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New Metallopolymers with Definite Properties

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The coordinative-radical polymerization of new monomers in the presence of azoizobutyronitrile (AIBN) as an initiator, in different solvents at 80°C has been studied.

The photoinitiated polymerization of several metal-containing monomers is described. Six metal chelates were investigated as monomeric units: copper (II), nickel (II), cobalt (II) complexes with 5-methyl-5-hexen-2,4-dione, 7-octen-2,4-dione and 3-allylpentan-2,4-dione in the photo polymerization processes which have been studied by the dilatometry.

Synthesized complexes (in very small quantities 1–5%) were copolymerized with styrene. The β -diketonates of Ni, Co, Cu can be used as new class of intrachain UV-absorbers.

Keywords: β -diketonates of Ni, Co, Cu; complexes; coordinative-radical polymerization; intrachain UV-absorbers; photoinitiated polymerization

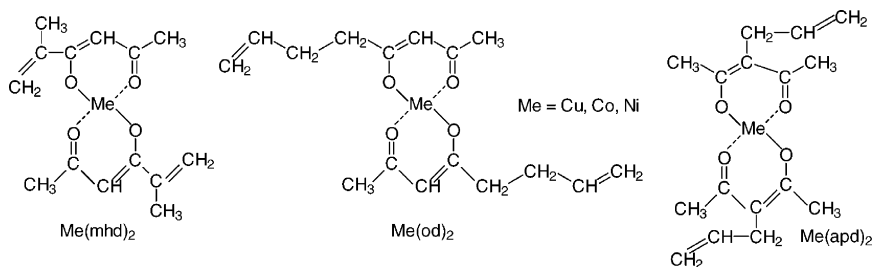
1. INTRODUCTION

The creation of polymers for special applications is a new direction in polymer synthesis. Metallopolymers – new functional materials are used for the alluvium of coatings from gaseous phase (CVD-method), as macroinitiators of the radical polymerization, perspective as superconductors, anisotropic optic systems, films in solar batteries [1,2].

The interest in these materials causes the elaboration of new methods of metallopolymer synthesis [3,4]. The polymerization process of

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some unsaturated β -diketonates – copper (II), nickel (II), cobalt (II) complexes with 5-methyl-5-hexen-2,4-dione (mhd), 7-octen-2,4-dione (od) and 3-allylpentan-2,4-dione (apd) with double bonds which are conjugated or unconjugated with chelates ring has been investigated.



2. RESULTS AND DISCUSSION

Complexes have been obtained by the exchange reaction between acetates of corresponding metal and β -diketonates in aqueous-alcohol solution and purified by recrystallization from ethanol. The structural peculiarities of the coordination site of obtained complexes have been studied by electronic, infrared and EPR-spectroscopies [3]. The chemical analysis on the metal, Carbon and Hydrogen achieved the structure of complexes corresponds to the formula $\text{Cu}(\beta\text{-dik})_2$ and $\text{Me}(\beta\text{-dik})_2 \cdot 2\text{H}_2\text{O}$, Me-Co, Ni. For Co-complexes in contrast to acetylacetonates the balance between dark blue tetrahedral shape of $\text{Co}(\beta\text{-dik})_2$ and pink octahedral $\text{Co}(\beta\text{-dik})_2 \cdot 2\text{H}_2\text{O}$ are observed in the electronic spectra of this complexes.

Earlier the kinetics of their coordinative-radical polymerization (AIBN as initiator, in different solvents, 80°C) we studied [4]. It was shown, that aprotic donor solvents such as dimethylformamide, pyridine accelerate the polymerization process as a result of the adduct formation. But in this conditions the polymerization of Cu β -diketonates is accompanied by the reduction Cu(II) to Cu(I) and even to metallic Cu. And so the polymer conversion was far lowed or Cu-based polymer were not obtained. Therefore, the photoinitiated polymerization of these complexes has been investigated since this process occurs at nearly room temperature and Cu β -diketonates would not be decomposed.

The photoinitiated polymerization of several metal-containing monomers has been studied by the dilatometry (with benzoin as photoinitiator, in different solvents, 30°C, UV-irradiation). The influence of metal nature and monomer structure on the rate of polymerization has been investigated (Fig. 1, Table 1).

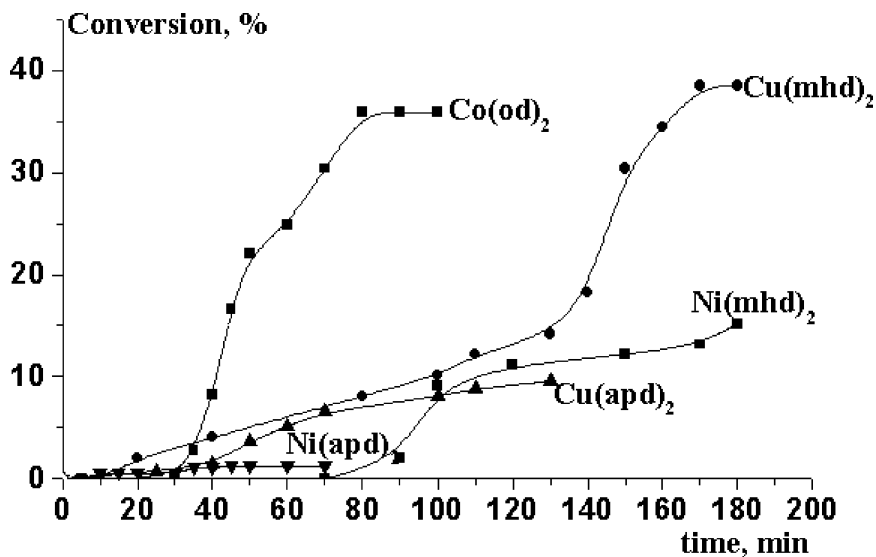


FIGURE 1 Kinetic of photoinitiated radical polymerization : 15% monomer in DMF with benzoin, argon atmosphere.

The highest rate of polymerization was observed for cobalt complexes among metals and in series of ligands – for complexes mhd, that is for β -diketone which have the double bond conjugated with the metalocycle.

The result proves that the reactive ability of metal-containing monomers based on β -diketones in the reaction of photopolymerization depends on the metal nature and β -diketone structure and it is determined by both electronic and steric factors.

It is known from the literature, that β -diketonate metal complexes are effective initiators of radical polymerization [5,6]. But the application of these complexes or binary systems based on them as photoinitiators of polymerization are not described.

TABLE 1 Kinetic Parameters of Photo Polymerization of Monomer Chelates

Monomer	$V/C \cdot 10^5, s^{-1}$	$V, \cdot 10^6, \text{mol/l} \cdot s$	$K_{\Sigma} \cdot 10^4$
Co(od) ₂	12,0	17,8	17,2
Ni(apd) ₂	0,19	0,28	0,27
Cu(apd) ₂	1,39	2,03	1,98
Cu(mhd) ₂	3,52	5,66	5,01
Ni(mhd) ₂	2,09	3,38	2,98

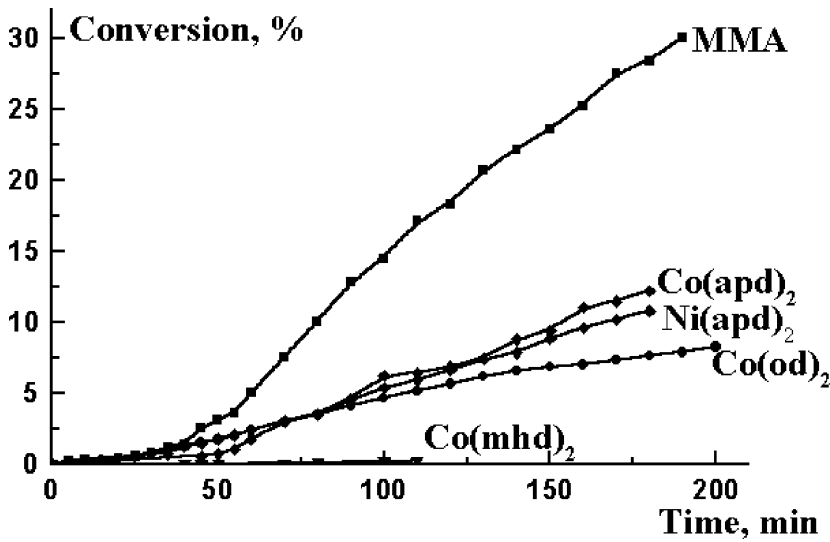


FIGURE 2 Kinetic of photoinitiated radical polymerization: 15% MMA in DMF, argon atmosphere with binary initiated system benzoin:chelate (2% : 1%).

Photopolymerization of methyl methacrylate (MMA) (15 mass.% in DMF) with mass.1% acetylacetonates Co, Ni, Cu and unsaturated β -diketonate metal complexes in combination with benzoin as photoinitiators of polymerization was studied. It was found that the photopolymerization of MMA with metal chelate is not observed. Binary systems based on the benzoin (2 mass.%) and metal chelates (1 mass.%) can initiate the polymerization of MMA with some peculiarities (Fig. 2, Table 2). In the case of binary systems with metal acetylacetonates some inhibition ($\text{Fe}(\text{acac})_3$) of the polymerization process can be occurred (Fig. 3, Table 3). Employing of the unsaturated β -diketonate metal complexes leads to the control of the length of kinetic and

TABLE 2 Kinetic Parameters of Photopolymerization of MMA with Binary Initiate System Benzoin : Chelate (2% : 1%)

Monomer	$V/C \cdot 10^6, s^{-1}$	$V, \cdot 10^6, \text{mol/l} \cdot s$	$K_{\Sigma} \cdot 10^4$
MMA	29,83	44,30	2,23
Co(od) ₂	7,62	0,114	0,57
Ni(apd) ₂	11,12	16,51	0,83
Co(apd) ₂	13,20	19,61	0,988

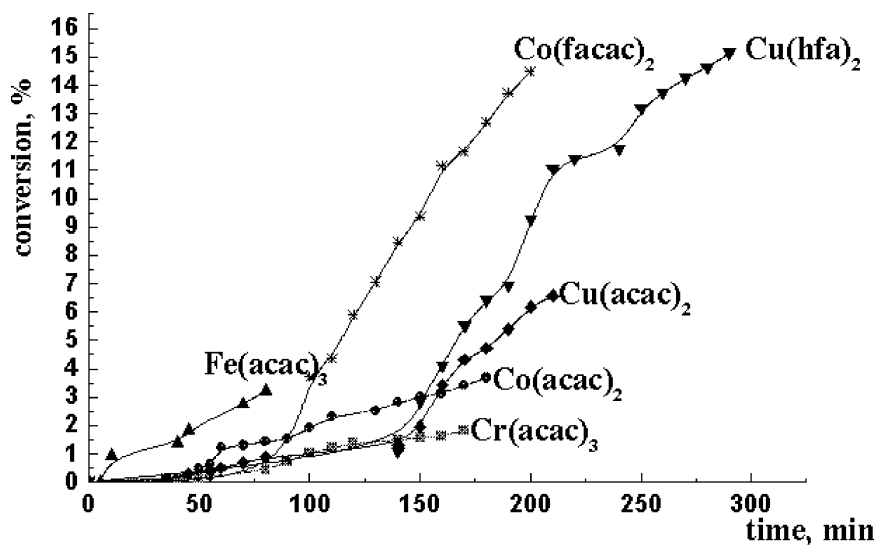


FIGURE 3 Kinetic of photoinitiated radical polymerization: 15% monomer MMA in DMF, argon atmosphere with binary initiated system benzoin: acetylacetonate metals (2% : 1%).

material polymer chains. Unexpectedly, $\text{Cu}(\text{mhd})_2$ is an inhibitor of polymerization in these conditions.

Metalorganic stabilizers were used for photostabilization of polyolefines, polyamides and polystyrene-based materials. The special monomers-modifiers were found in order to improve photostability of polystyrene. For the intrachain photostabilization of polystyrene they can be included to macromolecules by copolymerization [7,8].

Polystyrene and its copolymers with complexes have been obtained by the reaction of polymerization (1% AIBN as initiator), in DMF, 80°C. Structures of copolymers have been studied by electronic,

TABLE 3 Kinetic Parameters of Photopolymerization of MMA with Binary Initiate System Benzoin : Acetylacetonate Metals (2% : 1%)

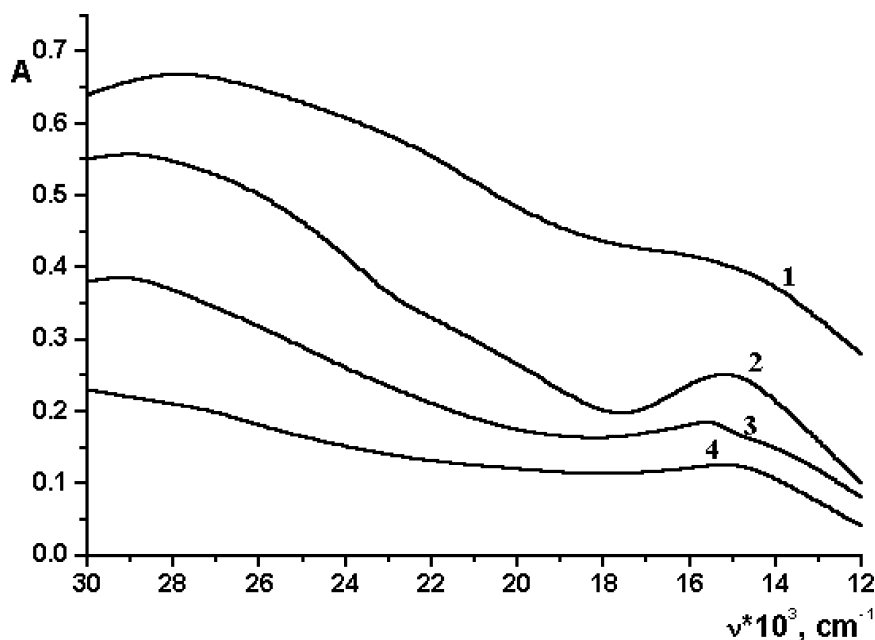
Monomer	$V/C \cdot 10^6, \text{sec}^{-1}$	$V, \cdot 10^6, \text{mol/sec} \cdot \text{l}$	$K_{\Sigma} \cdot 10^4$
MMA	29,83	44,30	2,23
$\text{Cu}(\text{ac})_2$	5,64	8,37	0,42
$\text{Co}(\text{ac})_2$	3,81	5,66	0,28
$\text{Fe}(\text{ac})_3$	6,32	9,39	0,47
$\text{Cr}(\text{ac})_3$	2,07	3,07	0,15
$\text{Cu}(\text{fac})_2$	14.51	21,55	1,09

TABLE 4 Parameters of Infrared Spectra of Styrene Copolymers with Complexes

No	Monomer	Ratio styrene : monomer, %	$\nu(\text{C-O})$	$\nu(\text{C-C})$	$\nu(\text{C=C})$	$\nu(\text{M-O})$
1.	Ni(mhd) ₂	99:1	1585	1600	—	>400
2.	Ni(od) ₂	99:1	1600	1600	—	>400
3.	Ni(apd) ₂	99:1	1600	1600	—	>400
4.	Co(mhd) ₂	99:1	1600	1600	—	>400
5.	Co(od) ₂	99:1	1595	1595	—	>400

infrared (Table 4) and diffusive reflection (Fig. 4) – spectroscopies. Electronic absorption spectra and diffusive reflection spectra have been recorded by Specord M-40 in area 25000–11000 cm⁻¹, and infrared spectra – by Specord M-80 in area 4000–400 cm⁻¹ with KBr.

General form of diffusive reflection spectra of copolymers in comparison with spectra of corresponding monomers [3] is not change, that permits to describe the neighborhood of nickel and cobalt in polymers as strained octahedral and cuprum – plane-square.

**FIGURE 4** Diffusive reflection spectra of some copolymers of styrene with complexes: 1 – Co(od)₂; 2 – Ni(od)₂; 3 – Ni(mhd)₂; 4 – Co(mhd)₂.

But the maximum of absorption of polymers in comparison with spectra of monomers moves to $150\text{--}200\text{ cm}^{-1}$ in low-frequency area, which indicate on attenuation of ligands field and more faint binding of metal - ligand. The results of electronic spectroscopy well correlate with data of infrared spectroscopy (Table 4).

Polymer films have been UV-irradiated (the temperature $20\text{--}22^\circ\text{C}$) during 3 hours. During irradiation the polystyrene films become friable and yellowish. The effect of photo stabilization of metal chelates is observed by changes in UV-absorption spectra of polystyrene (unstabilized and stabilized) after UV-irradiation (Fig. 5).

Photostabilization effect among β -diketonate complexes (Fig. 6) changes in a series: $\text{Cu(mhd)}_2 < \text{Co(od)}_2 < \text{Ni(od)}_2 < \text{Ni(mhd)}_2$, so Ni-complexes are best stabilizers.

It was found that the β -diketonates of Ni, Co, Cu can be used as new class of intrachain UV-absorbers.

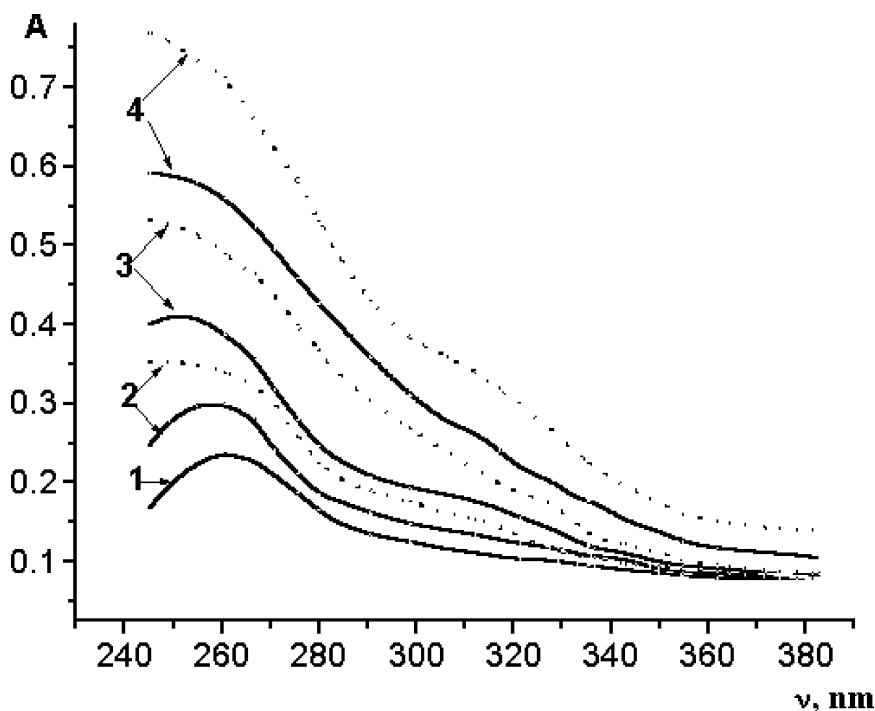


FIGURE 5 Changes of optical density in the UV-absorption spectra of unstabilized polystyrene (···) and stabilized Ni(mhd)_2 (—) after UV-irradiation, 1–0 min, 2–30 min, 3–90 min, 4–180 min.

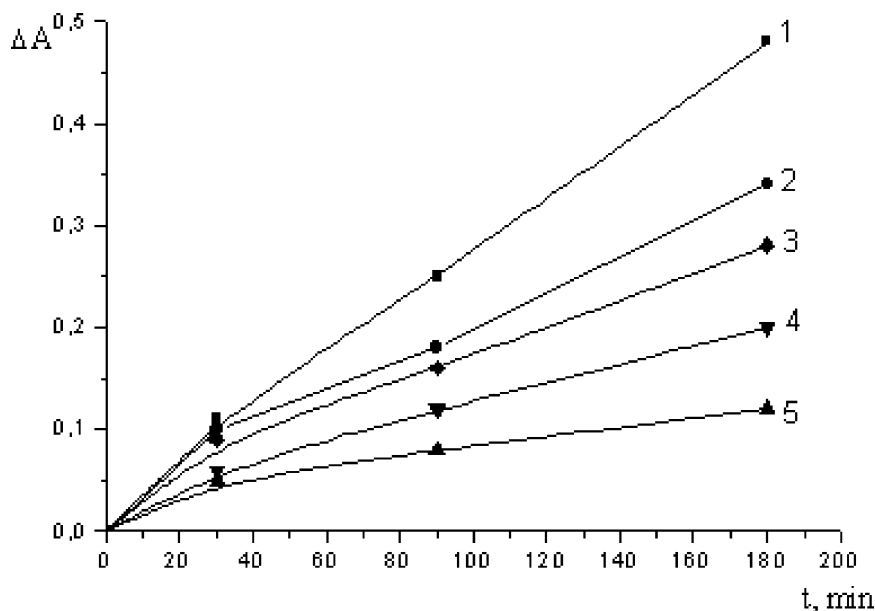


FIGURE 6 The dependence changes of optical density (ΔA) on $\lambda = 260$ nm on irradiation time for unstabilized polystyrene (1) and stabilized by: Cu(mhd)_2 (2), Co(od)_2 (3), Ni(od)_2 (4), Ni(mhd)_2 (5).

It is known from the literature [9], that metal complexes are effective thermostabilizers for polymeric materials. New styrene-nonyl methacrylate (4:1) copolymers with monomer chelates (2 mol.%) were obtained.

Thermogravimetric studies were made with thermobalances in vacuum. Antioxidative activity was studied in air using standard derivatograph OD-130. The monomer chelates units in the polymer chain were found to decrease the thermal stability of styrene copolymers at high temperatures (Table 5).

TABLE 5 Parameters of Thermogravimetric Studies of Thermooxidative Degradation of Styrene-Nonyl Methacrylate (ST:NMA) (4:1) Copolymers with 2% Metal Chelates

Copolymer	$T_d, ^\circ\text{C}$	$T_{10\%}, ^\circ\text{C}$
ST:NMA	273	300
ST:NMA + 2% Cu(mhd)_2	231	246
ST:NMA + 2% Co(od)_2	274	289

Hence, these metal complexes are not antioxidants but the β -diketonates of Ni, Co, Cu can be used as new class of intrachain UV-absorbers.

In the present work we obtained new metallopolymers containing metal ion in each monomer unit and found some fields of their application.

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