

Igor Voloshanovsky, Olga Shevchenko, Anastasiia Schastlyvets and Kateryna Burenkova

SYNTHESIS OF HETEROMETAL COPOLYMER COMPLEXES WITH FRAGMENTS OF Mn(II) AND Zn(II) *b*-DIKETONATES

Odessa Mechnikov Nationale University,
2, Dvoryanskaya str., Odessa, Ukraine; volis15@ukr.net

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Abstract. Heterometal polymer complexes with *b*-diketonate fragments have been obtained *via* styrene triple copolymerization with polyfunctional components of radical polymerization – vinyl-*b*-diketonates of 5-methyl-5-hexene-2,4-dionates Mn(II) and Zn(II). The process was carried out in a block and dimethylformamide solution in the presence and absence of additional initiator – benzoyl peroxide. Varying the chelated metals concentration, the presence of solvent and additional initiator one may control the concentration and metal ratio in the macromolecule, as well as products molecular weight.

Keywords: radical copolymerization, vinyl-*b*-diketonate, inhibitor, heterometal complex.

1. Introduction

It is well-known that *b*-diketonates of 3*d*-metals are active initiators of vinyl monomers polymerization [1, 2] and catalysts of many organic reactions [3]. Previously we demonstrated that vinyl-*b*-diketonates of 3*d*-metals are heterofunctional components of radical polymerization [4]. The presence of reactive double bond provides them with monomer properties and the chelated metals cycle makes them the initiators of radical polymerization [5]. Moreover, they have inhibiting properties at the concentration higher than $1 \cdot 10^{-2}$ mol/l [6]. Inhibition considerably depends on the metal nature and may be controlled by the temperature change and the presence of donor solvents [7]. The regularities of styrene and methylmethacrylate radical polymerization initiated by vinyl-*b*-diketonates essentially differ from the classic theory of radical polymerization. The obtained copolymers contain fragments of *b*-diketonates of 3*d*-metals providing them with properties of initiators and bactericides [8, 9] and increases polymers thermal stability [10].

Similarly, using triple copolymerization of styrene with vinyl-*b*-diketonates of two metals we may obtain copolymers with fragments of two *b*-diketonates, *i.e.* bimetal polymer metal complexes which have not been studied yet. Heterometal polymer complexes are of great interest as catalysts of different reactions, macroinitiators of radical polymerization, bactericide and fungicide materials, *etc.*

The aim of the present investigation is styrene radical polymerization initiated by 5-methyl-5-hexene-2,4-dionates Mn(II) (MXD-Mn) and Zn(II) (MHD-Zn), that allows to obtain copolymer metal complexes with Mn and Zn *b*-diketonates in the chain.

2. Experimental

5-Methyl-5-hexene-2,4-dion (MHD) was synthesized *via* methylmethacrylate condensation with acetone in the presence of sodium methylate [11]. The reaction products are extracted by diethyl ether and divided into two fractions by vacuum distillation. 5-Methyl-5-hexene-2,4-dionate of copper is precipitated from one of the fractions while adding copper acetate. Then the copper complex is recrystallized from methanol and decomposed by 10% H₂SO₄ while cooling. *Via* vacuum distillation we obtain MHD with $T_{boil} = 343\text{--}345$ K/2.3 kPa and $n_D^{20} = 0.9562$. MHD yield is 5–10%. MHD-Mn and MHD-Zn metal complexes are synthesized in the same way during interaction between MHD and Mn or Zn acetates [12].

Polymerization kinetics was studied by dilatometric and gravimetric methods. Molecular weight of polymers was determined by viscosimetry using the Ubellohde viscometer [13].

Metals content in the polymer was determined using the atomic adsorption spectrometer “Saturn”. The source of primary radiation is a 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_2H_2) 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 $\mu\text{g/ml}$ at standard deviation (S_r) ≤ 0.075 . The polymer sample (0.05–0.10 g) was previously dissolved at 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 $\mu\text{g/ml}$ of metal were prepared by step-by-step dilution by 2–10 times of the initial standard sample with the metal concentration of 1 $\mu\text{g/ml}$ (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

Before the estimation of kinetics of styrene triple copolymerization with Mn(II) and Zn(II) vinyl-*b*-diketonates we studied the initiating activity of these chelates taken separately. Kinetic and molecular weight characteristics of MHD-Mn initiation process are represented in Table 1.

The polymerization initial rates (V_{in}) insignificantly vary within chelate concentrations of $(0.5\text{--}3.0)\cdot 10^{-2}$ mol/l. This fact indicates that the inhibiting property of MHD-Mn is less than that of 5-methyl-5-hexene-2,4-dithionate of Co(II) [5]. In the case of Co at its concentration of $3.0\cdot 10^{-2}$ mol/l the styrene polymerization does not proceed. Moreover, there is a clear maximum on the dependence V_{pol} vs $\sqrt{C_{chel}}$. For MHD-Mn such maximum is absent. Molecular weights of obtained polymers also confirm lesser inhibiting effect of MHD-Mn. Within the range of

chelate concentrations $(0.5\text{--}3.0)\cdot 10^{-2}$ mol/l they vary slightly. It should be noted that under investigated conditions the molecular weight essentially depends on introduction of chelate groups into polymer during side chains grafting, as well as on break of growing chain on the chelated metal cycle.

At MHD-Mn concentrations of $(0.10\text{--}0.25)\cdot 10^{-2}$ mol/l a number of chelate groups introduced into polymer is small. Quantity of metal introduced into polymer points to this fact. Hence, grafting is actually absent and chelate inhibiting effect is preserved. The total effect of side chains grafting and the break of growing chains is shifted to the break. Molecular weights at mentioned concentrations of MHD-Mn sharply decrease.

The further decrease in chelate concentration decreases V_{in} to the rate of thermal polymerization. At the same time the inhibiting effect is also minimal that is confirmed by the agreement between V_{in} and V_{av} . The latter fact leads to the sharp increase in the molecular weight. Thus we may assert that MHD-Mn is the active initiator of styrene polymerization but its V_{av} is considerably less than V_{in} indicating the essential inhibiting effect of this chelate.

Table 1 also represents the kinetic parameters of styrene polymerization initiated by MHD-Zn at the concentration of $0.5\cdot 10^{-2}$ mol/l. The investigated chelate is not an initiator and provides the rates close to thermal polymerization but it has the inhibiting effect that is confirmed by the disagreement between V_{in} and V_{av} . Zn content in polymer is small under investigated concentration of chelate. The increase in MHD-Zn concentration is impossible due to its low solubility in styrene. Since the main aim of this work is obtaining of bimetal polymer complex, the further triple copolymerization was carried out in the solvent. For this purpose the donor solvent dimethylformamide (DMF) is used which not only dissolves MHD-Zn but should increase chelate initiating activity [1].

Table 1

Dependence of kinetic and molecular weight parameters of styrene polymerization initiated by MHD-Mn on chelate concentration at $T = 358$ K

$C_{init}\cdot 10^2$, mol/l	$V_{in}\cdot 10^5$, mol/(l·s)	$V_{av}\cdot 10^5$, mol/(l·s)	S_{dil} , %	S_{gr} , %	w_{Co} , wt %	$[\eta]$, cm^3/g	$M_n\cdot 10^{-5}$
3.00	16.9	9.7	9.9	8.0	0.42	0.98	2.63
2.00	20.4	10.1	10.5	8.2	0.46	0.95	2.52
1.00	18.8	8.0	10.2	9.7	0.20	1.10	3.07
0.50	19.5	8.0	10.3	6.4	0.15	0.97	2.58
0.25	9.5	5.3	9.9	8.7	0.04	0.55	1.17
0.10	6.1	4.5	10.5	9.0	0.01	0.73	1.76
0.05	3.4	3.3	9.9	9.6	0.01	2.31	8.65
0.50*	4.3	3.0	9.6	7.4	0.14	0.95	2.50
thermal	2.2	2.2	10.2	10.0	-	-	-

Notes: * – MHD-Zn was used as an initiator; V_{in} and V_{av} – initial and average polymerization rates, respectively; S_{dil} and S_{gr} – conversion determined by dilatometry and gravimetry, respectively; w – metal content; $[\eta]$ – intrinsic viscosity of polymer solution; M_n – average viscous molecular weight

Table 2

**Kinetic and molecular weight parameters of styrene polymerization initiated by MHD-Mn
on chelate concentration in DMF (1:1) at $T = 358$ K**

$C_{init} \cdot 10^2$, mol/l	$V_{in} \cdot 10^5$, mol/(l·s)	$V_{av} \cdot 10^5$, mol/(l·s)	S_{dil} , %	S_{gr} , %	w_{Me} , wt %	$[\eta]$, cm ³ /g	$M_{\eta} \cdot 10^{-5}$
3.00	42.1	14.0	9.9	5.2	0.47	1.18	3.39
2.00	36.6	12.6	11.2	5.7	0.20	1.16	3.31
1.00	23.7	4.9	9.2	6.3	0.19	1.37	4.20
0.50	24.9	5.3	9.8	8.6	0.10	1.75	5.86

Table 3

**Kinetic parameters of styrene polymerization initiated by MHD-Zn
on chelate concentration in DMF (1:1) at $T = 358$ K**

$C_{init} \cdot 10^2$, mol/l	$V_{in} \cdot 10^5$, mol/(l·s)	$V_{av} \cdot 10^5$, mol/(l·s)	S_{dil} , %	S_{gr} , %
3.00	3.6	3.3	8.9	8.2
2.00	5.4	4.3	8.9	8.6
1.00	3.2	2.2	9.8	9.0
0.50	3.1	2.9	9.6	9.0

Table 4

**Kinetic and molecular weight parameters of styrene polymerization initiated by MHD-Mn and MHD-Zn
on chelate concentration in DMF (1:1) at $T = 358$ K**

$C_{init} \cdot 10^2$, mol/l		$V_{in} \cdot 10^5$, mol/(l·s)	$V_{av} \cdot 10^5$, mol/(l·s)	S_{dil} , %	S_{gr} , %	w_{Me} , wt %		$[\eta]$, cm ³ /g	$M_{\eta} \cdot 10^{-5}$
MHD-Mn	MHD-Zn					Mn	Zn		
3.00	3.00	16.5	6.7	11.8	8.4	0.44	0.58	1.41	43
2.00	2.00	27.1	7.0	11.8	6.9	0.42	0.68	1.31	3.9
1.00	1.00	9.0	4.7	9.8	6.8	0.32	0.52	1.40	4.5
1.00	0.50	14.2	2.6	10.6	6.6	0.09	0.11	-	-
0.50	1.00	8.6	3.5	11.4	10.2	0.03	0.27	2.06	7.3

Kinetic parameters of styrene polymerization initiated by Mn and Zn chelates in DMF are represented in Tables 2 and 3.

The comparison of Tables 2 and 3 with Table 1 show that V_{in} and partially V_{av} increase for MHD-Mn in the solvent. Moreover, during polymerization in DMF the maximum polymerization rate is observed at $C_{chel} = 3.0 \cdot 10^{-2}$ mol/l while maximum in the block is achieved at $C_{chel} = 2.0 \cdot 10^{-2}$ mol/l and metal content varies slightly. Molecular weights considerably increase for all MHD-Mn concentrations. It means that in the donor solvent the initiation-inhibition ratio shifts to the initiation.

Concerning polymerization initiated by MHD-Zn in the solvent (Table 3), the polymerization rates do not practically depend on chelate concentrations and are close to the thermal polymerization rate. Thus we confirmed the selectivity of donor additives. K. Bemford [1] demonstrated that styrene polymerization initiated by Fe(III), Cu(II), Pb(II), Ni(II) and Co(II) acetylacetonates is accelerated using CCl₄ as a solvent; phenanthroline accelerates polymerization initiated by Mn(II), Mn(III), Fe(III), Co(III) and Cu(II) acetylacetonates, does not

affect the rate for Ni(II) acetylacetonate and inhibits polymerization for Co(II). Dipyridile accelerates the process for Mn(II) and Mn(III) acetylacetonates; pyridile – for Mn(III) only.

Kinetic and molecular weight parameters of styrene polymerization initiated by both MHD-Mn and MHD-Zn are represented in Table 4.

The comparison of Table 4 and Tables 1-3 allows to estimate the contribution of every initiator (MHD-Mn and MHD-Zn) in the general polymerization process. At equimolecular concentrations of both chelates ($C_{chel} = 3.0 \cdot 10^{-2}$ mol/l) the initial polymerization rate is considerably lower than that at initiation only by MHD-Mn. At the decrease in equimolecular concentrations till $2.0 \cdot 10^{-2}$ mol/l the rate sharply increases. The reason is that total concentration of two chelates is $6.0 \cdot 10^{-2}$ mol/l resulting in strong growth of inhibition, the same as for acetylacetonates [1]. In our previous investigations this fact leads even to polymerization closing. The decrease in chelates concentration till $1.0 \cdot 10^{-2}$ mol/l reduces the polymerization rate regularly.

Being initiated by chelates of different concentrations the polymerization rate is higher at MHD-Mn excess but in all cases the combined initiation by two chelates has considerably lower rate than that using only MHD-Mn.

Three factors should be taken into account during proceeding polymerization process: initiating activity of chelates, their inhibiting effect and selectivity of the donor solvent. These factors complicate the process but we may assert that the joint presence of both chelates decreases the initiating activity. In the investigated pair of chelates MHD-Mn serves as the initiator and MHD-Zn has the inhibiting effect (Table 1). The metal content in polymers is ~0.5 wt % at chelates equimolecular concentration. At the same time in all cases Zn content is higher than that of Mn. The possible reasons are constants of monomer copolymerization and high inhibiting activity of MHD-Zn, on the chelate cycle of which the growth of polymer radicals stops. It is interesting that at different concentrations of chelates $(0.5-1.0) \cdot 10^{-2}$ mol/l the content of both metals in the polymer sharply decreases. This fact requires additional investigations.

Molecular weights of polymers during combined initiation by two chelates are always higher than those during their individual application; usually they are above $3.9 \cdot 10^5$. Thus we may assert that under mentioned conditions the copolymers are formed containing fragments of Mn and Zn *b*-diketonates with satisfactory metal concentration and molecular weight. Varying chelates concentration we may vary metal ratio and concentration in the polymer.

The presence of inhibition at initiation by vinyl-*b*-diketonates retards the process even at low conversion that is obvious by values V_{in} and V_{av} . Therefore, to optimize the synthesis of bimetal polymer complexes *via* styrene triple copolymerization with MHD-Mn and MHD-Zn we used additional initiator – benzoyl peroxide (BP) with the concentration of $2.0 \cdot 10^{-2}$ mol/l. Polymerization was carried out in DMF and without it.

Previously we demonstrated that BP is not only additional initiator. Using initiating system *b*-diketonate–BP

it forms complex with chelated metals which provides accelerated decomposition of both components [14]. Using Mn(III) acetylacetonate–BP and Fe(III) acetylacetonate–BP systems the decomposition rate increases by 5–10 times depending on components ratio. For Fe(III) trifluorine acetylacetonate–BP system the decomposition rate is considerably higher. The same as for thermal decomposition, the polymerization rate of vinyl monomers initiated by the mentioned systems is also considerably higher than the rate at additive effect of the components [15]. The systems efficiency depends on the metal nature, the presence of substituents in the ligand and monomer nature. But while using the initiating systems and donor solvents the competition between the solvent and BP occurs for the formation of complex with *b*-diketonates. In our case it is possible that the process is shifted toward the complex formation with the solvent due to the higher concentration of DMF as compared with BP. Therefore we can assume that BP has the only function of additional initiator.

The results of triple copolymerization using BP are represented in Table 5.

The comparison of obtained results demonstrates the increase in polymerization rate by 5–6 times under equimolecular concentrations. The maximum rate is observed at component concentration of $2.0 \cdot 10^{-2}$ mol/l that corresponds to polymerization initiated by MHD-Mn (Table 1) and mixture of MHD-Mn and MHD-Zn (Table 4). Molecular weights of polymers considerably decrease and metal content slightly increases while using BP. At different concentrations of chelates the rates remain high. It should be noted that using BP and without its use the content of Zn in polymers are always higher than MHD-Zn content in the monomer mixture. Using BP it is possible to obtain polymers at styrene copolymerization with MHD-Zn only. Herewith high-molecular products with high content of Zn are formed.

Table 5

Kinetic and molecular weight parameters of styrene polymerization initiated by MHD-Mn and MHD-Zn on chelate concentration in DMF (1:1) at $T = 358$ K

$C_{init} \cdot 10^2$, mol/l		$V_{in} \cdot 10^5$, mol/(l·s)	$V_{av} \cdot 10^5$, mol/(l·s)	S_{dil} , %	S_{gr} , %	w_{Me} , wt %		$[\eta]$, cm ³ /g	$M_n \cdot 10^{-5}$	DMF presence
MHD-Mn	MHD-Zn					Mn	Zn			
3.00	3.00	97.7	64.1	11.8	8.8	0.62	0.86	0.21	0.31	in DMF
2.00	2.00	101.8	61.5	11.8	7.9	0.46	0.68			
1.00	1.00	74.7	53.4	11.8	10.5	0.28	0.48	0.50	1.03	
1.00	0.50	44.3	39.8	10.6	9.3	0.09	0.16			without DMF
0.50	1.00	80.1	45.2	11.0	6.1	0.11	0.45			in DMF
2.00	0.50	33.2	32.8	10.2	8.9	0.42	0.22	0.23	0.36	without DMF
0.50	2.00	56.1	49.3	10.9	10.7	0.06	0.52	0.36	0.66	in DMF
–	2.00	24.9	21.7	11.2	11.0	–	0.80	1.66	5.40	

Note: BP concentration is $2 \cdot 10^{-2}$ mol/l

4. Conclusions

Initiation of styrene polymerization in DMF by MHD-Mn and MHD-Zn vinyl-*b*-diketonates simultaneously results in formation of polymers with fragments of two *b*-diketonates in the macromolecule. In this process the used chelates have a function of comonomers and initiators. The optimum equimolecular concentrations of MHD-Mn and MHD-Zn are $2.0 \cdot 10^{-2}$ mol/l. At the same time copolymerization average rates are low due to the chelates inhibiting effect. Copolymer molecular weight is $\sim 4.0 \cdot 10^5$. To increase the polymerization average rate we used the additional initiator – benzoyl peroxide. In its presence the initial and average rates of the process are high, metal content in the polymer does not change and molecular weights of products considerably decrease. Thus the method of styrene triple copolymerization with MHD-Mn and MHD-Zn vinyl-*b*-diketonates in DMF may be used for producing heterometal polymer complexes containing fragments of Mn and Zn *b*-diketonates in the macromolecule. The metal concentration is not less than 0.5 wt %. Varying concentrations of vinyl-*b*-diketonates and the presence of additional initiator – benzoyl peroxide – we can vary the metal ratio in the polymer, polymerization rate and molecular weights of products.

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СИНТЕЗ ГЕТЕРОМЕТАЛІЧНИХ КОПОЛІМЕРНИХ КОМПЛЕКСІВ, ЯКІ МІСТЯТЬ ФРАГМЕНТИ β -ДИКЕТОНАТІВ Mn (II) ТА Zn(II)

Анотація. Методом потрібної кополімеризації сти-ролу з поліфункціональними компонентами радикальної полі-меризації – вініл- β -дикетонатами 5-метил-5-гексен-2,4-діо-натів Mn (II) та Zn (II) – отримані гетерометалічні полімерні комплекси з β -дикетонатними фрагментами. Процес про-води в блоці та у розчині диметилформаміду при відсутності та в присутності додаткового ініціатора – бензоїлпероксиду. Показано, що зміною концентрацій металохелатів, наявності розчинника та допоміжного ініціатора можливо регулювати концентрацію та співвідношення металів у макромолекулі та молекулярні маси продуктів.

Ключові слова: радикальна кополімеризація, вініл- β -дикетонат, інгібітор, гетерометалічний макрокомплекс.