NANOCOMPOSITES

The results of electron microscopic study of the products of metal-containing monomer transformations show that FeAcr3, CoMal, Fe2NiAcr, FeCoAcr and Fe2CoAcr have similar morphology. It is characterized by practically spherical electron-dense clusters having narrow size distribution and allotted in low electron-dense matrix. The clusters are either single particles or agglomerates of 3-10 particles. The nanosized particles are uniformly distributed in the matrix at an average distance of 8-10 nm.

The distinct crystalline reflections, which appeared in the XRD pattern, matched well the characteristic lines of metallic cobalt for the product of CoAAm thermolysis. The broad spectra suggested nanocrystalline structure. In fact the crystallites are very fine and their size depends on the thermolysis temperature. The Scherrer assessment gave the mean crystallite size 7 and 20 nm, for the samples thermolysed at temperatures and 1073 K, respectively. The latter temperature resulted also in the transformation of the single phase cobalt in the product formed at 873 K into two forms differing by the lattice constants; (i) cubic – a1 = 3.54470 Å, (ii) cubic – a2 = 3.61265Å, represented by double peaks on the X-ray pattern. The second contained some amount of dissolved carbon (CoCx).

The formation of magnetic particles proceeds during decarboxylation of metal-containing carboxylate groups at the final stages of thermal transformation. Ferromagnetic nanoparticles stabilized by a polymer matrix were obtained during solid phase polymerization of metal-containing monomers followed by controlled thermolysis of the products obtained. By varying the synthesis conditions, it is possible to obtain nanoparticles of metals, their oxides and of their carbides with the required size, shape and structure and homogeneity of size distribution through the matrix. The static magnetic properties of the sample are dominated by the interparticle magnetic interactions and glass-type freezing effects.

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