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Dvorianska St., 2, Odesa, 65082, Ukraine; e-mail: ovchev@ukr.net**CHELATES OF 3-ALLYLPENTAN-2,4-DIONE FOR
THE SYNTHESIS OF BRANCHED THERMOSTABLE
POLYMETHYL METHACRYLATE**

Radical polymerization of methyl methacrylate with the addition of Cu(II), Ni(II), Co(II) 3-allylpentan-2,4-dione chelates was carried out. It is shown that in the case of the cobalt complex, the process occurs at rates comparable to those of the traditional radical initiator, benzoyl peroxide. The resulting polymethyl methacrylate has large molecular weights and contains fragments of β -diketonates in the polymer, which graft side chains. The branched structure of the polymer is proven based on the calculation of the Zimm-Stockmeier factor. It has been established that the branched polymethyl methacrylate obtained on the basis of chelates has a higher thermal stability compared to the sample obtained using benzoyl peroxide.

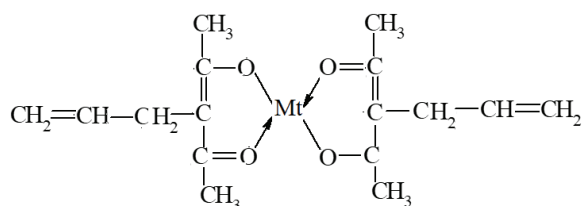
Keywords: polymethyl methacrylate, unsaturated β -diketonates of transition metals, thermo-oxidative destruction, branched polymers.

Polymethyl methacrylate (PMMA) is a transparent thermoplastic that is widely used as a structural material in many industries: construction, automotive, medicine, etc. In industry, the main methods of its extraction are mass radical polymerization and emulsion polymerization. The addition of various additives to PMMA ensures the creation of composites, which allows modification of the physicochemical and mechanical properties of this polymer. Therefore, the search for new inexpensive initiators for the synthesis of PMMA, which are also able to improve its properties, is an actual direction of polymer chemistry.

In our previous studies, it was shown that some unsaturated β -diketonates of transition metals, primarily cobalt(II), can initiate radical polymerization of vinyl monomers, while simultaneously acting as metallomonomers [1]. The introduction of chelate groups into the macromolecule provokes the formation of side branches, which can give such materials improved properties. Thus, in work [2], using polystyrene as an example, it was shown that the method of metal-containing polymers synthesis directly affects their structure and ability to thermo-oxidative destruction. It is also known that β -diketonates, added as compounds to the finished PMMA, are able to increase its stability to thermo-oxidative destruction [3]. The presented work investigated the possibility of using 3-allylpentane-2,4-dionates of some transition metals (APD-Mt, where Mt = Cu(II), Ni(II), Co(II)) for the synthesis of PMMA, their influence on the structure and thermo-oxidative properties of products.

MATERIALS AND RESEARCH METHODS

3-Allylpentan-2,4-dione and its metal chelates APD-Mt were synthesized according to the methods [4, 5], respectively. Cobalt(II) and nickel(II) complexes contain β -diketone ligand and two water molecules in the coordination sphere and are octahedra, APD-Cu has a planar-square structure.



3-allylpentan-2,4-dionate (APD-Mt),
Mt = Cu(II), Ni(II), Co(II)

Radical polymerization of MMA was carried out in a block at a temperature of 70 °C with APD-Mt concentrations, mol/l: Cu, Co – $(3,0-0,25) \cdot 10^{-2}$; Ni – $(1,0-0,1) \cdot 10^{-2}$. The upper concentration limit depends on the solubility of chelates in MMA. Initiation with cobalt chelate was carried out in a wider temperature range – 50–85 °C, and also with the use of some solvents: toluene, methyl ethyl ketone (MEK) and dimethylformamide (DMFA), while [MMA] = 3,54 mol/l. The calculation of the initial rate of polymerization (V_0) was carried out graphically by the tangent of the inclination angle to the curve of the dependence of conversion on time in the stationary section at a conversion (S) of approximately 10%. The content of metals (ω_{Mt}) was determined on the «Saturn» atomic adsorption spectrophotometer, having previously burned the organic part in a mixture of nitric and perchloric acids. The molecular weights of M_w and M_n were determined by gel permeation chromatography using a liquid chromatograph «Waters 200» on styrogel columns with exclusion limits of 10^3 , 500 and 200 Å (Set A) and $3 \cdot 10^3$, $3 \cdot 10^4$ and $3 \cdot 10^5$ Å (Set B), eluent – tetrahydrofuran, speed – 1,0 ml/min. The characteristic viscosity $[\eta]$ of PMMA was measured in benzene. The study of the thermo-oxidative destruction process was carried out by the method of dynamic thermogravimetry on the Derivatograph Q-1500D System F. Paulik, J. Paulik, L. Erdey in the temperature range of 20–700 °C in the air atmosphere with the simultaneous removal of gaseous products of destruction. Heating speed – 10 degrees/min. Sample weight was 50 mg. Based on the analysis of TG and DTA curves, thermogravimetric characteristics were calculated: T_B and T_E – temperatures of the beginning and the end of thermo-oxidative destruction, respectively.

RESULTS AND DISCUSSION

Kinetic studies revealed that the polymerization rate of MMA depends on the nature of the metal: Cu < Ni < Co (Table 1). At the same time, in comparison with the most widely used radical initiator – benzoyl peroxide (PB), at the same concentrations, cobalt(II) chelate shows comparable rates of the process. Polymerization of MMA under the influence of β -diketonates of transition metals occurs with induction periods (τ_{ind}), which is due to the ability of chelates to form intermolecular complexes with the carbonyl group of the monomer.

Table 1

Kinetic parameters of MMA polymerization and the amount of metal in polymers under the influence of initiators APD-Mt. $[APD-Mt] = 1 \cdot 10^{-2}$ mol/l

Initiator	Polymerization conditions	T, °C	$V_0 \cdot 10^5, \frac{\text{mol}}{\text{l} \cdot \text{sek}}$	$*V \cdot 10^5, \frac{\text{mol}}{\text{l} \cdot \text{sek}}$	S, %	$\tau_{\text{ind}}, \text{min}$	$\omega, 10^{\frac{\text{Mg}}{\%}}$
APD-Cu	blok	70	13,0	1,5	9,3	34	2,5
APD-Ni		70	16,2	1,8	9,6	10	3,8
APD-Co		70	34,5	3,9	9,4	230	2,6
		60	17,4	2,0	7,9	810	2,0
		85	78,3	8,8	10,4	39	7,0
		toluene	70	28,8	8,1	9,1	164
MEK	93,0	26,3		5,9	31	4,0	
DMFA	9,4	2,7		7,8	105	-	
PB	blok		44,3	5,0	9,8	0	-

$$*V = V_0/[M]$$

It is possible to reduce τ_{ind} and increase the reaction speed by using a donor solvent and higher synthesis temperatures, which was shown on the example of cobalt chelate (Fig. 1).

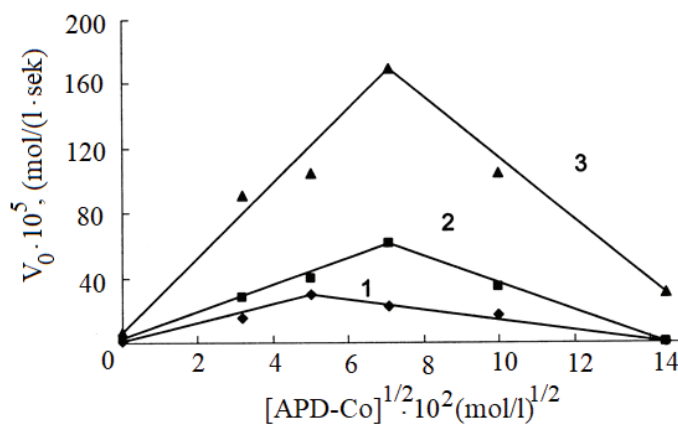


Fig.1. Dependence of MMA polymerization rate on APD-Co concentration.
T, °C: 1–60; 2–70; 3–85.

The logarithmic dependence of the polymerization rate on the concentration of chelate for APD-Cu and APD-Ni is linear (Fig. 2), the order of chelate is 0,5 and 0,3, respectively, which indicates the course of the process according to the usual free-radical mechanism. Initiation with cobalt chelate, as can be seen from Fig. 1, 2, has a certain feature, which is manifested in the nonlinear dependence of the polymerization rate on the concentration

of the initiator. This indicates the presence of polymerization inhibition after exceeding a certain concentration ($1 \cdot 10^{-2}$ mol/l), which begins to prevail over initiation. Therefore, determining the reaction order is possible only on the straight section of curve 1 (Fig. 2), which is in the concentration interval $(0,1-1,0) \cdot 10^{-2}$ mol/l. Inhibition is associated with a greater tendency of cobalt atoms to form complexes with free radicals, which makes their further activity in initiation impossible. A similar phenomenon was observed by us during the polymerization of styrene, which is known to have the donor character of radicals, so the inhibition for it is expressed to an even greater degree [1].

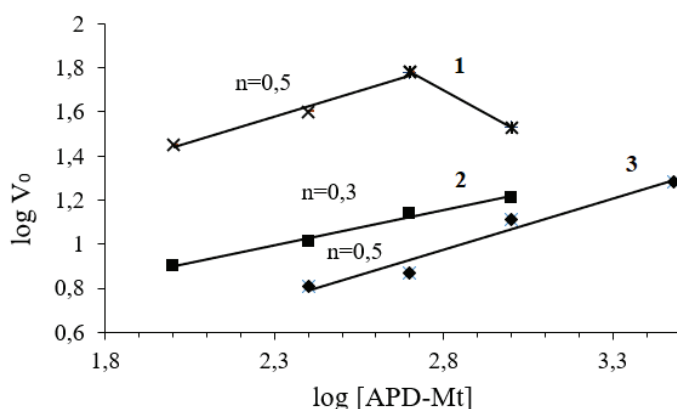


Fig.2. Logarithmic dependence of MMA polymerization rate on APD-Mt concentration:
1 – Co; 2 – Ni; 3 – Cu. T = 70 °C

Inhibition leads to a decrease in the metal content in the polymer, since a significant part of the metal is lost with low molecular weight fractions and is removed from the system. This is well illustrated by fig. 3 (curves 1, 2): APD-Co chelate, for which inhibition was observed, has a maximum metal content ($\omega_{Mt}, \%$), which coincides with the maximum of the reaction rate (Fig. 3, curve 1). For APD-Cu, the course of polymerization is not complicated by inhibition, the $[APD-Mt]-\omega_{Mt}$ dependence is linear (Fig. 3, line 3). From fig. 3 also shows that it is possible to increase the metal content in the polymer and shift the concentration limit if the reaction temperature is increased.

The presence of a significant amount of metal in the polymers proves that APD-Mt probably enters the macromolecule not only as an initiator, but also as a comonomer, since it has a double bond in the ligand. This fact can be indicated by an increase in the amount of metal with an increase in the polymerization temperature, as well as a reduced order according to the initiator (in the case of APD-Ni). Molecular masses (MM) of PMMA obtained with the participation of APD-Ni with the maximum concentration were $M_N=5,44 \cdot 10^5$; $M_w=9,78 \cdot 10^5$; $PDI=M_w/M_N=1,80$. Therefore, it can be seen that this chelate provides the formation of high-molecular PMMA with high, almost millions, MM with a low PDI, while the polymerization rates are also sufficiently high. Measurement of the metal content of the polymer showed that PMMA contains 0,038% of nickel, which, taking into account the M_w value, is 7 fragments of APD-Ni per one macromolecule. That is, the chelate simultaneously exhibits the functions of initiator and comonomer. Entering

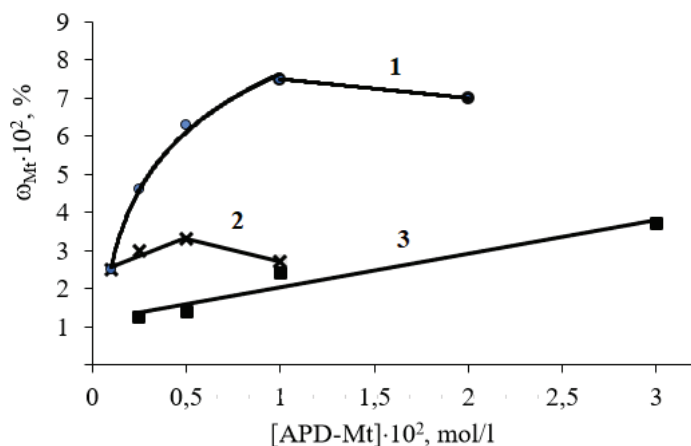


Fig. 3. Dependence of the amount of metal in br-PMMA on the initial concentration of chelates APD-Mt: 1 – Co (1, 2); 2 – Cu (3). T, °C: 1–85; 2–70 (2,3)

the chain as a comonomer, the chelate begins to initiate grafting of side chains, which determines the growth of the macromolecule from several sides, that is, the formation of branched PMMA (br-PMMA) with a high MM.

The branched structure of the formed products is also confirmed by the value of the Zimm-Stockmeier factor (g'), which is a measure of the polymer chain branching and is calculated as the ratio of the characteristic viscosities of the branched ($[\eta]_{br}$) and linear ($[\eta]_l$) products with the same MM [6]. The deviation of g' from 1 characterizes the degree of chain branching. To confirm the branched structure of PMMA, the g' factor was calculated for some samples, the value of which was 0,58–0,96 (table 2).

Table 2

Molecular mass characteristics and the Zimm-Stockmayer factor of br-PMMA samples synthesized by polymerization in a block with the participation of APD-Co. T=50 °C

[APD-Co] · 10², mol/l	ω _{Co} , 10²%	M _N · 10 ⁻⁵	M _w · 10 ⁻⁵	$\frac{M_w}{M_N}$	*[η] _{br} , dl/g	[η] _l , dl/g	g'
3,0	21,9	1,19	2,92	2,48	0,7377	0,7700	0,96
1,0	33,0	0,92	1,96	2,12	0,7166	0,9891	0,72
0,5	21,6	1,23	2,49	2,03	0,6869	1,1864	0,58

*[η]_{br} is measured experimentally, [η]_l calculated from M_w, using K=4,3 · 10⁻⁵; α=0,77 [7] for linear PMMA.

PMMA samples synthesized using APD-Mt were tested for resistance to thermo-oxidative destruction in order to determine the influence of β-diketonate fragments and branching of the chain on the temperature interval of decomposition. TG and DTA curves

of PMMA obtained with the participation of chelates with a similar metal content are shown in Fig. 4, a-c. The determined temperatures of the beginning (T_B) and the end (T_E) of the samples destruction were compared with the corresponding parameters of linear PMMA synthesized under similar conditions using PB (Fig. 4, d). The summarized results are presented in Table 3.

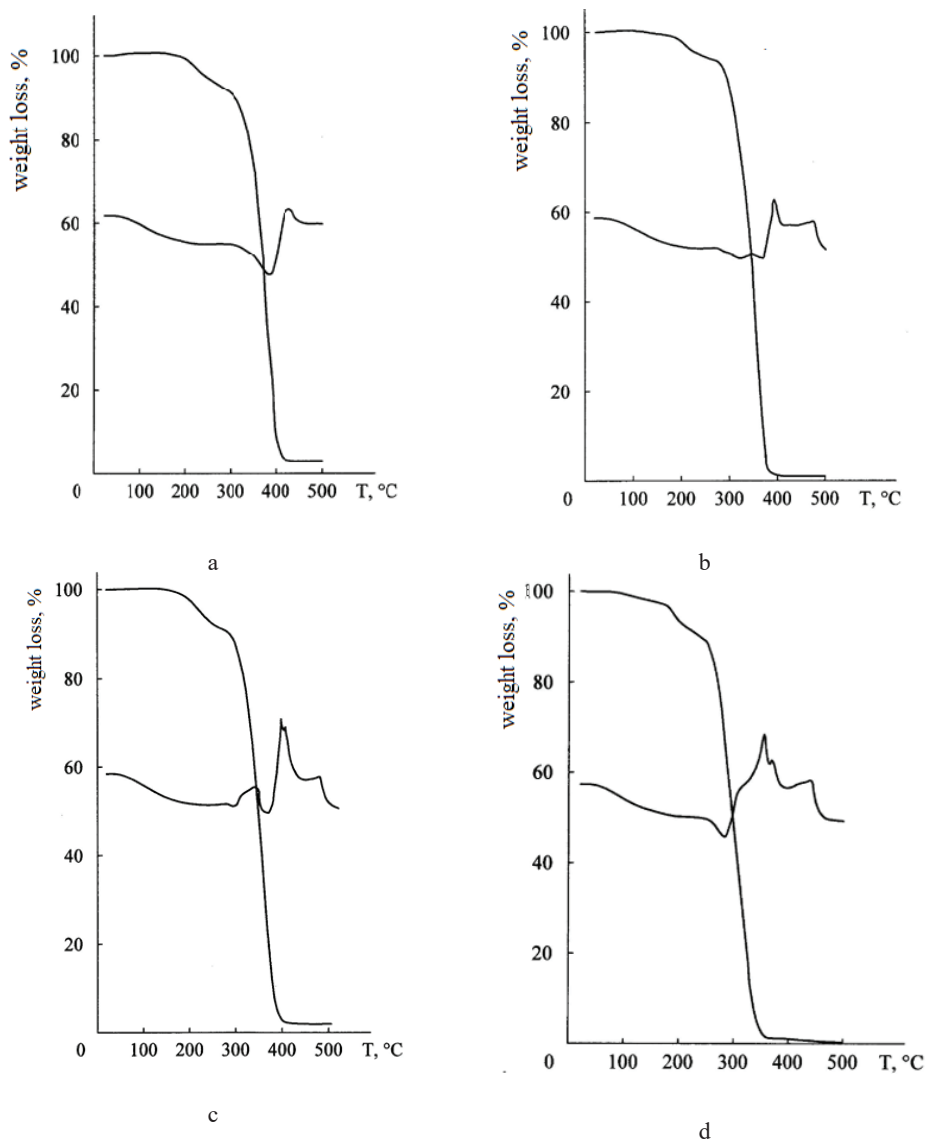


Fig. 4. TG and DTA curves of br-PMMA synthesized under the action of APD-Mt: a - Co; b - Ni; c - Cu; d - PB. $[APD-Mt]=[PB]=1 \cdot 10^{-2}$ mol/l. S ~ 10%. T = 70 °C.

Based on the results, it can be concluded that the presence of metal chelates in PMMA, regardless of the nature of the metal, significantly increases their resistance to thermo-oxidative destruction. T_B increases by 20–30 °C, and T_E – by 13–23 °C. The analysis of several PMMA samples with different cobalt content shows a clear tendency to increase T_B and T_E with an increase in the number of chelate fragments in the chain (Fig. 5)

Table 3

**The temperature of the beginning (T_B) and end (T_E) of destruction
br-PMMA, synthesized during the initiation of APD-Mt and PB.
[Initiator] = $1 \cdot 10^{-2}$ mol/l. Conversion ~ 10%. The temperature is 70 °C**

Initiator	$\omega_{Mt} \cdot 10^2, \%$	$T_B, ^\circ\text{C}$	$T_E, ^\circ\text{C}$
APD -Co	2,6	280	405
APD -Cu	2,5	269	415
APD -Ni	3,8	270	405
PB	0	250	392

The influence of metal β -diketonates can be observed in a change in the mechanism of destruction, primarily in the initial stages, because it is known that the destruction of PMMA begins in the range of 120–200 °C [8]. It is initiated by the splitting of anomalous sequences of links built according to the «head-to-head» principle, which are formed as a result of chain breakage by recombination. Further (200–300 °C), β -bonds are broken at the end links, which contain C=C bonds, formed as a result of breaking by disproportionation. Presumably, the presence of chelating fragments at the ends of the chains prevents these processes. In addition, branching can interfere with the diffusion of oxygen deep into the polymer ball, which also slows down degradation.

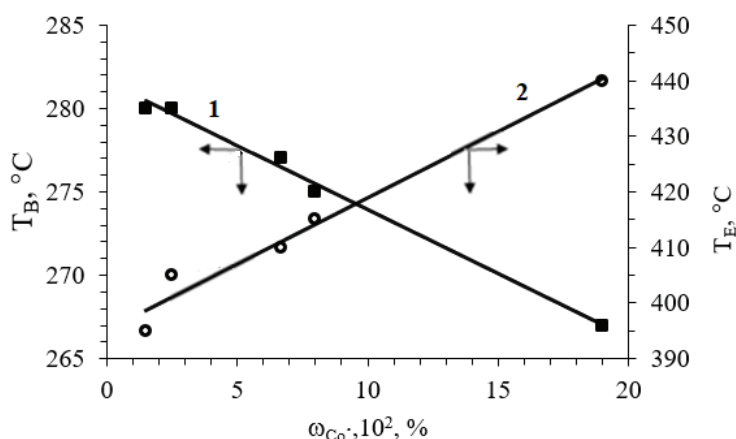


Fig.5. Graphical dependence of temperature of the beginning (T_B) (1) and the end (T_E) (2) of br-PMMA destruction on the amount of cobalt

Thus, it was found in our work that the use of 3-allylpentane-2,4-dionates Cu(II), Ni(II), Co(II) as initiators of MMA polymerization leads to the entry of chelates into the polymer chain in an amount proportional to the original metal complex. This contributes to the formation of PMMA with a branched structure. Cobalt chelate has the best initiator properties. The presence of a branched structure and metal β -diketonate fragments in the chain improves the resistance of PMMA to thermo-oxidative destruction compared to the linear product obtained using the industrial radical initiator PB.

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ХЕЛАТИ 3-АЛЛІПЕНТАН-2,4-ДИОНУ ДЛІЯ СИНТЕЗУ РОЗГАЛУЖЕНОГО ТЕРМОСТІЙКОГО ПОЛІМЕТИЛМЕТАКРИЛАТУ

Здійснено радикальну полімеризацію метилметакрилату із додаванням хелатів Cu(II), Ni(II), Co(II) 3-алілпентан-2,4-діону. Процес відбувається зі швидкостями, що залежать від природи металу, і збільшуються в ряду: Cu < Ni < Co. Показано, що у випадку кобальтового комплексу полімеризація в блоці здійснюється зі швидкостями співставними з традиційним радикальним ініціатором – пероксидом бензоїлу, але має певну особливість – швидкості полімеризації нелінійно залежать від концентрації ініціатора, що обумовлено взаємодією хелату із радикалами росту. Визначено, що граничну концентраційну межу можна зсунути у бік більших концентрацій, збільшивши температуру реакції та використавши розчинник донорного характеру. Подібним чином можна регулювати і вміст металу у полімері, який збільшується з температурою, що вказує на участь металокомплексів як комономерів.

Поліметилметакрилати (РММА), що утворюються, мають великі молекулярні маси та містять у складі полімерів фрагменти β-дикетонатів, кількість яких прямопропорційно зростає із збільшенням вихідної концентрації β-дикетоната. В ході синтезу полімеру вони прищеплюють бічні ланцюги, внаслідок цього РММА мають розгалуження. Розгалужена будова полімерів доведена на підставі розрахунку фактора Зімма-Штокмайера. Встановлено, що розгалужений РММА, отриманий на основі хелатів, незалежно від природи металу в хелаті має збільшену стійкість до термоокиснювальної деструкції порівняно зі зразком, отриманим за допомогою пероксиду бензоїлу. Температури початку деструкції збільшуються на 20–30 °С, кінцеві – на 13–20 °С. На прикладі хелату кобальту встановлена тенденція до зростання цих показників з підвищенням вмісту металу у полімері, що прямо доводить вплив β-дикетонатних фрагментів на термостабільність РММА. Зазначені вірогідні причини збільшення термостійкості поліметилметакрилату, отриманих під впливом хелатів.

Ключові слова: поліметилметакрилат, ненасичені β-дикетонати металів, термоокиснювальна деструкція, розгалужені полімери

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