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## METHOD FOR PRODUCING SILICONORGANIC COMPOUNDS

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**Abstract.** In this paper, the results of the synthesis of vinyl ethynyltriethoxysilane monomer are simulated on the basis of available industrial products of tetraethoxysilane and vinyl ethynyl magnesium bromide. The main physical properties of IR and UV spectroscopy have been determined, and a synthesis procedure has been developed that makes it possible to obtain compounds with high yields without laborious additional operations. The new substances obtained were identified by IR and UV spectroscopic methods and their melting point, refractive index, density, and other physical and chemical parameters were determined. The effect of the initial ratio of the components and the nature of the solvents on the yield of the polymer at different temperatures and the duration of the reaction was studied. The influence of the nature of organic solvents on the yield of this reaction product was studied. It is determined that the reaction rate increases with increasing polarity of the solvent .

**Keywords:** Monomer, tetraethoxysilane, vinyl ethynyl magnesium bromide, vinyl ethynyltriethoxysilane, polyvinylethynyltriethoxysilane, IR, UV-spectroscopy, boiling point, refractive index, density, specific viscosity.

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**Аннотация.** В работе приведены результаты синтеза мономера винилэтинилтриэтоксисилан на основе доступного промышленного продукта тетраэтоксисилана и винилэтинилмагнийбромид. Определены основные физические свойства методом ИК-, УФ-спектроскопии и разработана методика синтеза, позволяющая получать соединения с высокими выходами без трудоемких дополнительных операций. Полученные новые вещества идентифицированы методами ИК и УФ спектроскопии, определены температура их плавления, показатель преломления, плотность и другие физико-химические параметры. Было изучено влияние исходного соотношения компонентов и природы растворителей на выход полимера при различных температурах и продолжительности реакции. Определено, что скорость реакции увеличивается с увеличением полярности растворителя.

**Ключевые слова:** Мономер, тетраэтоксисилан, винилэтинилмагнийбромид, винилэтинилтриэтоксисилан, поливинилэтинилтриэтоксисилан, ИҚ-, УФ-спектрокопия, температура кипения, коэффициент преломления, плотность, удельная вязкость,.

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**Түйіндеме.** Бұл жұмыста қолжетімді өндірістік енім тетраэтоксисилан мен винилэтинилмагнийбромид негізіндегі винилэтинилтриэтоксисилан мономері синтезінң нәтижелері келтірілген. ИҚ және УК-спектрокопия әдісімен жасалған негізгі физикалық ерекшеліктері анықталып, кеп жұмысты қажет ететін қосымша операцияларсыз жоғары нәтижелі қосымшаларды алуға мүмкіндік беретін синтездеу әдісі жасалды. Алынған жаңа заттар ИҚ және УК-спектрокопия әдістерімен теңестіріліп, олардың балқу температурасы, сыну керсеткіші, тығыздығы және басқа да физикалық-химиялық параметрлері анықталды. Полимердің шығуына әртүрлі температурада және реакцияларының ұзақтығына қарай компоненттердің және еріткіштер табиғатының бастапқы байланысының әсері зерттелді. Реакция жылдамдығының еріткіштің қарама-қарсылығының артуына қарай есетіні анықталды.

**Түйінді сөздер:** Мономер, тетраэтоксисилан, винилэтинилмагнийбромид, винилэтинилтриэтоксисилан, поливинилэтинилтриэтоксисилан, ИҚ және УК-спектрокопия, қайнау температурасы, сыну коэффициенті, тығыздық, меншікті тұтқырлық.

**Introduction.** As is known, organosilicon compounds have surprising properties, which are manifested when applied to the surface of materials. At the same time, the formation of the thinnest film is observed, which in turn, bypassing the air, does not allow water or moisture to pass through. These films have a relatively high resistance to external influences such as low and high temperature, are chemically stable and have mechanical strength. In connection with this, there has been a recent increase in the interest in studies related to the production of organosilicon compounds and their applications in various industries.

From the literature review, one can find out in the works of scientists Kiping, Friedel and Crafts, Grignard, K.K. Kuvatbaev, K.A. Andrianov, S.V. Zakharova, M.M. Kabachkin, T.V. Koroleva, M.B. Lotharev, A.N. Polovanov, V.M. Kopylov, V.V. Kireev, A.I. Demchenko, A.A. Arshinov, D.O. Anashkin, and I.M. Raigorodskii used the following methods for the preparation of organosilicon compounds: disproportion, pyrolysis, Würz method, thermocatalytic pyrolysis, organometallic synthesis, direct synthesis. In the above methods, specific conditions are required, such as high tempera-

ture, complexity of instruments, etc. In our opinion, a convenient method of obtaining organosilicon compounds is the Grignard reaction [1].

**Experimental part:**

Synthesis of vinyl ethynyl magnesium bromide –  $\text{CH}_2=\text{CH}-\text{C}\equiv\text{C}-\text{MgBr}$ . Upon careful cooling with a mixture of snow and  $\text{CaCl}_2$  and constant stirring, vinyl acetylene was introduced into the ethereal solution of ethylmagnesium bromide. The reaction time is about 5.0 hours. The resulting product vinyl ethynylmagnesium bromide is readily soluble in ethyl ether. The yield is 67% [2].

Synthesis of polyvinylethynyltriethoxysilane. To synthesize vinyl ethynyltriethoxysilane in a 1000 ml four-necked flask, 210 ml (2.0 moles) of ethyl ether (or other solutions: benzene, THF, etc.) were poured in with a mechanical stirrer with a stopper, thermometer, dropping funnel and reflux condenser, and 110 ml (1.0 mole) of tetraethoxysilane were added to the stirring. The temperature was then raised to 45-50 °C, and 140 ml (1.0 mole) of vinyl ethynyl magnesium bromide was charged in portions over a period of 45-50 minutes. Then, with vigorous stirring, the temperature was raised to 55-60 °C and the reaction continued for another 4.0-5.0 hours. At the end of the time, the agitator was stopped, allowed to cool for 2.0 hours and cooled to 10.0 ± 2.0 °C.

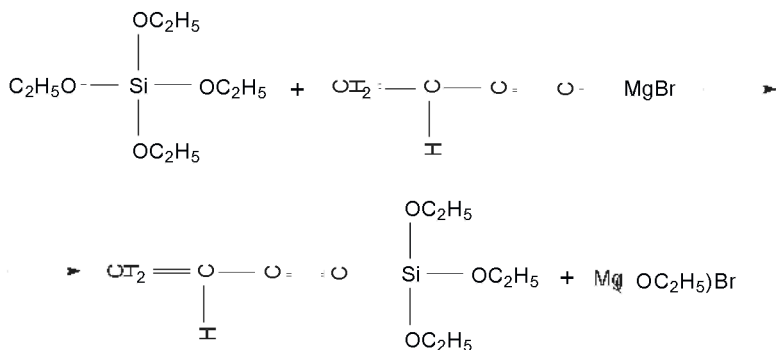
Then, in small quantities, the reaction mixture was transferred to a separatory funnel, several times washed with bidistilled water (until bromine ions appeared in the wash water, with a silver nitrate probe) to remove magnesium ethoxy bromide. The ethyl ether was distilled off at a temperature of

35.6 °C (or benzene at 80.1 °C) by vacuum distillation with a vacuum pump with a pressure of 1.8-2.0 for ethyl ether or 5.0-5.2 millimeter of mercury.

The interaction of tetraethoxysilane and vinyl ethynyl magnesium bromide in equimolecular proportions leads to the formation of vinyl ethynyltriethoxysilane according to the following scheme:

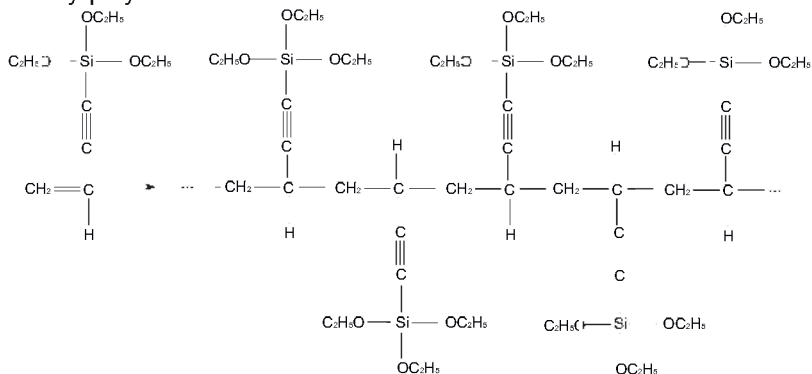
Unlike dry ether and benzene, reactions carried out in the medium of other solvents such as toluene, dioxane, etc. give a lower yield of the final product.

Synthesized vinyl ethynyltriethoxysilane is an oily liquid, light yellow in color, highly soluble in esters, benzene, chloroform, tetrahydrofuran, dioxane, hexane, poorly soluble in acetone, pyridine, dimethylformamide, dimethylsulfoxide and absolutely insoluble in water and alcohols.



The most common method of polymerization of organosilicon polymers is the thermopolymerization of monomers.

The resulting vinyl ethynyltriethoxysilane monomer is polymerized, followed by polymer formation:



Then, the desired product of polyvinylethynyltriethoxysilane was subjected to rectification, and a product of polyvinylethynyltriethoxysilane with ethyl ether 150 ml (50%) or benzene 140 ml (48%)  $n_D^{20} 1,4560$  was obtained;  $d_4^{20} 1,0183$ . (48 %).

Viscous polyvinylethynyltriethoxysilane is a colorless, non-toxic substance that is odorless and insoluble in water. Not soluble in lower alcohols, however, it dissolves in many organic solvents, has increased chemical stability. Thermostable, characterized by a small change in viscosity with temperature. In Table 1. some basic physical properties of the obtained products are given.

**Table 1 - The basic physical properties of organoelemental mono(poly)mer measures based on silicon**

Products	Density at 25 °C, g / cm <sup>3</sup>	Coefficient of refraction, $n_D^{25}$	Specific viscosity, at 25 °C, ccm
Vinyl Ethyltriethoxysilane	1,1154	1,13526	120
Polyvinylethynyltriethoxysilane	1,3372	1,3862	410

**The discussion of the results.** It is determined that even at a low conversion rate, the polymer yield also depends on the initial component ratio and temperature. It was found that with initial conversions the yield of the product increases linearly in accordance with the duration of the reaction.

In order to determine the effect of temperature on kinetics, the reaction was carried out in the temperature range of 0-50 °C at different ratios of the initial reagents. An increase in temperature led to an increase in the rate of the process, and an increase in the yield of the polymer. Note that the resulting product had a lower intrinsic viscosity, which is clearly seen from Figure 1.

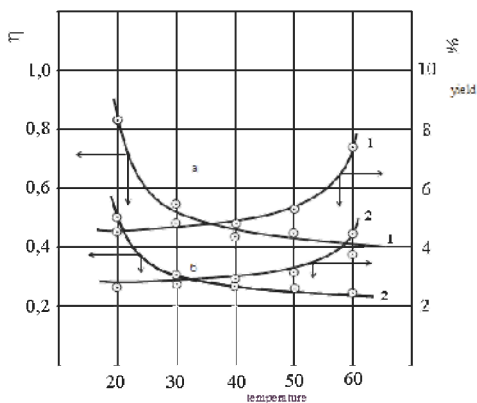


Figure 1 - Change in the intrinsic viscosity, and the yield from the temperature in the 50: 1 ratio and (2 b) ratio of 50: 5 benzene. The starting ratio of tetrachlorosilane and vinyl ethynyl magnesium bromide is 50:50. Duration 1 hour.

Thus, it has been found that the viscosity of the product varies with different ratios and concentrations.

Study of the thermo-oxidative degradation of polyvinylethynyltriethoxysilane. We used the differential thermal analysis (DTA) method. With its help it is easy to fix the temperatures (T) of the samples and, most importantly, the integral and differential curves of the mass change (TG and DTG), as well as the enthalpy (DTA). Thermooxidative degradation of polyvinylethynyltriethoxysilane was studied in the temperature range 200 - 400 °C.

Studies were conducted on a NETZSCH STA-409 PG TG-DSC analyzer, equipped with a K-type (Low RG Silver) thermocouple and using aluminum crucibles. The amount of sample was taken in the range of 5-6 mg. All measurements were carried out in an inert atmosphere of nitrogen with a purge rate of 50 ml/min. The heating rate was 10 K/min. The measuring system was calibrated using standard substances – indium, bismuth, tin, zinc, and cesium chloride.

Under the experimental conditions, polyvinylethynyltriethoxysilane was treated with benzoyl peroxide. The consumption of benzoyl peroxide was 2.5% of the weight of the polymer. The results of the study of the thermal oxidative degradation of polyvinylethynyl dihydroxychlorosilane are shown in Figure 2.

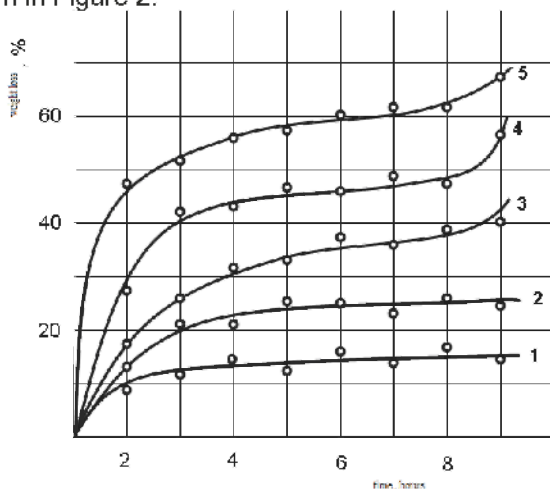


Figure 2 - Dependence of the degree of degradation (in% weight loss) of polyvinylethynyltriethoxysilane on the temperature and duration of thermal oxidation. Temperature of thermal oxidation in °C: 1- 200; 2-250; 3-300; 4-350 and 5-400.

From the data obtained it was found that polyvinylethynyltriethoxysilane at 200°C undergoes a slight degradation, and at 250-350 °C, an intensive decomposition of the polymer occurs. The greatest destruction with complete destruction of polyvinylethynyltriethoxysilane is observed at 400°C.

From the data obtained (Figure 2), it can be seen that the thermo-oxidative degradation of polyvinylethynyltriethoxysilane is S-shaped in regression-transcendental diagrams. Analysis of the dependence of the degree of degradation of the forming products after thermal oxidation at different temperatures (Table 2) shows that at 250°C, as a result of thermal degradation, after the 3 hours of the process, weight loss is 21,85%, and at 400°C, respectively, weight loss is 52,44% of the initial weight. As a result of the analysis of polyvinylethynyltriethoxysilane subjected to thermal-oxidative degradation, in the presence of benzoyl peroxide, are shown in Table 2.

**Table 2 - Analysis of polyvinylethynyltriethoxysilane after thermal oxidative degradation in the presence (2.5% by weight) of benzoyl peroxide**

Conditions for destruction		Weight loss, %
Temperature, °C	Time, per hour	
250	3	21,85
	9	24,36
400	3	52,44
	9	66,74

The decomposition of the elemental composition of polyvinylethynyltriethoxysilane has a linear dependence on the loss of mass (Table 2). This is apparently due to the fact that the thermo-oxidative degradation of polyvinylethynyltriethoxysilane occurs both with the breakdown of COO-Si and with the breakage of Si-C bonds.

The complete removal of carbon upon the breakdown of the Si-C bond into polyvinylethynyl-triethoxysilane is due to the fact that, during

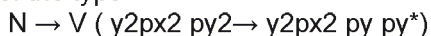
thermal-oxidative degradation, along with the separation of ethynyl groups between the silicon atoms, the formation of oxygen bridges takes place, which probably hinders the ethynyl group with oxygen (steric effect). To identify the structure and determine the qualitative characteristics of the obtained substances, we used the IR spectroscopy method in a wide range of spectra - in the regions 500-3500  $\text{cm}^{-1}$ . The average intensity absorption bands in the 1400, 1465, 1250  $\text{cm}^{-1}$  region, characterizing stretching vibrations of a single C-C bond, are noted. The absorption bands of about 1025 and 1095  $\text{cm}^{-1}$  vibration frequencies indicate, respectively, the presence of Si-O and Si-C bonds.

The characteristic bands of stretching vibrations of the multiple bond for the ethylene group ( $\nu_{(\text{C}=\text{C})}$ ) are found in the region 1795, 1740, 1680  $\text{cm}^{-1}$ . In the spectra of a polyvinylethynyltriethoxysilane compound, such characteristic absorption bands are also present [3-5].

For the objects studied in the work, UV spectra were also used. In particular, UV spectra were obtained for solutions of polyvinyl ethynyltriethoxysilane in ethyl ether.

Chromoforems are for the most part groups of atoms with unsaturated bonds. However, polyvinyl ethynyltriethoxysilane containing unsaturated bonds C = C absorbs only in the spectral region  $> 200$ .

The ethynyl group  $\text{—C}\equiv\text{C—}$  in the samples has a wide band up to 240 nm and it must be assumed that it is due to the possibility of a transition of the type



A wide diffuse band is also found in the region of 180-165 nm and two systems of bands, of the Ribberg series, in the region of 152-105 nm. Further, the presence of conjugations of two double bonds between carbon atoms was established, which leads to the appearance of intense absorption in the region of 225 nm.

It is known that C-C bonds between carbon atoms usually only absorb in the long ultraviolet region. Also, the absorption band of the chromophore group, depending on the conditions in which the chromoform is located (neighboring atoms, solvent, etc.), can shift within certain limits.

**Conclusions.** Synthesis of organosilicon monomers and polymers based on them, including the monomer vinyl ethynyltriethoxysilane, was obtained. The new substances obtained were identified by IR and UV spectroscopic methods and their melting point, refractive index, density, and other physical and chemical parameters were determined. The effect



of the initial ratio of the components and the nature of the solvents on the yield of the polymer at different temperatures and the duration of the reaction was studied. The influence of the nature of organic solvents on the yield of this reaction product was studied. It is determined that the reaction rate increases with increasing polarity of the solvent .

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