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**MICROBIOSTATIC EFFECT OF POLYMETHYL  
METHACRYLATE MODIFIED  
WITH A COBALT METAL COMPLEX.**

**МІКРОБІОСТАТИЧНА ДІЯ ПОЛІМЕТИЛМЕТАКРИЛАТУ  
МОДИФІКОВАНОГО КОБАЛЬТОВИМ  
МЕТАЛОКОМПЛЕКСОМ**

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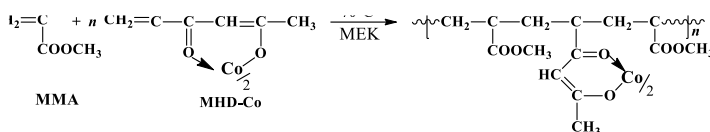
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Polymethyl methacrylate (PMMA) is a thermoplastic polymer with transparency and good strength characteristics, therefore it finds a variety of applications in various industries: from the automotive industry and construction to cosmetology and aesthetic medicine. Due to its bio- and hemocompatibility, resistance to biological environments, PMMA is widely used for medical purposes as bone cements [1], a material for the manufacture of dentures, drug delivery [2], and for coating the surface of mechanical devices implanted in the human body [3] and etc.

It is known that adding special additives to polymer materials can additionally provide them with antimicrobial properties. Commonly, metal-containing compounds are used as such additives, which are simply mixed with polymers or composite materials are prepared based on them [4]. However, the use of metal compounds as additives can lead to their loss during use of the material and to toxicity if used in vivo. Much more effective is the fixation of antimicrobial agents by chemical bonds on a polymer matrix during their synthesis. Our previous studies showed that the introduction of unsaturated cobalt chelates into polystyrene during its production gives it bactericidal properties [5]. In the presented work, we studied the effect of cobalt (II) 5-methyl-5-hexene-2,4-dionate (MHD-Co) immobilized on PMMA during its synthesis on biological activity.

In industry, PMMA is produced primarily by free radical polymerization of methyl methacrylate (MMA) at moderate temperatures, initiated by organic and

inorganic peroxides and some redox systems. Polymerization of methyl methacrylates can be carried out in a mass (block), suspension, emulsion or solution. In our experiment, we prepared PMMA by its radical polymerization in the presence of cobalt (II) 5-methyl-5-hexene-2,4-dionate under the following conditions: reaction temperature – 70 °C,  $[\text{MHD-Co}] = 5 \cdot 10^{-3} \text{ mol/l}$ ,  $[\text{MMA}] = 3.54 \text{ mol/l}$ . The solvent is methyl ethyl ketone (MEK). Under these conditions, polymerization took place at a rate of  $10.1 \cdot 10^{-5} \text{ mol/(l}\cdot\text{s)}$ . The conversion at which the product was isolated was 10%. As can be seen, from the indicated conditions, the synthesis took place without an additional initiator, since MHD-Co itself is an excellent initiator of the radical polymerization of MMA. Moreover, due to the presence of a double bond in its ligand, it copolymerizes with MMA and thus becomes part of PMMA:

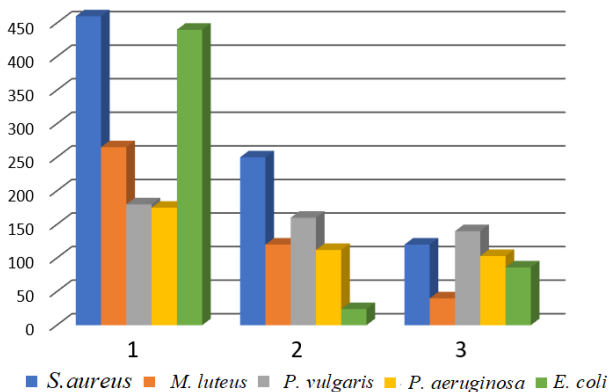


We confirmed the fact of copolymerization by analyzing the metal content in the polymer, which was carried out by atomic adsorption spectroscopy. The polymer contained 0.23% cobalt. If PMMA is prepared under similar conditions using a saturated analog of cobalt acetylacetonate ( $\text{Co}(\text{acac})_2$ ), which can also initiate radical polymerization of PMMA, then the polymer contains cobalt in trace amounts (0.01%) as end groups.

PMMA with immobilized MHD-Co chelate (sample 3) was tested for biological activity against certain microorganisms: *Staphylococcus aureus* ATCC 25923, *Micrococcus luteus* ATCC 4698, *Proteus vulgaris* ATCC 6896, *Escherichia coli* ATCC 25922, *Pseudomonas aeruginosa* ATCC 27853. Moreover, for assessments Based on the influence of the polymer matrix itself, under identical conditions, a PMMA sample was synthesized that did not contain metal. It was obtained by radical polymerization under the influence of the industrial initiator benzoyl peroxide (sample 2). A clean glass plate, which was not coated with polymer, also served as a control (sample 1). The results of the study are presented in Fig. 1.

The figure shows that coating a glass plate with polymethyl methacrylate film significantly increases its bacteriological safety. In all cases, the survival rate of microorganisms is significantly reduced compared to a glass surface. Modification of PMMA with cobalt  $\beta$ -diketonate leads to an even greater bacteriostatic effect, however, this can only be stated for gram-positive microorganisms – *S. aureus* and especially *M. luteus*. For gram-negative

bacteria, the use of the polymer matrix itself is quite effective, especially in the case of *E. coli*. On a polymethyl methacrylate coating for 30 minutes, only 5.5% of cells retained their viability compared to the control sample.



**Fig. 1. Number of colony-forming units on the studied samples:**  
**1 – glass plate without polymer coating;**  
**2 – PMMA polymer film without MHD-Co;**  
**3 – PMMA polymer film with immobilized MHD-Co**

Thus, the conducted studies showed the prospects of modifying PMMA with metal  $\beta$ -diketonates, in particular cobalt, in relation to gram-positive microorganisms. It should be noted that the use of transition metals in fairly small quantities allows synthesis to be carried out without additional initiators under fairly mild conditions. Further experiments will be aimed at expanding the range of used metals.

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