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STUDY OF THE SYNTHESIS MECHANISM AND SOME PROPERTIES OF OLIGOMERS BASED ON EPICHLOROHYDRIN AND DIPHENYLGUANIDINE

Rovshan Israilovich Ismailov

Tashkent State Technical University, Tashkent city, Republic of Uzbekistan, Professor, DSc, i.ravshan1972@mail.ru, <https://orcid.org/0000-0002-1130-9228>; i.ravshan1972@mail.ru

Normuhamad Edgarov

Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, Tashkent city, Republic of Uzbekistan, Professor, DSc, yodgarov.n@mail.ru, <https://orcid.org/0000-0003-1296-3843>; yodgarov.n@mail.ru

Alisher Israilovich Ismailov

Tashkent State Technical University, Tashkent city, Republic of Uzbekistan, PhD, alisher3637@mail.ru, <https://orcid.org/0009-0005-6798-2412>, alisher3637@mail.ru



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STUDY OF THE SYNTHESIS MECHANISM AND SOME PROPERTIES OF OLIGOMERS BASED ON EPICHLOROHYDRIN AND DIPHENYLGUANIDINE

A.I.ISMOILOV¹, N.EDGOROV², R.I.ISMOILOV¹ (1 – Tashkent State Technical University; 2 – Institute of General and Inorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan, Tashkent city, Republic of Uzbekistan)*

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Abstract. In this work, the synthesis and the scheme for obtaining an oligomer based on epichlorohydrin with diphenylguanidine were studied, the proportions of epichlorohydrin in the initial mixture, the yield of oligomers, and the reduced viscosity were studied. The results of spectroscopic and elemental analyzes are obtained, which show that changes in the ratio of monomers have almost no effect on the iodine content in the oligomer. This is apparently due to the fact that epichlorohydrin is much more active in reactions than amino compounds. By studying the degree of conversion on the viscosity of the oligomerization products, the effects on the intrinsic viscosity of the oligomer were determined. The use of epichlorohydrin is due to its high reactivity due to the activity of the epoxy group and the mobility of the iodine atom of the iodomethyl group. In addition, based on a study of literary sources, we found that most of the substances intended to stabilize and slow down the combustion of polymer compositions contain ionically or covalently bound iodine, which gives them such valuable specific properties. The properties of surfactants are formed in the process of their synthesis, since the mechanism and patterns of synthesis are interrelated with the properties of the compounds. We have studied the interaction of epichlorohydrin with diphenylguanidine and found that spontaneous oligomerization occurs at a sufficient rate in bulk at room temperature. Spontaneous polymerization of epichlorohydrin with diphenylguanidine was studied by the dilatometric method, and the contraction coefficient, which determines the degree of change in the volume of the monomer mixture, was also studied. The mechanism of synthesis, the structure of the final product, technological and kinetic regularities of the process make it possible to predict the physical and colloid-chemical properties of oligomers. Determining the properties of products in conjunction with mathematical modeling of synthesis is the subject of further research.

Keywords. synthesis, oligomer, kinetics, epichlorohydrin, diphenylguanidine, spectroscopy, physic-chemical properties.

Annotatsiya. Ushbu ishda difenilguanidin bilan epiklorogidrin asosidagi oligomerni olish sintezi va sxemasi, epiklorogidrinning dastlabki aralashmadagi nisbati, oligomerlar unumi, qovushqoqligi pasayganligi o'rganildi. Spektroskopik va elementar tahlillar natijalari olingan bo'lib, monomerlar nisbatidagi o'zgarishlar oligomeridagi yod miqdoriga deyarli ta'sir qilmaydi. Bu, ehtimol, epiklorogidrinning aminokislotalarga qaraganda ancha faol reaksiyaga kirishishi bilan bog'liq. Oligomerlanish mahsulotlarining qovushqoqligiga konversiya darajasini o'rganish orqali oligomerning ichki yopishqoqligiga ta'siri aniqlandi. Epiklorogidrinidan foydalanish epoksi guruhining faolligi va yodometil guruhining yod atomining harakatchanligi tufayli uning yuqori reaktivligi bilan bog'liq. Bundan tashqari, adabiy manbalarni o'rganish asosida biz polimer kompozitsiyalarining yonishini barqarorlashtirish va sekinlashtirish uchun mo'ljallangan ko'pchilik moddalarda ion yoki kovalent bog'langan yod borligini aniqladik, bu ularga shunday qimmatli o'ziga xos xususiyatlarni beradi. Sirt faol moddalarning xossalari ularning sintezi jarayonida hosil bo'ladi, chunki sintez mexanizmi va sxemasi birikmalarning xossalari bilan o'zaro bog'liqdir. Biz epiklorogidrinning difenilguanidin bilan o'zaro ta'sirini o'rganib chiqdik va xona haroratida o'z-o'zidan oligomerizatsiya massada etarli tezlikda sodir bo'lishini aniqladik. Epiklorogidrinning difenilguanidin bilan o'z-o'zidan polimerlanishi dilatometrik usulda, monomer aralashmasi hajmining o'zgarish darajasini belgilovchi qisqarish koeffitsienti ham o'rganildi. Sintez mexanizmi, yakuniy mahsulotning tuzilishi, jarayonning texnologik va kinetik qonuniyatlari oligomerlarning fizik va kolloid-kimyoviy xususiyatlarini oldindan aytish imkonini beradi.

Tayanch so'zlar: sintez, oligomer, kinetik, epiklorogidrin, difenilguanidin, spektroskopiya, fizik-kimyoviy xossalalar.

*Ismailov Rovshan Israilovich – Professor, DSc, i.ravshan1972@mail.ru, <https://orcid.org/0000-0002-1130-9228>;

Edgarov Normuhamad – Professor, DSc, yodgarov.n@mail.ru, <https://orcid.org/0000-0003-1296-3843>;

Ismailov Alisher Israilovich – PhD, alisher3637@mail.ru, <https://orcid.org/0009-0005-6708-2412>.

Аннотация. В работе исследован синтез и схема получения олигомера на основе эпишодгидрина с дифенилгуанидином, изучены доли эпишодгидрина в исходной смеси, выход олигомеров, приведенная вязкость. Получены результаты спектроскопических и элементных анализов, которые показывают, что изменения соотношения мономеров почти не влияет на содержание иода в олигомере. Это по-видимому связано с тем, что эпишодгидрин намного активнее вступает в реакции, чем аминосоединения. Изучением степени превращения на вязкость продуктов олигомеризации определены действия на характеристическую вязкость олигомера. Использование эпишодгидрина обусловлено его высокой реакционной способностью вследствие активности эпокси группы и подвижности атома иода иодметильной группы. Кроме того, на основании исследования литературных источников, нами установлено, что большинство веществ, предназначенных для стабилизации и замедления горения полимерных композиций, содержат ионно- или ковалентно связанный иодом, который придает им столь ценные специфические свойства. Свойства поверхностно-активных веществ формируются в процессе их синтеза, поскольку механизм и закономерность синтеза взаимосвязаны со свойствами соединений. Нами изучено взаимодействие эпишодгидрина с дифенилгуанидином и установлено, что при комнатной температуре с достаточной скоростью в массе происходит самопроизвольная олигомеризация. Самопроизвольную полимеризацию эпишодгидрина с дифенилгуанидином изучали dilatометрическим методом, также был изучен коэффициент контракции, определяющий степень изменения объема мономерной смеси. Механизм синтеза, структура конечного продукта, технологические и кинетические закономерности процесса позволяют прогнозировать физические и коллоидно-химические свойства олигомеров.

Ключевые слова: синтез, олигомер, кинетика, эпишодгидрин, дифенилгуанидин, спектроскопия, физико-химические свойства.

Introduction

Research in the field of synthesis and study of the properties of oligomers containing active reactive groups is of certain theoretical and practical interest. The most common methods for the synthesis of reactive oligomers are ionic and radical polymerization of reactive monomers, the method of chemical transformations, etc. As is known, these methods are characterized by multi-stage and complexity of oligomerization and are often accompanied by side reactions. In this aspect, it is of particular interest to obtain reactive oligomers by spontaneous polymerization at relatively low temperatures and in the absence of an initiator. It is known that the method of stabilizing polymers and reducing their flammability by introducing organic and inorganic additives used in the production of composite building materials has significant disadvantages, such as migration, toxicity, heterogeneity, large shrinkage of additives and deterioration of some physical and mechanical properties of polymers. Elimination of these disadvantages can be achieved by introducing polymer or oligomeric stabilizers and combustion inhibitors into the compositions [1-6].

By reacting epihalohydrin (EHH) with various nitrogen-containing compounds, a huge number of compounds with a complex of valuable properties have been synthesized. At the same time, the reaction of interaction between EHH and amino compounds has been the most studied. This is due to the fact that when EHH interacts with amino compounds, new compounds are formed that have valuable properties. It is advisable to obtain quaternary ammonium compounds and polyfunctional polyelectrolytes

based on the products of the interaction of epihalohydrin with amino compounds [7-9].

In works [10-13], the processes of spontaneous oligomerization of epiodohydrin (EIH) with amino compounds: benzoxazolinone, its methyl methacrylic esters, and α -amino acids were considered for the first time. The dependence of the oligomerization process on various factors (ratio of reagents, temperature, polarity of the reaction solvent, time) was studied. Six new ammonium oligomers were obtained. The kinetics of the reaction in terms of product yield was studied depending on the concentration of EIH, amino compounds and temperature. The reaction kinetics equations were determined and it was found that the rate of spontaneous oligomerization is practically proportional to the molar concentration of both EIH and amino compounds.

EIG is one of the important and accessible compounds for the synthesis of oligomers. When EIG interacts with amino compounds as a result of the Menshutkin reaction, quaternary ammonium salts are formed, which undergo spontaneous oligomerization. There is a sufficient number of literary sources devoted to the synthesis, patterns of formation, study of physicochemical properties and areas of application of EIH oligomers and various amino compounds. But in these works, due attention is not paid to the colloidal chemical, including surface-active properties of the synthesized oligomers [14-16].

Oligomers obtained by the interaction of EIG with nitrogen- and silicon-containing compounds seem interesting and promising. If stable oligomeric products are obtained by reacting ECH with these compounds, then their properties can be predicted.

They must have surface activity, micelle-forming and solubilizing ability, adhesive properties, and be heat and heat resistant. They can be used as components of adhesive compositions, co-hardeners of epoxy resins, stabilizers and modifying reagents for various composite systems.

Materials and Methods

We studied the kinetics of oligomerization of epiiodohydrin with diphenylguanidine (DPG) by dilatometry. In order to determine the optimal conditions for the process and quantitatively analyze the influence of various factors on the properties of oligomers, the kinetics of spontaneous oligomerization of EIH with DPG was studied. The effect of temperature on the rate of spontaneous oligomerization of EIH with DPG in ethanol solution was studied [17-20]. The dependences of the rate, spontaneous oligomerization, oligomer yield, and also spectroscopic studies were studied.

Spontaneous polymerization of EIH with DPG was studied using the dilatometric method (as well as the gravimetric method to study the kinetics of polymer formation at high degrees of conversion), which makes it possible to determine the polymer yield by selecting the reaction mixture during polymerization.

The degree of conversion of monomer to polymer q (weight fraction in %) was calculated using the formula

$$Q = \Delta V / V_0 K$$

where V_0 - is the initial volume of the reaction mixture at a given polymerization temperature, ml; ΔV -change in the volume of the reaction mixture over a period of time, ml; K is the contraction coefficient, which determines the degree of change in the volume of the monomer mixture at a given temperature as a result of the complete conversion of monomers into polymer.

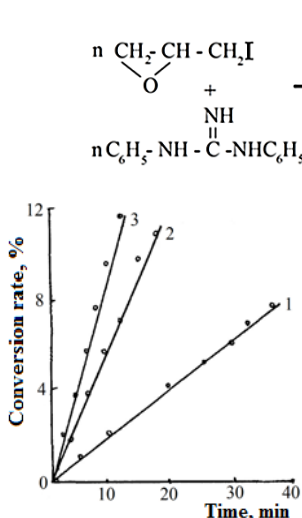


Fig 1. Dependence of the yield of the EIH oligomer with DPG on the reaction duration at various temperatures: 1-313K; 2-323K; 3-333K

The contraction coefficient depends on the density of the monomer and polymer and is calculated by the formula:

$$K = \frac{\frac{1}{\rho_m} - \frac{1}{\rho_n}}{\frac{1}{\rho_n}}$$

where ρ_m, ρ_n - are the densities of the monomer and polymer, respectively, g/sm^3 .

Stirring of the reaction mixture was carried out using a magnetic stirrer, which promoted the rotation of a magnet sealed in glass inside the dilatometer.

Before carrying out systematic experiments, in all cases, preliminary checks of the reproducibility of the results were carried out. The resulting final products were dissolved in ethyl alcohol and precipitated with ether to remove unreacted monomer. After this, the resulting polymer was dried in a vacuum oven at room temperature to constant weight.

Results and Discussion

The average reaction rates were determined at the initial stage of the reaction at 313-333K. As can be seen from table. 1, with increasing temperature, the rate of polymerization increases. Based on these results, the nature of the dependence of $lg \frac{100}{100-x}$ on time was determined (Fig. 1-2), where x is the amount of unreacted monomer. The linear nature of the dependence indicates that the overall rate of oligomerization is described by a second-order equation.

As a result of these reactions, soluble ammonium oligomers of a regular structure and insoluble ammonium oligomers of a three-dimensional structure are formed.

A mechanism for spontaneous polymerization has been proposed, which involves the formation of a zwitterion that begins chain growth according to the anionic oligomerization mechanism.

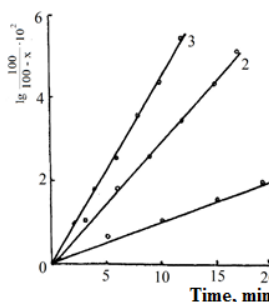
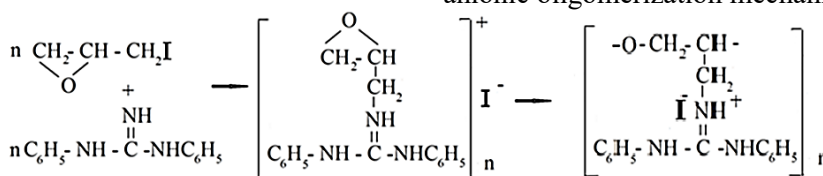


Fig 2. Dependence of $lg \frac{100}{100-x}$ on the duration of spontaneous oligomerization of EIH with DPG at temperatures: 1-313 K; 2-323K; 3-333K

Spontaneous oligomerization of EIH with DPG occurs at low temperatures, in the absence of initiators, at a sufficiently high rate.

Table 1

Dependence of the rate of spontaneous oligomerization at interaction of EIH with DPG in ethanol. DPG concentration is 1.5 mol/l

Temperature, K	Time, min	Exit, %	$lg \frac{100}{100-x}$	$K_{average} \cdot 10^5$	Average rate of spontaneous oligomerization	
					%/min	$\frac{mol}{l \cdot sec} \cdot 10^3$
313	5	1,4	0,00612	3,6	0,21	2,33
	10	2,2	0,00966			
	15	3,4	0,01502			
	20	4,2	0,01863			
	25	5,1	0,02273			
	30	6,0	0,02687			
323	3	1,7	0,00744	10,6	0,62	6,89
	6	3,8	0,01682			
	9	5,6	0,02502			
	12	7,5	0,03385			
	15	9,5	0,04312			
	18	10,8	0,04963			
333	2	2,0	0,00877	17,2	0,98	10,86
	4	3,8	0,01682			
	6	5,6	0,02502			
	8	7,7	0,03479			
	10	9,5	0,04335			
	12	11,7	0,05403			

Quaternization of the EIH molecule with the DPG molecule reduces the value of the potential barrier during the interaction of quaternized epiiodohydrin molecules. The mobile hydrogen of the quaternary ammonium group opens the ring, forming an oligomer with flame retardant properties.

The activation energy was determined graphically. The activation energy of the oligomerization process is 33.3 kJ/mol. To elucidate the mechanism of the reaction between EIH and DPG, IR- and PMR- spectra of the starting components and the final product were recorded at room temperature.

In the PMR spectrum recorded with methanol, new signals appear in the form of a doublet-doublet at 4.3 ppm. characteristic of the hydrogen atoms of the N-CH₂ group. The aromatic ring signals shift to a weaker region and appear at 7.5 ppm. moderate signal. The characteristic signal for the methylene group associated with the oxygen atom shifts to the region of 3.00 ppm and appears in the form of a doublet-doublet. The proton signals from the methyl group bonded to the oxygen atom appear at 4.65 ppm.

In the IR spectra of the synthesized oligomer, the bending vibrations of the =NH group (1545 cm⁻¹) of diphenylguanidine, connected to the carbon atom

through a double bond due to the formation of ammonium groups, disappear. In this case, new signals are formed for asymmetric vibrations of the ether (-C-O-C-) bond in the region of 1125 cm⁻¹. The signals also disappear due to the opening of epoxy groups (1235, 935, 860 cm⁻¹) during spontaneous oligomerization.

It can be assumed that the oligomerization reaction occurs due to the quaternization of the =NH group. NH groups bound to the phenyl group do not react at 313-333K. Apparently, this is due to the shielding of NH groups associated with the phenyl radical. The formation of soluble products is also proof of this assumption.

In order to clarify the influence of the monomer ratio on the oligomerization process, the dependence of the oligomer yield on the ratio of EIH to DPG was studied. It was determined that the rate of oligomerization increases linearly with increasing concentration of epiiodohydrin in solution.

To determine the effect of the initial concentration of monomers, we studied the dependence of the oligomer yield at different concentrations of monomers at 323 K and the ratio of EIH to DPG equal to 2:1. As the initial concentration

of monomers increases, the rate of oligomerization increases.

Of great interest is the study of the influence of solvents. The polymerization reaction proceeds faster in polar solvents. The dependence of the oligomer yield on polarity at 323 K was studied in a mixture of alcohol and water solvents, creating different dielectric constants of the medium. Dielectric constant values varied from 81 to 24.3. The highest rate of oligomerization and the yield of oligomer are directly proportional to the dielectric constant of the medium. The increase in the rate of spontaneous oligomerization with increasing dielectric constant of the solvent is apparently explained by the fact that in this case the Menshutkin reaction, responsible for the process, accelerates.

Thus, when EIH interacts with DPG, due to the high reactivity of the iodine atom of EIH and the high nucleophilicity of DPG, a positive charge appears on the nitrogen atom in the intermediate product. It enhances the activity of interacting functional groups, and this increases the rate of spontaneous oligomerization.

The rate of spontaneous oligomerization does not depend on the content of radical inhibitors in the reaction medium. In order to study the effect of radical oligomerization inhibitors, the oligomerization reaction was carried out in the presence of hydroquinone, atmospheric oxygen, diphenylpicrylhydrazine and 2,2,6,6-tetramethylpiperidyl nitroxide. The obtained result indicates the non-radical nature of the process.

To prove the mechanism of spontaneous oligomerization of EIH with DPG, a similar reaction of epiodohydrin and diphenylthiourea was performed. At a temperature of 313-333K, the reaction between EIH and diphenylthiourea molecules does not occur. It can be assumed that the spontaneous oligomerization reaction of EIH occurs due to the =NH group of DPG with the formation of quaternized groups. Shielded NH groups of DPG, as we see in the example of diphenylthiourea, do not participate in the reaction.

It has been established that during the interaction of EIH with DPG, spontaneous oligomerization occurs in the absence of initiators and catalysts in a wide temperature range (293-373 K) with the formation of reaction products and a molecular weight of 3000-6000 cu.

Oligomers of EIP with DPG are slightly yellow powders. They are highly soluble in ethanol, dimethylformamide, dimethyl sulfoxide and other highly polar solvents, but insoluble in water, dioxane, and benzene. Oligomers can be crushed with a mortar or mixed with polymer powders by extrusion.

Of great interest is the study of the time dependence of the yield of the EIH oligomer with DPG at high degrees of conversion.

The dependences of the reduced viscosity and iodine content in the EIH oligomer with DPG on the nature of the solvents were determined (Table 2), as can be seen with increasing solvent polarity, the values of the intrinsic viscosity of the oligomer decrease.

Table 2
Some physicochemical properties of oligomers synthesized on the basis of EIH with DPG. $S_{DfG}=1.5 \text{ mol/l}$
 $\tau=1 \text{ hour, } T=333\text{K}$

Solvent	Exit, %	η 0.5% solution	Bromine content, %
Ethanol	48,0	0,07	22,8
Acetone	8,8	0,09	22,6
Dimethylformamide	2,3	0,08	22,1

Table 3
Oligomerization conditions and some physicochemical properties of oligomers synthesized on the basis of EIH with DPG in ethyl alcohol, $\tau=1 \text{ hour}$

EIH:DFG molar ratio	Temperature, K	Exit, %	η 0,5% solution	Nitrogen content, %
1:1	313	13,66	0,05	14,00
2:1	313	20,33	0,06	13,58
1:2	313	7,22	0,06	13,66
4:1	313	18,61	0,06	12,63
1:1	323	25,58	0,05	14,07
2:1	323	27,46	0,06	13,62
1:2	323	12,63	0,05	13,16
4:1	323	21,84	0,05	13,11
1:1	333	43,89	0,07	13,87
2:1	333	48,00	0,06	13,53

EIH:DFG molar ratio	Temperature, K	Exit, %	η 0,5% solution	Nitrogen content, %
1:2	333	22,02	0,06	13,74
4:1	333	37,36	0,08	13,25

The dependence of the intrinsic viscosity on the ratio of EIG to DPG was studied (Table 3). Oligomerization occurs at high speed in bulk and highly polar solvents.

Conclusion

Thus, by increasing the proportion of epiiodohydrin in the initial mixture, the yield and reduced viscosity increase. The results of elemental analysis show that changes in the ratio of monomers have almost no effect on the bromine content in the oligomer. This is apparently due to the fact that epiiodohydrin reacts much more actively than amino compounds. The degree of conversion affects the viscosity of the oligomerization products.

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