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SYNTHESIS OF 1-(P-VINYLPHENYL)-2-DIETHYLAMINOMETHYLCYCLOPROPANE AND ITS RADICAL COPOLYMERIZATION WITH METHYL METHACRYLATE

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Abstract: *The radical copolymerization of 1-(p-vinylphenyl)-2-diethylaminomethylcyclopropane with methyl methacrylate was carried out and some regularities of the process examined. Values of constants of relative activity of monomers were determined and Q-e parameters calculated on Alfrey and Price. Copolymerization constants of this compound (r_1) with methyl methacrylate (r_2), calculated on the Fineman-Ross method, are as follows: r_1 = 0.95, r_2 = 0.33, Q and e parameter values: Q_1 = 1.80, e_1 = -0.72, respectively. The photochemical structuring of the copolymer was studied. It was established that the obtained copolymer has a sufficiently high biomedical activity which opens up the possibility of its using as bactericides and fungicides.*

Keywords: *1-(p-vinylphenyl)-2-diethylaminomethylcyclopropane, biological activity, bactericide, fungicide.*
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Introduction

The polymers containing functionally active groups in their composition have a wide range of biomedical activity and are used as bactericides, fungicides, medical products. Most frequently, monomers of vinyl and new monomer series containing carbonyls and amino-groups in the structure are used for preparation of such polymers [1-4].

It was known that the cyclopropane-containing compounds are effective and relatively safe biocidal substances. In considering pseudo-unsaturated nature of cyclopropane ring and high biological activity of many compounds cyclopropane series [5-8], the present article sets an aim to synthesize a new monomer 1-(p-vinylphenyl)-2-diethylamino-methyl cyclopropane (VPhDEC) and its sopolymerization with methylmetacrylate as well as research into bactericide properties of obtained sopolymers of different composition**.**

Experimental part

Synthesis of 1-(n-vinylphenyl)-2-diethylaminomethyl cyclopropane 22.8 g (0.1 mol) of p-chlorophenol in ethylmethyl ketone (EMK, 150 ml) was dissolved in a three-necked flask equipped with a mechanical stirrer, a thermometer and a dropping funnel; the contents were cooled to 0°C. Then 7.3 g (0.1 mol) of diethylamine in 30 ml of EMC was added drop by drop for 30 min. with constant stirring and cooling. The reaction mixture was stirred for 30 min and another 20 min at room temperature.

The obtained residue was extracted with sulfur ether and the resulting product was dried with anhydrous Na_2SO_4 and then evaporated using a rotary spoiler. The main product was distilled in vacuum and obtained VPhDEC with yield 87%. B.p. 110-112°C/0.5 mm merc.c.

Elemental analysis is (%): C=83.11; H=10.38 N=6.06 (calculated); C=83.07; H=10.33; N=6.02 (found).

The copolymerization was carried out in benzene at 333 K in the presence of AIBN and for revealing the regularity, The copolymerization synthesized in VPhDEC with MMA was carried out in an ampoule of benzene solution in the presence of 0.5% of dinitrilazoisobutyric acid (AIBN) (of total mass of monomers) at 70°C. The forming copolymer was purified by twofold precipitation from benzene solution into methanol and dried in vacuum (15-20 mm merc.c) at 30°C to a constant mass. The characteristic viscosity was determined in benzene in Ubbelode viscometer. The molecular weight value (MM ≈ 350000-420000) was estimated on the characteristic viscosity ([η]= 0.93 dl/g).

The copolymer composition was determined according to the data of elemental analysis on the nitrogen atom content.

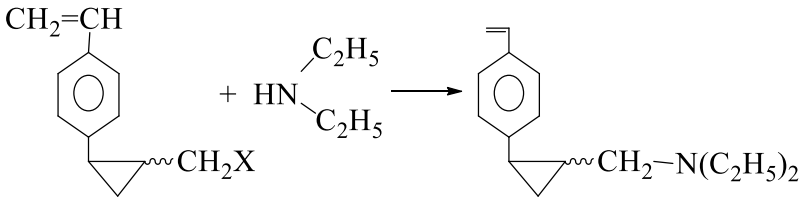
The IR spectra of copolymers were registered on a spectrometer "Agilent Cary 630 FTIR", PMR spectra – on a spectrometer BS-487B Tesla (80 Mhz) in a solution of deuterated chloroform.

For investigation of the photochemical structuring of the copolymer, 2-10% copolymer solutions were prepared and then applied to a glass substrate by size of 60×90 mm. The application was carried out by means of centrifugation method at 2500 rev·min^{-1}. The resist layer thickness after its drying for 10 min at room temperature and for 20 min at 25°C/10 mm merc.c was 0.15-0.20 mcm.

A mercury lamp DRT-220 (current strength – 2.2 A, distance from the radiation source – 15 cm, the exponometer mobile shutter rate – 720 mm·h^{-1}, exposure time – 5-10 sec.) was used as UV irradiation source. The content of the insoluble copolymer was calculated on the residue mass.

Results and discussion

This work is a continuation of the investigations carried out in the synthesis of cyclopropane-containing monomers and copolymers.



X= Br

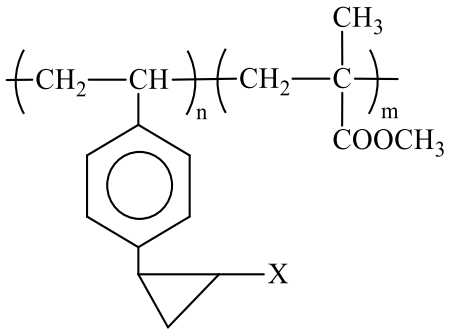
It revealed that the copolymerization proceeds under the studied conditions without induction period with constant initial rate, the ratio of co-monomers of 1-(p-vinylphenyl)-2-diethylaminomethylcyclopropane and MMA was changed in the wide range of mol %, the total concentration of copolymers was determined on the elemental analysis using the Fineman-Ross method [9] on the nitrogen atom content [10]. The obtained results are shown in Table 1.

Table 1. The copolymerization of VPhDEC (M_1) with MMA (M_2).

Quantity of monomers in the initial mixture, mol %		Quantity of monomer residues in the copolymer, mol %		r_1	r_2	$r_1 \cdot r_2$	Parameters of the copolymer microstructure		
M_1	M_2	m_1	m_2				L_{M_1}	L_{M_2}	R

10	90	35.10	64.90				1.90	2.13	59.71
25	75	3.24	96.76				1.09	29.7	6.52
50	50	8.76	91.24	0.95	0.33	0.313	1.01	10.5	16.20
75	25	20.13	79.87				1.08	4.1	37.01
90	10	35.32	64.68				1.16	2.05	62.60

As is evident from Table, the VPhDEC exhibits higher activity during copolymerization which is probably due to the conjugation in VPhDEC molecule.



X=$-CH_2N(C_2H_5)_2$

It revealed that the system remains homogeneous in benzene up to high conversion values (96%). The obtained copolymers after precipitation and drying to a constant mass are a white powder, well soluble in benzene, chlorinated hydrocarbon, dimethylformamide, and in other solvents.

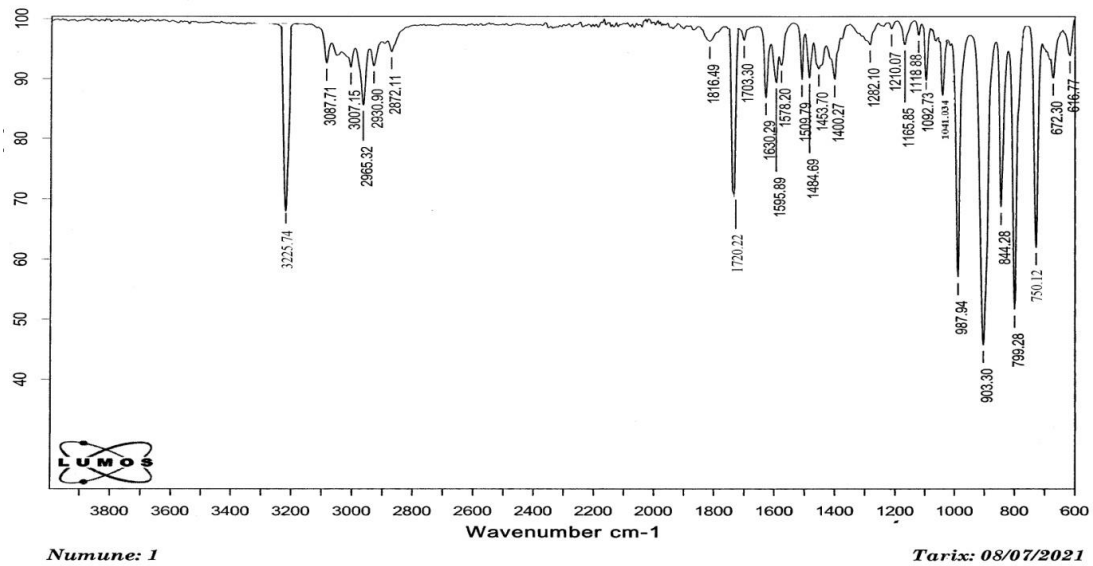
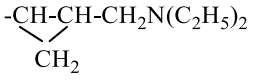


Fig.1. IR spectrum of the copolymer of 1-(n-vinylphenyl)-2-dimethylaminomethyl cyclopropane (VPhDEC) with methyl methacrylate (MMA).

The structure of the synthesized polymer was studied through IR and PMR spectroscopy. The identification of the structure of macromolecules of copolymers isolated at various degrees of conversion and containing links of both monomers in macrochains was carried out by means of IR and PMR spectroscopy. In the IR spectra (Fig.1) of the samples of the obtained copolymers at various ratios of the initial monomers, there is an intensive absorption band at 1720 cm^{-1} corresponding to the valence vibrations of the carbonyl group, and also the absorption bands at 1035-1040 cm^{-1} belonging to the cyclopropane ring. It should be noted that in the IR spectra of all samples of the studied polymer of tertiary amines, in the field of 672, 750 cm^{-1} and 3200-3400 cm^{-1}, there are wide absorption bands corresponding to the valence vibrations of amino-groups, the bands of average intensity in the field of 1400-1509 cm^{-1} and 1578 cm^{-1} referring to the valence vibrations of the benzene ring, the bands of low intensity in the field of 1000-1027 cm^{-1} representing planar deformation vibrations of C-H bond of the same ring.

The PMR spectrum (Fig. 2) contains resonant signals for protons of benzene (δ=6.85-7.25 ppm) and cyclopropane (δ=0.75-1.75)  rings. It revealed that the resonant signals of protons of the vinyl group (δ=4.50-5.05) completely disappear after polymerization.

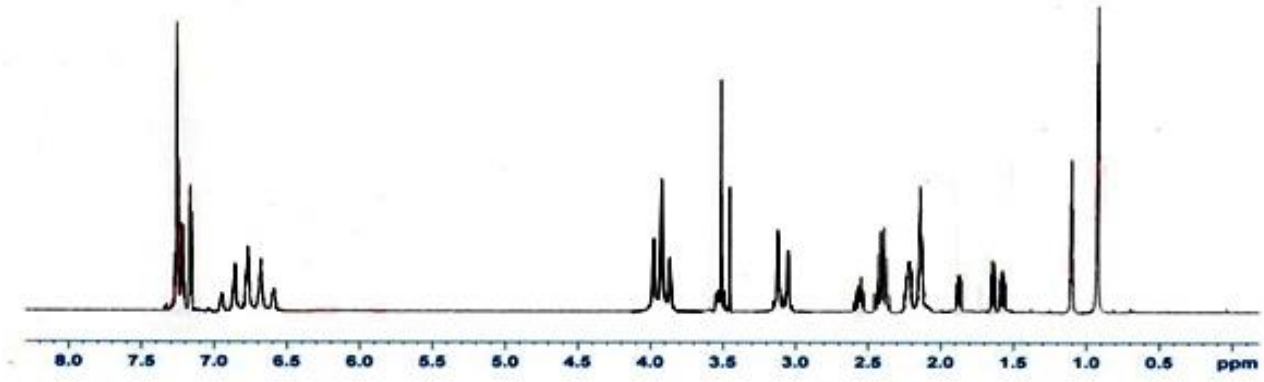


Fig.2. PMR spectrum of the copolymer of 1-(n-vinylphenyl)-2-dimethylaminomethyl cyclopropane (VPhDEC) with methyl methacrylate (MMA).

Owing to the availability of the reactive groups of various chemical nature in the macromolecule of the copolymer, it is of interest to investigate the photochemical structuring of the obtained copolymer arising from cross-linking under the effect of UV irradiation. As a result, these polymers prove to be negative photoresists. The obtained copolymers are notable for high photosensitivity (52-54 cm^2/J), good solubility before irradiation and resistance to solvents after structuring and relatively good thermal stability which is very important for photoresist. It revealed that the synthesized copolymers are capable for formation of thin films and long-term conservation of good lithographic properties. The films formed from this copolymer show the elasticity, following which the cracks are not formed.

The preliminary biological tests showed the sufficiently high bactericidal (E.coli=1.5, St.aur.=1.0) and fungicidal (Can.alb=0.8) activity of the obtained copolymer of VPhDEC with MMA (VPhDEC : MMA = 64 : 36 mol.%).

Conclusions

As a result of the investigation, the samples of copolymers of 1-(p-viniphenyl)-2-diethylaminomethylcyclopropane with MMA of various co-monomer composition with high

yield (up to 95%) and with various viscosity characteristics were obtained for the first time. It found that the copolymerization of 1-(p-vinylphenyl)-2-diethylaminomethylcyclopropane with methyl methacrylate is exposed to the basic regularities of the radical polymerization: an increase of the co-monomers concentration in the initial solution leads to the rise in conversion and characteristic viscosity, and a considerable decrease of the radical initiator concentration results in sharp decrease of the copolymer yield. It revealed that the synthesized VPhDEC and its copolymer show the high bactericidal and fungicidal properties.

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1-(P-VİNİLFENİL)-2-DİETİLAMİNOMETİL TSİKLOPROPANIN SİNTEZİ VƏ ONUN METİLMETAKRİLAT İLƏ RADİKAL SOPOLİMERLƏŞMƏS

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1-(p-Vinilfenil)-2-dietilaminometil tsiklopropanın metilmetakrilatla radikal sopolimerləşməsi aparılmış və prosesin bəzi qanunauyğunluqları öyrənilmişdir. Monomerlərin nisbi aktivlik

sabitlərinin qiymətləri müəyyən edilmiş, Alfrey və Prays əsasında Q-e parametrləri hesablanmışdır. Göstərilən birləşmənin (r_1) metilmetakrilat (r_2) ilə sopolimerləşmə sabitləri Faynman-Ross metodu ilə hesablanmış və $r_1 = 0.95$, $r_2 = 0.33$, Q-e parametrlərinin qiyməti müvafiq olaraq $Q_1 = 1.80$, $e_1 = -0.72$ təşkil etmişdir. Sopolimerin fotokimyəvi quruluşu tədqiq edilmişdir. Müəyyən edilmişdir ki, alınan sopolimer kifayət qədər yüksək tibbi-bioloji aktivliyə malikdir ki, bu da ondan bakterisid və funqisid kimi istifadə etmək imkanını yaradır.

Açar sözlər: *1-(p-vinilfenil)-2-dietilaminometiltsiklopropan, bioloji aktivlik, bakterisid, funqisid.*

СИНТЕЗ 1-(П-ВИНИЛФЕНИЛ)-2-ДИЭТИЛАМИНОМЕТИЛЦИКЛОПРОПАНА И ЕГО РАДИКАЛЬНАЯ СОПОЛИМЕРИЗАЦИЯ С МЕТИЛМЕТАКРИЛАТОМ

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Проведена радикальная сополимеризация 1-(п-винилфенил)-2-диэтиламинометилциклопропана с метилметакрилатом и изучены некоторые закономерности процесса. Определены значения констант относительной активности мономеров и рассчитаны параметры Q-e по Алфрею и Прайсу. Константы сополимеризации указанного соединения (r_1) с метилметакрилатом (r_2), рассчитанные по методу Файнмана-Росса, составляют: $r_1 = 0.95$, $r_2 = 0.33$, значения параметров Q и e: $Q_1 = 1.80$, $e_1 = -0.72$, соответственно. Исследовано фотохимическое структурирование сополимера. Установлено, что полученный сополимер обладает достаточно высокой медико-биологической активностью, что открывает возможность использования его в качестве бактерицида и фунгицида.

Ключевые слова: *1-(п-винилфенил)-2-диэтиламинометилциклопропан, биологическая активность, бактерицид, фунгицид.*