

УДК 542.952:547.442:542.978

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EFFECT OF SOME METAL β -DIKETONATES ON THE BACTERICIDAL ACTIVITY OF POLYMER FILMS AGAINST GRAM-POSITIVE MICROORGANISMS

It is shown that the β -diketonates inclusion in polystyrene and polymethylmethacrylate films through covalent binding allows obtaining polymeric materials with high bactericidal activity against gram-positive bacteria *S. aureus* and *M. luteus*. Thereat, the nature and quantity of the introduced metal and the polymer matrix play an important role.

Keywords: vinyl- β -diketonates, polymeric metal complexes, the bactericidal activity.

In the past decade, the synthesis of new polymeric biocides is a top trend in the polymer chemistry for special purposes. Metal containing polymer materials have a special place among of polymeric biocides. As a biocide fragments of compounds containing toxic metals, for example Hg, Pb, Sn, As, were used firstly [1-2]. Currently the possibility for the application of metals with lesser toxic effects – Ag, Zn, Cu, etc. is studied [3-6]. An important way to reduce the toxicity of the metal components of the biocides is to obtain polymers in which the metal is bonded to the macromolecule through the chemical bond and metal is not released during operation. This trend is the most promising.

Previously, authors studied the antibacterial properties of polystyrene with the β -diketonates fragments of certain metals against gram-positive microorganisms *P.aeruginosa* and *E.coli* [7]. A significant effect of the metal nature as well as the macro chain nature and structure on bactericidal properties was demonstrated.

A continuation of above mentioned research is given work aimed at the study of polystyrene and polymethylmethacrylate containing chain β -diketonates of silver (I), cobalt (II), (III) and copper (II), covalently bonded to the macromolecule, the bactericidal activity of polymer coatings against the gram-positive microorganisms *S.aureus* and *M.luteus*.

Materials and research methods

Vinyl- β -diketone 5-methyl-5-hexene-2,4-dione (MHD) was prepared as in [8], and its cobalt complex (MHD-Co (II)), according to [9]. Metal – containing polymers based on polystyrene (PS) and polymethylmethacrylate (PMMA) were synthesized by several methods (for details: see Table 1.). Before use, they were subjected to two-fold reprecipitation from benzene solution in cold ethanol. They were air dried to constant weight.

The metal content in the polymer was determined by atomic absorption spectrophotometer “Saturn”. Sample of the polymer (0.05-0.10 g) was preliminary dissolved at the heating on a sand bath in 25-30 ml mixture of concentrated nitric and perchloric acid (5:3). The resulting solution was diluted to 10 ml with distilled water.

Metal-content in such samples is relatively low. This is due to the limited solubility of MHD-Co (II) in the monomers as well as due to the presence of certain limit concentration ($\sim 1 \cdot 10^{-2}$ mol/l), above which MHD – Co (II) behaves itself as an inhibitor of the radical polymerization [11].

Table 1

Method, the conditions for obtaining of polymers samples and metal content in these samples

Sample №	Metal polymer	w_M , mas. %	Method of obtaining	Conditions
1	PS	–	Radical polymerization in mass	Initiator – PB. T= 85°C. $C_{in} = 5 \cdot 10^{-3}$ mol/l
2	PS -Co(II)	0,19	The same	Initiator – MHD-Co(II). $C_{in} = 5 \cdot 10^{-3}$ mol/l. T= 85°C
3	PS -Co(II)	0,92	Complexation of polymeric ligand with a metal salt	$m_{(CH_3COO)_2Co \cdot 4H_2O} = 0,031$ g. T= 25°C
4	PS -Co(III)	0,53	The same	$m_{(CH_3COO)_2Co \cdot 4H_2O} = 0,031$ g. $m_{PB} = 0,200$ g. T= 50°C
5	PS-Cu(II)	1,90	The same	$m_{(CH_3COO)_2Cu \cdot 2H_2O} = 0,025$ g. T= 25°C
6	PS-Ag(I)	1,57	The same	$m_{AgNO_3} = 0,063$ g. T= 25°C
7	PS -Ag(I)-PS	0,02	Grafted radical polymerization of styrene on the sample 6	Initiator – sample 6. $C_{in} = 0,2$ mas.%. T=70°C
8	PS -Ag(I)-PMMA	0,05	Grafted radical polymerization of MMA on the sample 6	The same
9	PMMA	–	Radical polymerization in mass	Initiator – PB. T= 70°C. $C_{in} = 10 \cdot 10^{-3}$ mol/l
10	PMMA-Co(II)	0,23	Radical polymerization in solution	Solvent – methylethylketon. Initiator – MHD-Co(II). $C_{in} = 5 \cdot 10^{-3}$ mol/l. T= 70°C.
11	Control	–	–	The surface of the glass plate

Two samples **1** and **9** – are the PS and PMMA respectively, obtained at the initiation of benzene by peroxide (PB). They contain no metal and were used as a reference samples, as well as to evaluate the effect of the polymer matrix on the bactericidal properties. Sample **11** was a clean glass plate and served as the control one.

Samples **3-6** are PS containing chain fragments MHD-M (M = Co (II), Co (III), Cu (II), Ag (I)). These samples were obtained through the method of complexation. Schematically, the process is depicted in Figure 2. First, the polymer ligand (Stage I, Figure 2) was obtained at 80 °C through the styrene radical copolymerization with MHD

The data in the Table 2, indicate that the nature of metal in the polystyrene strongly influences its bactericidal activity against *S.aureus*. Polystyrene with β -diketonate copper fragments (sample 5) has the highest bactericidal activity. It is in 34 times more active than the metal-free PC and in 46 times higher than the control sample.

Table 2

Bactericidal properties of metal polymer films relatively to the gram-positive bacteria *S. aureus* and *M. luteus*

Sample	<i>Staphylococcus aureus</i>		<i>Micrococcus luteus</i>	
	Number of colony forming units (CFU)	Colony diameter,mm	Number of colony forming units (CFU)	Colony diameter,mm
1	340±18	1-3	130±10	1-2
2	260±8	1-4	250±21	1-2
3	200±11	2-3	130±14	1-2
4	230±14	1-3	130±10	1-2
5	10±2	2-3	130±24	1-2
6	45±5	1-2	100±8	1-2
7	450±12	2-3	160±26	1-2
8	300±26	1-2	20±4	1-2
9	250±29	2-3	120±11	1-2
10	120±13	1-2	40±9	1-2
11	460±47	2-3	265±17	2-3

The sample 6, containing silver, demonstrates quite good bactericide ability as well. It is in 8 times more active than the PS containing no metal. However, the reduction of silver content in the polymer as a result of grafting (samples 7, 8) dramatically decreases its bactericidal properties. Cobalt macrocomplexes though they have a somewhat higher activity than the reference samples, but in comparison with polymers containing the copper- and silver- their bactericidal activity can not be referred as a high. Thus, as can be seen from the Table 2, method of obtaining as well as the metal valence in practice does not affect the number of CFU.

In the case of *M.luteus* as for *S.aureus* and PS, and PMMA matrix have a weak bactericidal activity, but in 2 times higher than the control sample. However, the influence of the matrix associated with of β -diketonates fragments for *M.luteus* is manifested in an interesting way.

If the inclusion of the metal atoms in PS-film, irrespective of their nature and quantity, has almost no effect on their antibacterial properties, then for PMMA pattern it is completely different. Inclusion of MHD-M fragments into the PMMA chain increases bactericidal activity of polymer films essentially. Thus for PMMA containing just only

0,23 wt.% of Cobalt (sample 9), its bactericidal activity is increased 3 times as compared to the metal-free PMMA.

The fact that it is namely the combination of PMMA-M leads to the improved bactericidal activity and the fact that polystyrene (sample 6), containing 1,57 wt.% of silver has CFU = 100, which is slightly different from the reference sample (CFU = 130). Grafting of PMMA to this sample leads to a drastic reduction in the amount of silver in the polymer (0,05 wt.%), but it increases significantly its bactericidal activity. It is 5 times higher than the initial macroinitiator (sample 6) and 8 times higher than the same amount for the sample 7, which is grafted by PS.

Our studies allow to suggest, that varying the nature and quantity of the metal as well as the nature of the polymer matrix, which is bonded to metal chelates, then universal polymeric materials, possessing bactericidal action against several microorganisms, could be obtained. Another way for the creation of such materials is combination of several metal complexes used for immobilization. For example, to obtain coating with high bactericidal activity against to both microorganisms studied in given report, then it could be the PMMA film, containing both copper and silver β -diketonates in its composition. These assumptions need to be clarified in this research direction and, above all, the development of approaches to the synthesis of heterometallic polymer materials is necessary.

References

1. Биологическая активность полимеров, полученных радикальной полимеризацией с использованием металлорганических инициаторов / Г.А. Воскобойников, Л.М. Мазанова, Ю.Д. Семчиков [и др.] // Вестник ННГУ. Сер. Химия. – Н. Новгород, 1998. - № 1, с. 113-117.
2. Применение биоцидных оловосодержащих препаратов в качестве средств защиты бумаги от биоповреждений плесневыми грибами / К.П. Заботин, Н.Ю. Новоспасская, В.Ф. Смирнов [и др.] // Вестник ННГУ. Сер. Химия. – Н. Новгород, 1998. - № 1, с. 93-97.
3. Биологически активные олово и цинксодержащие сополимеры широкого спектра действия / З.Г. Чернукова, Н.Ю. Новоспасская, В.Ф. Смирнов [и др.] // Вестник ННГУ. Сер. Химия. – Н. Новгород, 2001. - № 1, с. 14-18.
4. Пат. 5199977 США МКИ С 09 D 5/14. Antifouling paint compositions / Yamamori N., Yokoi I., Higo K., Matsuda M.; Nippon Paint Comp. – № 732882 Заявл. 19.07.91. Оpubл. 06.04.93.
5. Пат. 4970117 США, МКИ В 05 D 7/00. Coatings with neutralized carboxylated polymers / Duvdevan I., Manalastas P., Drake E.; Exxon Research and Engineering Comp. - № 263851 Заявл. 28.10.88. Оpubл. 13.11.90.
6. Использование цинксодержащих полимерных биоцидов в качестве средств защиты промышленных материалов от биоповреждений / Н.В. Кузнецова, Л.В. Кабанова, О.Н. Смирнова [и др.] // Вестник ННГУ. Сер. Химия. – Н. Новгород, 2001. - № 1, с. 38-42.
7. Бактерицидные свойства полимерных пленок с β -дикетонатными группами по отношению к грамотрицательным микроорганизмам / И.С. Волошановский, О.Ю. Зинченко, О.В. Шевченко [и др.] // Вісник ОНУ. Хімія. - 2011. – Т.16, № 4. – С.50-56.
8. Teysse Ph., Smets S. Synthesis and polymerization of methacryloylacetone // Makromol. Chem. – 1958. – Bd.26, N 3. – P.245-251.
9. Синтез и полимеризация непредельных β -дикетонатов кобальта / В.Я. Зуб, А.С. Бережницкая, И.А. Савченко [и др.] / Координац. химия. — 2004. – Т.30, № 10. – С.753-757.
10. Винил- β -дикетонаты кобальта (II) – полифункциональные компоненты радикальной полимеризации / О.В. Шевченко, И.С. Волошановский, Т.И. Бербат // Вопросы химии и хим. технологии. – 2003. - № 6. – С.111-115.
11. β -Дикетоны и их металлокомплексы в реакциях ингибирования радикальных процессов / О.В. Шевченко, Т.И. Бербат, Е.В. Буренкова // Вісник ОНУ. Хімія. - 2006. – Т.11, № 1-2. – С.106-111.

Стаття надійшла до редакції 08.09.12

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ВПЛИВ β -ДИКЕТОНАТІВ ДЕЯКИХ МЕТАЛІВ НА БАКТЕРИЦИДНУ АКТИВНІСТЬ ПОЛІМЕРНИХ ПЛІВОК ПО ВІДНОШЕННЮ ДО ГРАМПозИТИВНИХ МІКРООРГАНІЗМІВ

Резюме

Показано, що введення β -дикетонатів металів в полістирольні та поліметил-метакрилатні плівки шляхом ковалентного зв'язування, дозволяє одержувати полімерні матеріали, які мають бактерицидну активність по відношенню до грампозитивних бактерій *S. aureus* и *M. luteus*. При цьому важливу роль мають як природа та кількість металу, що вводиться, так і полімерна матриця.

Ключові слова: виніл- β -дикетонати, полімерні металокомплекси, бактерицидна активність.

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ВЛИЯНИЕ β -ДИКЕТОНАТОВ НЕКОТОРЫХ МЕТАЛЛОВ НА БАКТЕРИЦИДНУЮ АКТИВНОСТЬ ПОЛИМЕРНЫХ ПЛЕНОК ПО ОТНОШЕНИЮ К ГРАМПОЛОЖИТЕЛЬНЫМ МИКРООРГАНИЗМАМ

Резюме

Показано, что введение β -дикетонатов металлов в полистирольные и полиметилметакрилатные пленки, путем ковалентного связывания, позволяет получить полимерные материалы, обладающие высокой бактерицидной активностью по отношению к грамположительным бактериям *S. aureus* и *M. luteus*. При этом существенную роль играют как природа и количество вводимого металла, так и полимерная матрица.

Ключевые слова: винил- β -дикетонаты, полимерные металлокомплексы, бактерицидная активность.