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PREPARATION AND STUDY OF COPOLYMER OF N,N'-(p-PHENYLENE) BISMALEIMIDE WITH ALLYL ESTER OF SALICYLIC ACID

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Abstract: *The reaction of radical copolymerization of N,N'-(p-phenylene)bismaleinimide with allyl ester of salicylic acid was carried out. Conditions of the implementation of the copolymerization reaction, the rate, content and molecular weight of the obtained copolymers, as well as the dependence of these parameters on the composition of the initial mixture of monomers determined. It established that the copolymerization reaction was accompanied by the formation of donor-acceptor complexes between monomer pairs. The copolymerization reaction proceeded on radical-complex mechanism and the relative activities of monomers in the copolymerization reaction calculated: (r_1=0.03; r_2=0.04). The copolymerization constant values close to zero indicate the tendency of the monomer to copolymerization reaction and the formation of macromolecules with alternating structure analyzed. The composition and structure of the obtained polymer was determined by methods of physical-chemical and spectral analysis, and also its antibacterial properties studied. It found that in spite of the fact that the investigated polymer showed an active effect on separate cultures of microorganisms in the case of concentrate, it had weak antimicrobial activity. It also revealed that the effect of the polymer on the cells of fungi (C.albicans) is more effective.*

***Key words*:** *Bismaleimide, allyl ester of salicylic acid, donor-acceptor complexes, relative activity, alternating polymers, antibacterial polymers.*
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Introduction

As is known, the polymer materials used in the food industry, medicine and everyday life, etc., along with properties such as mechanical strength and impact resistance, are considered important from availability of antibacterial properties as well [1, 2, 3]. This is due to the fact that that the products made of polymer materials are widely used in everyday life and contain various bacteria that pose a great threat for human health. Therefore, there is a need for polymer materials with sterile, bactericidal and fungicidal properties [4, 5, 6].

Recently, in the field of macromolecular chemistry, the attention has been paid to the preparation of the polymer materials on the basis of unsaturated cyclic (bis)imides. In particular, the extensive investigations are being carried out in the field of thermostable and antibacterial polymers formed as a result of radical, anionic, alternating and stepwise copolymerization reactions of monomers on the basis of itacon, citracone and maleimides [7-11].

The development of technology of the preparation of the antimicrobial polymer materials (APM) is carried out in several directions, one of which is the inclusion of the natural and synthetic antimicrobial additives in the process of processing the polymer materials [12].

Washing them off the surface of the antibacterial composite materials made with the use of simple molecular additives reduces the service life of products in a short period of time and negatively influences on other properties. A perspective direction in this field is the use of polymers containing biologically active groups as antibacterial additives in the preparation of

the antibacterial polymer compositions for extension of the service life.

In our previous investigations, information on the synthesis of copolymers containing biologically active groups on the basis of bisimides of maleic acid and their use as biologically active polymer additives in the preparation of the antibacterial composite materials has been provided [8, 9, 12-14].

The purpose of this paper is the investigation of the regularities of the copolymerization reaction of allyl ester of salicylic acid (Al_{sal}) with N,N'-(p-phenylene)bismaleinimide (PhBMI) for preparation of polymers containing biologically active groups and the properties of the biological activity of the obtained copolymer.

Experimental part

Al_{sal} copolymerization reactions of N,N'-(p-phenylene)bismaleinimide were carried out in a glass ampoule in the presence of 0,2% of benzene peroxide (BP) in a solution of methyl ethyl ketone at temperature 650°C for 8 h. Total density of the initial mixture of monomers is constant and equal to 1.0 mol/l. The proportion of monomers varies, as shown in Table 1. The obtained copolymers are precipitated several times from a solution of methyl ethyl ketone into methanol, dried in vacuum (30-40 mm merc.c) at 400°C until a constant mass is obtained. The copolymers obtained as a white powder are well soluble in methyl ethyl ketone and chloroorganic solvents. The composition of copolymers was determined on the esterification number value [15].

^{1}H and ^{13}C NMR spectra of the copolymers were recorded on "Bruker Fourier" device with working frequency of 300 MHz (solvent – $CDCl_3$).

The IR spectrum of the copolymer of PhBMI with Al_{sal} was recorded on the spectrometer Agilent Cary 630 FTIR of firm "Agilent Technologies" in the range of 600-4000 cm^{-1}.

The initial antibacterial and antifungal action of the investigated substance was studied by the disco-diffusion method [16]. To study these properties, according to the generally accepted rule as a test culture, Staphylococcus aureus as a representative of Gram-positive bacteria, which is the main causative agent of purulent-inflammatory processes, from the gram-negative bacteria Escherichia coli (intestinal bacteria), Pseudomonas aeruginosa (blue-green pus bacillus) of pigment-forming gram-negative bacteria, Candida albicans (candida) of yeast-like fungi as a representative fungus, Bacillus anthracoides was taken as representative of spore-forming gram-positive bacilli and Klebsiella pneumoniae was taken as representative of capsule bacteria.

In the disk-diffusion method, a suspension containing 1 billion microbial cells per 1 ml is prepared from a daily culture of microorganisms, that is, a small amount is taken from the daily microbial culture on the left agar surface with a bacteriological loop on a sterile physiological solution, a suspension is prepared, and adjusted to the standard, it is brought to the limit of 1 billion microbial cells in 1 ml. The individual microbial suspensions are then poured into Petri dishes containing MPA (meat-peptone agar) and Sabouraud agar. The bowls are gently moved to ensure that the suspension is evenly distributed in all directions. The remaining suspension was then vacuumed off through a pipette and thrown into the disinfectant solution. The bowls were kept at a temperature of 37°C for 10 minutes for the solution to dry slightly. After that, the bowls are removed from the thermostat, and the sterile disks soaked in the pre-presented substances for 3-5 minutes are arranged on the surface of the nutrient medium planted with microbes, gently pressed with tweezers so that the disks are well-wet. The bowls with MPA are then placed in a thermostat at 37°C and the seedlings in Sabouraud medium at 28°C. When the disks get wet, the substance they absorbed diffuses into the agar and kills the microbe. After 24-48 hours, the bowls are removed from the thermostat and the results are recorded.

The antimicrobial action of the synthesized new polymer substances and controls is studied. The investigated substance shows a various influence on different types of microorganisms, but all synthesized substances have antimicrobial activity.

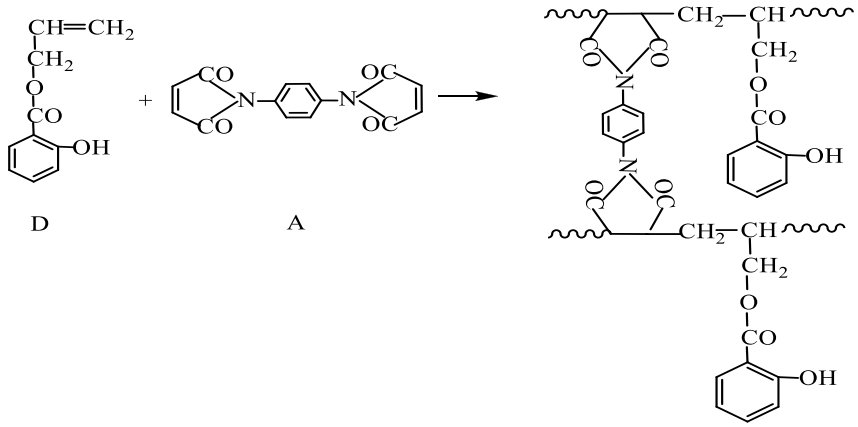
The synthesized substance showed more active antimicrobial properties against gram-positive microbes and *Candida*. For example: the preparations of PhBMI copolymer (5%) with allylsalicylate at ratio 1:400 destroyed *St. aureus* in 20 min. (in control was the end).

The preparation of Al_{sal}-N,N'-(p-phenylene) bismaleinimide destroyed Candida fungus at ratio 1:400 in 10 min. and at ratio 1:800 in 20 min. In the control there was an end even in 1 h at ratio 1:800. The preparation (drug) of Al_{sal}-PhBMI (10%) copolymer destroyed *Candida*, as well as staphylococci and green purulent bacillus at ratio 1:800 in 1 h.

It established as a result that the investigated copolymer Al_{sal} - bismaleinimide can be used both as a bactericide and a fungicide.

Results and discussion

The purpose of the selection of allyl ester of salicylic acid as a comonomer is the preparation of polyfunctional copolymers containing both phenol and imide groups and the study of their antibacterial and antifungal properties. The formation of a complex of donor (D) – acceptor (A) type between Al_{sal} and PhBMI molecules (charge transfer complex) is known in the literature [14].



It has to be kept in mind that the NMR spectra of monomers were recorded separately and in a mixture in various proportions. In the NMR spectrum of mixture of PhBMI and Al_{sal} monomers of various composition (A>>D), changes in the proton chemical shift values belonging to PhBMI molecule indicate the formation of the complex of type [D]...A].

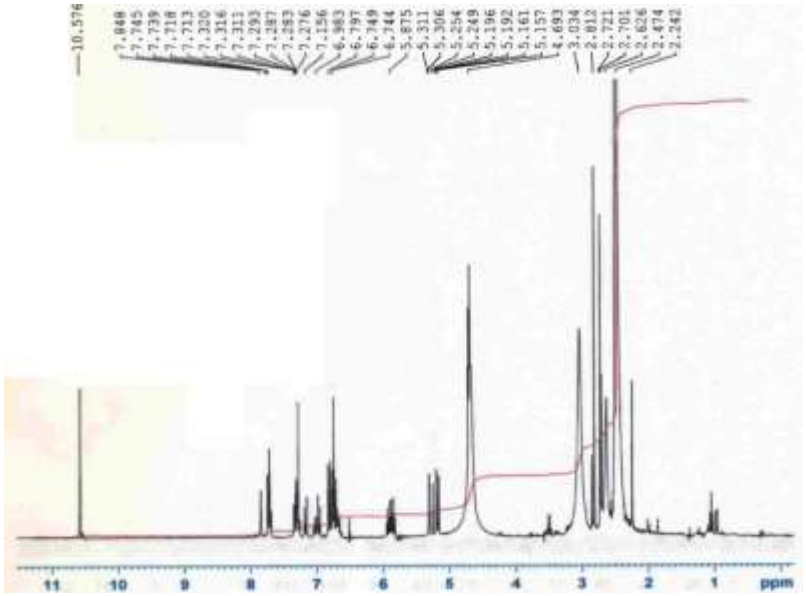


Fig. 1. ^{1}H NMR spectrum of Al_{st} copolymer of N,N′(p-phenylene)bismaleinimide

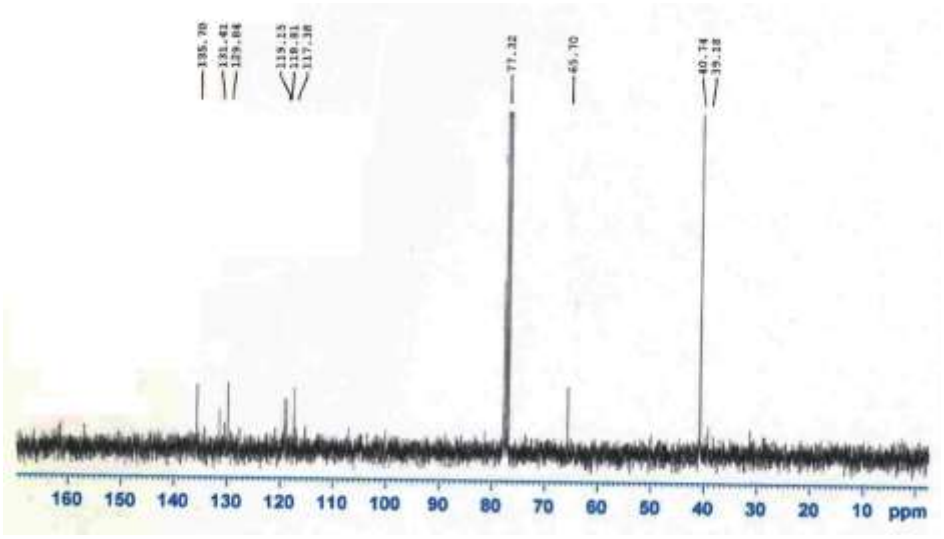


Fig. 2. ^{13}C NMR spectrum of Al_{st} copolymer of N,N′(p-phenylene)bismaleinimide

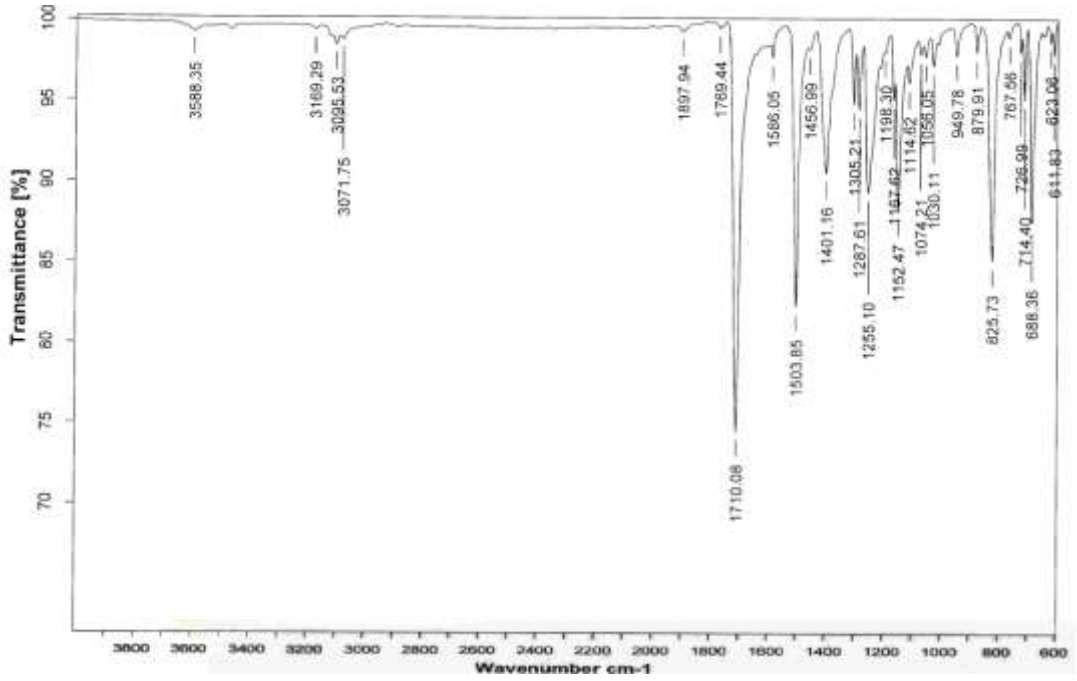


Fig. 3. IR spectrum of Al_{st} copolymer of N,N′(p-phenylene)bismaleinimide

The availability of C=O (1710 cm^{-1}), C-O-C (1152 cm^{-1}) absorption bands in the IR spectrum of copolymers and the absence of absorption band characteristic for C=C bond (1630-1640 cm^{-1}) are the main factors proving the formation of copolymers.

As mole fraction of the donor in the mixture of monomers rises, the changes in the value of this shift are grown. Independently of the ratio of monomers in the initial monomer mixture, the presence of links in the copolymer is close to the equimolar ratio, which is one of the factors proving that the reaction proceeds with the formation of a donor-acceptor complex (the complex formed with charge transfer). The equilibrium constant (Cc) of the complex-formation process was established as a graph using the Ketaalar equation (Table 3.3).

$$[D]+[A]\xleftrightarrow{Kc}[D...A]$$

$$Kc=\frac{[D...A]}{[D]\cdot[A]}$$

Table 1. Indices for calculation of the complex-formation constants of (Cc) of allylsalicates (D) with N,N'-(p-phenylene)bis maleinimide (A)

	[A] mol/l	[D] mol/l	1/Δeks, ppm^{-1}	1/D l/mol
Al_{sal} – PhBMI	0.1	1.0	42.0	1.00
	0.1	2.0	17.0	0.50
	0.1	3.0	12	0.33
	0.1	4.0	8	0.25
	0.1	5.0	3	0.20

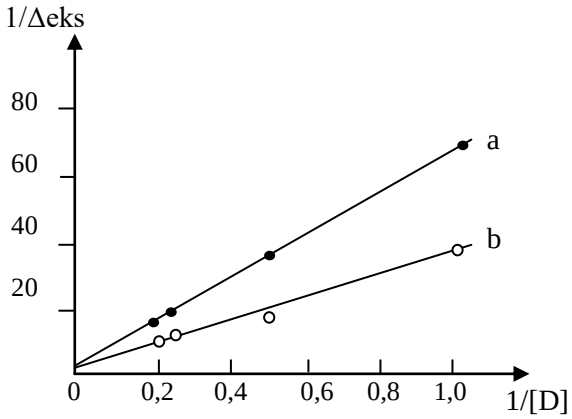


Fig. 4. Calculation of equilibrium constants of the complex formed between pairs of Al_{sal}-PhBMI monomers by NMR spectroscopy method.

According to calculations C_c= 0.096 for Al_{sal}-PhBMI monomeric pair.

Naturally, it can be concluded that the complex formed between monomers shows a serious influence on their relative reactivity. PhBMI macroradicals formed from PhBMI molecule from monomer pairs cannot be combined with PhBMI molecule or the formimng BMI-Al_{sal} complex by means of PhBMI component. The formed complex behaves as a free monomer. The relative activitities of monomers in the copolymerization reactions are calculated by means of the Mayo-Lewis equation [15]. The dependence of the total rate of copolymerization reactions on the composition of the monomer mixture for both pairs of monomers is studied. As can be seen from the Fig. 4, this dependence has an extremal character. There is observed a displacement in the maximum of the curves depending on the total density of the monomer mixture. This fact proves that both free monomers and the complex participate in the copolymerization reactions.

In this case, there are used a table and graphics of the dependence of the composition of copolymers on the composition of the initial mixture of monomers in the copolymerization reactions (Table 2 and Fig. 2).

Table 2. Experimental indices of the radical copolymerization reaction of PhBMI (M_2) with A_{sal} (M_1): t = 65°C, solvent – dioxane (75%), initiator – benzoyl peroxide (0.2%), reaction time -8 h.

Initial mixture of monomers		Quantity of monomer in copolymer composition mol%		r_1	r_2	$r_1 \cdot r_2$	Microstructure of copolymers		
M_1	M_2	m_1	m_2				L_{M_1}	L_{M_2}	R
10	90	43.5	56.5	0.03	0.04	0.0012	1.003	1.36	84.62
25	75	50.3	49.7				1.01	1.12	93.9
50	50	49.8	50.2				1.03	1.04	96.61
75	25	51.7	48.3				1.09	1.01	95.09
90	10	55.8	44.2				1.27	1.27	87.93

L_{M_1} and L_{M_2} – ratio of monomer blocks; R – Harwood block coefficient

r_1= 0.03 and r_2=0.04 for Al_{sal}-PhBMI monomer pair.

Table 3. The influence of their composition on properties of copolymers obtained in copolymerization reactions N,N'-(p-phenylene)bis maleimide (M_1) and Al_{sal}(M_2).

№	Quantity of Al_{sal} in the monomer mixture, mass %	Quantity of m_1 on the copolymer composition, mass %	Yield, %	$[\eta]$ dl/g.	Viscous fluidity, T°C
1	0.0	0	84.0	0.78	83
2	5.0	0.32	20.5	0.66	77
3	10.0	1.20	15.2	0.43	72
4	25.0	2.5	12.00	0.30	70
5	50.0	4.0	10.5	0.22	66

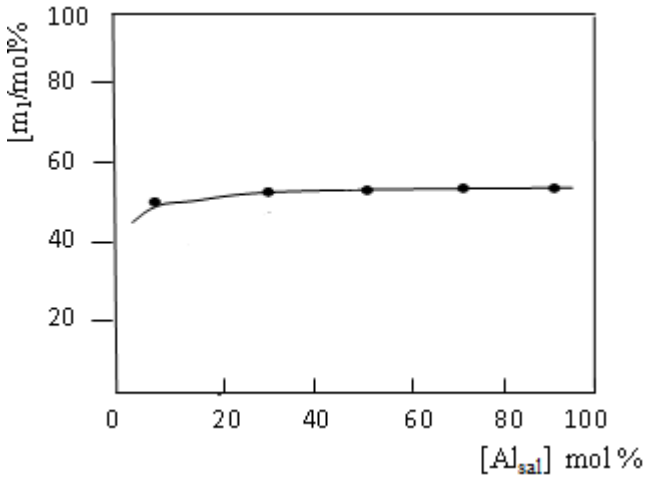


Fig. 5. Dependence of the total rate of the copolymerization reaction on the composition of the initial mixture of monomers.

The values of the relative activity of monomers in copolymerization reactions close to zero prove that the copolymers have an alternating (alternating) structure.

Conclusions

With the aim of preparation of the polymers containing a cyclic imide group, the copolymerization reaction of (N,N'-(p-phenylene)bismaleinimide with allyl ester of salicylic acid was carried out and the properties of the biological activity of the obtained copolymer investigated. It established that the copolymerization reaction was accompanied by the formation of donor-acceptor complexes between monomer pairs. The copolymerization reaction proceeds on radical-complex mechanism. The results of investigation show that as a result of the copolymerization reaction of (bis)maleimides with allyl ester of salicylic acid, the copolymers of an alternative (alternating) structure are obtained.

The composition and structure of the obtained polymer were established by methods of physical-chemical and spectral analysis (NMR, IR) and its antibacterial properties studied.

The synthesized copolymer can be used in the preparation of antibacterial polymer materials with a long-term influence used in agriculture and medicine. It was established that the investigated copolymer Al_{sal} – (N,N'-(p-phenylene)bismaleinimide could be used both as a bactericide and a fungicide.

References

1. Shtilman M.I. Polymers of medical-biological purpose. Moscow: Akademkniga Publ., 2006, 420 p.
2. Dontsova E.P., Zharnenkova O.A., Snezhko A.G., Uzdensky A.V. Polymer materials with antimicrobial properties. *Plastic*, 2014, vol. 131, no. 1-2, pp. 30-35.
3. Afinogenov G.E., Panarin E.F. Antimicrobial polymers. St.Petersburg: Hippocrates Publ., 1993, 264 p.
4. Shtilman M.I., Tzatzarakis M., Lotter M.M., Tcakatsakis A.M. Polymer fungicides // *Vysokomolekulyarniye soed. [High-molecular compounds]*. Series B. 1999, no. 8, pp.1363-1376. (In russian).
5. Badulin N.A., Plotnikov V.M. Antitumor, antibacterial and antivirus pharmaceutical composition, Pat RF № 2319491, 2006.
6. Bonilla A.M., Garcia M.F. Polymeric materials with antimicrobial activity. *Progress in Polymer. Sci.* 2012, vol. 37, pp. 281-339. DOI: 10.1016/j.progpolymsci.2011.08.005
7. Alikhanova A.İ., Rasulzadeh N.Sh., Zeynalova S.Q., Rasulov N.Sh. Investigation of the antibacterial properties of polychlorinated cyclic bisimides. *Intern. Journal of Chemical Engineering Research.* 2019, vol. 6, issue 1, pp. 4-6. http://doi.org/10.14445/23945370/IJCER-V6I1P102
8. Alikhanova A.I., Rasulzadeh N.S. Preparation and investigation of copolymers of cyclic bisimides with styrene. IV All-Russian Conference "Chemistry and chemical technology: achievements and prospects", T.F. Gorbachev Kuzbass State Technical University, 2020, pp. 671 – 672.
9. Alikhanova A.I., Rasulzadeh N.Sh. Preparation and study of the properties of the copolymer of cyclic unsaturated bismaleimide with styrene. *Azerbaijan Chem. J.*, Baku, 2021, no. 4, pp. 25-29. http://doi.org/10.32737/0005-2531-2021-4-25-29
10. Cozan V., Hulubei C., Airinei A., Morariu S. Maleimide copolymers containing azobenzene moieties – synthesis and study of liquid crystalline and optical properties. *RSC Advances*, 2016, issue 104, **6**, pp. 101900-101910 http://doi.org/10.1039/C6RA21072D
11. Kolyamshin O.A., Danilov V.A., Koltsov N.I. Peculiarities of synthesis and properties of some maleinimides. *Butlerov Communications*. 2012, vol. 32, no.12, pp. 26-30.
12. Alikhanova A.I., Rasulzadeh N.Sh. Preparation and invstigation of ethylene(bis)maleimide copolymers with allyl ester of salicylic acid. VIII International Scientific Conference "Chemistry of coordination compounds"

dedicated to the 85th anniversary of the Department “Analytical Chemistry”. 2020, pp. 103-104.
13. Alikhanova A.I., Rasulzadeh N.Sh., Bakhshaliyeva K.F., Muradov P.Z. Preparation and research of antibacterial polypropylene composition materials based on the cyclic bisimides. *International Journal of Advanced Research in Science, Engineering and Technology*, 2019, vol. 6, issue 10, pp. 10995 – 10999.
14. Rzaev Z.M. Polymers and copolymers of malein anhydride. Baku: Elm Publ., 1984. 157 p.
15. Toroptseva A.M., Belogorodskaya K.V., Bondarenko V.M. Laboratory workshop on chemistry and technology of high-molecular compounds. Leningrad: Khimiya Publ., 1972, 386 p.
16. Pozdeev O.K., Pokrovsky V.I. Medical microbiology. Textbook for universities GEOTAR MED 2001. – 768 p.
17. Prech E., Bulmann F., Affolter K. Determination of the structure of organic compounds. Tables of spectral data. Moscow: Mir, Publ., 2012, 438 p.
18. Trujillo-Ferrara F.J., Santillan R., Beltrán H.I., Farfán N., Höpfl H. ^{1}H and ^{13}C NMR spectra for a series of arylmaleamic acids, arylmaleimides, arylsuccinamic acids and arylsuccinimides. *Magnetic Resonance in Chemistry*, 1999, vol. 37(9): pp. 682-686. https://doi.org/10.1002/(sici)1097-458x(199909)37:9<682::aid-mrc500>3.0.co;2-%23

BİSMALEİNİMİDLƏRİN SALİSİL TURŞUSUNUN ALLİL EFİRİ İLƏ BİRGƏPOLİMERLƏRİNİN ALINMASI VƏ TƏDQİQİ

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Xülasə: N,N'-(p-fenilen) bismaleinimidin salisil turşunun allil efiri ilə radikal birgəpolimerləşmə reaksiyası həyata keçirilmişdir. Birgəpolimerləşmə reaksiyasının aparılma şəraiti, sürəti, alınmış birgəpolimerlərin tərkibi və molekul kütlə göstəriciləri və bu parametrlərin ilkin monomer qarışığının tərkibindən asılılığı müəyyən edilmişdir. Müəyyən edilmişdir ki, birgəpolimerləşmə reaksiyası monomer cütləri arasında donor-akseptor komplekslərinin yaranması ilə müşayət olunur. Birgəpolimerləşmə reaksiyası radikalkompleks mexanizmi ilə baş verir. Birgəpolimerləşmə reaksiyasında monomerlərin nisbi aktivlikləri hesablanmışdır: (r_1=0.03; r_2=0.04) Birgəpolimerləşmə sabitlərinin qiymətlərinin sıfıra yaxın olması monomerin birgəpolimerləşmə reaksiyalarına meylli olduğunu və növbəli quruluşa malik makromolekulların əmələ gəlməsini göstərir. Alınmış polimerin tərkibi və quruluşu fiziki-kimyəvi və spektral analiz üsulları ilə müəyyən edilmiş, həmçinin onun antibakterial xassələri öyrənilmişdir. Məlum olmuşdur ki, təqiq edilən polimer konsentrat halda seçilmiş mikroorqanizm kulturalarına aktiv təsir göstərdiyi halda zəif antimikrob aktivliyə malikdirlər. Polimerin göbələk hüceyrələrinə (C.albicans) təsirinin daha effektli oldugu da müşahidə edilmişdir.

Açar sözlər: Bismaleimid, salisil turşunun allil efiri, donor-akseptor kompleksləri, nisbi aktivlik, növbəli quruluşlu polimerlər, antibakterial polimerlər.

ПОЛУЧЕНИЕ И ИЗУЧЕНИЕ СОПОЛИМЕРА N,N'-(п-ФЕНИЛЕН) БИСМАЛЕИМИДА С АЛЛИЛОВЫМ ЭФИРОМ САЛИЦИЛОВОЙ КИСЛОТЫ

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Аннотация: Проведена реакция радикальной сополимеризации N,N'-(п-фенилен)бисмалеинимида с аллиловым эфиром салициловой кислоты. Определены условия протекания реакции сополимеризации, скорость, состав и показатели молекулярной массы полученных сополимеров, а также зависимость этих параметров от состава исходной смеси мономеров. Установлено, что реакция сополимеризации сопровождается образованием донорно-акцепторных комплексов между мономерными парами. Реакция сополимеризации протекает по радикально-комплексному механизму. Рассчитаны относительные активности мономеров в реакции сополимеризации: (r_1=0.03; r_2=0.04). Значения констант сополимеризации, близкие к нулю, свидетельствуют о склонности мономера к реакциям сополимеризации и образованию макромолекул с чередующей структурой. Методами физико-химического и спектрального анализа определены состав и структура полученного полимера, а также изучены его антибактериальные свойства. Установлено, что исследуемый полимерный концентрат обладает слабой антимикробной активностью, одновременно оказывает активное воздействие на отдельные культуры микроорганизмов. Также было замечено, что воздействие полимера на клетки грибов (C.albicans) более эффективно.

***Ключевые слова*:** Бисмалеимид, аллиловый эфир салициловой кислоты, донорно-кцепторные комплексы, относительная активность, антибактериальные полимеры