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ABSTRACT

of the dissertation for the degree of Doktor of Science

INVESTIGATION OF THE STRUCTURAL INHOMOGENEITY IN MACROMOLECULES AND CREATION OF POLYMERS WITH REGULATED PROPERTIES ON THEIR BASIS

Speciality: 2304.01 – Chemistry of macromolecules

Field of science: Chemistry

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INTRODUCTION

Actuality and degree of development of the dissertation work: The synthesis of polymers with given properties and creation of materials on their basis one of the actual directions of modern polymer chemistry. The structural inhomogeneity, being an important property of polymers, includes inhomogeneity on molecular weight (molecular weight distribution – MWD), on number and type of end functional groups – distribution on types of functionality (DTF), on topological structure of the macrochain (availability of linear, branched and cyclic macromolecules), and in a case of copolymers – distribution along length of the polymer blocks, etc[1].

In this connection, for the development and improvement of the synthesis methods, it is necessary to establish a bond between structural inhomogeneity and properties of the polymers. Thus, an actuality of study of the structural inhomogeneity has been connected with problem of development of the directed synthesis of the polymers of regulated structure[2]. In solution of this problem, the methods of high-performance liquid chromatography (HPLC), namely, exclusive and adsorption HPLC (ELC and ALC), occupy a special place. In order to characterize various types of the structural inhomogeneity, a combination of various chromatographic methods and detectors selective for a defined type of inhomogeneity is also used. This method is often called multidimensional chromatography. Critical chromatography or chromatography at the point of phase transition from adsorption of macromolecules to exclusion is currently purposefully used for to study of special types of structural heterogeneity, such as heterogeneity on end groups, on the composition of copolymers, in topology.

When elucidating the mechanism of polymerization processes, a complex study of various types of structural in

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[1] Kricheldorf, Hans. Polycondensation. History and new rezults / Hans Kricheldorf – Hamburg: Springer – 2014. – 302p.`

[2] Rovkina N. M. Chemistry and technology of polymers. Preparation of polymers by methods of polycondensation and polymer-analogous transformations. / N. M. Rovkina, A. A. Lyapkov. - St. Petersburg: Lan, - 2019. - 432 p.

homogeneities is of great importance, which has received little attention in the known literature.

The determination of the distribution of structural heterogeneity in the composition of a number of synthesized and existing polymers compounds in this work, allows, to obtain polymer and polymer-composite materials with high operational properties for various purposes, biologically active polymer-based materials, as well as antimicrobial drugs of various effects, etc, by targeted carrying out of polymer–anologous conversations.

Objects and subject of research. The objects of study of the dissertation work were polymers of different classes - oligoazomethinephenols and metal polymer complexes on their basis, oligoepichlorohydrins, phenolformaldehyde oligomers, oligoacrylates, episulfide oligomers, olgosulfoimides, furan resins, polyethylene and oligomers of α-olefins, polyesters of various classes, natural polysaccahides, etc. The subjects of the study is the study of the structural heterogeneity of these polymers.

Purpose of dissertation work: Study of the structural inhomogeneity of the above-mentioned classes of polymers and investigation of interrelation of molecular inhomogeneity with synthesis conditions for purpose of directed regulation of properties of the end products.

Development of new effective chromatographic systems allowing to analyze the various types of the structural inhomogeneity of macromolecules appearing during polymerization as well as destruction processes of the polymers, which could reveal the regularities proceeding in fundamental and side reactions.

Using combined or multidimensional HPLC including, in particular, two-detector ELC and ALC at normal and reversed phases, in isocratic and gradient (critical chromatography) modes of elution, to characterize the occurring conversions of products formed during intra- and intermolecular interaction of macromolecules in a number of polymer (oligomer) systems tested in work.

Quantitative assessment the possibility of separation of certain fractions with various functional structure and parameters of

MWD and to establish control for their formation depending on the synthesis conditions.

Scientific novelty: By a method of multidimensional chromatography with combination of various variants of two-detector ALC and ELC in the composition of the investigated oligomers, there have been established such types of inhomogeneity as MWD, DTF, on topology, distribution of macromolecules on the isomer structure, etc.

With the use of critical HPLC in the composition of epichlorohydrin oligomerization products, it has been fixed in parallel a distribution on MW and functionality, 7 types, including one cyclic and 6 linear bifunctional macromolecules with various MWD parameters have been detected.

Two-detector chromatographic system has been developed, due which it was possible to determine the distribution on isomer structure in the composition of side oligomer fractions formed during amination of α-olefins.

According to the results of chromatographic investigations and spectral analyses the properties of MWD and DTF of nonionic SAS on the basis of alkoxy derivatives and alkylolamides of naphthenic acids have been studied, bi- and trifunctional macromolecules with end OH and COOH groups in various combinations have been revealed and their bond with SAS properties has been established.

Parallel interpretation of the readings of various detectors allowed to establish three types of structural inhomogeneity – on MWD, DTF, as well as on topological structure in the composition of the secondary product of high-pressure PE and consequently, two types of branched macromolecules consisting of functional (double bond) and non-functional (without double bond) fragments of polyethylene macromolecules have been detected.

MWD and fractional compositions of natural polysaccharides and polyacetylenes formed during microbiological synthesis with basidial fungi have been also studied in the multidimensional chromatographic system using two-detector ELC and ALC.

Theoretical and practical value: The carried out investigations have a theoretical and practical value since the obtained results show the possibility of regulation of properties and composition of polymers and also materials on their basis by study of the structural inhomogeneity in the various synthesis conditions

The obtained results of investigation of the structural inhomogeneity in the various reaction conditions can be used in preparation of the following oligomers with given structural parameters and different fractional compositions: oligoaminopyridines, oligophenylazomethinephenols and polymer metal complexes on their basis, low-molecular polyacrylates, low-molecular oligomers of α-olefins, polyesters on the basis of synthetic and oil naphthenic acids, oligoepichlorohydrins, oligosulfoimides, sulphur-containing linear polyamines, halogen-containing unsaturated polyesters on the basis of hexachloronorbornene dicarboxylic acid and also in the synthesis of phenolformaldehyde oligomers modified by nitrogen-containing organic compounds and products of their high temperature interaction with soybean oil, etc.

The results of study of the structural inhomogeneity of the secondary product of high-pressure polyethylene (HPPE) production, as well as the products of the secondary processing of materials on the basis of polyethylene have a practical value.

The developed chromatographic method of investigation of the formation process of the natural polymers and individual organic substances by micromycetes (basidiomycetes, etc.) by microbiological degradation opens up the possibility of synthesis of the individual organic compounds in a technologically easy way, which does not require large economic costs.

Many of the investigated objects are important both from a practical and fundamental point of view and can be used in the study of regularities of various processes of polycondensation, cationic polymerization of organic oxides, processes of synthesis of oligomers of low-molecular α-olefins, side reactions of production of a number of industrial polymers, aging processes during exploitation of the polymer materials, and also in the study of the microbiological synthesis processes of natural polymers, etc.

Personal contribution of the author. The work of Bektashi N.R. is an independent scientific-research work, which testifies to the professional competence of its author. The applicant has independently determined the purpose and tasks of the investigations, has correctly selected and skillfully used the set of chromatographic methods of analysis corresponding to the task, has directly participated in carrying out of the experiments in all sections of the work, has analyzed and generalized the results of investigations and has laconically formulated the conclusions.

The following positions are made for defense (shall be defended):

1. In the conditions of oxidative polycondensation by means of air oxygen and NaOCI in water-alkaline medium, the preparation of oligoaminopyridines and oligophenols with Schiff's substituents and their polymer complexes with two-valence transition metals (Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Pb^{2+}) with regulated MWD parameters, possessing high heat- and thermal stability, magnetic sensitivity and antibiotic activity against a number of testmicrocultures.

2. In the presence of recirculated chloroaluminate ionic liquids, and also in their combination with Ti-containing complexes with grafted “ion-liquid” ligands, the oligomerization of α-olefins with oligoalkyl naphthenic structure with low polydispersity and regulated molecular-mass characteristics.

3. Photoelectrochemical synthesis of oligosulfoimides, oligoacrylates, furan resins, binary and ternary copolymers of MA with α-olefins and (meth)acrylic acid, and also the preparation of oligomers on the basis of polyaminothiocarbamide macromonomers with regulated MWD parameters and functionality.

4. Results of the investigation of the structural inhomogeneity of oligoepichlorohydrins synthesized in a medium of methyl benzenes by a method of two-detector exclusion and critical chromatography and also polycondensation of anhydride of norbornene dicarboxylic acid with propylene glycol and methacrylic acid, allowing to obtain the bifunctional oligomers of different type and various MWD parameters.

5. Synthesis of polyfunctional polymer complexes on the basis of polyamines and thiocarbamide containing episulfide heterocycles, nitrile, amine and amide groups as well as fragments of quaternary amines and chlorine in macrochain, allowing to establish the necessary conditions of preparation of the polymer complexes with given functionality and MW.

6. Results of the investigation (multidimensional chromatography – ELC, ALC) on study of inhomogeneity of the low-molecular side products of HPPE production, products of amination of α-hexene, nonionic SAS on the basis of oil naphthenic acids and polyglycols and also natural polysaccahrides and polyacetylenes obtained in biosynthesis process, the sources of which were basidiomycetes of the genus *Ganoderma lucidum* and *Pleurotus ostreatus.*

Approbation of the work. Based on the materials of this work, the papers have been presented at the following National and International scientific conferences: XIII, XVI, XXIII, XXIV, XXV National Chemistry Congress (Samsun-1999, Konya – 2002, Sivas – 2009, Zonguldak – 2010, Erzurum – 2011, Yalova-2023), 9 National chromatography congress (Trabzon, 2009), V and IX Baku International Petrochemical Conference dedicated to the memory of academician Yu.G.Mamedaliyev (Baku, 2002, 2016), International Workshop/Conference, Liquid Chromatographic Procedures for Separation of Macromolecules (Bratislava, 2001), Republic Scientific Conference dedicated to 95th and 110th anniversary of academician M.F.Nagiev (Baku, 2003 and 2018), 21 National Biology Congresses with International participation (Bishkek, 2012). IX International Scientific-practical Conference “Latest scientific achievements" (Sofia, 2013), V Ulusal Polimer Bilim ve Teknolojisi kongresi (Tokat, 2014), V International conference-schools on chemistry and physical chemistry of oligomers (Volgograd, 2015), International Scientific Conference dedicated to 50th jubilee of Institute of Polymer Materials, ANAS, (Sumgait, 2016), XII International conference-schools on chemistry and physical chemistry of oligomers “Oligomers – 2017” (Chernogolovka, 2017), International Scientific-technical Conference dedicated to 100th anniversary of academician B.G.Zeynalov (Baku, 2017). International conference "Modern problems of science and education" (Moscow, 2020) IX international conference on the physical chemistry of plant polymers (Arkhangelsk, 2021). Republican conference dedicated to the 90th anniversary of academician S. Aliyev (Baku, 2023).

Publications on the topic of the dissertation. The results of the investigations have been reflected in 60 printed works, including 36 papers in national and foreign scientific publications, 24 abstracts of papers of national and international conferences.

Structure and scope of the dissertation. The dissertation consists of contents, list of symbols, introduction, general characteristics of the work, 5 chapters, conclusion and 282 references. The dissertation is presented on 285 pages of typewritten text, including 70 figures and 48 tables. The total number of characters in the dissertation work (excluding tables, figures and references) is 308956 characters, including 34313 (first chapter), 10052 (second chapter), 137553 (third chapter), 55415 (fourth chapter), 51523 (fifth chapter) and 6672 characters (conclusions).

In the introduction, the author substantiates the actuality of the topic, defines the object and subject, the purpose and tasks of the investigation, methodological bases, scientific novelty, theoretical and practical value**.**

In the first chapter a review and analysis of the literature devoted to the study of the structural inhomogeneity of polymers has been presented. The review is in chronological order.

In the second chapter the peculiarities of practical application of these methods have been considered, the concrete chromatographical conditions of carrying out of the analyses have been presented, and also a brief description of objects and other physical-chemical methods of the investigation is provided.

The third chapter has been devoted to the investigation of molecular-weight distribution of the polymers by a method of exclusion liquid chromatography in the mono-detector system.

In the fourth chapter the results of the investigation of the structural inhomogeneites of the polymers carried out by a method of two-detector liquid chromatography are presented.

In the fifth chapter the results of complex study of various kinds of the structural inhomogeneites in multidimensional chromatographical system are presented.

In conclusion, the main results and conclusions obtained in the dissertation have been listed, and also a list of references has been presented.

MAIN CONTENT OF THE WORK

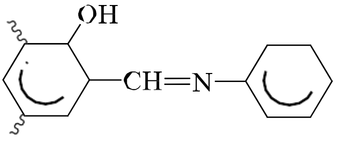
1. Investigation of inhomogeneity of polymers on MW by a method of ELC in mono-detector chromatographic system

The traditional method of determination of MW and MWD of polymers is size exclusion or gel-permeation chromatography with use of refractometric detector. During analysis, information about the molecular inhomogeneity of the polymer is obtained by means of a refractometric detector. The results of investigations of MWD of the polymers synthesized by various methods of polymerization are presented below.

1.1. Synthesis and investigation of MWD and structure of oligophenylazomethine phenol and metal complexes on its basis

The exclusion-chromatographic investigations of MWD of oligomerization products of phenylazomethine phenyl (PhAMPh) (Fig.1) showed that oligophenylazomethine phenol (OPhAMPh-1) consists of mixture of di- and trimers, and other two fractions (OPhAMPh-2, OPhAMPh-3) are the oligomers with M_n and M_w 880, 920 and 2070, 2200), respectively. A degree of polydispersity of these compounds are high and vibrated in small ranges M_w / M_n =2,35-2,4. Unlike OPhAMPh-1, OPhAMPh-2 and OPhAMPh-3 consist of two low- and high-molecular fractions (NF, HF) sharply differing on MWD parameters.

The dynamics of PhAMPh conversion during process was controlled by a method of high-performance exclusion chromatography with UV-spectrophotometric detection on change of the area of the corresponding peak. The structure of OPhAMPh consisting of PhAMPh links is as follows:



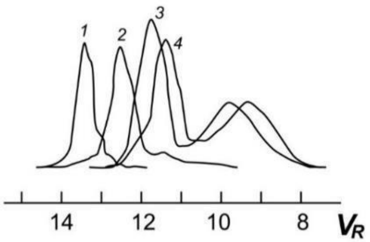


Fig. 1 Exclusion curves of MWD, OPhAMPh and metal complexes on its basis.

The first peak on MWD curve of these compounds with maximum at V_R=13.5 is referred to oligomer fraction with M_w and M_n 890 and 730 prevailing by content 65-85%. As follows from figure OPhAMPh-2 and OPhAMPh-3 (curves 3 and 4) are characterized considerably high MW, the values of which are changed in a low interval (M_n = 6140, 6300 and M_w =6300 and 7100).

The oligomers synthesized at room temperature interact with metal acetals Zn^{+2}, Cu^{+2}, Co^{+2} and Ni^{+2} in a mixture methanol-dioxane. In this case, the solutions are immediately colored red-brown (Co^{+2}), yellow-brown (Ni^{+2} and Zn^{+2}) and dark-green (Cu^{+2}) color and after 15-20 minutes the precipitations are formed. In boiling of the reaction mixture, the metal-polymer complexes (MPC) with quantitative yields are formed. After isolation from the reaction mixture and drying, these complexes acquire gray and dark-brown colors. They are partially dissolved in DMFA and in interaction with concentrated sulfuric acid and aqueous solutions of alkalis are decomposed into soluble products. MPC of OPhAMPh-1 and OPhAMPh-2 are not melted to 250^{o}C. The gravimetric analyses showed that the complexes of OPhAMPh-2 contain Zn^{+2} – 9,70 % (14.36%), Cu^{+2} – 12.23 % (14.01%), Co^{+2} – 11.75% (13.11), Ni^{+2} 11.02% (13.08 %) in the compositions. OPhAMPh-3 in aqueous solution actively reacts with Cu^{+2} acetate and completely precipitates. In this case, the brown color is converted into green.

The results of ELC investigations of PhAMPh oligomer products, in particular, the study of the dynamics of changes of their

MWD at transition to the complex form shows a very complex mechanism of the process behavior. It has been shown that MPC formation proceeds simultaneously with a decrease of MW of macromolecules due to chain break with splitting of shorter chains, and also with an increase of MW of oligomers due to the formation of bridging intermolecular bonds [1,2,3,4,8,20,38, 46,47,52].

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1.2 Molecular characteristics of oligoalkyl naphthenic oils obtained with oligomerization of C_6-C_{12} α-olefins in the presence of ion-liquid catalytic systems

In recent years, the synthetic polyalphaolefin oils (PAOO) have been widely used, the world production of which currently exceeds~400 thousand tons per year. Period of exploitation of the synthetic lubricant materials can reach 8000 h (petroleum oils – only 500-2000 h). Especially strict requirements for all types of oils are made on the degree of their residual unsaturation, which has been connected with the requirements of their thermal-oxidative stability. These properties of PAOO largely depend on character of molecular-weight distribution (MWD). So, the narrowest MWD values have a positive effect on their exploitation properties. In this work, the dynamics of changes of MWD and fractional composition, and also the structure of oligoalkyl naphthenic oils obtained in the oligomerization process of C_8–C_{12} of α-olefins in the presence of new effective ion-liquid catalytic systems (ILCS-1) on the basis of $[(C_2H_5)2NH_2]+[Al_2Cl_7]^-$ and their modifiers with Ti-phenolate complexes (ILCS-2) have been investigated with use of ELC and mass spectrometry.

The results of exclusion-chromatographic investigations of the oligomerization products of α-olefins (C_6-C_{12}) synthesized in the presence of the recirculated catalysts on the basis of chloroaluminate ionic liquids and also in their combination with Ti- and Ni-containing complexes with grafted “ion-liquid” ligands have been presented. It has been established that depending on synthesis conditions it is observed a growth of macrochains in the oligomerization process at transition from one catalytic system to other. The conditions of preparation of oligomers with regulated MWD parameters with defined MW have been also revealed.

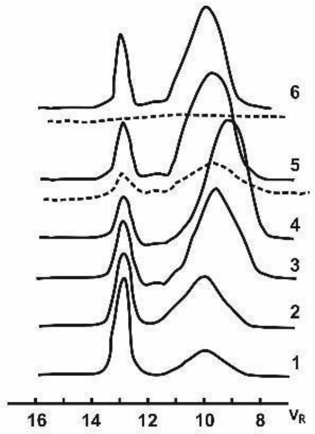


Fig. 2 MWD curves of the oligomerization reaction products of α-octene (curves 1 and 2), α-decene (curves 3 and 4) and α-dodecene (curves 5 and 6) synthesized in the presence of ILCS-1 and ILCS-2.

So, the low-molecular fractions (LM) of pentamers and tetramers ($V_R = 12$) and high-molecular fractions (HM) on MW value changing in a relatively wide range-3000-6890 (M_w) and 2500-5300 (M_n) ($V_R = 8\text{-}12$) have been found in the composition of the reaction products. In all cases, during formation of oligomers, the transition from catalytic system of type ILCS-1 to ILCS-2 is accompanied with increase of their MW. For example, in the composition of the oil fraction (OF-2) of oligooctene obtained by distillation of the reaction product higher 350°C, the transition to the catalytic system of ILCS-2 is accompanied with increase of M_w and M_n values corresponding to HM oligomers from 3000 to 3900 and from 2500 to 3700 in the composition of the oligomers, respectively.

It is observed a decrease of a quantity of HM fraction from 25 to 15% and is correspondingly fixed a fall of the intensities of the corresponding peaks (Fig. 2, curves *1* and *2*). It should be noted that the transition to the catalytic system of ILCS-2 in a case of oligomerization of α-decene and α-dodecene occurs also with decrease of a quantity of HM fraction in the composition of the obtained products and intensity of the corresponding peaks. In this case the similar regularities are detected.

Table 1

MWD characteristics of oligo- and α-olefins (C_8–C_{12}) synthesized in the presence of ILCS-1 and ILCS-2 ($V_R = C_1 – C_2 \lg M$, where $C_1 = 24.4$, $C_2 = 4$)

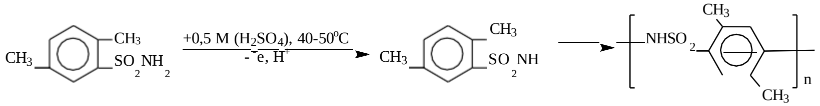
№	Modi-fier	Catalyst	LMF, %	MWD			V_R max	M_p
				M_w	M_n	M_w/M_n		
1	α- C_8	ILCS-1	25	3000	2500	11.2	10.68	2720
2		ILCS -2	15	3900	3700	1.05	10.00	3800
3	α – C_{10}	ILCS-1	20	4450	3740	1.19	9.96	4100
4		ILCS -2	15	5180	4540	1.14	9.60	4860
5	α – C_{12}	ILCS-1	20	4820	4310	1.12	9.76	4580
6		ILCS-2	10	6890	5300	1.30	9.28	6100

Note – samples 1 and 2 pentamers, 3–6 tetramers. M_p – MM in peaks maximum.

The obtained hydrocarbons are named oligoalkyl naphthene hydrocarbons, and the synthetic oils with corresponding structure – oligoalkyl naphthenic oils. A presence of naphthenic rings and absence of double bonds (or presence in small quantities) in these products lead to their use without hydrogenation processes in further. The possibility of the selective preparation of products with oligoalkyl naphthenic structure with narrow MWD characterizing by absence of the double bonds have been revealed. The possibility of regulation of MW of the oligomer products by change of molar ratio of components of the catalytic system has been established. [5,19,22].

1.3 Oligomers of *p*-xylene sulfamid

In this section the results of the investigation of the preparation process of oligomers of *p*-xylene sulfamide by a method of electrolysis in an aqueous solution of sulfuric acid at temperature 40-50°C have been presented. The following complete scheme of the electrochemical oxidative polycondensation of p-xylene sulfamide is proposed.



The composition and structure of the obtained oligomer have been determined by a method of IR spectroscopy. It has been established that the intensity of the absorption bands in the fields of 1320-1350 and 1140-1180 cm^{-1} corresponds to the valence vibrations of SO_2N bond. The influence of a quantity of passed electricity (Q) on the process of the electrochemical oxidative polycondensation of *p*-xylene sulfamide has been studied. It has been established that with an increase in the quantity of electricity from 8 to 14 A·h, the yield of the synthesized oligomers of *p*-xylene sulfamide is increased from 52 to 75% on substance.

During the study of the influence of current density on the yield of the obtained oligomers, a high value is observed at a current density 0,1 A/cm^2 and is 75%. In further increase of the current density, the yield of the obtained oligomers is decreased, which has been connected with overheating of the electrolyte, favoring, apparently, the occurrence of the side reactions. The molecular weight and molecular-weight distribution of the synthesized products have been studied by high-performance liquid chromatography in the exclusive mode.

Table 2

Results of the influence of a quantity of passed electricity (Q) on MWD of the reaction products of the radical oxidative polycondensation of *p*-xylene sulfamide initiated by electrochemical current.

Sam-ple	Quantity of electricity, Q, A·p	Conver-sion, %	MWD			Oligomer yield, %
			M_w	M_n	M_w/M_n	
1	8	65	3200	2450	1.3	35
2	12	45	3800	2900	1.31	55
3	14	25	4200	3150	1.33	75

It can be seen from the results of exclusive-chromatographic investigations of the reaction products of the radical oxidative polycondensation of *p*-xylene sulfamide, presented in Table 2, that the conversion of the initial monomer largely depends on the quantity of the passed current. So, the lowest yield of the oligomer has been fixed at a value Q = 8 A·h. In this case, the quantity of unreacted monomer in the composition of the reaction mixture of the product was 65%, i.e. the quantity of the formed oligomer is 35% (sample 1). The further growth of the value of the quantity of the passed current to 14 A·h leads to an increase of yield up to 75% (sample 3). As expected, the tendency of growth for M_w and M_n of the formed oligomers in the ranges of 3200, 4200 and 2450, 3150 is observed respectively.

It is clearly seen from the obtained results and from MWD curves of the synthesized products that they have bimodality (Fig. 3). The first of them characterizes the unreacted part of the monomer (curves 1-3), and the second – the forming oligomer (curves 1'-3'). In this case, on increase of Q passed through the medium, the ratio between the curve modalities is changed in accordance with their values indicated in Table. The synchronous displacement of MWD curves of oligomers towards high molecular weights is observed.

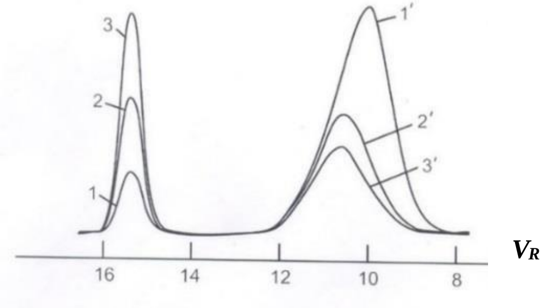


Fig. 3. Curves of dependence of MWD of the products of the radical OP of *p*-xylene sulfamide initiated electrochemically on the quantity of Q. Curves 1 (1'), 2 (2') and 3 (3')-Q=8, 12 и 14 A·h, respectively.

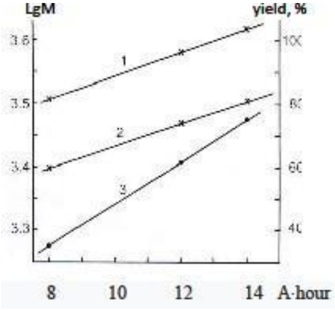
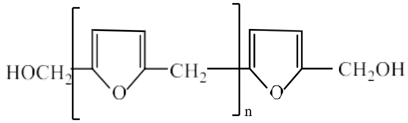


Fig. 4. Dynamics of changes of M_w (curve 1), M_n (curve 2) and product yields (curve 3) of the radical oxidative polycondensation of *p*-xylene sulfamide initiated electrochemically, depending on Q.

The linear character of the curves and the synchronicity of changes in M_W and M_n under the conditions of the electrochemical oligomerization of *p*-xylene sulfamide, as already indicated, show that the chain growth order during the formation of macromolecules is stable. These factors favor the study of the kinetic regularities of the process, and also allow the synthesis of oligomers with controlled molecular weight [28,31,33,36].

1.4 Molecular weight distribution of furan resins synthesized by electro(photo)chemical method

The synthesis of furan resins has been carried out by methods of electro- and photoelectrochemical initiated polymerization of furfuryl alcohol and its propylene chlorohydrin ether. These methods have a number of advantages over chemical methods. Fistly, the reaction products are the films localized already on the surface of the electrode and having good electrical conductivity. Another advantage of the method is the high stoichiometry of the process, allowing to regulate the properties of the molecular-weight distribution of polymer in the process of its preparation. The results of size-exclusion chromatographic investigations showed that the polymerization process of these compounds by these methods occurs by two various mechanisms. So, in the first case, the polymerization proceeds with the formation of a low-molecular furan resin as an individual trimer and pentamer, and in the second case (I , II) (Fig.5).



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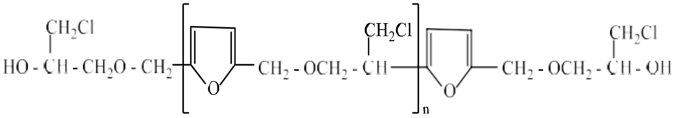

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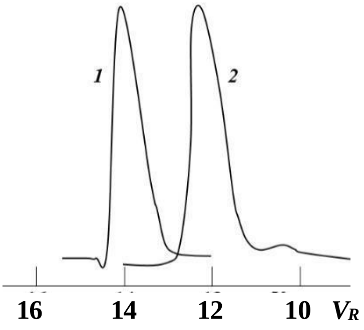
with photoelectrochemical initiation, the reaction occurs on the polymerization mechanism of dienes formed in opening of the furan ring with the formation of linear oligodienes consisting of elementary units with one double bond (III and IV)(Fig. 5).

$$-[CH(HO)-CH=CH-CH(R)(R')]_n-$$

Where R и R' → CH_2OH (**III**) and fragments $-CH_2-OCH_2-CH(OH)-CH_2Cl$ **(IV)**



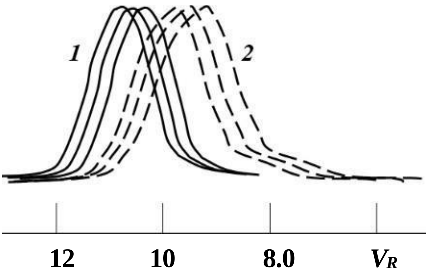


Fig. 5 Exclusion curves of the MWD of furan resin synthesized by polymerization of furfuryl alcohol (curve 1) and its propylene chlorohydrin ether (curve 2) by electrochemical method

Fig. 6 Exclusion curves of the MWD of furan resin synthesized by polymerization of furfuryl alcohol (curves 1, solid lines) and its propylene chlorohydrin ether (curves 2 - dotted lines)

It has been shown that in this case, the illuminance grows from $20 \cdot 10^3$ to $30 \cdot 10^3$ Lux, the initiation of furfuryl alcohol is accompanied by the formation of oligomers, molecular weights vibrating in the range of 3220-4175 (M_w) and 2300-2960 (M_n), and the initiation of propylenechlorohydrin ether under the same conditions leads to the formation of oligomers with growing values of the molecular weights from 7345 to 9430 and from 4680 to 6110 (M_n), to M_w=9430 and M_n =6110. The yield of polymerization products of the initial monomers is also increasing from about 45% to 70%. The electro- and photoelectrochemical initiation of monomers has been carried out under the same conditions. Only in the second case, the incandescent lamps of various capacities (150, 300 and 500 watts) have been used, the graphite served as the anode and cathode. Electrolyte – an aqueous solution of sulfuric acid (0.5 M H_2SO_4). The sample dissolved in dimethylformamide together with the background electrolyte was placed in an electrolyzer equipped with a graphite cathode and anode. With irradiation of the reaction zone with visible light, the initiation was carried out at a current density of 0.1-0.15 A/cm^2 and temperature in the range of 40–50°C. The time required for oxidative polycondensation – from 8 to 10 h. [53,99,60].

2. Investigation of the structural inhomogeneity of polymers by a method of ELC in two-detector chromatographic system

2.1 MWD and DTF of oligoepichlorohydrins

The study of MWD and DTF of oligoepichlorohydrins (OECH) forming in toluene under action of BF_3OEt_2 by a method of two-detector GPC showed that the composition of oligomers includes basically two types of bifunctional macromolecules. First – macromolecules with end epoxide and aromatic groups forming as a result of chain transfer to solvent molecules, i.e. toluene (alkylation); second – macromolecules with end epoxide groups and double bond.

However, with methods of exclusive and adsorption chromatography, a quantitative estimation of DTF is not possible, since in both regimes, a division on type of functionality is imposed on separation by MW. The analysis of MWD and DTF in parallel with exclusion and critical chromatography allows to establish the functional composition of oligomers. The MWD and DTF of oligoepichlorohydrins obtained at cation polymerization on Lewis acids in a number of solvents have been studied. As the objects of investigation the various samples of OECH were used (Table 2).

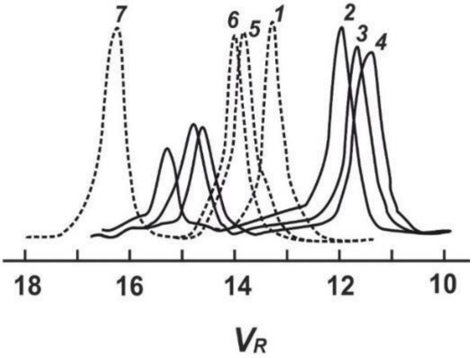


Fig.7. Curves of MWD of OECH samples obtained in exclusion regime of separation. Adsorbent "Separon SGX»" D = 100 Å, eluent – DMFA, 0.2 ml/min, sample volume – 1-4 mcl, T = 295 K.

An interaction of ECH with toluene at 333 K in the presence of BF_3OEt_2 (Fig.7, sample 1) proceeds completely to the side of formation of alkylated products, i.e. dominating role belongs to the chain transfer to the solvent molecule with formation of macromolecules of type 1 (Table 4). However, judging by the values of f_n for separate groups (Table. 3, sample 1) it can be seen that in the composition of the oligomer, besides molecules of type I, there are two other types of macromolecules. So, exceeding the value of f_n on epoxide groups higher one (1.33) can indicate to the availability of linear macromolecules with two terminal epoxide groups in the oligomer composition, i.e. diepoxide (Table. 3, type V). Such diepoxide can be formed at chain break by recombination of the active centers. An availability of the double bonds (f=0.33) in the sample shows the possibility of formation of linear macromolecules of OECH with end bonds C=C (type III). In other words, in spite of the unimodal character of chromatograms obtained in the exclusive regime, this sample may contain at least three types of bifunctional macromolecules.

The study of influence of nature of the catalysts on MWD and DTF of oligomers (Table 2) showed that at transition from BF_3OEt_2 (sample 1) to $AlCl_3$ (sample 2), $SnCl_4$ (sample 3) and $ZnCl_2$ (sample 4) their molecular parameters are noticeably changed. Unlike OECH synthesized under action of BF_3OEt_2, the exclusion chromatograms of the samples synthesized under action of other catalysts are differed with biomodality (Fig.7, samples 2-4). The peaks at V_R = 14.5-15.5 apparently, correspond to low-molecular fractions of OECH not containing aromatic fragments. MW of these fractions is much higher than MW of the corresponding fractions in the composition of oligomers synthesized at lower temperatures in a medium of the toluene, and also the fractions of OECH synthesized under conditions of the cation polymerization of ECH (Table 3 and Fig.7, sample 7).

Table 3

Molecular weight characteristics and average-numeral functionality f_n of OECH samples determined in the exclusion regime of separation

№	MWD			Functional groups*, mass %			f_n		
	M_w	M_n	M_w/M_n	E	A	D	E	A	D
1	1780	1400	1.27	4.1	3.25	0.60	1.33	0.50	0.31
2	590 3000 2570	550 2600 1870	1.07 1.15 1.37	1.37	2.50	1.00	0.81	0.51	0.69
3	680 3400 3115	650 2900 2100	1.04 1.17 1.49	1.42	1.82	0.95	0.74	0.45	0.79
4	780 3500 3350	730 3000 2200	1.06 1.16 1.52	1.30	1.68	0.90	0.70	0.43	0.77
5	1400	1200	1.16	3.23	8.20	-	0.94	0.93	-
6	1070	970	1.08	3.95	12.5	-	0.89	1.02	-
7	460	360	1.27	3.40	-	2.65	0.28	-	0.65

***E, A and D – epoxide, aromatic groups and double bonds.**

If in the last two cases the tetramers are formed, then in a case of the samples 2-4, the fractions corresponding to hexa-, hepta- and octamers (Fig.7) on MW with content of 32, 42 and 45% are formed, respectively. The peaks detected in the high-molecular field of chromatogram of the samples 2-4 (V_R = 11-13) show (Table 3)the availability of up to 52-68% of macromolecules II. It is seen from data of Table 3 that the transition to p-xylene and mesitylene leads to a decrease of MW and polydispersity of oligomers (Fig. 7, samples 1, 5, 6). An increase of f_n on aromatic groups and the absence of C=C bonds in the samples indicates to the predominance of the chain transfer reaction to molecules of aromatic solvent with the formation of type I macromolecules (95, 96%). So, according to the results of MWD analysis of OECH in the exclusion regime and f_n for different groups, it was possible to show that there are three types of functional macromolecules in the investigated samples (I, III and V) (Table 4).

Table 4

DTF of OECH samples in the critical regime of separation

Macromolecule	Type of functionality	DTF (mass %) for samples						
		1	2	3	4	5	6	7
I	Ar ---Δ	82.7	63.1	50.05	47.20	96.15	95.25	-
II	Ar -CH	2	55.05	4.52	5.20	3.85	4.75	-
III	=-----Δ	5.52	20.02	23.92	22.98	-	-	45.50
IV	= ---CH	4.35	1.65	1.48	1.20	-	-	3.32
V	Δ----- Δ	1.56	-	-	-	-	-	-
VI	CH -CH	4.15	-	-	-	-	-	-
VII	□	1.70	10.13	20.03	24.12	-	-	51.18

More efficient method of separation – liquid chromatography in the critical conditions, i.e. separation at the border of exclusion and adsorption regimes was used for DTF analysis. In this regime, the division of macromolecules on MW disappears and the observed chromatogram gives direct information about the types of functionality or other types of the structural inhomogeneity of oligomers. In Fig.7 the typical chromatograms of the studied OECH samples, the separation of which has been carried out in the critical conditions, have been presented. As follows from the figure, unlike mono-and bimodal curves obtained in the exclusion regime, these chromatograms are characterized by availability of a number of well-resolved peaks corresponding to macromolecules of different types of functionality. Based on the data obtained in exclusion regime (see above), it can be assumed that the peaks at the values of V_R = 21, 22 and 24 on chromatogram of the samples 1 (curve *1*) correspond to the macromolecules of type V, III and I (Table 4), a content of which is 4.15, 4.35 and 82.7%, respectively.

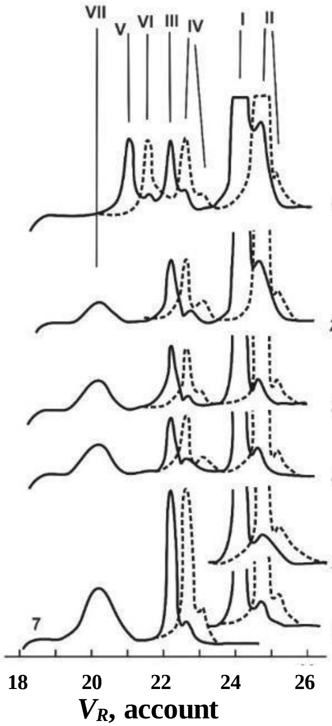


Fig. 8. DTF-chromatograms of OECH samples obtained in the critical regimeof separation. Adsorbent “Separon SGX”, D = 100 Å, eluent – benzene: DMFA =50:50 rev.%, 0.2 ml/min, sample volume – 0.5-2mcl.

The weak signals fixed from right of the basic peaks apparently correspond to macromolecules with end chlorohydrin groups not converted into epoxide form during dehydrochlorination reaction with alkali. For their identification, the samples were used, in which the epoxide groups were partially substituted with hydrochloride groups. In this case, the chromatograms showed a displacement of peaks by 0.5 accounts towards large V_R (dashed line). In other words, instead of peaks corresponding to the epoxide forms of macromolecules (V, III, and I), the signals related to macromolecules VI (1.7%), IV (1.56%) and II (5.52) were appeared.

On the chromatograms of the samples 2, 3 and 4 synthesized in the presence of specified number of the catalysts, as expected, the peaks of diepoxide macromolecules of OECH of type V (f_n on epoxide groups – 0.43-0.51, Table 3) are absent. Besides linear macromolecules of type III (V_R = 22) characteristic for these samples, the chromatograms have relatively wide peaks at (V_R = 20), which remain unchanged during the transition to the hydrochloride form and back. The identical peak has been also fixed on the chromatogram of OECH sample (Fig. 6, curve *7*), obtained in the conditions of cation polymerization of ECH in a medium of inert solvent. It can be assumed that this peak corresponds to cyclic oligomers of ECH (type VII), the formation of which usually occurs during cation polymerization of cyclic esters. The formation of a large quantity of cyclic oligomers on the products of cation polymerization was also observed by a method of ELC. The analysis of DTF of the samples 5 and 6 synthesized in a medium of p-xylene and mesitylene (Fig.8, curves *5* and *6*) in the critical regime of separation showed that they consist of macromolecules of type II (5%). An availability of small peaks (V_R = 23 and 25) on the chromatograms of chlorohydrin forms of oligomers (samples 1-7) clearly indicates to the presence of a small quantity of macromolecules with β-chlorohydrin group, the formation of which is characteristic of such processes .

The results of DTF analysis of a series of OECH samples in the critical regime showed that depending on the synthesis conditions, they contain macromolecules belonging to seven various types of functionality: six linear and one cyclic. It has been also established by a method of GPC that the content of cyclic macromolecules (tetra-, hexa-, hepta- and octamers) reaches 50% in the composition of oligomer fraction with low MW (for ECH homopolymer without aromatic fragments) [5,35,50]. .

2.2 Investigation of regularities of the synthesis of halogen-containing unsaturated polyesters

We have previously studied the regularities of modification process of epoxy diane resins with unsaturated polyesters and established some physical-mechanical properties of the obtained products. In this section the results of synthesis and investigations of new polyhalogen-containing unsaturated polyesters (HUPE) on the basis of propylene glycol (PG), maleic anhydride (MA) and anhydride of 1.4.5.6.7.7-hexachloro(hexabromo)bicyclo [2.2.1]-hept-5-en-2,3-dicarboxylic acid or anhydride of hexachloro-(hexabromo)norbornene dicarboxylic acid (HC- and HB-NBDA) are presented.

The dynamics of change of MWD and functionality of polycondensation products in this system of components has been studied by a method of two-detector exclusion chromatography. By comparison of the data obtained by one-and two-stage methods, an attempt is made to find out the process mechanism and side reactions proceeding during this process. The polycondensation reaction of PG with these anhydrides and MA at molar ratio 1.1:0.5:0.5 was carried out in a melt at 190°C in a nitrogen atmosphere.

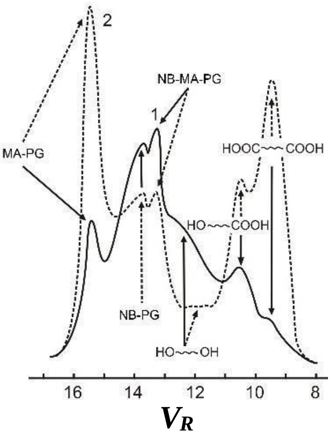
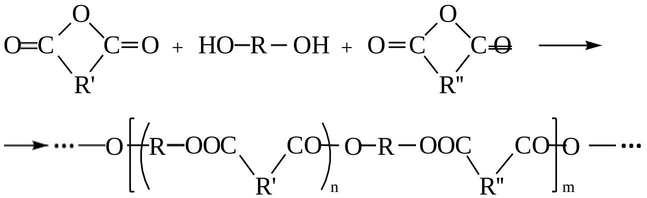
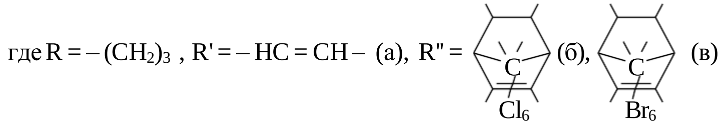


Fig. 9. Exclusion curves of formation of HUPE at joint one-stage polycondensation of MA, PG and anhydride of PG and anhydride of HB-NBDA.

The scheme of this reaction can be presented as follows:



(Ia-в)



The course of synthesis process of HUPE was controlled by a method of two-detector ELC. In this case, the dynamics of change of MWD and functionality in the product composition was observed in parallel with refractometric and UV-spectrophotometric detectors. As follows from the chromatogram of the polycondensation product synthesized by one-stage method (Fig. 9) and from the data of Table (samples 1-3), the investigated products are characterized by polymodality and, consequently, high polydispersity (M_w and M_n) reaching 2.6.

It has been established that, depending on synthesis conditions in a case of one-stage method, a quantity of purposeful product (MW ≈ 3000) doesn't exceed 30%. The reaction products consist, mainly, of low-molecular adducts formed independently between each anhydride and PG. On the chromatogram of the presented sample (Table 5, sample 2), taken with refractometer (curve 1), a narrow peak with a maximum at $V_R = 15.5$ ($M_n = 165$), corresponding to a fraction consisting only of monoester molecules (IIa-c), condensation product of MA and PG ($M_{theor.} = 174$) has been fixed.

There have been also detected the fractions with M_w and M_n, equal, respectively to 320, 300 and 950, 790, consisting, mainly, of molecules of mono- (IIa-c) and diesters (IIIa-c), forming in interaction of HC(HB)-anhydride with PG, and also at joint condensation of HC(HB), MA and PG (Ia-c). This is evidenced by the peaks fixed at $V_R = 13.75$ ($M_n = 460$) and 13.25 ($M_n = 610$), which correspond to the theoretically calculated MW values of mono- and diesters shown above, equal to 447 and 618.

Table 5.

Molecular-weight characteristics of the polycondensation reaction products of HC- and HB-NBDA, propylene glycol and maleic anhydride synthesized with one-stage (samples 1-3) and two-stage (samples 4-7) methods.

Sample №	Frac-tions, %	MMD parameters			Content of functional groups, %		f_n	
		M_w	M_n	M_w / M_n	OH	COOH	OH	COOH
1	70	1025	526	1.95				
	30	monoester*						
	–	785	330	2.34	6.35	10.1	1.23	0.74
2	15	3400	3100	1.09				
	50	950	790	1.2				
	20	320	300	1.06				
	15	monoester *						
	–	1070	450	2.38	2.72	12.6	0.72	1.26
3	9	4515	4090	1.1				
	37	1040	810	1.28				
	22	310	300	1.03				
	32	monoester *						
	–	910	350	2.6	4.37	11.37	0.91	0.88
4	85	1500	1130	1.15				
	15	2300	1982	1.16				
	–	1450	1220	1.19	2.5	0.55	1.79	0.15
5	83	2100	1550	1.35				
	17	3900	2360	1.65				
	–	2400	1640	1.46	1.87	0.47	1.8	0.17
6	–	3880	3210	1.21	0.38	1.25	0.2	1.75
7	–	4500	3800	1.18	0.08	2.08	0.18	1.76
8	–	4580	3850	1.18	0.09	2.08	0.19	1.78
9	–	5850	4800	1.22	0.06	1.70	017	1.81

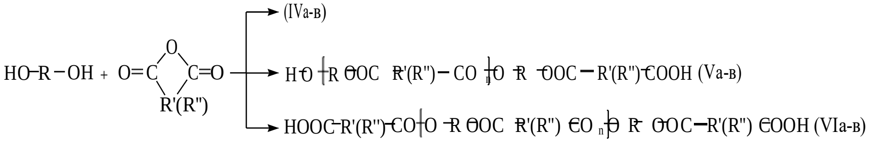
Note: Last column numbers – total values of M_w and M_n.

The band with a sharp decline, detected at V_R ~ 13-11 or in range of MW values 700-2500 (Fig.9), limited by a fraction with modality at V_R = 10.5 (M_n = 3000) actually shows the formation of oligomer macromolecules in the process. It has been established that

f_n values on these groups depending on synthesis conditions and molar ratio of reagents are vibrated in the range of 0.72-1.2 (on OH) and 0.74-1.26 (on COOH). Here, the exceeding of f_n values per unit in a case of the samples 1 and 2 (Table 5) confirms the availability of the forming products of macromolecules containing two identical end groups, noted above – oligoesterdiols (IVa-c) and oligoesterdiacids (IIIa-c) in the composition.

The results obtained on one-stage method can be of great importance in elucidation of the formation process mechanism of HUPE, since the used chromatographic system, besides MWD, allowed to detect DTF in their composition.

In order to obtain HUPE with more homogeneous composition, it has been carried out a two-stage method, in the first stage of which one of the initial anhydrides (MA or HC (HB) is separately subjected to the polycondensation reaction with PG. The synthesis of HUPE has been carried out in both variants, i.e. both MA (sample 4) and HC(HB)-anhydride (sample 5) were used as initial components at the first stage of the process. The purpose of this stage is to suppress the formation of side products, to obtain oligomer esters of strictly diol form, allowing to carry out the reaction with the next anhydride also on the polycondensation mechanism at the final stage of the process. The reaction scheme at the first stage of the process can be described as follows:



Oligoesterdiol (IVa-c) at this stage is the purposeful product of the process, but by changing the molar ratio of the initial components, the reaction can be directed mainly towards the formation of a product with structure (Va-c) or (VIa-c).

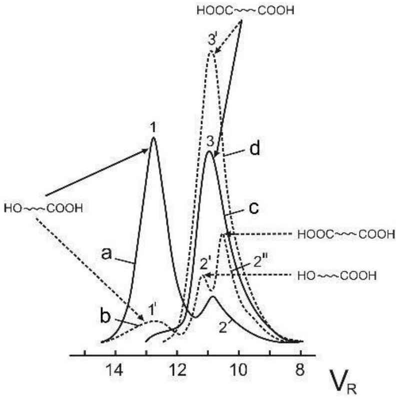
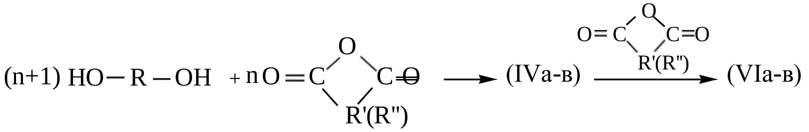


Fig. 10. Exclusion curves of formation of HUPE at joint two-stage polycondensation of maleic anhydride of HC-NBDA, propylene glycol and anhydride 1. Curves "a" and "b" – first stage, curves "c" and "d" – second stage.

On the chromatogram of the product synthesized at the first stage of the process, presented in Fig.10, two fractions of the oligomer structure are detected. First, more low-molecular fraction (M_w = 1300, M_n = 1130) (Table 5, sample 4), by 85% (curve "a", peak 1) is oligoesterdiol (IVa-c) – main purposeful product at the first stage of the polycondensation process. The weak absorption of this fraction on UV-detector (curve "b", peak 1'), possessing high intensity on refractometer, confirms its attribution to polyester macromolecules of type HO– ··· –OH non-absorbing in the UV-area. The existing absorption, although weak, as already noted, occurs due to unsaturated bonds (C=C) spreading along oligomer chain. The second fraction with higher MW (M_w = 2300, M_n = 1982) with unimodal peak on MWD (peak 2) has bimodality on UV-detector (curve "b", peak 2' and 2") with various intensities. This has been connected with availability of two sub-fractions with close MW but various types of functionality in the composition of this fraction. It can be assumed that the first peak with relatively weak intensity (peak 2') is referred to macromolecules of HO– ··· –COOH type (Va-c), and the second (peak 2"), more intensive – to macromolecules of HOOC– ··· –COOH type (VIa-c). Then the interaction products of MA and PG (or HC (HB) and PG) at the second stage of the process are subjected to the polycondensation with next anhydride – HC (HB) (in the second variant with MA) on scheme:



It is seen from data of Table that unlike one-stage method, the end products in a case of two-stage method are the oligomers with comparatively high homogeneity. M_w/M_n values synthesized with the participation of anhydrides HC-NBDA (samples 6 and 7) and HB-NBDA (samples 8 and 9) are close and are approximately 1.2.

As follows from the chromatogram of the same sample taken by refractometric detector (Fig. 10), the formation of HUPE at the final stage of the process is accompanied by displacement of the signal of the low-molecular oligoesterdiol subjected to the polycondensation reaction towards high MW (curve "b", peak 3), and the second high-molecular fraction does not lead to an essential change in the character of MWD at the transition to the next stage and its signal is practically covered by the signal of the first fraction, which has been connected with the absence of oligodiol molecules in the second fraction, favoring interaction with other anhydride molecules of dicarboxylic acids on polycondensation mechanism. A noticeable change at the final stage occurs in a character of UV-chromatogram (curve "d"). The low-molecular oligoesterdiol with low intensity (peak 1') non-absorbing in the UV-area at the final stage is fixed as an intensive peak with unimodal character (peak 3'). It has been established that the purposeful products (HUPE) synthesized in shown system of components by two-stage method possess sufficiently high homogeneity not only on MWD but also on functionality. This is evidenced by f_n values of the purposeful products on COOH, which are 1.75 and 1.76 (samples 6 and 7) and close to zero on OH (0.18, 0.2).

For bromine-containing HPE f_n values on COOH and OH are almost not differed from chlorine-containing analogues and are 1.78, 1.81 and 0.19, 0.17, respectively. Thus, all composition of the purposeful products (VIa-c) consists practically of bifunctional molecules with regular alternation of ester fragments and unsaturated links.

Thus, comparing the signal intensities of fractions fixed on UV and refractometric detector and on corresponding MW, the unsaturated esters with wide range of MW, beginning from adducts consisting of initial components and ending with oligoester macromolecules with M_n=1000-4800, referring to various types of functionality have been revealed in the composition of the reaction products. The chromatographic system used together with chemical and other physical-chemical methods allows to identify and estimate quantitatively the intensity of proceeding of the side reactions and, as a whole, to obtain the most close data on the mechanism of the formation process of polyfunctional unsaturated polyesters [26].

2.3. Study of the dynamics of changes of the parameters of molecular-weight distribution in the aging process during the exploitation of materials on the basis of polyethylene

This section has been devoted to the study of the dynamics of changes of MWD in the exploitation process of the polymer films on the basis of HPPE, and also to the investigation of the modification process of polyethylene waste with dichlorocarbene formed as a result of thermolysis of sodium trichloroacetate.

The initial samples were unused polymer film, as well as films kept in the open air for 16, 18, 21 months before and after modification. The content of C=C bonds was determined by a method of spectral ozonation. The quantity of carbonyl groups was determined by elemental analysis on oxygen content. MWD parameters of the samples were determined by ELC method. The average calculated functionality (f_n) on double bonds and carbonyl groups were calculated using the formula: $f_n = M_n / M_{eqv}$, the equivalent molecular weight value M_{eqv} was determined from the ratio 2600:D and 2800:K, where D and K are the contents of double bonds and carbonyl groups. The modification process of the investigated objects was controlled by UV detection. It has been established that the introduction of CCl_2 fragments into the polymer macromolecule is accompanied by a decrease of the intensities of the detector signals to the complete consumption of C=C bonds.

Table 6

Dynamics of changes of MW characteristics and functionality of the polymer films on the basis of HPPE.

№ of samples	Fraction, %	*Molecular weight			f_n	
		M_w	M_n	M_w/M_n	$f_{n\,C=C}$	$f_{n\,C=O}$
1	**100**	**29000**	**27000**	**1.07**	-	-
	95	32000	2900	1.1		
	5	5200	4200	1.24		
2	**100**	**23800**	**22200**	1.18	**1.01**	**1.11**
	75	27000	25000	1.08		
	25	16300	12900	1.26		
3	**100**	**19000**	**12000**	**1.58**	**1.75**	**1.75**
	15	29000	27000	1.07		
	50	18700	17000	1.10		
	35	4500	3600	1.25		

Note: The original HPPE before (sample 1) and after 18, 21 and 24 months of exploitation (samples 2, 3 and 4). *The first numbers of the columns (bold) are the total values of MW samples.

ELC investigation of MWD of polyethylene films on the basis of HPPE during exploitation showed that the main change in their composition is observed 18 months from the beginning of exploitation. In this case, in the composition of the initial sample, consisting of 95% fractions with M_w=32000 and M_n= 29000 and 5% fractions with M_w =5200, M_n=4200 (Table 6 and Fig. 11, curve 1), after the specified exploitation time due to the destruction of macromolecules on ELC curves of the sample, the low molecular weight fractions with M_w and M_n, equal to 16300 and 12900 are respectively appeared as widely diffuse bands. At the same time, the displacement of the peak of the initial sample by 0.25 counts towards high V_R or low MW (curve 2) is observed.

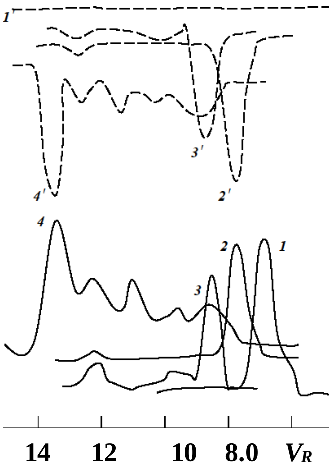


Fig. 11. Curves of MWD films on the basis of HPPE of the initial sample (*1* and *1*′) and the samples after 18 (*2* and *2*′), 21 (*3* and *3*′) and 24 months (*4* and *4*′) exploitation; *1-4* and *1*′ and *4*′ – signals of refractometric and UV detector, respectively.

On the character of MWD curves, it can be noted that after 18 months, the further development of destruction occurs much faster, and after 21 months two more fractions with maxima at V_R=8 (M_w =18700 and M_n=17000) and a wide band at V_R=10-13 (M_w=4500 and M_n=3600) in quantities of 35 and 50% respectively, are appeared in the composition of the investigated sample, i.e. practically only 15% of the basic composition of the initial sample remains (curve 3). And 24 months after the beginning of exploitation, besides these fractions, 3 more new fractions with peak maxima at V_R=9 (M_w =13500, M_n=11000), 10.5 (M_w =6500 and M_n=5000) and 12.25 (M_w =3500, M_n=2900) have been fixed on the chromatograms of the analyzed film. In this case, the composition of the polymer sample consists only of fractions formed during exploitation by the destruction of polyethylene macromolecules, and consequently only traces of the original polymer composition remain.

It can be seen from the data in Table 6 that the aging of the polymer films on the basis of HPPE for two years leads to a decrease of the total values of M_w and M_n from 29000 and 27000 to 7400 and 5300, respectively. The tendency of increase of polydispersity from 1.07 to 1.58 is observed. The parallel UV spectrophotometric detection of the investigated samples showed that the changes in the aging process occur not only in the molecular, but also in the chemical structure of macromolecules. So, in the spectrum of the initial film, which do not absorb in the UV field (Fig.11, curve 1), the symmetrical signals (curves 2, 3 and 4), similar to the signals of MWD curves taken by a refractometric detector are appeared after 18 months. According to the analysis of the composition and structure of the samples, the appearance of signals in the UV field, and increasing during the aging process, has been connected with the formation of C=C bonds and carbonyl groups, being active chromophores, well absorbing in the working wavelength of the UV detector (254 nm).

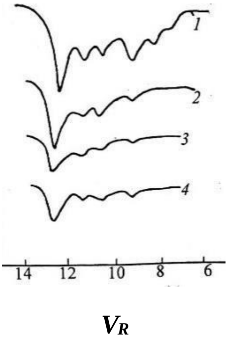


Fig. 12. Dynamics of changes of the character of MWD curves in the UV field (254 nm) during modification of the samples with dichlorocarbene. CCl_2 concentration, % of the total polymer mass: 0-(1), 0.5 (2), 1.0 (3) and 1.5 (4).

The study of the functional composition of the investigated samples showed that the content of these groups in their composition does not exceed 1%. In this case, the functionality for the same groups, calculated according to MWD data, is f_n =1.0-1.75, i.e. the average number of the formed C=C bonds and C=O groups per polymer molecule does not exceed 2. The occurrence of these groups in HPPE macromolecules during aging or loss of working capacity of products gives them a greater tendency to various modification processes

It has been shown that the sodium salt of trichloroacetic acid subjecting to thermolysis under conditions of processing PE, forms the carbon dioxide, sodium chloride and dichlorocarbene (CCl_2). The latter one reacts easily with functional groups of PE. In this case, its addition on double bonds, and also its implementation on C-H bond of the methylene group adjacent to the carbonyl group occur. The process is completed with the disappearance of the double bonds. This can be seen from the chromatograms of the samples modified with CCl_2 taken by UV detector (Fig. 12)

As follows from the figure, at modification of a fraction characterized by higher quantity of C=C bonds and C=O groups (0.85, 0.81%, respectively) and an equimolar quantity of dichlorocarbene, it is firstly observed a decrease in the intensity of the detector signal (curves 1-3). Further, the excess quantity of CCl_2 does not influence on the intensity of the spectrum (curve 4). It can be assumed that after the complete consumption of C=C bonds, the remaining weak signal characterizes only the carbonyl groups existing in macromolecules. IR spectral analysis confirmed these assumptions. So, in the spectra of the samples, with an increase in the degree of modification, the absorption bands of C=C bonds gradually disappear at 1640 cm^{-1} and the bands characteristic for chlorine atoms are appeared.

The results of ELC investigations of the aging processes and modification after it show that during aging, the destruction reaction takes place, which proceed according to the law of chance. As a result of the random splitting of macromolecules, their properties are deteriorated and they become unsuitable for further use. Thus, the results of the carried investigations may be of interest both from the methodological point of view and from the point of view of use of the materials obtained under conditions of re-processing of PE [10].

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3. Investigation of the structural inhomogeneity of polymers in a multidimensional chromatographic system.

In many cases, a separation within one chromatographic system is not sufficient for a complete analysis of the polymer. In this case, the complex application of different chromatographic methods (multidimensional chromatography) allows to obtain much more information about the structural inhomogeneity of polymers. The combination of several types of the polymers separation can be realized with use both of different chromatographic systems, and in one chromatographic system. The results of investigations of the structural inhomogeneity obtained by analysis of various compounds in a multidimensional chromatographic system are presented below.

3.1 Peculiarities of the structural inhomogeneity of oligomerization products formed during amination process of α-olefins

The structural inhomogeneities of the amination products of α-hexene in the synthesized oxidative-reduction system $NH_2OH\cdot HCl$-$TiCl_3$ by method of two-detector ELC and reverse-phase ALC. Two-detector variants of these methods with use of UV spectrophotometric and refractometric detectors have been selected. Eluents: methanol+water (75:25 rev. %) and dimethylformamide, respectively. Their feeing rate – 0,3 ml/min. T=20-25°C.

The study of properties of the amination products of α-hexene in these chromatographic systems showed that the obtained products are the complex mixture of fractions differing not only on molecular weight (MW) but also on isomer composition. This can be seen from the data presented in Table 5 and chromatograms of the analyzed products (Fig. 13 and 14) taken by these methods. Five fractions have been fixed on the chromatograms of products taken with refractometer in both systems. Based on the results of spectral analyses, and also from data on amination of α-olefins previously obtained by us, one can assume that the fraction detected at V_R=3 ml (Fig.13) corresponds to 1-aminohexene, being main isomer of monoamine of hexene-1 (70%) on content. The fraction revealed at

V_R=2.5 ml (5%) corresponds to the mixture of isomers of diamine compounds, i.e. 5.8 and 6.7 diamine dodecane (DADD), being the products of dimerization of aminoalkyl radicals formed during radical attack of NH_2 on molecules of *α*–olefins. In this case, it occurs the proton transfer from carbon atom C_1 to C_2 and from C_2 to C_1 respectively with formation of radicals [$NH_2–CH_2–\dot{C}H–(CH_2)_3–CH_3$)] and [$\dot{C}H_2–CH(NH_2) – (CH_2)_3$-$CH_3$)]. It has been established that a series of fractions fixed on the chromatogram at V_R =1.5, 1.7 and 1.88 ml values corresponds to telomers with M_n = 794, 660 and 478 with content of 5, 14 and 6 %, respectively (Fig.13). In this case, the total MW of telomere fractions, a total number of which is 25%, is M_n=630. A content of double bonds in their composition reaches 1.1 %. It has been established on the basis of values shown above that the average-numeral functionality of fraction of telomers on C=C bond is f_n =1.06, i.e. each telomer molecule contains one double bond.

Table 7.

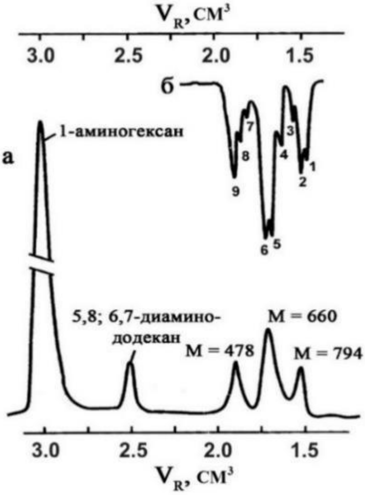
MWD parameters and fractional compositions of the amination products of α-AH identified by methods of ALC and ELC

Fraction	MWD*					
	Fraction, %		ALC		ELC	
	ALC	ELC	M_n, g/mol	M_w/M_n *	M_n, g/mol	M_w/M_n
OH	5	4	794	1,02	800	1,03
OH	14	16	660	1.03	670	1.05
OH	6	8	478	1.02	460	1.02
Mixture DADD	5	4	200	---	200	---
α-AH	70	68	100	---	100	---

$^*M_w = M_n \times M_w / M_n$.

The quantitative ratio of fractional composition of the investigated product has been also confirmed with two-detector ELC. As follows from Fig. 10 on ELC chromatogram of the same sample, taken with refractometric detector (curve 1), there have been fixed the fractions on MW corresponding to mono- and diamine compounds or, as indicated above, 1-aminohexane and 5,8 and 6,7 diamine dodecane with content of 68 and 68, respectively. A series of signals fixed in this regime clearly separated telomer fractions are appeared in trimodal form. These fractions are approximately identical to the parameters obtained in the ALC regime on MW (M_n = 800, 670, 460), on content (5, 14 and 8%) and also on average-numeral functionality on double bonds (f_n = 0.98).

It has been established that in the composition of the investigated amino product, a decrease of the polarity of the fraction coincides with a decrease of their MW and, correspondingly, the separation occurs on an exclusion mechanism. At UV-detection in both variants of the chromatographic system, the signals are appeared in the initial part of the sample chromatogram, i.e. only telomer fractions are fixed (Fig. 13 and 14, curves *b*), and the signals of mono- and diamine compounds unlike refractometric data are absent.



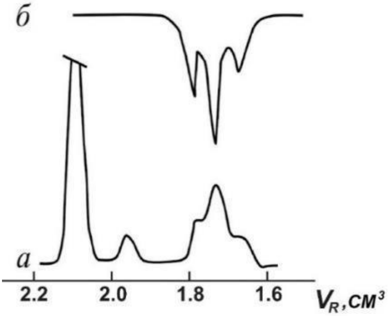


Fig. 13. Adsorption curves of MWD of the amination products of α-hexene. Adsorbent – *Separon SGX C18*, eluent – methanol:water (75:25 %), 0.3 ml/min, T=20-25 ^{0}C. Here in Fig. 4.9 detectors: refractometer (*a*), UV spectrophotometer (λ=254 nm)(*b*).

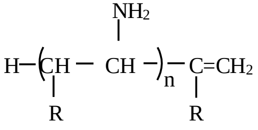
Fig. 14. Exclusion curves of MWD of the amination products of α-hexene.

has been connected with availability of end chromophore C=C bonds absorbing well in the UV area in the composition of telomers. If in refractometric detection, the separation is observed only on MW, then in a case of UV detection in ALC regime, the fraction separation is also fixed on isomeric composition. This is evidenced by the multiplet character of the signals of telomers fraction (Fig. 13, curve *b*).

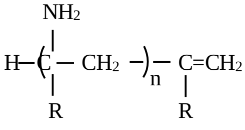
As follows from Figure, in the ranges of the same MW (V_R=1.5, 1.7 and 1.88 ml) each fraction is characterized by three maxima differing with various intensity. The first two maxima can be referred to more polar α- and β-aminooligohexenes (maxima 1, 2, 4, 5, 7 and 8) forming at 1, 2 and 2, 1 hydrogen migration, and the third less polar isomer corresponds to the oligoaminohexene formed at hydrogen migration either from the second to the third, or to the fourth carbon atom (maxima 3, 6 and 9).

In the IR spectra there are intensive absorption bands in the field of 1379 cm^{-1} and 1469 cm^{-1} characteristic for CH_3 and CH_2 groups, and also a band at 720-740 cm^{-1} corresponding to deformation C-H vibrations in unbranched chains – $(CH_2)_n$. The weak absorption band detected in the field of 966 cm^{-1} shows the availability of a small quantity of substituted double bond located at the end of the telomer chain $-RC=CH_2$. Due to the high content of monoamine in the composition of product in the field of 1600 cm^{-1}, the strong absorption bands corresponding to primary amine group of NH_2 have been fixed. The bands of valence vibrations characteristic for NH_2 groups are also observed at 3400- 3200 cm^{-1}.

The structure of obtaining oligomers can be presented as follows:

1. 

$H-(\underset{R}{CH}-\overset{NH_2}{CH}-)_n-\underset{R}{C}=CH_2$

2. 

$H-(\underset{R}{\overset{NH_2}{C}}-CH_2-)_n-\underset{R}{C}=CH_2$

$R \rightarrow -(CH_2)_3-CH_3$, n=4-7

The NMR^{1}H spectra confirmed the IR spectroscopic data of the products.

Thus, it has been established by a method of two-detector ELC that in the composition of amination products of α-hexene, along with individual aminoalkanes, it occurs an oligomerization of α-hexene leading to the appearance of three fractions with MW in the range of 460-800. The method of reverse-phase ALC allowed to reveal the distribution of products on isomer composition in the products, in this case, each telomer fraction consists of a mixture of three isomers, which are separated in order of decreasing their polarity [43,50].

3.2 Investigation of the structural inhomogeneity in the side products of HPPE production

As it was known, in the production of high-pressure polyethylene (HPPE), the low-molecular side products (SP) differing by instability of composition and structure are formed. This work has been devoted to the study of various types of the structural inhomogeneity of SP of HPPE production with joint use of the methods of high-performance ELC and ALC.

The sam les taken from various batches of SP of HPPE production were used as objects of investigation. In the exclusion and adsorption regimes of separation, DMFA (0.2 ml/min) and benzene (0.3 ml/min) served as eluents, respectively. In a case of ALC, two-detector system of separation consisting of refractometric and UV spectrophotometric detector has been used.

The obtained results show that the investigated samples, although are close on values of total MW (M_n= 700-800) but are considerably differed on fractional compositions and have a wide MWD, are characterized by different content of the double bonds, and consequently, by various f_n values on C=C bonds (Table 8). For ex., if the sample 1 consists of (95%) low-molecular fractions with M_w =900 and M_n =740 (5% MW with 2000) with content of C=C bonds equal to 2% and with f_n =0.5 (Fig.15, curves 1), then in the composition of the sample 2 (curve 2) a content of the high-molecular fractions with M_w =10000 and M_n=9500 reaches 20%, and the sample possesses comparatively high content of C=C bonds (5%, f_n=1.5).

Table 8

Molecular-weight and functional characteristics of SP of HPPE production

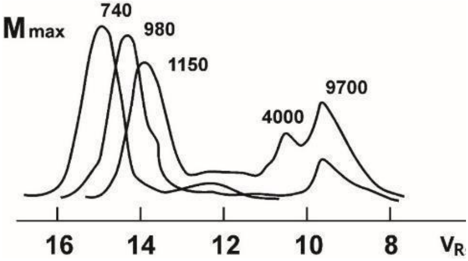
Sample	MWD			Content, %		f_n on C=C
	M_w	M_n	M_w/M_n	fraction	C=C	
1	900	740	1.21	-	2.0	0.57
2	700 10000 2100	620 9500 790	1.12 1.05 2.65	80 20 -	5.0	1.5
3	640 4350 11400 2840	500 3500 11200 800	1.28 1.24 1.02 3.5	63 17 20 -	10	3.07

Note: lower numbers of the columns (samples 2 and 3) – total values of MW samples.

The sample 3 was more complex on its fractional composition. As is seen from Fig.15 (curve 3), it consists mainly of three fractions with different MW. The firs with M_w and M_n 11400 and 11200 with maximum at its V_R=9.25 value, and the second – with M_w and M_n 4350 and 3510 at V_R =10.75 and the last – with M_w and M_n 640 and 500 at V_R=14.25, in quantities 20, 17 and 63%, respectively. A content of C=C bonds in its composition is much more than in other ones and is 10% (f_n= 3.07). It should be noted that in this case the total MW of the sample is low (M_w =2840, M_n=800) and the product has a sufficiently wide MWD (M_w/ M_n=3.5). This is evidenced by the low degree of crystallinity of this product (65%). However, as expected, according to the theory, a low degree of crystallinity, indicating to the availability of amorphous and crystalline structures simultaneously, has been also connected with structural inhomogeneity, leading to an increase of a degree of disordering of the polymers.

The IR-spectral analysis of structure of the samples taken from various batches of SP of HPPE production showed that their main peculiarity is the availability of unsaturated double bonds (2-10%) and carbonyl groups in the composition, in the fields of 1650 and 1720 cm^{-1} the double bonds and weak signals of carbonyl groups have been fixed, respectively. MWD parameters established by a method of ELC and content of C=C bonds determined by a method of spectral ozonation allowed to calculate the average-numeral functionality f_n of the samples on C=C bonds.

On ALC chromatogram, taken by a refractometric detector, there have been fixed two well-resolved peaks of energy, characterizing fractions consisting of linear and branched PE macromolecules (Fig. 15, curve 1), a ratio of which is 60:40 %. For identification of the peaks as a model sample, the analysis involved PE of strictly linear structure synthesized by the Ziegler method and it has been established that it corresponds to the first peak on the chromatogram of the sample 3 (Fig. 15, curve 2) on volume of V_R retention, and the second, in all probability, corresponds to the PE macromolecules of branched structure (V_R =0.8 ml).



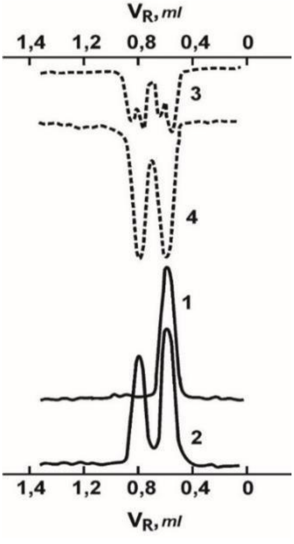


Fig.15. Exclusion curves of MWD of side products of HPPE production. Refractometric detector. Adsorbent – Separon SGX, D=100 Å, eluent – DMFA, rate – 0.2 ml/min, T=20^{0}C.1 account = 0.1 ml.

Fig.16. Adsorption curves of distribution of side products of HPPE production on topology (curves 1 and 2) and on DTF (curves 3 and 4), taken in two-detector system of chromatography. Continuous lines – refractometer, dotted lines – UV spectrophotometer (254nm). Adsorbent – Separon SGX , D=100 Å, eluent – benzene, rate – 0.3ml/min. T=20-25^{0}C.

On the chromatogram, taken by UV detector, the same fractions correspond to two clearly resolved bimodal curves (curve 3). The bimodal character of the peaks of linear and branched PE fractions on the UV detector has been obviously connected with availability of two various types of macromolecules in their compositions, one of which contains fragments of C=C bonds, being active chromophore, selectively absorbing in the UV area. This shows that each fraction is separately divided on types of functionality, which are detected only on UV detector. The bond between bimodality of UV curves and unsaturation of fraction has been proved at chlorination of the investigated sample 3, as a result of which the bimodality disappears and the peaks acquiring a unimodal character correspond to the chlorinated PE macromolecules with linear and branched structure (Fig. 16, curve 4). The proof of this is the absence of the double bonds in the composition of the chlorinated sample. Thus, it is seen that the chlorination occurs in two directions on usual dehydrogenation reaction and at the opening of the double bonds.

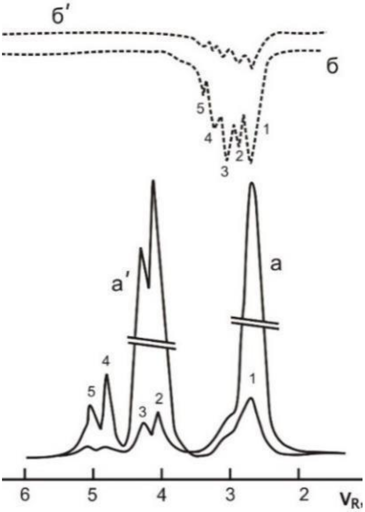
On the other hand, it has been established that the change of a content (2-10%), consequently, and functionality of the samples (f_n=0.5-3) on C=C bonds (Table 7) is accompanied by change of intensity of the peaks at V_R=0.5 and 0.8 ml (Fig.16, curve 3). The available modalities at these V_R values correspond to PE macromolecules with unsaturated C=C fragments, and the less intensive peaks at V_R=0.6 and 0.9 correspond to PE macromolecules without double bonds. It is clearly seen on f_n value for the first sample (0.5) that one of the two molecules contains one double bond. Taking into account the fact that in the IR spectra of the investigated samples, besides C=C bonds, the weak signal of the carbonyl group also being a chromophore and well absorbing in the UV area has been detected, it can be assumed that the less intensive peaks characterize PE macromolecules with functional carbonyl groups.

Thus, the complex use of HPLC methods allowed to establish the following types of the structural inhomogeneity in the composition of SP of HPPE production: First – inhomogeneity on ME (ELC), second – inhomogeneity on topology, i.e. on structure of chain and the last – on type of functionality (two-detector ALC). The obtained results on the composition and structure of SP of HPPE production allow carrying out polymer-analogous conversions purposefully and obtaining low-molecular PE with various properties using various substitution reactions, which, in turn, would allow it to be used as a plasticizer, modifier, etc. [6,7].

3.3 Investigation of the structural inhomogeneity in the process of microbiological synthesis of natural polysaccharides and polyethylenes

In this work, the molecular-weight distribution and functional compositions of natural polysaccharides (PS) and polyacetylenes (PA), the sources of which were basidiomycetes of the genus *Ganoderma lucidum Pleurotus ostreatus*, have been investigated with complex use of two-detector ELC and reverse-phase ALC. There have been used two-detector variants of these methods (refractometer, UV spectrophotometer) allowing to evaluate the quality and functional characteristics of the synthesized products in parallel**.** The results of ELC and ALC investigations of aqueous and ether extracts obtained after processing of the cultural liquid of the corresponding basidial fungi are presented in Table 9 and in Fig.17 and 18.

It has been established that there is a great similarity between the results obtained in a case of these types of basidial fungi (Fig. 17). It can be assumed in both cases on character of ALC chromatogram that the analyzed products consist of a mixture of fractions belonging to two different types of compounds. Since the first fraction is simultaneously fixed on refractometer (curves *a* and a^{I}, peaks 1) and on UV-detector having a multiplet character with five maxima with different intensities (curve b, peaks 1-5). This indicates to the availability of five sub-fractions of different functionality in its composition, well absorbed in the UV area. The individual character of the signal of fraction on refractometer has been connected with closeness of the physical-chemical parameters, especially the optical densities of the compounds existing in its composition. According to the results of physical-chemical analyses, their correspondence to PA compounds with a high degree of unsaturation, containing numerous triple and double bonds, i.e. active chromophore groups well absorbing in the UV area. The other 4 fractions are fixed only on refractometer and are referred to PS well soluble in water, in the composition of which the basic functional groups are auxochromic hydroxyl groups not absorbed in the UV area (curve *a*, peaks 2-5). It is seen on character of the chromatograms that in ether extracts, the quantitative advantage is PA (curve *a*), and in aqueous extracts – PS (curve a^I). In both cases, the quantity of PA and PS isolated from biomass of the corresponding basidiomycetes reaches 70-80%.



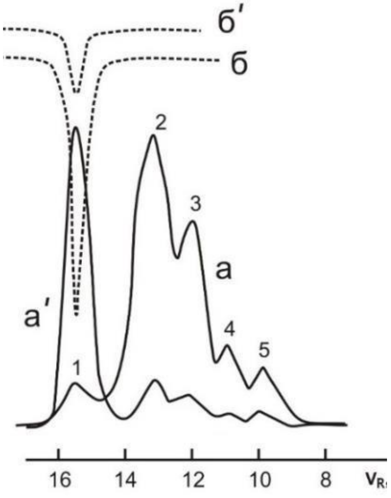


Fig.17. ALC curves of a mixture of PA and PS obtained in the biosynthesis process with basidial fungi of the genus *Ganoderma lucidum,* isolated during extraction with methyl ether (curves *a* and *b*) and water (curves *a'* and *b'* (dashed line). Adsorbent – Separon SGX C 18, edluent – acetonitrile+H_2O (75:25 %), 0.3 ml/min.

Fig.18. MWD curves of a mixture of PA and PS taken in ELC regime, isolated during extraction with methyl ether (кривые *a* и *б*) и водой (curves *a'* and *b'*). Adsorbent – Separon SGX, eluent – DMFA, 0.3 ml/min. Here in Fig.13 detectors: refractometric (continuous line), UV spectrometric (dashed line).

During growing of these fungi in the deep cultivation, it was possible to isolate the fractions from extracts with a SP value in a sufficiently low range of 1.0-1.2. Data of Table also shows that in both cases, in use of basidiomycetes of the genus *Ganoderma lucidum* and *Pleurotus ostreatus*, the identical regularities are observed; only a small difference at quantitative ratios of fractions in the composition of the investigated extracts is fixed.

Table 9

Molecular-weight characteristics of PA and PSobtained in the biosynthesis process with basidiomycetes *Ganoderma licidum* (fractions 1-7) and *Pleurotus ostreatus* (fractions 7-14). V_R= C_1-$C_2 lgM$, C_1=24.4, C_2=4

Name of fraction	Content of fraction,%		MWD		M_w/M_n	V_R (max)	M_p
	In ME	In water	M_w	M_n			
PA	74	6.0	180	180	1.0	15.35	180
Hexaoze	11	42.5	1085	1085	1.0	13.1	1085
Heptaoze	18	31	1260	1260	1.0	12.15	1260
OS	3.0	11.5	4390	3600	1.22	10.86	2430
OS	4.0	10	5450	4500	1.21	9.7	4730
OS (water)	-	-	1912	1260	1.82	-	-
OS (ME)	-	-	829	229	3.62	-	-
PA	71	8.0	180	180	1.0	15.35	180
Hexaoze	12	40	1085	1085	1.0	13.1	1085
Heptaoze	7.0	33	1260	1260	1.0	12.15	1260
OS	5.0	12	4600	3500	1.31	10.5	2985
OS	5.0	7.0	5600	4650	1.2	10.0	4000
OS (water)	-		1806	893	2.02	-	-
OS (ME)	-		855	244	3.5	-	-

Note: OS-oligosaccaride. Bold numbers – total parameters of MWD of product in aqueous and in ME extract. M_p^*- M_n in the maximum of peaks.

The changes of MW of these fractions in such wide range are consequently reflected in values of a degree polydispersity (SP). The total values of SP of ME extracts are sufficiently high (3.62 and 3.5) (Table 9) than aqueous extracts (1.82 and 2.02) (fractions 6 and 13). This shows about the fact that in the selected conditions of growing biomass of the investigated basidial fungi, as expected, the mechanisms of their action are the same. A comparison of UV chromatograms taken in ELC and ALC regimes shows that in the last case, a selectivity of system on functionality of PA compounds is high. So, the multiplet signals of PA fraction fixed in a case of ALC (Fig.17, curve *b* and $b^{\prime}$) are differed with monomodality in ELC system (Fig.18, curve *b* and $b^{\prime}$).

In order to study the chemical composition, the detected PA fractions were subjected to preparative separation. It was provided in the conditions of higher concentration of extract with multiple collection of the fraction according to the corresponding peaks of ALC fixed on UV-detector, which were then subjected to structural analysis. As a result of investigations carried out on study of the chemical composition and structure of PA mixtures grown by basidial fungi, 5 known compounds of the following structure have been respectively identified on peaks 1-5 (Fig.18, curve *b*). These compounds have been fixed sequentially in the following order:

1 - cis-undeca-3,9,10-triene-5,7-diine acid

$H_2C=C=CH-C\equiv C-C\equiv C-CH=CH-CH_2-COOH$;

2 - cis-undeca-2-ene-4,6,10-triine acid

$HC\equiv C-CH_2-CH_2-C\equiv C-C\equiv C-CH=CH_2-COOH$;

3 - cis-nona-4-ene-6,8-diine acid

$HC\equiv C-C\equiv C-CH=CH-CH_2-CH_2-COOH$;

4 - cis-undeca-3-ene-5,7,10-triine-1-ol-

$HC\equiv C-CH_2-C\equiv C-C\equiv C-CH=CH-CH_2-CH_2OH$;

5 - deca-cis-2-trans-8-dien-4,6- diine-1-ol-

$CH_3-CH=CH-C\equiv C-C\equiv C-CH=CH-CH_2OH$.

Successfully selected chromatographic conditions of carrying out of analysis allow not only to control the conditions of cultivation, but also the composition and structure of biosynthesis products, the effectiveness of various fungi separately. The methodology of preparation of PS and PA has been developed, and the factors regulating their ratios have been revealed [30, 55, 57].

CONCLUSIONS

I. Investigation of inhomogeneity of polymers on MW by a method of ELC in mono-detector chromatographic system

- The conditions of the oxidative polycondensation of phenylazomethine phenols by air oxygen and NaOCI in aqueous-alkaline medium have been considered. It has been shown that the tested planar di-, tri- and oligophenols with Schiff's substutuents in normal conditions interact actively with acetates of two-valence transition metals (Cu^{2+}, Co^{2+}, Zn^{2+}, Ni^{2+} and Pb^{2+}) with formation of the metal-polymer complexes with regulated MWD parameters in the wide range, possessing magnetic sensitivity and antibiotic activity against a number of testmicrocultures [2,3,4,8,20,38, 46,47,52].

- The oligomers of 2- and 4-aminopyridines, previously synthesized only by electrolysis, under has been firstly obtained by us, under the above menfioned conditions and the dependence of the molecular weight distribution on the reaction conditions has been established. It has been shown that the complexes of these oligomers with acetates of transition metal acetates, with adjustable MWD parameters, can be used as highly efficient catalysts in esterification, hydrolysis, amidation, epoxidation reactionns and other processes [1].

- In the presence of recycled chloroaluminate ionic liquids, and also in their combination with Ti-containing complexes with grafted "ion-liquid" ligands, the oligomerization of α-olefins has been carried out. MWD has been studied and the possibility of selective preparation of products with oligoalkyl naphthenic structure with low polydispersity and regulated molecular-weight characteristics has been shown [5,19,22].

- It has been carried out the exclusion-chromatographic control over photoelectrochemical synthesis process of oligosulfoimides, oligoacrylates, furan resins, binary and ternary copolymers of MA with α-olefins and (meth)acrylic acid and also over oligomerization process of polyaminocarbamide macromonomers and depending on conditions of electrolysis there have been synthesized the corresponding oligomers with regulated

MWD parameters and functionality, [11,14,28,31,33,36,37, 39,41,42,44, 53,59,60].

- MWD of monoalkyl (C_8-C_{12}) phenolformaldehyde oligomers modified with nitrogen-containing organic compounds and products of their high-temperature interaction with soybean oil has been investigated. It has been revealed the dependence of polymolecularity of the initial components and end products on degree of modification of the oligomer, on mass ratio of the initial components [34,40,45,48,49].

II. Investigation of the structural inhomogeneity of polymers by a method of ELC in two-detector chromatographic system

- The study of the structural inhomogeneity of oligoepichlorohydrins synthesized in a medium of methyl benzenes by a method of two-detector exclusion HPLC and critical chromatography showed that besides with MMP, it is also observed a distribution on types of functionality in its composition. So, seven types, including one cyclic and six linear bifunctional macromolecules with various MWD parameters have been detected in the composition of oligomer products [5,35,50].
- MWDs of polyfunctional polymer complexes on the basis of polyamines and thiocarbamide containing episulfide heterocycles, nitrile, amine and amide groups, as well as fragments of quaternary amines and chlorine in macrochain have been investigated by a method of ELC. Depending on the synthesis conditions, the various fractions from adducts consisting of initial components up to oligomers with MW in the ranges of 3500-4500 have been detected in the composition of the polymer complexes. Two-detector system of chromatography allowed to establish the necessary conditions for preparation of the polymer complexes with given functionality and MW [9,12].
- The regularities of formation of the polycondensation reaction products of anhydride of norbornene dicarboxylic acid with ethylene glycol and maleic anhydride have been studied. Two-detector system of chromatography allowed to

reveal six types of bifunctional macromolecules and also molecules of individual adducts forming at various combinations of the initial compounds in the composition of the investigated products [26].

- By a method of two-detector ELC it has been investigated the process of one-stage synthesis of alkyd resins on the basis of glycerin, phthalic acid and vegetable oils with use of new sulfocationites and Ti-containing metal-polymer nanocomposites as the catalyst. The possibilities of regulation of the molecular-weight distribution of the obtained alkyd resins depending on nature of the catalyst and conditions of realization of the reaction have been revealed [22,23,27].
- The dynamics of changes of the molecular structure and functionality of the polymer films on the basis of HPPE during exploitation in the natural conditions has been investigated by a method of ELC and the process of modification of polyethylene samples with dichlorocarbene formed as a result of thermolysis of sodium trichloroacetate has been also studied. It has been shown that under the influence of destructive natural factors, a series of low-molecular fractions containing double bonds and carbonyl groups is formed in the composition of the polymer films [10].

III. Investigation of the structural inhomogeneity of polymers in a multidimensional chromatographic system.

- The structural inhomogeneities of low-molecular side products of HPPE production have been investigated in the multidimensional chromatographic system with use of the methods of ELC and normal-phase ALC. It has been shown that in the composition of the investigated products, besides MWD and DTF, there is a inhomogeneity on topology of macromolecules. Thus, the used chromatographic system allowed to detect the linear and branched oligoethylene macromolecules with and without functional end double bond in the composition of the investigated products[6,7].
- The methods of ELC and reverse-phase ALC (multidimensional chromatography) allowed to reveal the separation on isomer composition in the composition of amination products of

α-hexene. It has been shown that in this case each telomer fraction consists of a mixture of three isomers, the separation of which occurs in order of decrease of their polarity, i.e., the first two isomers correspond to the more polar α- and β-oligoaminohexenes formed during 1,2 and 2,1 hydrogen migrations, and the third – less polar oligoaminohexene formed during the hydrogen migration either from the second to the third, or to the fourth carbon atom (γ- isomer) [24,43,58].

- The methology of analysis of the structural inhomogeneity of the interaction reaction products of naphtenic acids with polyyglycols and alcyl amine been developed. It has been shown that by changing the conditions of esterification, one can regulate a quantity of low-molecular mono-, di- and triesters, as well as high-molecular polyesters in the composition of products and obtain LSAS with various degree of hydrophilicity, having an important value in the development of the oil demulsifiers [51].
- The complex use of the methods of ALC and ELC (multidimensional chromatography) allowed to reveal the synthetic naphthenic acids in the composition of aliphatic esters obtained in the presence of nanocatalysts on the basis of sulfated polystyrene, besides individual alkyl esters and high-molecular oligoesters being products of the side reesterification reaction. It has been established that the availability of metal nanoparticles in the composition of the catalysts at low concentrations allows to regulate MWD parameters of products and increase the role of this or that reaction in the process [29].
- MWD and functional compositions of polysaccharides and polyacetylenes obtained in the biosynthesis, the sources of which were basidiomycetes of the genus *Ganoderma lucidum Pleurotus ostreatus*, have been investigated with complex use of two-detector ELC and reverse-phase ALC. During growing of these fungi in the deep cultivation, four fractions of polysaccharides with different MWD parameters and five fractions of polyacetylene compounds with conjugated unsaturated bonds of various functionality have been isolated and identified in the composition of their mycelium [15,16,17,18. 21,25,30,32,55,57].

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