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SYNTHESIS, POLYMERIZATION AND COPOLYMERIZATION OF GEM-DISUBSTITUTED CYCLOPROPYL VINYL ESTERS WITH MALEIC ANHYDRIDE

Speciality: 2304.01 – Macromolecular chemistry

Area of science: Chemistry

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AUTOABSTRACT

of the dissertation for the degree of Doctor of Philosophy

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The work has been carried out at the Institute of Polymer Materials of the Ministry of Science and Education of the Republic of Azerbaijan and Sumgait State University.

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GENERAL CHARACTERISTICS OF THE WORK

The actuality of theme and the degree of its development. Currently, special attention is paid to the synthesis of new monomers, the development of effective methods for obtaining functional polymers based on them, the preparation of thermo- and chemically resistant polymers, the selection of biologically active polymers and polymer carriers. For creation of a new generation of this type of polymers, the extensive and intensive scientificresearch works are being carried out in the direction of creation of the functional monomers for various purposes on the basis of fine organic synthesis¹. The level of development of technique sets a task of creation of polymers with special properties and for various purposes and composition materials based on them with higher exploitation indices for specialists working in the field of polymer chemistry. From this point of view, the copolymers of maleic anhydride are of particular importance. The easy opening of the anhydride group during chemical reactions in the macromolecule of copolymers allows to obtain the new thermoplastic and thermoreactive polymers, water-soluble, coating-forming and other important materials on their basis.

The availability of unsaturated groups in the side chain of polymer macromolecules, the reactions of their thermal conversion or homopolymerization, or radical copolymerization with various vinyl monomers provide an easy conversion into three-dimensional structure. The materials obtained as a result of polymerization are used in the production of adhesives, reinforcing plastic connectors, photo- and electronic resists. One of the main methods of preparation of this type of materials is the esterification reaction of copolymers containing anhydride groups with unsaturated alcohols.

Object and subject of the investigation. The main object of the investigation is the synthesis of various vinyloxy- and (2-vinyloxy)ethoxy-

¹ Anuj K. Additive-Free Synthesis of Trifluoromethylated Spiro Cyclopropanes and Their Transformation into Trifluoromethylated Building Blocks / K.Anuj, F.J.Muhammad, T.Shilpa [et.al] // Asian Journal of Organic Chemistry, Germany.– 2021. –v.10. –Is.6. – p.1536-1541

substituted cyclopropylacetal monomers, carrying out of the model reactions of combination with mono- and dithiols in the presence of free radicals, preparation of homo- and copolymers in the presence of radical initiators and cationic catalysts determining their structure, properties and application possibilities.

The subject of the investigation is the synthesis of synthesized monomers, S-containing adducts and copolymers with maleic anhydride, the study of their properties, including the properties of biological activity, the use of anhydride-containing copolymers as a hardener for epoxide resin, and also the study of photosensitivity and other properties of compositions obtained on the basis of the obtained products.

Purposes and tasks of the investigation. The synthesis of functional, photochemically structured polymers containing acetal- substituted cyclopropyl and anhydride groups in macromolecules, the establishment of the dependence between their properties and structure and determination of areas of practical application is the main purpose of investigation.

For achievement of this purpose, it was necessary to solve the following problems:

- synthesis of vinyl cyclopropyl esters containing functional groups in the molecule and their polymerization in the presence of free radical initiators and cationic catalysts;
- radical homopolymerization of the synthesized monomers of vinyloxycyclopropylacetal and copolymerization with maleic anhydride;
- determination of structural properties and physical-chemical properties of the obtained homo- and copolymers and composition materials on their basis;
- study of the reactivity of synthesized monomers in the investigated reactions;
- investigation of complexes of donor-acceptor type formed between monomers during copolymerization with maleic anhydride;
- determination of photosensitivity, biological activity, the possibility of use of epoxide resins as a hardener and other exploitation characteristics of the synthesized polymers and composition materials based on them.

Methods of investigation. The structure and composition of the synthesized monomers, adducts, homo- and copolymers have been studied by IR-, PMR spectroscopy, derivatography, GLC, viscometry and other generally accepted modern methods of analysis.

Main positions submitted for defense:

- Results of the investigation of the synthesis of vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetals and their structural properties;
- Peculiarities of radical and cationic polymerization of synthesized substituted cyclopropyl acetals;
- Peculiarities of radical copolymerization of the synthesized esters with maleic anhydride and results of chemical modification of anhydride-containing copolymers and their discussion;
- Results of the investigation of photosensitivity of homo- and copolymers of substituted cyclopropyl acetals, properties of biological activity of the synthesized monomers and their adducts with thiols.

Scientific novelty of the investigation. The investigation of the processes of synthesis and polymerization of acetal-substituted vinyl cyclopropyl monomers and the preparation of polymer materials with new properties, the implementation of the copolymerization process in the presence of maleic anhydride with complex-formation between comonomers, the revealing of interaction between the structures of the synthesized monomers and their polymerization activity, the preparation of more important new materials by carrying out of various chemical reactions of the obtained high-molecular compounds determine the scientific novelty of the dissertation. The kinetic properties of radical polymerization of (2-vinyloxy)ethoxy-4,7-dioxaspiro-[2,4,0]-heptane, as well as the influence of radical polymerization of the synthesized monomers have been also investigated and the composition of the polymerization reaction on monomer and initiator has been determined.

Theoretical and practical significance of the investigation. The synthesis of new functional monomers and the development of a method of the preparation of homo- and copolymers containing acetal-substituted cyclopropyl groups in the side chains, the preparation of composition

materials with high antimicrobial properties, the creation of photosensitive resists and other materials are of theoretical importance.

Personal participation of the author. The applicant has an important share at each stage connected with the solution of the problems posed in the scientific-research work, the practical implementation of investigations, carrying out of analyses, analysis of the obtained results, the compilation of scientific papers and dissertations on research work.

Approbation and application. The main provisions covering the content of the dissertation work have been published in 9 papers (2 without co-authors) and 9 conference materials in scientific publications recommended by the Higher Attestation Commission of the Azerbaijan Republic. The published scientific papers fully reflect the content of the dissertation.

The obtained results: Akademik A.A.Əfəndiyevin 75 illik yubileyinə həsr olunmuş "Makromolekullar kimyasının fundamental və tətbiqi problemləri" Respublika elmi konfransında (Sumqayıt, 2013), Tacikistan Respublikası EA-nın V.İ.Nikitin adına Kimya İnstitutunda keçirilən Əbu Bəkr Məhəmməd İbn Zəkəriyə Razinin 1150 illik yubileyinə həsr olunmuş Beynəlxalq elmi-praktiki konfransında (Düşənbə, 2015), 4th İnternational Caucasian Symposium on Polymers and illik Advanced Materials (Batumi, 2015), Sumqayıt Dövlət Universitetinin 55 illik yubileyinə həsr olunmuş "Funksional polimerlər və xüsusi xassəli polimer materiallar: problemlər, perspektivlər və praktiki baxışlar" mövzusunda keçirilən Beynəlxalq elmi konfransında (Sumqayıt, 2017), Azərbaycan Respublikası Təhsil Nazirliyi Gəncə Dövlət Universitetində "Müasir təbiət və iqtisad elmlərinin aktual problemləri" Beynəlxalq elmi konfransında (Gəncə, 2018), İvane Javakhishvili Tbilisi State University, World Forum on Advanced Materials (Tbilisi, 2018), 6th International Caucasian Symposium on Polymers and Advanced Materials (Batumi, 2019), Sumqayıt şəhərinin 70 illik yubileyinə həsr olunmuş "Kimya texnologiyası və mühəndisliyinin innovativ inkişaf perspektivləri" mövzusunda keçirilən Beynəlxalq elmi konfransında (Sumqayıt, 2019), Nizami Gəncəvinin anadan olmasının 880 illiyinə həsr olunmuş "Kimyanın müasir problemləri" adlı Respublika Elmi Konfransında (Sumgayıt, 2021).

Name of the institution, where the dissertation work has been carried out. The dissertation work has been carried out in accordance with

the scientific-research plan in the laboratory "Functional smart polymers", operating at the Institute of Polymer Materials of of the Ministry of Science and Education of the Republic of Azerbaijan and at the Department "Petrochemistry and Chemical Technology" of Sumgayit State University.

Volume of the structural sections of the dissertation separately and the total volume with a mark. The scientific work consists of 161 pages (189770), including Introduction (9635), chapter I (48345), chapter II (26287), chapter III (60631), chapter IV (25176), chapter V (16480), conclusion (3216), 23 figures and 25 tables.

The first chapter includes 1,1-cycloaddition of dichlorocarbene to C=C-double bond and preparation of dichlorocyclopropane-containing adducts, dichlorocyclopropanation of vinyloxy- and (2-vinyloxy)ethoxy)-substituted unsaturated hydrocarbons, synthesis and polymerization of the obtained alkyl (cycloalkyl) esters, complex-formation in the alternative copolymerization process and a literature review devoted to the areas of application of cyclopropane-containing compounds.

The second chapter consists of an experimental part devoted to the synthesis of the initial monomers and their physical-chemical parameters, homo- and copolymerization, the preparation of composition materials and other problems.

In the third chapter the results obtained in the investigation of the synthesis and polymerization of vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetals and their discussion have been reflected.

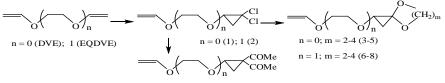
The fourth chapter has been devoted to the discussion of the defined peculiarities of the copolymerization of vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetals with maleic anhydride.

In the fifth chapter, the possibilities of practical use of adducts, homoand copolymers based on vinyloxy- and (2-vinyloxy)ethoxycyclopropyl acetals have been investigated.

MAIN CONTENT OF THE WORK

Vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclo-propylacetal (cyclic and non-cyclic) monomers have been synthesized according to the

following scheme with the aim of prepartion of the polymers of linear structure containing highly reactive groups in the side chain:



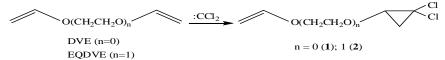
n = 0 (9); 1 (10)

The synthesized vinyloxycyclopropyl esters contain cyclic acetal and non-cyclic ketal groups in a cyclopropane ring.

Synthesis of *gem*-dichloro-substituted cyclopropyl vinyl esters

It was known that dichlorocarbene under conditions of interphase catalysis selectively combines to double bonds of alkenes. diene hydrocarbons, vinyl esters and other compounds for formation of gemdichloro-substituted cyclopropane compounds. The compounds of this type containing chlorocyclopropane formed as a result of this reaction are used as biological products, additives to fuels, oils and polymers, intermediates in the preparation of solvents of special purpose, etc, and are of particular importance. In addition to all this, the compounds of ethers with cyclopropane (or substituted cyclopropane) ring and vinyl groups in the molecule are of particular interest as monomers in the chemistry of macromolecules, and on their basis one can obtain the functional polymers for special purposes. From this point of view, in this work it is intended to obtain a number of vinylto study the reactions of substituted cyclopropyl acetals, their copolymerization with homo- and maleic anhydrides, to determine the composition, structure and properties of the obtained products.

The reaction of initially synthesized divinyl ether and divinyl ether of ethylene glycol with dichlorocarbene obtained under the conditions of interphase catalysis was carried out as primary unsaturated hydrocarbons:



For a more detailed investigation of the reaction of synthesized divinyl ethers

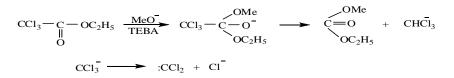
with dichlorocarbene, the preparation reactions of dichlorocarbene have been used on two various methods.

In the first case, the reaction of dichlorocarbene with divinyl ethers obtained at hydrolysis of chloroform with alkali under conditions of interphase catalysis has been carried out:

$$CHCl_3 \xrightarrow{\text{NaOH}} CCl_3 + H_2O$$

$$CCl_3 \longrightarrow :CCl_2 + Cl^2$$

The second method is based on the reaction of divinyl ethers of dichlorocarbene obtained by the interaction of ethyl ether of trichloroacetic acid with Na-methylate (in the conditions of interphase catalysis):

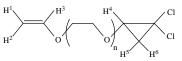


It has been established as a result of the carried out investigations that under the selected optimal conditions (divinyl ether:chloroform = 1:1,2; NaOH – 4 mol (as 50% solution in water; TEBA – 0.025 mol), the yield of monoadduct in the reaction products is 40% for 2 h., for more than 2 h, the preparation up to 15% *bis*-adduct is observed along with monoadduct. At the initial stage of the process, the reaction proceeds faster and a further increase of the reaction time does not show an essential influence on the yield of the purposeful product, and the optimal conditions correspond to 2.0 hours.

In the IR spectra of synthesized *gem*-dichlorocyclopropylvinyl ethers corresponding to the vinyl group, cyclopropane ring, ether and C-Cl bonds, the absorption bands in the frequency range of 1640-1650 cm⁻¹, 1030-1040 cm⁻¹, 1130-1140 cm⁻¹, 760-800 cm⁻¹ are observed, respectively.

By analysis of the PMR spectra of these compounds, the chemical shifts related to the corresponding proton-containing groups have been investigated and shown in Table 1.

Table 1



Chemical shifts of proton-containing groups

| Compound | Chemical formula | H^{1} | H^2 | H^3 | H^4 | H^5 | H^6 | OCH ₂ CH ₂ O |
|----------|---------------------|------------------|---------|----------|----------------|---------|---------|------------------------------------|
| 1 | | 4.02(d) | 4.13(d) | 6.43(dd) | 2.90(m) | 1.30(m) | 1.10(m) | - |
| 2 | | 4.06(d) | 4.16(d) | 6.46(dd) | 2.86(m) | 0.96(m) | 0.76(m) | 3.70; 4.10 (m) |

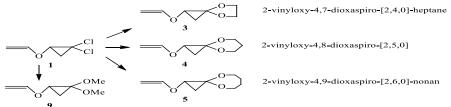
Preparation of vinyloxy- and (2-vinyloxy)ethoxysubstituted cyclopropyl acetals

As a result of the reaction of vinyloxy substituted *gem*dichlorocyclopropane monomers with various alkanediols in the presence of NaOH, the vinyloxy- and (2-vinyloxy)ethoxy substituted cyclopropyl acetals have been synthesized. The reaction proceeds on the following scheme:

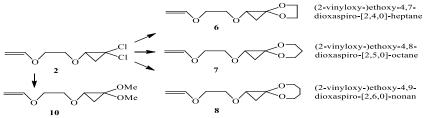
$$= \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)} \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}}_{O(1)}) \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}} (C_{1} \cap H_{0})_{m}) \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m} (C_{1} \cap H_{0})_{m}) \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m} (C_{1} \cap H_{0})_{m})) \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m} (C_{1} \cap H_{0})_{m})) \longrightarrow \underbrace{(\bigcup_{0 \in \mathcal{O}_{n}} (C_{1} \cap H_{0})_{m}$$

The cyclic and non-cyclic vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetals with the following structural formulas have been synthesized under the established optimal conditions, their composition and structure have been determined by analytical methods.

The acetals obtained on the basis of *gem*-dichlorocyclopropyl vinyl ether:



(2-vinyloxy)ethoxy substituted cyclopropyl acetals as well as 2-vinyloxy-4,7dioxaspiro-[2,4,0]-heptane, 2-vinyloxy-4,8-dioxaspiro-[2,5,0]-octane, 2vinyloxy-4,9-dioxaspiro[2,6,0]-nonane compounds have obtained and investigated according to the following scheme in the conditions of synthesis:

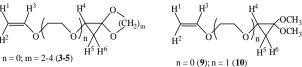


The compounds (3-8) isolated after the reaction have been analyzed using GL chromatography and their degree of purity has been determined.

The chemical shifts recorded in the PMR spectra of synthesized compounds are presented in Table 2. It can be seen from Table that in the PMR spectrum of the compound 7, the signals characteristic for the protons of the group – OCH₂CH₂O– are located in the fields of δ =3.74–4.13 ppm, and the protons of CH₂-group in the cyclopropane ring having δ =0.76-1.42 ppm are registered as doublet signals and are observed in relatively weak areas. The signal at δ =1.82-2.86 ppm should be attributed to CH-proton of the cyclopropane ring adjacent to the oxygen atom. The protons of the methylene group belonging to the double bond are observed in the fields of CH₂=CH– δ =4.04 ppm and δ =5.06 ppm.

Table 2

Results of PMR spectra of vinyloxy- and (2-vinyloxy-)ethyloxy substituted cyclopropyl acetals



| | | n | = 1; m = 2 | -4 (0-8) | | | | |
|---------|------------------|----------------|------------|-------------------|----------|-----------|-------------------|----------------------|
| | | Cher | nical sh | ifts of pro | tons and | l proton- | containing groups | |
| Monomer | | | | | δ, ppi | m | | |
| Code | H^{1} | H^2 | H^3 | H^4 | H^5 | H^6 | –OCH2–, –OCH3 | C-CH ₂ -C |
| 3 | 4.16 | 5.04 | 5.87 | 1.97- 2.25 | 1.03 | 1.37 | 3.95-4.05 | — |
| 4 | 4.15 | 5.03 | 6.45 | 2.86 | 0.94 | 0.69 | 3.99-4.09 | 1.83- 1.88 |
| 5 | 4.13 | 5.03 | 6.45 | 2.86 | 0.94 | 0.69 | 3.70-3.60 | 1.53- 1.55 |
| 6 | 4.18 | 4.06 | 6.43 | 2.21 | 0.73 | 0.48 | 3.74-4.13 | - |

2 4 (6 9)

| 7 | 4.18 | 4.03 | 6.45 | 2.23 | 0.72 | 0.48 | 3.74-4.13 | 1.83- 1.88 |
|----|------|------|------|------|------|------|-----------------|---------------|
| 8 | 4.16 | 4.04 | 6.43 | 2.22 | 0.70 | 0.48 | 3.60-4.13 | 1.53- 1.55 |
| 9 | 4.15 | 5.06 | 6.44 | 2.86 | 0.94 | 0.69 | 3.30 | - |
| 10 | 4.15 | 4.04 | 6.43 | 2.22 | 0.73 | 0.48 | 3.74-4.13; 3.30 | - |

J values characterizing the interaction between the protons of the double bond are as follows for compound 6:

 $J^{1,2}$ (geminal interaction) = 2.4 Hs

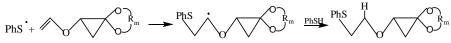
 $H^{1}_{H^{2}} = C + H^{3}_{O-}$ J^{1,3} (*cis*- interaction) = 8.0 Hs

 $J^{2,3}$ (*trans*- interaction) = 16.0 Hs

The various alkanediols, including 1,2-ethanediol, 1,3-propanediol and 1,4-butanediol, have been used in the preparation of cyclopropyl acetals together with dichlorocyclopropyl component. The obtained compounds are differed on quantity of members included in the acetal cycle. Naturally, the influence of cycles of different sizes on the overall reactivity of the molecule, as well as on the vinyl group, should also be different. For confirmation of these considerations, in the subsequent investigations, the activity of these synthesized monomers in various conversion reactions, polymerization and copolymerization processes has been studied.

Free radical combination of thiols with vinyloxy- and (2-vinyloxy)ethoxy substituted cyclopropyl acetals

The reaction of the initial components – monomer: thiil = 1:1.1 (mol) in the presence of initiator of a radical type (in a quantity of 0.5% on mass) of the synthesized vinyloxycyclopropyl acetals has been carried out in a nitrogen atmosphere at 70^oC for 1.5 h. Thiil radicals formed as a result of the spin exchange of a radical with thiophenol as a result of the thermal decomposition of the initiator are combined to double bonds of monomers to form an intermediate radical. The latter causes the formation of an adduct due to the removal of proton from thiophenol molecule. $J \xrightarrow{\Delta} 2\dot{R} R + PhSH \longrightarrow RH + PhS'$



The results of our investigations show that the yield of the obtained adducts is quite high and is 87-93% independently of *m*- value (the quantity of methylene groups) in acetals containing cyclopropane ring.

The results of spectral analysis show that the radical addition of thiophenol to the synthesized monomers occurs in 1,2-position and leads to the formation of monoadducts.

It is seen from the IR spectrum that the availability of an absorption band in the frequency range of 1020-1040 cm⁻¹ indicates the availability of cyclopropane group, and the thiophenol compound occurs only in the presence of double bond of vinyl group.

In the PMR spectra of the synthesized adducts, the absence of signals at δ =5.0-6.0 ppm referring to protons of double bond and the presence of the proton signals belonging to SCH₂ group at δ =2.94-3.1 ppm., confirms that the reaction proceeds due to the vinyl group.

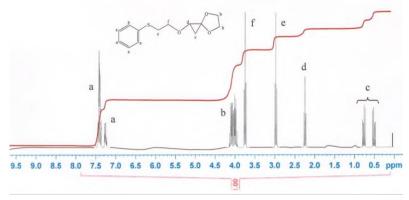
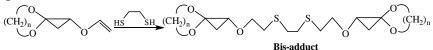


Fig. 1. PMR spectrum of monoadduct obyained from 2-vinyloxy- 4,7dioxaspiro-[2,4,0]heptane with thiophenol

The structure of compounds obtained as a result of the reaction with thiophenol has been studied using IR- and PMR spectra. The results of the investigation of the spectra showed that depending on the ratio of the initial components, the reaction is completed with the preparation of mono- or *bis*-

adducts. Only the vinyl group of vinyloxycyclopropyl acetals regioselectively participates in the combination reaction:



The study of PMR spectra of adducts obtained during the addition reaction showed that the chemical shifts characteristic of protons near the double bond in the initial substrate are not observed in the spectrum of adducts obtained during the reaction (δ =5.0-6.0 ppm.), i.e. only the vinyl group participates in the reaction. In addition, in the spectrum, the signals registered in the field of δ =2.7-3.0 ppm indicate the availability of –SCH₂-fragment in the adduct structure. The character of the spin-spin interaction in the spectrum, the chemical shifts values and integral signal intensities are agreed with the assumed structure of mono- and bis-adducts.

Table 3

Results of PMR spectra of adducts obtained from thiophenol and vinyloxycyclopropyl acetals

| Initial | Structural formula of | Cherr | nical shifts | s of protor | n-contair | ning groups (& | , ppm.) |
|---------|--|----------------------------------|---------------------|---------------------|-----------|-------------------------------|---------------------------------------|
| nonomer | monoadducts | C ₆ H ₅ S- | -SCH ₂ - | -OCH ₂ - | -OCH3- | -CH-C< | -O(CH ₂) _n - |
| 3 | $PhS(CH_2)_2OCH - C C O(CH_2)_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH_2 CH$ | 7.20- 7.36 (m) | 2.94 (t) | 3.71(t) | _ | 2.21(t); 0.46; 0.73 (m) | 3.95-4.05 (m) |
| 4 | $\underset{CH_2}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\overset{O}{\underset{CH_2}{\overset{O}{\overset{O}{\underset{CH_2}{\atopO}{\underset{CH_2}{\atopO}{\atopCH_2}{\overset{O}{\underset{CH_2}{\atopO}{\underset{CH_2}{\atopO}{\underset{CH_2}{\atopO}{\underset{CH_2}{\atopO}{\atopO}{\underset{CH_2}{\atopO}{\atopO}{\underset{CH_2}{\atopO}{\atopO}{\atopO}{I}{I}}}}}}}}}}}}}}}}}}}}}}$ | 7.21-7.33 (m) | 2.96 (t) | 3.71(t) | - | 2.22(t); 0.48; 0.71 (m) | 3.98- 4.08(m); 1.88(m) |
| 5 | PhS(CH ₂) ₂ OCH CC CH ₂) ₄ | 7.21- 7.37 (m) | 2.97 (t) | 3.71(t) | _ | 2.21(t); 0.48; 0.71 (m) | 3.60- 3.70(m); 1.53- 1.57(m) |
| 6 | $\underset{CH_2}{PhS(CH_2CH_2O)_2CH} \xrightarrow{C} \underset{CH_2}{\overset{O}{}} \underset{CH_2}{} \underset{CH_2}{\overset{O}{}} \underset{CH_2}{} \underset$ | 7.18- 7.34 (m) | 3.24 (t) | 3.71(t); 3.52(s) | _ | 2.20(t); 0.48; 0.73 (m) | 3.93- 4.04(m) |
| 7 | PhS(CH ₂ CH ₂ O) ₂ CH ₂ CCCO CH ₂ CCCO CH ₂ CCCCO CH ₂ CCCCO CH ₂ O | 7.17- 7.33 (m) | 3.25 (t) | 3.71(t); 3.55(s) | _ | 2.18(t); 0.48; 0.73 (m) | 3.99- 4.10(m); 1.87(m) |

| 8 | $PhS(CH_2CH_2O)_2CH C C C C C C C C C C C C C C C C C C $ | 7.19- 7.40 (m) | 3.25 (t) | 3.71(t); 3.56(s) | _ | 2.16(t); 0.48; 0.73 (m) | 3.63- 3.71(m); 1.54- 1.58(m) |
|----|---|-------------------|----------|---------------------|----------|-------------------------------|---------------------------------------|
| 9 | PhS(CH ₂) ₂ OCH—CCCH ₃ CH ₂ CH ₂ CCH ₃ | 7.21- 7.35 (m) | 3.20 (t) | 3.81(t) | 3.33 (s) | 2.21(t); 0.48; 0.73 (m) | _ |
| 10 | PhS(CH ₂ CH ₂ O) ₂ OCH C OCH ₃ CH ₂ CH ₂ CH ₂ | 7.22- 7.38 (m) | 3.21 (t) | 3.80(t); 3.46(s) | 3.31 (s) | 2.21(t); 0.48; 0.73 (m) | _ |

Polymerization in the presence of free radicals

The results of numerous investigations show that the synthesized monomers of vinyl cyclopropyl referring to the group of vinyl esters, are polymerized with great difficulty on the radical mechanism, and the reaction products consist of low-molecular compounds, i.e. oligomers. The monomers of this type are usually polymerized well on the cationic mechanism. However, the participation of the monomers synthesized by us in cationic polymerization has been connected with a number of difficulties. Thus, besides the vinyl group, a cyclopropane ring can also participate in the polymerization process. This leads to the formation of an insoluble fraction during the reaction. Therefore, it is difficult to investigate the mechanism of the cationic polymerization process of this type of monomers and to obtain polymer products with certain stable composition and structure.

Taking all this into account, we have carried out the radical polymerization process of vinyloxy- and (2-vinyloxy)ethoxy- substituted cyclopropyl acetals and investigated them with extensive use of the gas-liquid chromatography method. Chlorobenzene was used as an internal standard, the process was carried out at various concentrations of the monomer and initiator and temperature ranges. For carrying out of preliminary experiments, the various solvents (methylene chloride, diethyl ether, toluene) have been tested. The products obtained as a result of polymerization of the synthesized monomers (3-8) in the presence of radical initiators are highly soluble in polar solvents (DMF, THF, acetone, chlorinated hydrocarbons, etc.). The composition and structures of the obtained functional polymers have been determined by use of corresponding analytical methods, including spectral analysis. The polymerization process has been carried out in the presence of dinitrile azobisiso-fatty acid, benzoyl peroxide and tert-butyl peroxide at various temperatures both in the solvent (benzene) and in the mass. The obtained experimental results showed that the macromolecular compounds formed during polymerization have a relatively low molecular weight (independently of the reaction conditions, the average degree of polymerization is 15-30). During polymerization of monomer 3, the macromolecular compounds with higher average molecular weight are observed. This result has been determined by determination of the characteristic viscosity of the obtained oligomeric products and investigation of their gel-penetrating chromatograms.

It should be noted that the polymerization of monomers (3-10) occurs selectively due to the opening of the double bond, and the cyclopropylacetal groups in the side chain remain unaffected.

$$n \longrightarrow O (CH_2)_m \longrightarrow O (CH_2)_n$$

The polymerization process proceeds without an induction period and with sufficiently high yield. The obtained experimental results show that the polymer yield is low at low temperatures. The temperature rise also increases the polymer yield. Thus, the polymer yield for 6 h in the presence of dinitrile azo-*bis*-iso-fatty acid at 60° C is less than the yield obtained at 100° C. The conversion of monomers into polymers usually occurs with the participation of various elementary particles. Thus, the polymerization of monomers occurs on cationic, anionic or radical mechanisms, and the particles participated in the polymerization process can be carbocation, carbon or radicals. The functional groups in monomer molecules or alicyclic fragments containing strain bonds in the molecule influence on the reactivity of monomers during polymerization process. In the presence of functional groups with +J effect in its molecule, the reactivity of the monomer and also the yield of polymers as the end product (naturally, the polymerization reaction rate is increased in this case) is increased. In a case of groups with -J

effect, the reactivity of the monomer molecule is decreased and at the same time the reaction rate is also decreased

In this work, along with determination of the general regularities of the synthesized monomer taken for polymerization, the kinetics of the process, i.e. the factors influencing on the polymerization rate of the used monomer: on its concentration, as well as on the initiator concentration and the influence of the reaction temperature on the process has been studied.

It has been established that when the monomer density changes from 0.18 mol/l to 1.00 mol/l, its polymerization rate is increased from 1.22 mol/l sec to 7.10 mol/l sec.

At the same time, the results obtained from the investigation of the influence of the initiator concentration on the polymerization rate and temperature on the process course are presented in Table 4.

Table 4

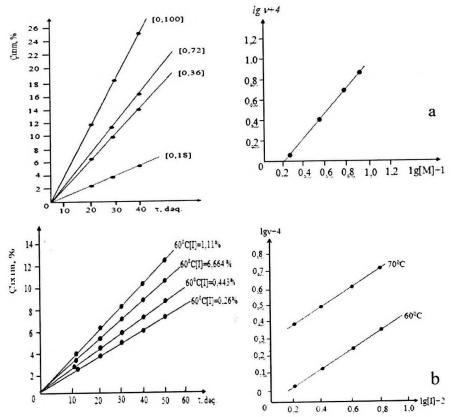
| N⁰ | [M], mol/l | [AİBN], mol/l | T,K | $\vartheta \cdot 10^4 \text{ mol/l·sec}$ |
|----|------------|---------------|-----|--|
| 1 | 1.0 | 0.0152 | 333 | 1.262 |
| 2 | "" | 0.0256 | "" | 1.59 |
| 3 | "" | 0.0384 | "" | 1.92 |
| 4 | "" | 0.0640 | "" | 2.64 |
| 5 | "" | 0.0152 | 343 | 2.62 |
| 6 | "" | 0.0256 | "" | 3.03 |
| 7 | "" | 0.0384 | "" | 3.94 |
| 8 | "" | 0.0640 | "" | 5.29 |
| 9 | 0.18 | 0.075 | 343 | 1.22 |
| 10 | 0.36 | "" | "" | 2.57 |
| 11 | 0.72 | "" | "" | 5.03 |
| 12 | 1.00 | "" | "" | 6.69 |
| 13 | 1.00 | 0.0152 | 333 | 1.27 |
| 14 | "" | "" | 338 | 1.77 |
| 15 | "" | "" | 343 | 2.61 |
| 16 | "" | "" | 348 | 4.28 |
| 17 | "" | "" | 353 | 7.63 |

Kinetics of polymerization reaction

Based on the obtained experimental results, a graphics of the dependence of the polymer concentration (x) on the polymerization time has

been constructed and the polymerization rate on the angle tangent value of the obtained angular dependence has been determined. The dependences of the logarithm of the polymerization rate on the logarithms of the concentrations of the monomer and initiator have the form of a straight line (Fig. 2).

According to these dependences, the reaction order has been determined both on the monomer and on the initiator.



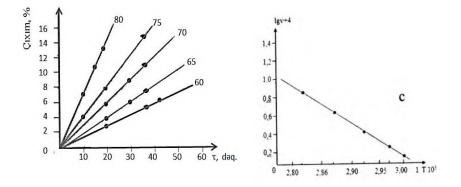


Fig.2. Dependence of the polymerization rate on the monomer density (a), the initiator density (b), the influence of temperature (c)

The activation energy of the process has been determined using the Arrhenius equation based on the graphics of the temperature dependence of logarithm of the polymerization rate at various temperatures. The general kinetic equation of the reaction

$W = k[M]^{1.0}[J]^{0.5}$

For example, the activation energy value of the polymerization reaction of (2-vinyloxy-)ethoxy-4,7-dioxaspiro-[4,2,0] heptane is 78.80 kJ/mol.

Table5

| Monomer code | Τ, ⁰ C | Type of initiator | Quantity of initiator, mol % | Yield of polymer, % | [η]**, dl/g | MW*** |
|-----------------|-------------------|-------------------|------------------------------|------------------------|-------------|-------|
| | 60 | AIBN | 0.5 | 42 | 0.481 | 2800 |
| 3 | 80 | BP | 0.3 | 37 | 0.465 | 2700 |
| | 120 | DTBP | 0.3 | 48 | 0.353 | 2000 |
| | 60 | AIBN | 0.6 | 38 | 0.435 | 2500 |
| 4 | 80 | BP | 0.3 | 33 | 0.386 | 2200 |
| | 120 | DTBP | 0.3 | 47 | 0.356 | 2100 |
| 5 | 60 | AIBN | 0.6 | 17 | 0.356 | 2000 |

Conditions and results of radical polymerization of synthesized monomers 3-10 (polymerization time - 48 hours*)

| 6 | 60 | AIBN | 0.6 | 39 | 0.379 | 2200 |
|----|----|------|-----|----|-------|------|
| 7 | 80 | BP | 0.3 | 32 | 0.360 | 2100 |
| 8 | 80 | BP | 0.3 | 30 | 0.352 | 2000 |
| 9 | 60 | AIBN | 0.6 | 49 | 0.495 | 2900 |
| 10 | 80 | BP | 0.3 | 41 | 0.482 | 2800 |

* – The polymerization time at 60°C for 3,4,5 monomers is 30 hours;

** – 0.5 g in 100 ml was determined in tetrahydrofuran at 20° C

*** – It was calculated based on the values K= $3.98 \cdot 10^{-4}$ and $\alpha=0.75$.

An increase of the initiator concentration during polymerization does not practically influence on MW of the polymer and its characteristic viscosity. In some cases, it even increases the quantity values. This becomes evident from the results of GC analysis of the obtained polymers. MW of the obtained polymers is not changed even with increase of the polymerization time. Only an increase of the polymerization time influences on the yield of the obtained polymers and increases them.

For establishment of the dependence between the structure of the synthesized monomers (3-10) and their polymerization ability, the polymerization of these monomers has been carried out under the same conditions and in the presence of the same initiator (initiator – AIBN, solvent – toluene, $\tau - 5$ h, t = 70°C). It has been established that monomer 3 has high activity, and monomer 8 – the least activity.

An increase of a number of members in the rings of the acetal group in cyclopropane fragments somewhat decreases their reactivity. So, the activity is decreased during the transition from monomer 3 to monomer 5 and from monomer 6 to monomer 8. The most active monomer is 5-membered acetal ring, and the weakest - 7-membered acetal ring. It can be assumed that such activity of monomers has been connected with spatial difficulties caused by acetal groups.

Polymerization in the presence of cationic catalysts

The cationic polymerization of the synthesized vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetal monomers (3-10) in the presence of BF_3 ·O(C₂H₅)₂ catalyst has been carried out both in mass and in solution (in various solvents) at low temperatures. It has been established that

the polymer obtained during the polymerization process in the mass has both a regular spatial structure and high molecular weight indices..

The cationic polymerization of monomers 3-10 has been carried out in the presence of $BF_3 \cdot O(C_2H_5)_2$ catalyst in ether at -15 ^{0}C , in CH_2Cl_2 solution at -40 ^{0}C and in toluene at -75 ^{0}C in a dry nitrogen atmosphere. The conversion has been controlled using GL chromatography (internal standard – chlorobenzene). The results of the carried out experiments showed that the induction period during polymerization is not observed, and the yield of polymer products due to the monomer is almost quantitative.

The obtained results indicate that the polymerization of acetalsubstituted cyclopropyl monomers (3-10) occurs due to the opening of the double bond of the vinyl group and the polymers with functionally substituted cyclopropyl groups in the side chain are obtained:

$$= \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{n} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{CH_{2}CH_{2}} \underbrace{\bigcirc}_{m} \underbrace{\xrightarrow{BF_{3}O(C_{2}H_{3})_{2}}}_{nO} \underbrace{\bigcirc}_{nO} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{n} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{CH_{2}CH_{2}} \underbrace{\bigcirc}_{m} \underbrace{\bigcirc}_{nO} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{CH_{2}CH_{2}} \underbrace{\bigcirc}_{m} \underbrace{\bigcirc}_{nO} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{CH_{2}CH_{2}} \underbrace{\bigcirc}_{m} \underbrace{\bigcirc}_{O} \underbrace{O} \underbrace{\bigcirc}_{O} \underbrace{\bigcirc}_{O} \underbrace{$$

In spite of the fact that the polymerization process proceeds with the opening of double bonds, an insoluble fraction also participates in the reaction products. These products, formed in small quantities and having a closed structure, have been most likely connected with the opening of the cyclopropane or acetal ring.

The polymerization conditions of the synthesized monomers (3-10) in the presence of the cationic catalyst and some indices of the obtained polymers are presented in the following Table.

Table 6

Polymerization conditions and obtained results of vinyloxy- and (2vinyloxy)ethoxy substituted cyclopropylacetal monomers (3-10) in the presence of

a cationic catalyst $(BF_3O(C_2H_5)_2)$

| N / | | Quantity of | | Yield of p | olymer,% | ſ]¥ | |
|-------------------|-------|-----------------------------|------------|------------------|--------------------|---------------|------|
| Monomer's code | T, ⁰C | initiator, Solvent mol % | | Soluble fraction | Insoluble fraction | [η]*, dl/g | MW** |
| 3 | -40 | 3.5 | CH_2Cl_2 | 80.2 | 16.2 | 0.11 | 1800 |
| 3 | -70 | 5.0 | toluol | 46.0 | 18.6 | 0.153 | 2900 |
| 4 | -60 | 3.0 | toluol | 82.0 | 15.8 | 0.14 | 2500 |
| 5 | -70 | 4.5 | toluol | 83.2 | 15.6 | 0.17 | 3200 |

(polymerization time – 30 hours)

| 6 | -40 | 4.0 | CH ₂ Cl ₂ | 75.6 | 17.0 | 0.12 | 2000 |
|----|-----|-----|---------------------------------|------|------|------|------|
| 7 | -60 | 3.5 | toluol | 76.0 | 17.2 | 0.13 | 2200 |
| 8 | -70 | 5.0 | toluol | 77.0 | 16.6 | 0.15 | 2800 |
| 9 | -40 | 4.0 | CH_2Cl_2 | 80.3 | 15.6 | 0.14 | 2500 |
| 10 | -60 | 3.5 | CH_2Cl_2 | 82.2 | 14.8 | 0.16 | 3000 |

*-0.5 g in 100 ml was determined in tetrahydrofuran at 20°C;

** – It was calculated based on the values K=3.98 $\cdot 10^{-4}$ and α =0.75.

The obtained polymers are well soluble in polar solvents – DMFA, THF, chlorinated aliphatic and aromatic hydrocarbons.

Copolymerization with maleic anhydride

The investigations showed that the composition of polymer products obtained by copolymerization of vinyl esters with maleic anhydride in the initial mixture of monomers always remains practically constant, and the elementary links formed from various monomers are in equimolar ratios (Table 7). The comparison of the values of characteristic viscosity $[\eta]_{char.}$ shows that the molecular weight of copolymers obtained by copolymerization of vinyl esters with maleic anhydride at ratio of monomers 1:1 is higher than the molecular weight of copolymers obtained under conditions differing from the equimolar molar ratio of monomers (Table 7), so, in other cases, $[\eta]_{char.}$ values of copolymer is somewhat lower.

Table 7

Copolymerization with monomers of vinyloxysubstituted cyclopropyl acetal – (M_1) , maleic anhydride – (M_2)

Composition of [η]*, Composition of the initial monomers. Yield, % MW** M_1 code copolymer, mol.% dl/g mol.% $[M_1]_0$ $[M_2]_0$ $[M_1]_t$ $[M_2]_t$ 90.0 10.0 8.6 50.1 49.9 0.41 2350 70.0 30.0 10.8 50.0 50.0 0.42 2400 3 50.0 15.2 0.46 50.0 50.0 50.0 2700 0.43 30.0 70.0 12.1 49.9 50.1 2500

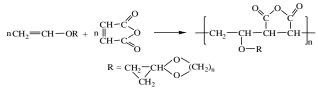
([I]= $0.02 \text{ mol/l}, \text{T}=70^{\circ}\text{C}, \text{ solvent} - \text{benzene}$).

| | 10.0 | 90.0 | 9.4 | 49.8 | 50.2 | 0.39 | 2250 |
|---|------|------|------|------|------|------|------|
| | 90 | 10 | 3.2 | 54.3 | 45.7 | 0.40 | 2300 |
| | 70 | 30 | 6.8 | 53.2 | 46.8 | 0.41 | 2350 |
| 4 | 50 | 50 | 14.7 | 52.8 | 47.2 | 0.42 | 2400 |
| | 30 | 70 | 11.0 | 54.5 | 45.5 | 0.41 | 2350 |
| | 10 | 90 | 7.2 | 52.0 | 48.0 | 0.38 | 2250 |

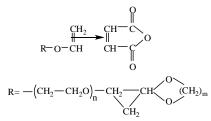
*-0.5 g in 100 ml was determined in tetrahydrofuran at 20°C;

** – It was calculated based on the values $K=4.11 \cdot 10^{-4}$ and $\alpha=0.89$.

The maximum rate of the copolymerization process with an equimolar ratio of comonomers is explained by the formation of molecular complexes as a result of donor-acceptor interaction of comonomers. So, as a result of the decisive role and participation of this type of complexes in the phase of elongation of copolymerization, the copolymer macromolecules of regular alternating structure are formed.



In the IR spectra of the obtained copolymers, the absorption bands belonging to the anhydride group at frequencies of 1765-, 1845 cm⁻¹ and absorption bands at frequency of 1020-1050 cm⁻¹ belonging to the threemembered ring have been registered. However, the absorption band at frequency of 1640-1645 cm⁻¹, characterizing C = C bond is not observed in the spectrum. Thus, it can be concluded based on the obtained results of the study of IR spectra that the copolymerization process of the investigated compounds with maleic anhydride proceeds in the direction of preparation of copolymers of a linear structure with the participation of their double bonds. So, the electron density of π -bond in the monomer molecule of vinyl cyclopropyl ester is increased due to the electron-donor cyclopropoxy-group, and, as a consequence, at their radical copolymerization with maleic anhydride, the possibility of formation of π - π complexes increases:



It should be noted that there are no essential differences in the IR spectra of copolymers obtained at various ratios of the initial monomers. This indicates that the copolymerization process proceeds with the participation of both comonomers, independently of the molar ratio of the initial comonomers and the depth of copolymerization, and the copolymers with an equimolar link content are obtained.

It is also seen from the indices in Table 8 that independently of the initial relative quantities of the initial comonomers, the copolymers obtained in all cases have an equimolar link content, which is characteristic for the copolymerization processes of monomers of electron-donor nature in the presence of maleic anhydride. Based on the values in Table, the copolymerization constants r_1 and r_2 have been calculated on the Feynman-Ross method.

The copolymerization of the synthesized monomers with maleic anhydride is accompanied by the formation of a weak donor-acceptor complex between the initial comonomers.

Table 8

Equilibrium constants of complexes formed during copolymerization of vinyloxy- and (2-vinyloxy)ethoxy substituted cyclopropyl acetals with maleic anhydride

 \cap

| | m(H | H ₂ C) | | | ∖ ►[| | |
|------------|-----|-------------------|------|------------------------|-------------|----------|------|
| Compound's | R | ł | | K _t , l/mol | | ΔΗ, | ΔS, |
| code | Ν | m | 25°C | 45 ⁰ C | 60°C | kcal/mol | e.u. |
| 3 | 0 | 2 | 0.24 | 0.19 | 0.15 | 1.175 | 6.06 |
| 4 | 0 | 3 | 0.26 | 0.20 | 0.16 | 1.183 | 5.84 |
| 5 | 0 | 4 | 0.28 | 0.22 | 0.18 | 1.105 | 5.50 |
| 6 | 1 | 2 | 0.25 | 0.23 | 0.20 | 1.160 | 5.92 |

| 7 | 1 | 3 | 0.23 | 0.22 | 0.20 | 1.165 | 6.02 |
|----|---|---|------|------|------|-------|------|
| 8 | 1 | 4 | 0.22 | 0.20 | 0.17 | 1.171 | 6.14 |
| 9 | 0 | I | 0.22 | 0.18 | 0.16 | 0.798 | 5.44 |
| 10 | 1 | | 0.21 | 0.19 | 0.16 | 1.173 | 5.74 |

The chemical shift of protons of maleic anhydride in the presence of these monomers confirms the formation of a donor-acceptor complex. The complex-formation constant values (K_p , l/mol) of complexes formed by the used comonomers with maleic anhydride at 25^oC are 0,21÷0,28 mol/l, respectively (Table 8).

In determination of the composition of the investigated complex using the PMR spectrum, observing the linear dependence of $\frac{1}{\Delta}$ on $\frac{1}{[D]}$, it is seen that the

complex is in a molar content of 1:1.

It can be seen from Table 8 that the changes in the structure of the donor monomer strongly influence on the complex-formation constant. Thus, the radical copolymerization of maleic anhydride with vinyloxy-*gem*-dichlorocyclopropane and its cyclic acetal leads to the formation of regularly structured copolymers containing reactive anhydride fragment and cyclopropane ring undergoing the stage of complex-formation with charge transfer.

Practical use of vinyloxy- and (2-vinyloxy)ethoxycyclopropyl acetals and products based on them

The synthesized initial compounds, adducts, homo- and copolymers obtained on their basis, developed composition materials have been tested for determination of their physical-chemical and physicalmechanical parameters and the possibilities of their application in areas corresponding to their parameters have been determined.

1. The results of experimental investigations showed that the tested samples 4a (2-vinyloxy-4,8-dioxaspiro-[2,5,0]-octylphenyl sulfide), 4b (ethylene-bis-(vinyloxy-4,8-dioxaspiro-[2,5,0]-octyl)sulfide, 7a (2-vinyloxy-)ethoxy-4,8-dioxaspiro-[2,5,0]-octylphenyl sulfide and 7b (ethylene-bis-(2-vinyloxy-)ethoxy-4,8-dioxaspiro-[2,5,0]-octyl)sulfide samples have antimicrobial and antifungal properties. So, the compounds 4a and 7a showed the greatest activity against

golden staphylococcuses (*Staphylococcus aureus*). The destructive effect of these adducts is observed in these substances at concentration 1:400 and after 20 min. This effect occurs after 40 min., when the concentration changes by 1:800. It has been established that the investigated compounds show higher antimicrobial properties than ethyl alcohol, rivanol, furacillin, nitrofungin possessing known antimicrobial properties. This effect is slightly weaker than effect of chloramine. Considering the above-mentioned one, one can use the investigated compounds as antiseptics and prepare the biocidal composition materials on their basis.

2. The crosslinking process of modified copolymers under the action of photoradiation has been investigated and the degree of crosslinking of the irradiated copolymer layers has been determined. In this case, the copolymers with different degrees of esterification were used, and layers of the required thickness were prepared from their solutions of various concentrations.

In the dichloromethane solution of the modifier (vinyl carbinol) used in the modification of the copolymer, the absorption band with a maximum of 204 nm is observed in the UV spectrum, which is directly connected with the availability of a vinyl group. Due to UV rays, the intensity of this absorption band decreases depending on the irradiation duration.

The changing of the intensities of the absorption bands depending on time have been also recorded using IR spectra. For this, the changing of the relative intensities of the absorption band at 980 cm⁻¹ (for C = C-double bond) has been taken into account. It should be noted that 2 min. after the irradiation period, the obtained thin polymer layers lose solubility. This is directly connected with the participation of the double bonds in the crosslinking irradiation process.

It has been determined that the maximum degree of crosslinking of copolymer samples is 90% and is completed after 40 sec.

Along with photochemical conversions of the modified copolymers, the thermal conversions are also important. The fact that the modified copolymers have high polymerization activity under the influence of UV rays allows them to be used in the creation of photo- and electronic resists.

3. For determination of the suitability of the synthesized adducts as plasticizers for PVC, their freezing temperatures have been firstly determined (Table 9). Then the thermal stability of these compounds and compositions prepared in the presence of polyvinyl chloride has been determined at 180^oC. It has been shown that the thermal stability and some other properties of

compositions on the basis of PVC in the presence of adducts exceed the corresponding properties of compositions made with the participation of the well-known plasticizer DDPh (Table 9).

Table 9

| | Prepared bis-adduct | | | | |
|--------------------------------------|---------------------|-------------|-------------|--|--|
| Indices | From | From | DDPh | | |
| | monomer 5 | monomer 7 | DDFII | | |
| Color | Straw | Light straw | Light straw | | |
| Density at 20°C, g/cm ³ | 0.9435 | 0.9420 | 0.9700 | | |
| Refraction index at 20°C | 1.4510 | 1.4530 | 1.479-1.484 | | |
| Acid number, mg KON/g | — | — | _ | | |
| Viscosity, cPz, at 20°C | 12.68 | 13.60 | 13.82 | | |
| Flash temperature, ^o C | 188 | 219 | 232 | | |
| Freezing temperature, ^o C | -68 | -65 | _ | | |
| Quantity of volatile substances, % | 0.270 | 0.116 | 0.026 | | |
| (for 6 hours at 100°C | 0.270 | 0.110 | | | |
| Saponification number, mg KON/g | _ | _ | 249 | | |

Some properties of *bis*-adducts of the mixing reaction of acetal-substituted cyclopropyl vinyl esters with EDT

The tensile strength and specific elongation on the basis of compositions of PVC are changed depending on the quantity of bis-adduct plasticizer as follows: when the quantity of bis-adduct plasticizer changes by $5\div40\%$ mass%, the tensile strength of the obtained compositions is $19.9\div23.2$ MPa, and the specific elongation is $295\%\div240\%$.

The physical-mechanical parameters of the polymer layers or plasticizers made on the basis of PVC with use of bis-adducts are very close to the parameters of plasticizers prepared in the presence of standard DDPh. In some cases, their tensile strength, elongation and modulus (100%) values are slightly higher. From the point of view of frost resistance, the compositions on the basis of PVC with the participation of bis-adduct are preferable.

RESULTS

1. The various vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetals have been synthesized, their composition and structure have been determined, the model addition reactions with mono- and dithiols

in the presence of free radicals have been carried out, homo- and copolymerization reactions have been realized, the areas of application of low- and high-molecular compounds have been determined [1,2,4,17].

2. 1,1-gem-dichlorosubstituted cyclopropyl-containing vinyl esters by the interaction of divinyl ether and divinyl ether of ethylene glycol with dichlorocarbene obtained by hydrolysis of chloroform in the presence of alkali, in the condition of interphase catalysis have been synthesized and their compositions and structures have been determined. It has been shown that depending on the ratio of the initial components, the reaction proceeds in the direction of preparation of mono- and bis-1,1-gem-dichlorosubstituted cyclopropyl adducts. The reaction carried out at 40°C at ratio divinyl ether:chloroform = 1:1, with the participation of TEBA, proceeds in the direction of preparation of mono-adducts with high yield [1,5,9,10].

3. The corresponding cyclopropyl acetals have been obtained by the interaction of vinyloxy- and (2-vinyloxy)ethoxy-substituted 1,1-dichlorocyclopropanes with glycols in the presence of NaH and their addition reactions with mono- and dithiols in the presence of free radical initiator and it has been established that as a result of the reaction the monoadducts are formed with thiophenol, and with ethandithiol – biadducts. The structure of the obtained sulfur-containing acetal-substituted cyclopropane esters has been confirmed by spectroscopic methods [3,14].

4. The polymerization process of synthesized vinyloxy- and (2-vinyloxy)ethoxy-substituted cyclopropyl acetal monomers in the presence of radical initiators and cationic catalysts has been investigated and it has been shown during these reactions that the low molecular weight oligomers are obtained, only vinyl groups of the synthesized monomers participate in the polymerization process and the reaction proceeds due to the opening of C=C double bond, while the acetal-substituted cyclopropane rings remain unaffected [6,7,8,17].

5. The kinetics of radical homopolymerization of (2-vinyloxy)ethoxy-4,7-dioxaspiro-[4,2,0]heptane has been investigated and it has been established that during polymerization in solution (in a benzene medium) in the presence of dinitrile azo-*bis*-iso-fatty acid, the reaction order was 1.0 on the monomer, on the initiator – 0.5, which corresponds to the regularities of free radical polymerization of most vinyl monomers. 6. The copolymerization reactions of vinyloxy- and (2vinyloxy)ethoxy-substituted cyclopropyl acetal monomers with maleic anhydride has been studied and it has been established that independently of the ratio of the initial monomer mixtures, the equimolar copolymers are obtained in all cases, the process is accompanied by the formation of intermediate complexes of the donor-acceptor type. The parameters characterizing the process (r_1 . r_2 , Q, e) have been determined, the equilibrium constant values of the forming complexes have been determined by spectroscopic methods, and the values of thermodynamic parameters have been calculated [5,12].

7. There have been determined the possibilities of use of the synthesized monomers, adducts, homo- and copolymers and composition materials based on them and it has been shown that:

- The initial monomers, S-containing adducts and copolymers formed with maleic anhydride, have biologically active properties [15,18];

- The compositions on the basis of PVC in the presence of adducts of the synthesized monomers and thiols have biocidal properties [15,16];

- Anhydride-containing copolymers can form the thin polymer films and are suitable for use in the preparation of photoresists in photolithographic processes [11];

The results of the dissertation are presented in the following scientific papers:

1. Alıyeva, Ş.H. Viniltsiklik asetaləvəzli tsiklopropil efirlərinin sintezi və polimerləşməsi / Ş.H.Alıyeva, R.Z.Şahnəzərli, A.M.Quliyev //Akademik A.A.Əfəndiyevin 75 illik yubleyinə həsr olunmuş Makromolekullar kimyasının fundamental və tətbiqi polimerləri Respublika elmi konfransının materialları, -Sumqayıt: – 27-28 iyun. – 2013. – s.64-65.

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