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## SYNTHESIS AND INITIATING ACTIVITY OF Co(II)-Mn(II) BIMETALLIC MACROINITIATORS OF *b*-DIKETONATE TYPE

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*Received: September 29, 2014 / Revised: December 08, 2014 / Accepted: February 18, 2015*

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**Abstract.** Bimetallic macroinitiators have been obtained *via* styrene triple copolymerization with cobalt(II) and manganese(II) vinyl-*b*-diketonates. The copolymerization kinetic parameters have been studied. Metal chelates were found to be as comonomers, initiators and inhibitors at the same time during copolymerization process. The macroinitiators synthesis optimal conditions have been examined. They may be used for the production of grafted polymers.

**Keywords:** vinyl-*b*-diketonate, radical copolymerization, macroinitiator, inhibition, bimetallic macrochelate.

### 1. Introduction

One of the priority directions of the chemistry of highmolecular substances is modification of polymeric materials providing the improvement of physico-chemical characteristics of the polymers and increasing the possibility of their usage in different branches of industry. One of the modification methods is application of macroinitiators allowing to obtain grafted polymers with a branched structure.

There are few types of polymeric initiators (macroinitiators, MI). The most common method of their obtaining consists of two stages. At the first stage monomer initiators containing the double bond are synthesized; the bond is capable of homo- and copolymerization with vinyl monomers. At the second stage homo- and copolymerization of the synthesized monomers is carrying out. As a result the polymer with initiating groups is obtained. Monomer initiators with peroxy groups were synthesized firstly [1]. But the general study of the permonomers was started in the sixties of the XX century. At that time various perethers of acrylic and methacrylic acids were synthesized. These compounds are easily homo- and copolymerized with vinyl and dienic monomers and form MI of the peroxy

type [2]. Then MI of the peroxy type were studied in different homogeneous and heterogeneous processes of the polymeric materials synthesis and modification. MI with the active organometallic end-groups may be obtained *via* initiating polymerization of the vinyl monomers by the systems with metalloorganic compounds. While using such metalloorganic MI during block-copolymerization their viscosity increases by 10 times [3]. MI with diazogroups in the macromolecule are known, as well [4]. Macrophotoinitiators possessing the initiating activity together with the properties of surface-active substances, stiffeners, stabilizers, *etc.* were synthesized and studied. H. Ohar *et al.* [5] synthesized macrophotoinitiators based on maleic anhydride and benzoine cooligomers which are well adsorbed on the surface of mineral dispersive particles.

Previously we obtained a new type of MI containing fragments of *b*-diketonates of 3*d*-metals in its macromolecule. For this purpose we synthesized vinyl-*b*-diketonates with a reactive double bond [6]. Co(II), Ni(II) and Cu(II) vinyl-*b*-diketonates were synthesized on their basis [7]. The initiating of vinyl monomers radical polymerization by means of the mentioned compounds leads to the synthesis of MI capable to graft side chains and obtain branched and grafted polymers [8]. It was shown by us [9] that vinyl-*b*-diketonates with the concentration of above  $5 \cdot 10^{-3}$  mol/l exhibit the inhibiting activity; the dependence  $V_{pol} \sim \sqrt{C_{chel}}$  is nonlinear for them, *i.e.* their behavior as an initiator does not correspond to the conception of classical theory of radical polymerization [9]. It is the reason for the great difference between the initial (rate in the straight zone) and average (rate at  $\sim 10\%$  conversion) polymerization rates. The greater difference between the mentioned parameters the higher inhibitory action. For the most used initiators (*e.g.* benzoyl peroxide) these parameters are equal because the dependence of polymerization rate on time is a linear one.

Co(II) vinyl-*b*-diketonates have the most initiating activity during styrene polymerization. It is well-known that acetylacetonates of 3*d* metals are initiators of radical polymerization. Manganese acetylacetonate has the highest initiating activity among examined acetylacetonates [10].

So, it should be interesting to synthesize and study the initiating activity of MI containing Co(II) and Mn(II) vinyl-*b*-diketonates in the same macromolecule. Moreover, the effect of two diketonates simultaneous presence on the polymerization kinetics is still indeterminate. Such heterometallic polymeric macroinitiators of *b*-type are not described in the literature. They may be interesting as the catalysts for organic reactions, as well as bactericidal and fungicidal materials with a wide spectrum of action.

## 2. Experimental

5-Methyl-5-hexene-2,4-dion (MHD) was synthesized *via* methylmethacrylate condensation with acetone in the presence of sodium methylate [11]. MHD-Mn and MHD-Co metal complexes are synthesized in the same way while interaction between MHD and Mn or Co acetates [7].

MHD-Mn(II), MHD-Co(II) and styrene block-copolymerization was carried out at 358 K and polymerization in methylethylketone (MEK) solution – at 353 K (styrene:MEK (v/v) = 1:2). To study the kinetic regularities the process was carried out till ~ 10 % conversion.

Polymerization kinetics was studied by dilatometric and gravimetric methods. Molecular weight of polymers was determined by viscosimetry using the Ubbelohde viscometer [12].

Metals content in the polymer was determined using the atomic adsorption spectrometer “Saturn”. The source of primary radiation is spectral lamp with a hollow cathode LSP-1; cobalt analytic line – 240.7 nm; manganese analytic line – 279.5 nm; slit width of monochromator – 0.1 mm. The investigated solutions were sprayed into the flame of slot burner acetylene-air at gas (C<sub>2</sub>H<sub>2</sub>) consumption of 2.17 l/min and oxidizer (air) consumption of 11.33 l/min. The height of flame photometry zone over burner slit – 1.5–2.0 mm. Under the mentioned conditions the determined range of metal concentration is 0.25–10 µg/ml at the standard deviation ( $S_r$ ) ≤ 0.075. The polymer sample (0.05–0.10 g) was previously dissolved while heating on a sand bath in 25–30 ml of nitric and chloric acids mixture (5 : 3). The obtained solution was diluted by distilled water till 10 ml volume. Standard solutions with 0.5; 1; 2; 5; 10; 25 and 50 µg/ml of metal were prepared by step-by-step dilution

by 2–10 times of the initial standard sample with the metal concentration of 1 µg/ml (provided by Physico-Chemical Institute, Odessa, Ukraine). To avoid possible errors caused by the mentioned mineral acids (nitric and chloric), their contents in analyzed and standard solutions were equalized.

## 3. Results and Discussion

To estimate the role of every fragments of Co(II) and Mn(II) *b*-diketonates we examined styrene polymerization initiated by Co(II) and Mn(II) chelates separately. The obtained results are represented in Tables 1 and 2.

When comparing Tables 1 and 2 one can see that at the conversion close to 10 % the initial and average rates of polymerization are entirely different values. It means that the inhibition process takes place. Discrepancy between  $S_{dil}$  and  $S_{grav}$  also confirms the inhibition presence.  $S_{grav}$  has lower values due to the partial losses of low-molecular fractions during polymerization. Moreover, MHD-Co(II) provides higher  $V_{init.}$  but lower  $V_{av.}$  values compared with those provided by MHD-Mn(II). The difference between conversion values determined by dilatometric and gravimetric methods is greater for MHD-Co(II) compared with MHD-Mn(II), that also indicates the greater inhibiting activity [9]. On the basis of the results presented in Tables 1 and 2 we plotted the dependencies of  $V_{init.}$  on MHD-Me concentration (Fig. 1). This dependence is non-linear in contrast to the peroxide initiators. The increase in MHD-Me concentration after the maximum retards  $V_{init.}$  for both chelates but it is more intensive for MHD-Co(II). When initiating the styrene polymerization by MHD-Co(II) at the concentration of  $20 \cdot 10^{-3}$  mol/l the cross-linked product is formed. In case of MHD-Mn(II) soluble polymers are formed even at higher concentrations. The cross-linking process occurs due to the break of growing radicals on the metal centre of MHD-Co(II). All mentioned kinetic characteristics indicate that MHD-Co(II) has more intensive inhibiting activity compared with that of MHD-Mn(II). The metal contents in both chelates are almost the same.

The dependence of characteristic viscosity [ $h$ ] on the initiator concentration is also of interest. The decrease in chelates concentration decreases both initiating and inhibiting activities but the latter one decreases more intensively. The close values of  $V_{init.}$  and  $V_{av.}$  as well as  $S_{dil}$  and  $S_{grav}$  at low concentrations of chelates reveal this fact. Moreover, *b*-diketonates fragments, introduced into the macromolecule, initiate the side chains grafting. This fact also affects [ $h$ ] value, especially with the conversion growth [13]. The joint influence of several factors leads to the sharp increase in [ $h$ ] value for both *b*-diketonates at the concentration of  $0.5 \cdot 10^{-3}$  mol/l.

Table 1

Dependence of kinetic parameters of styrene polymerization initiated by MHD-Co(II) on the initiator concentration and characteristics of the obtained polymers;  $T = 358\text{ K}$

$C_{in} \cdot 10^3$ , mol/l	$V_{init.} \cdot 10^5$ , mol/l·s	$V_{av.} \cdot 10^5$ , mol/l·s	$S_{dil.}$ , %	$S_{grav.}$ , %	$w_{Co}$ , wt %	$[\eta]$ , dl/g	MI symbol
20.0	6.3	3.1	8.9	11.9	0.53	cross-linked	I-Co
10.0	22.6	3.2	9.9	5.5	0.32	1.89	II-Co
5.0	22.6	2.9	9.1	6.5	0.23	1.82	III-Co
2.5	17.0	4.1	9.9	8.6	0.10	1.24	IV-Co
1.0	13.6	5.0	9.9	8.4	0.05	0.85	V-Co
0.5	12.0	5.2	9.8	8.7	0.02	1.67	VI-Co
0	2.2	2.2	10.0	10.0	–	–	–

Notes:  $V_{init.}$  and  $V_{av.}$  – the initial and average rate of polymerization, respectively;  $S_{dil.}$  and  $S_{grav.}$  – conversion determined by dilatometry and gravimetry, respectively;  $w$  – metal content;  $[\eta]$  – characteristic viscosity of the polymeric solution

Table 2

Dependence of kinetic parameters of styrene polymerization initiated by MHD-Mn(II) on the initiator concentration and characteristics of the obtained polymers;  $T = 358\text{ K}$

$C_{in} \cdot 10^3$ , mol/l	$V_{init.} \cdot 10^5$ , mol/l·s	$V_{av.} \cdot 10^5$ , mol/l·s	$S_{dil.}$ , %	$S_{grav.}$ , %	$w_{Mn}$ , wt %	$[\eta]$ , dl/g	MI symbol
30.0	16.9	9.7	9.9	8.0	0.42	0.98	I-Mn
20.0	20.4	10.1	10.5	8.2	0.46	0.95	II-Mn
10.0	18.8	8.0	10.2	9.7	0.20	1.10	III-Mn
5.0	19.5	8.0	10.3	6.4	0.15	0.97	IV-Mn
2.5	9.5	5.3	9.9	8.7	0.04	0.55	V-Mn
1.0	6.1	4.5	10.5	9.0	0.01	0.73	VI-Mn
0.5	3.4	3.3	9.9	9.6	0.01	2.31	VII-Mn
0	2.2	2.2	10.0	10.0	–	–	–

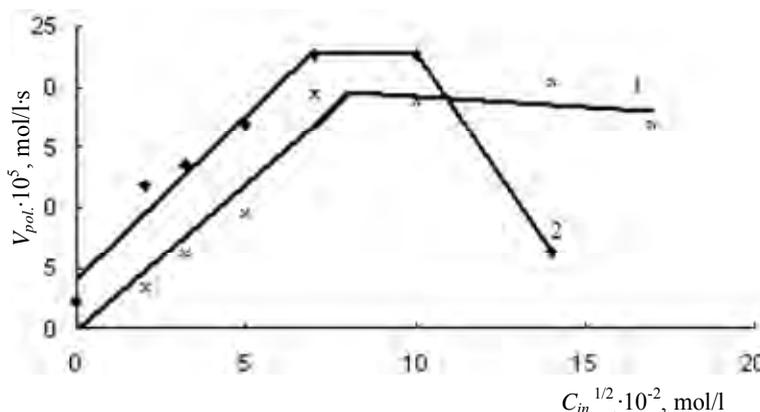


Fig. 1. The polymerization initial rate vs. MHD-Mn(II) (1) and MHD-Co(II) (2) concentration

The next stage of investigations was styrene polymerization initiated by MHD-Co(II) and MHD-Mn(II) mixtures. Taking into account that *b*-diketonates has a double bond in their structure these chelates form a triple copolymer with styrene.

The used metal-monomers contain two unsaturated *b*-diketonate fragments but mainly one double bond participates in the copolymerization process. The presence of unused multiple bonds in the obtained polymers

confirms this fact [14]. The reasons are considerable decrease in the mobility of *b*-diketonate fragment after its introduction into a macromolecule and steric barriers.

The kinetic parameters of the triple copolymerization and the properties of obtained polymers are represented in Table 3. At high concentrations of both chelates the polymerization rates are less than the sum of initiating rates of the individual chelates (Fig. 2). But at the concentration of  $2.5 \cdot 10^{-3}$  mol/l  $V_{init.}$  for the mixture is

$14.9 \cdot 10^{-5}$  mol/l, that differs in a less degree from the sum value of the individual chelates rates. It means that while initiating by the mixtures the inhibiting component increases with the concentration growth in a great extent compared with the initiating component. This fact is determined by metal total quantity in the system rather than its nature. And just cobalt chelate plays the key role

because it is a stronger inhibitor. The additional confirmation is the fact that there is a regularity in the system with non-equimolar ratio of metallic complexes: the greater part of MHD-Co(II) in the mixture, the lower polymerization rate. The increase of MHD-Mn(II) amount in the mixture increases the initial and average rates of the process.

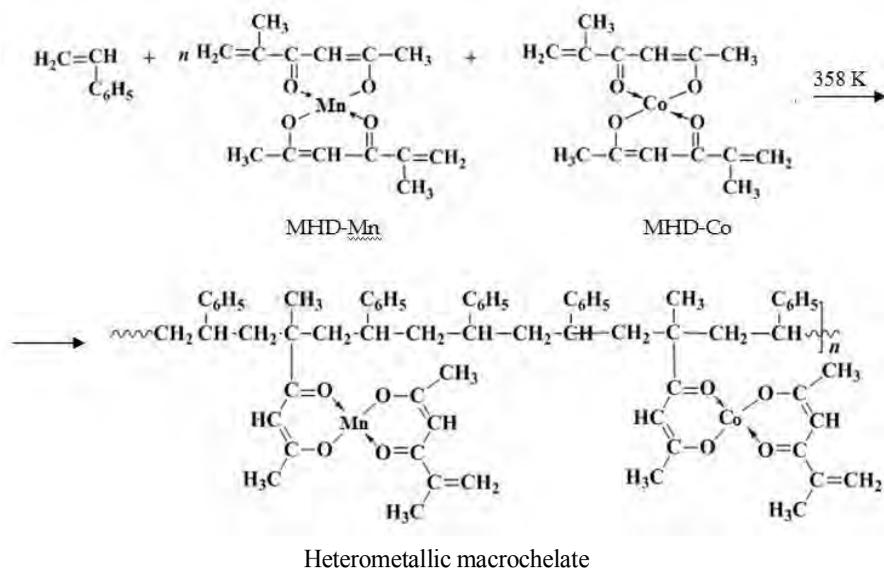
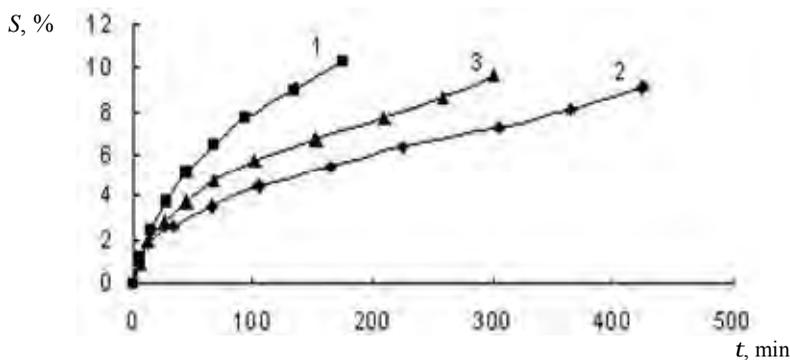


Table 3

**Dependence of kinetic parameters of styrene polymerization initiated by MHD-Co(II) and MHD-Mn(II) mixtures on the initiator concentration and characteristics of the obtained polymers;  $T = 358$  K**

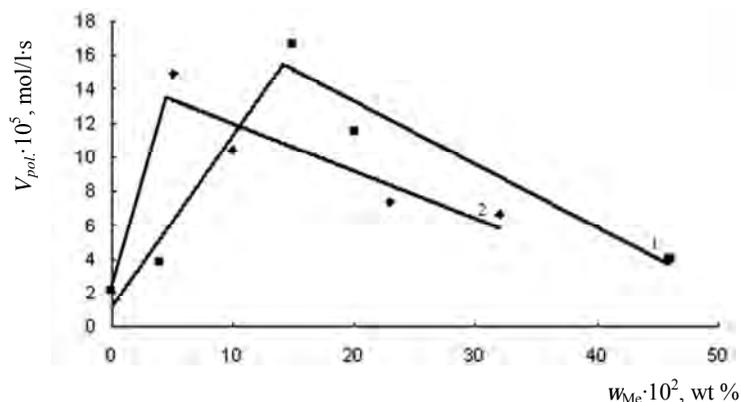
$C_{in} \cdot 10^3, \text{ mol/l}$		$V_{init} \cdot 10^5, \text{ mol/l}\cdot\text{s}$	$V_{av} \cdot 10^5, \text{ mol/l}\cdot\text{s}$	$S_{dil}, \%$	$S_{grav}, \%$	$w_{Me}, \text{ wt } \%$		$[\eta], \text{ dl/g}$	MI symbol
MHD-Co	MHD-Mn					Co	Mn		
*30.0	*30.0	5.7	3.8	10.2	6.2	3.0	3.5	cross-linked	I
10.0	10.0	5.4	1.7	9.6	4.5	0.40	0.32	3.21	II
5.0	5.0	19.0	4.4	9.6	7.5	0.27	0.25	1.64	III
2.5	2.5	14.9	4.6	9.9	7.2	–	–	–	IV
5.0	2.5	10.9	2.7	9.8	7.3	0.16	0.01	–	V
5.0	1.5	12.2	2.8	9.8	5.1	0.18	0.01	–	VI
2.5	5.0	15.4	6.1	9.3	7.7	0.10	0.12	0.86	VII
1.5	5.0	18.1	6.1	10.4	9.7	0.04	0.10	0.95	VIII

Note: \* – polymerization in MEK solution



**Fig. 2.** Conversion vs. time of styrene polymerization initiated by MHD-Co(II) and MHD-Mn(I):

$C_{\text{MHD-Mn(II)}} = 5 \cdot 10^{-3} \text{ mol/l}$  (1);  
 $C_{\text{MHD-Co(II)}} = 5 \cdot 10^{-3} \text{ mol/l}$  (2) and  
 $C_{\text{MHD-Mn(II)+MHD-Co(II)}} = 5 \cdot 10^{-3} \text{ mol/l}$  (3)



**Fig. 3.** Dependence of the initial rate of styrene grafted polymerization on the metal concentration in the macroinitiator: MI with MHD-Mn(II) fragments (1) and MI with MHD-Co(II) fragments

Table 4

**Kinetic parameters of styrene grafted polymerization on monometallic MI;  $T = 358\text{ K}$ ,  $C_{MI} = 0.01\text{ wt \%}$**

Macroinitiator parameters			Grafted polymerization parameters					
Symbol	$w_{Me}, \%$		$[h], \text{dl/g}$	$V_{init.}, \text{mol/l}\cdot\text{s}$	$V_{av.}, \text{mol/l}\cdot\text{s}$	$S_{dil.}, \%$	$S_{grav.}, \%$	$[h], \text{dl/g}$
	Mn	Co						
II-Co		0.32	1.89	6.7	5.6	9.9	8.8	3.54
III-Co		0.23	1.82	7.4	7.1	10.0	7.9	3.78
IV-Co		0.10	1.24	10.4	6.3	9.9	9.2	4.03
V-Co		0.05	0.85	14.9	4.6	9.9	9.4	2.04
VI-Co		0.02	1.67	3.4	2.9	9.9	8.9	2.80
II-Mn	0.46		0.95	4.0	3.8	10.3	9.0	2.47
III-Mn	0.20		1.10	11.5	5.7	9.9	7.8	2.16
IV-Mn	0.15		0.97	16.7	4.7	9.9	8.8	2.23
V-Mn	0.04		0.55	3.8	3.0	9.9	8.8	1.89
VI-Mn	0.01		0.73	4.7	4.5	10.7	9.2	3.36
Thermo-	0	0	–	2.2	2.2	10.0	10.0	–

Table 5

**Kinetic parameters of styrene grafted polymerization on bimetallic MI;  $T = 358\text{ K}$ ,  $C_{MI} = 0.01\text{ wt \%}$**

Macroinitiator parameters			Grafted polymerization parameters					
Symbol	$w_{Me}, \%$		$[h], \text{dl/g}$	$V_{init.}, \text{mol/l}\cdot\text{s}$	$V_{av.}, \text{mol/l}\cdot\text{s}$	$S_{dil.}, \%$	$S_{grav.}, \%$	$[h], \text{dl/g}$
	Mn	Co						
II	0.32	0.40	1.72	6.8	6.0	9.8	8.0	3.95
III	0.25	0.27	1.64	6.7	4.9	9.9	8.1	2.30
VI	0.01	0.18	2.03	6.3	5.0	9.9	8.2	3.43
VII	0.12	0.10	0.86	4.5	3.8	9.9	8.0	5.03
VIII	0.10	0.04	0.95	7.9	5.6	9.3	8.7	2.18

When using equimolar amount of *b*-diketonates the content of metals in the polymer is similar and may be controlled by concentrations varying. To increase the metal content in the polymer the process was carried out in the solvent – methylethylketone (MEK), which is a donor additive. The ratio styrene : MEK = 1:2 allows to solve chelates with higher concentrations  $C_{MHD-Mn(II)} = C_{MHD-Co(II)} = 30 \cdot 10^{-3} \text{ mol/l}$  and decreases their inhibiting activity [9]. However, the polymerization rates are low ( $V_{init.} = 5.7 \text{ mol/l}$  and  $V_{av.} = 3.8 \text{ mol/l}$ ) and the metal content in the formed polymer is high ( $w_{Mn} = 3.5 \text{ wt \%}$  and  $w_{Co} = 3.0 \text{ wt \%}$ ).

To estimate the initiating activity of heterometallic copolymeric complexes at the styrene polymerization we preliminary studied the initiating activity of monometallic MI described above. The process was carried out at 358 K. MI amount was 0.1 wt % from the styrene amount. The results are given in Table 4.

Maximum initial rate for the cobalt MI is found for cobalt concentration of 0.05 wt % and for manganese MI – at 0.15 wt %. The graphical dependence of  $V_{init.}$  on metal concentration in MI is given in Fig. 3. In such a case the dependence is similar to the dependence  $V_{init.}$  vs.  $C_{in.}^{1/2}$  (Fig. 2). Average rates for cobalt MI are maximal at

$C_{Co} = 0.23$  wt % and for manganese MI – at  $C_{Mn} = 0.20$  wt %. It is connected with a greater number of active centers on the macromolecule where styrene is grafted. It should be noted that chelates inhibiting activity is lower when initiated by MI compared with initiating by monomeric MHD-Mn(II) and MHD-Co(II). The less difference between  $V_{init.}$  and  $V_{av.}$  reveals this fact (*vide* Tables 1, 2, 4). The possible reason is a difficult break of growing chain on the metal centre due to the steric reasons and minor mobility of macroradicals. The 2-3 time increase in characteristic viscosity of obtained polymers compared with that of the initial MI indicates the formation of branched polymers (*vide* Tables 1-3). It should be noted that at close values of  $V_{init.}$  and  $V_{av.}$  the  $[h]$  value of obtained polymers is higher if we use cobalt MI. The possible reason is that the chelate comonomer introduces into the macromolecule due to the multiple bonds (copolymerization) and break of growing chains on the metallic centre (inhibition). In case of MHD-Co(II) the break of growing chains is more essential.

The obtained heterometallic MI (their characteristics are represented in Table 3) were used for styrene grafting under the conditions similar to those when monometallic MI were used. The obtained results are represented in Table 5.

When comparing the results from Tables 3 and 5 one can see that the difference between  $V_{init.}$  and  $V_{av.}$  is less while initiated by MI compared with initiating by the mixtures (Table 3). Similar to the results in Table 4 the polymerization rates for heterometallic MI are lower than they should be according to the additive rule. Moreover, at similar content of manganese in the polymer the polymerization rates increase with the decrease of cobalt content (samples VII and VIII). The highest rate has the sample VIII, in which both chelates concentrations are close to the concentration maxima for monometallic MI. The characteristic viscosities of grafted polymers considerably exceed the values for heterometallic MI that is the evidence of grafting high degree. Thus, the obtained heterometallic macroinitiators containing fragments of cobalt and manganese *b*-diketonates may be used for the production of grafted polymers.

## 4. Conclusions

The comparison of the initial and average rates of styrene polymerization initiated separately by MHD-Mn(II) and MHD-Co(II) and by their mixtures exhibits a stronger inhibiting activity of MHD-Co(II) compared with MHD-Mn(II). At the separate initiating by close concentrations Co-chelate ensures the formation of cross-linking due to the break of macroradicals on cobalt atom. During joint initiating by above-mentioned *b*-diketonates the increase in MHD-Co(II) concentration in the mixture leads to the decrease of the initial and average

polymerization rates; the increase in MHD-Mn(II) concentration has the opposite effect. When varying the metallic complex concentrations and using the solvent it is possible to control the amount and ratio of metallic complex groups in the polymeric bimetallic macrocomplexes used as macroinitiators.

The initiating activity of monometallic and bimetallic MI was compared. In both cases the inhibiting activity of chelate groups introduced into the polymer is lower due to the steric and diffusive reasons. The highest polymerization rate has MI, in which both chelates concentrations are close to the concentration maxima for monometallic MI. The obtained polystyrene has higher values of characteristic viscosity than that of the initial MI. This fact indicates the formation of grafted polymers.

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## СИНТЕЗ ТА ІНІЦІОЮЧА АКТИВНІСТЬ Co (II)–Mn (II) БІМЕТАЛІЧНИХ МАКРОІНІЦІАТОРІВ β-ДИКЕТОНАТНОГО ТИПУ

**Анотація.** *Методом потрібної кополімеризації стиролу з вініл-β-дикетонатами Mn (II) та Co (II) отримані біметалічні макроініціатори. Досліджені кінетичні параметри кополімеризації. Показано, що металохелати в процесі кополімеризації одночасно виконують функції мономерів, ініціаторів та інгібіторів. Знайдено оптимальні умови синтезу MI. Показана можливість використання отриманих макроініціаторів для одержання прищеплених полімерів.*

**Ключові слова:** *вініл-β-дикетонат, радикальна кополімеризація, макроініціатор, інгібування, біметалічний макрохелат.*