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Research of Physico-Chemical Properties of Synthesized Thiocol Oligomer Based on Sodium Polysulphide, Monochlorohydrine and Ammonium Phosphate

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Abstract: The purpose of this study is the synthesis and study of thiokol oligomer ДКА-4 brand based on sodium tetrasulfide, epichlorohydrin and ammonium phosphate, which is intended for use as a main component Thiokol sealant. To achieve this goal, a thiokol oligomer based on sodium tetrasulfide, epichlorohydrin, and ammonium phosphate was synthesized and investigated, and the optimal conditions for the synthesis of a thiokol oligomer were determined. Research has been carried out on the influence of the molar ratios of the starting substances on the composition and physicochemical properties of the synthesized thiocol oligomer. The optimum polycondensation temperature was taken as 80o-85o C, the reaction time is 1.5-2 hours, as a result, the yield of the target product reaches 93%. As a result of the studies carried out, the thiokol oligomer with the best performance was obtained at a 1: 1: 1 molar ratio of sodium tetrasulfide, epichlorohydrin, and ammonium phosphate, respectively. Based on the results of IR spectroscopy and differential scanning calorimetry, a reaction for the formation of a thiokol oligomer is proposed.

Keywords: thiokol, polysulfide oligomer, polycondensation, IR spectroscopy, thermal analysis.

Introduction

Polysulfide oligomers are of undoubted interest for the development of sealing and protective coatings. The consumption of sealing materials in construction today reaches 50% of their total production. Recently, sealing materials based on reactive oligomers have become widespread. A special place among them is occupied by sealants based on liquid thiokol. Currently, there are many new methods for the synthesis of thiokol oligomers and their modified analogues [1].

Polysulfide polymers, as an important class of polymers, are used in various applications as sealants, adhesives, etc. They are usually synthesized by the reaction of disodium polysulfides with dihalogenated compounds to produce liquid or solid polymers. Their most important advantages are excellent adhesion to various surfaces, the absence of sealant defects under load

and pressure, resistance to fuel and solvents, very low gas and vapor permeability, as well as high resistance to ozone and ultraviolet radiation [2].

In industry, the synthesis of liquid thiokols is carried out by polycondensation of aqueous solutions of sodium polysulfide with organic halides to obtain a dispersion of high molecular weight rubber, followed by splitting it at disulfide bonds and obtaining a liquid thiol with terminal SH-groups. Organic di- and trihalo derivatives and sodium polysulfides of various compositions are widely used as starting monomers for the preparation of thiokol oligomers [3]. Unlike carbon chain rubbers, thiokol oligomers contain a significant amount of sulfur atoms in the main chain, and there are no unsaturated bonds in macromolecules. Earlier in the literature, copolymer liquid thiocols based on 2,2-dichlorodiethylformal and epichlorohydrin [4] were synthesized;)methane and hypercrosslinked polydisulfide based on it [6]. In [7], the results of studying the polycondensation of elemental sulfur with mono- and disubstituted arenes are summarized: features of the synthesis and structure of the resulting products, their physicochemical properties. Variants of a polysulfide polymer are also proposed: obtained by polycondensation of di- and polyhalides with sodium polysulfide in the presence of a dispersant, followed by washing, splitting and coagulation of the split dispersion with an acidic reagent; and obtained by the interaction of di- and polyhalides with sodium hydrosulfide and sulfur in the presence of quaternary ammonium halides, and in both cases mixtures of chlorine-containing monomers were used as dihalogenide: 2,2'-dichlorodiethylformal in combination with 1,2-dichloroethane and epichlorohydrin or 2,2 '-dichlorodiethylformal in combination with chloroparaffin of the formula CnH_2n—mClm, where n=10—20, m=2—6 [8].

Most authors today use the term thiolene to describe the reaction of thiols with a wide range of unsaturated functional groups, such as maleimides, acrylates, and norbornenes, in addition to unactivated carbon-carbon double bonds. In some of these cases, the reaction can proceed according to a mixed mechanism, including the classical radical addition, as well as nucleophilic addition according to the Michaelou type [9-14]. In [15], a new aromatic amino-terminated polysulfide oligomer was synthesized from a thiol-terminated polysulfide oligomer and bis(4-aminophenyl) disulfide via the disulfide metathesis mechanism. The authors of [16] synthesized polysulfide oligomers from elemental sulfur and methacrylic acid esters; new polysulfide materials were also synthesized from butadiene, styrene, isoprene, and methacrylate monomers [17]. In addition, new polysulfide polymers were obtained [18] using a new process from vinyl monomers, elemental sulfur and metallic sodium in THF. A kinetic study of reactions at -40°C showed that the whole process can be described as a competition between a slow reaction (initiation of the monomer by an alkali metal) and a fast reaction (deactivation of the carbanion formed by elemental sulfur).

In recent years, several new oligomeric thiols have been synthesized and put into production, opening up new applications or types of improved properties. For example, dithiol polyesters and its derivatives open up new opportunities for thiol semicrystalline materials [19, 20]. The use of oligomeric thiols has the distinct advantage of low shrinkage and reduced stress during the depolymerization process [21] or lower glass transition temperature and more uniform materials [22]. In another work, thiocarbamate oligomers used in the preparation of photocured or thermoset films with a high glass transition temperature were used to obtain excellent hardness and impact resistance [23].

Thus, the purpose of this study is the synthesis and study of a thiokol oligomer based on sodium polysulfide, monochlorohydrin, and ammonium phosphate, which is intended for use as the main component of a thiokol sealant.

Research Materials.

The object of the study is the obtained thiokol oligomer brand NEP-13 based on sodium tetrasulfide, dichlorohydrin and urea adduct. Reagents of the brand “pure” and “chemically pure” were used in the work.

Research Methods.

IR-spectrum analaysis. IR spectroscopic studies of the oligomer were carried out at the center for the collective use of unique scientific equipment of the Institute of Bioorganic Chemistry of the Academy of Sciences of the Republic of Uzbekistan. The IR spectrum of the oligomer was recorded on an Avatarsystem 360 FT-IR spectrometer from the Nikolet Justument Corporation (USA) (range 400–4000 cm–1, resolution 4 cm–1) by the powder method. The spectra were interpreted using basic software that implements automatic measurement of spectra, has tools for graphical display of spectra and their fragments, and forms the work with the user's spectrum library.

Thermoanalytical analysis. Thermoanalytical studies were carried out on a Netzsch Simultaneous Analyzer STA 409 PG instrument (Germany), with a K-type thermocouple (Low RG Silver) and aluminum crucibles. All measurements were carried out in an inert nitrogen atmosphere with a nitrogen flow rate of 50 ml/min. The temperature range of measurements was 25-370°C, the heating rate was 5K/min. The amount of sample per measurement is 5-10 mg. The measuring system was calibrated with a standard set of substances KNO_3, In, Bi, Sn, Zn.

When determining the density of the resulting oligomer used GOST 15139-69. Determination of the content of sulfhydryl groups in liquid thiokol oligomer was carried out in accordance with GOST 12812-80 "Liquid thiokols". The test result was taken as the arithmetic mean of two parallel determinations, the discrepancy between which did not exceed 0.20% at a confidence level of 0.95%.

Synthesis of thiokol oligomer DKA-4 based on sodium tetrasulfide, dichlorohydrin and urea adduct. In a 500 ml three-necked flask equipped with a stirrer, reflux condenser, thermometer and addition funnel, dissolve 31.5 g (0.40 mol) of sodium sulfide in 150 ml of water. 37.5 g (1.17 mol) of sulfur are added to the solution, the mixture is heated and boiled for 1 hour with stirring. Then the solution is filtered off and 0.22 g (0.0013 mol) of an ionic liquid (tetraethylammonium chloride) is added.

27.8 g (0.30 mol) of dichlorohydrin are added to this solution for 1 hour with stirring at 700C. Then 0.26 g (0.0013 mol) of urea adduct is added and the reaction mixture is kept at 800-850C for another 1 hour. After that, it is allowed to cool and the upper layer is decanted from the yellow rubbery product, which is washed three times with boiling water. After drying under a fume hood. Receive 63.5 g of the oligomer (99% of theory). Sulfur content 50.8%. During the synthesis of thiokol oligomers, the dependence of the reaction yield on the reaction time at a temperature of 80°-850C was studied. A highly efficient reaction yield was obtained with a reaction time of 1.5–2 hours [24].

Results and Discussion.

This work is devoted to obtaining the main component of thiokol sealant based on sulfur, nitrogen and phosphorus-containing oligomer. Experiments have shown that in order to obtain a high yield of the thiokol oligomer, it is obviously necessary to take the equimolar ratio of the reagents according to Table 1. and Fig.1.

Table 1. Dependence of the yield of the reaction for obtaining a thiokol oligomer on the molar ratio of the initial monomers (85-90oC, τ=1.5-2 hours)

Monomer ratio, mol	Reaction yield, %	Average molecular weight (cryoscopically)	Appearance	Sulfur content, %	
				Calculated	Found
1:1:1	93	3750	Brown viscous substance	54,3	52,2
1:2:1	78	4610		38,6	38,1
1:2:2	67	4460		30,1	30,4

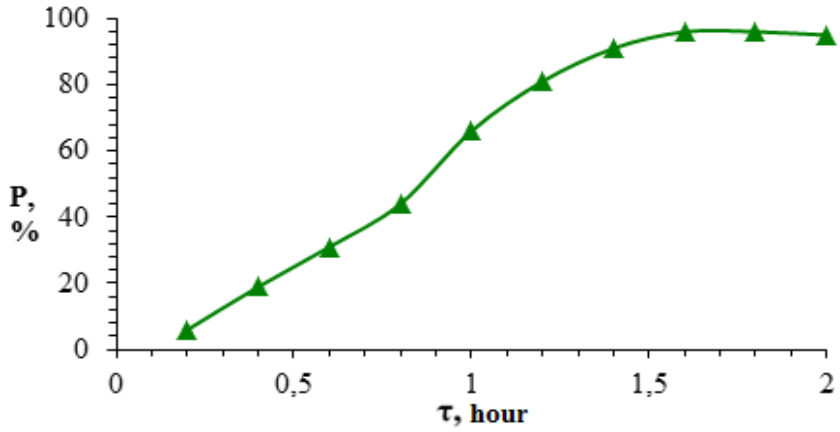


Fig. 1. Dependence of the yield of thiokol oligomer on the duration of the reaction at 85-90°C.

In the IR spectrum of DKA-4 in the regions of 2852-2920 cm^{-1} there are absorption bands confirming the presence of -CH_2- groups, and absorption bands in the region of 1651 cm-1, confirming the presence of the –$CONH_2$ group in the free state. The bending vibrations of all active groups appear as strong narrow bands between the usual bending vibration bands –CH_2–CO– in the region of 1440 – 1400 cm^{-1}. The absorption bands at 1022 and 1332 cm-1 confirm the presence of –NH2 groups. The presence of groups containing phosphorus P=O and P–O–C in the region of 1165 cm^{-1} is confirmed by a wide intense band and sulfur-containing compounds in the regions of 900-400 cm^{-1}, 1060-1040 cm^{-1}. In addition, narrow low-intensity bands containing bonds of a sulfur-containing compound appear on IR spectroscopy in the regions of 450-550 cm^{-1} and 1460 cm^{-1} (Fig. 2).

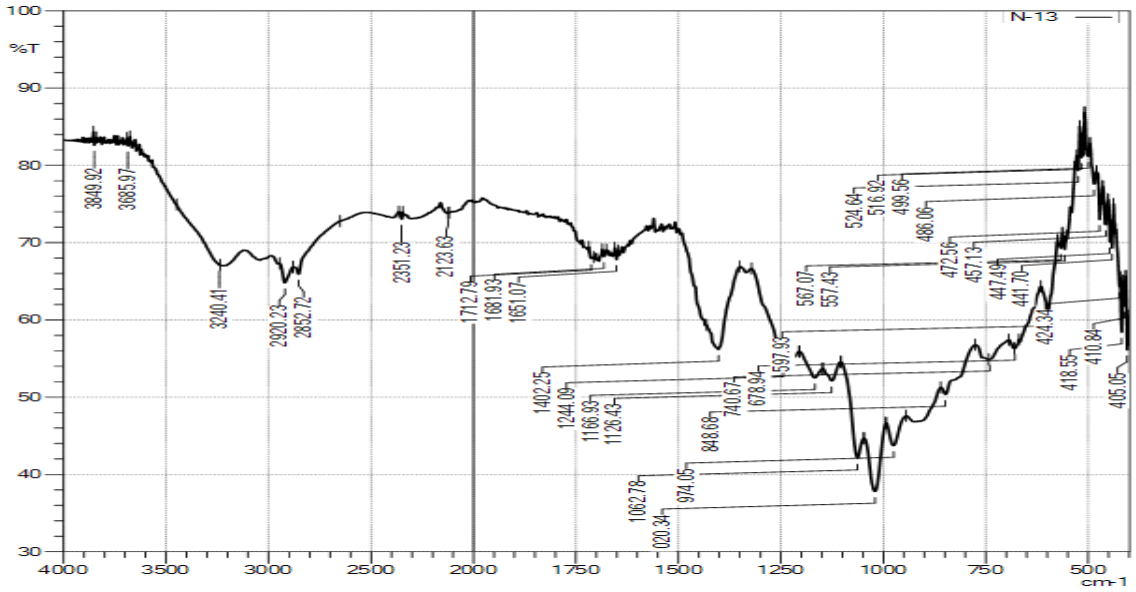


Fig.2. IR spectrum of sulfur-, nitrogen- and phosphorus-containing oligomer grade DKA-4

Changes in sulfur-, nitrogen-, and phosphorus-containing oligomer grade DKA-4 during thermal decomposition were studied by differential scanning calorimetry (DSC) [25, 26]. The thermal decomposition data of the resulting thiokol oligomer are shown in Fig.3. From Fig.3. It can be seen that the mass of the DKA-4 sample does not change up to 200°C. On the DSC curve in this temperature range of 20-200°C, one small endothermic peak (171°C) is observed, which may correspond to sample melting or structural rearrangement. Above a temperature of 200°C, the sample begins to decompose in one stage - (in the range of 200-270°C at a rate of 7% / min with a weight loss of 66%. The decomposition reaction is endothermic, the total decomposition energy is -261 J / g. Fig.3.

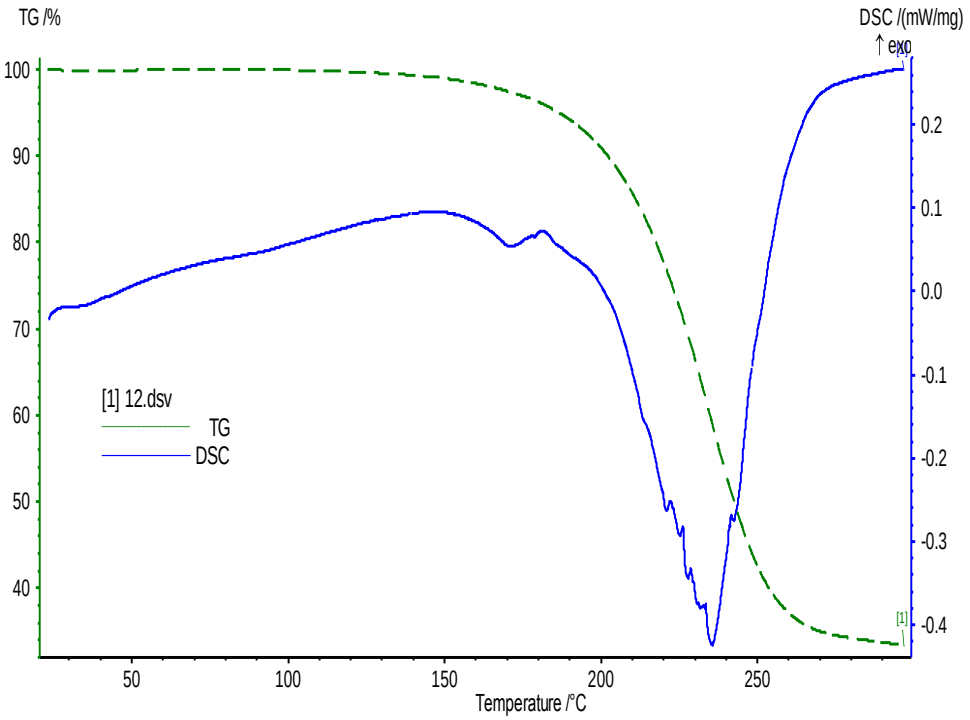
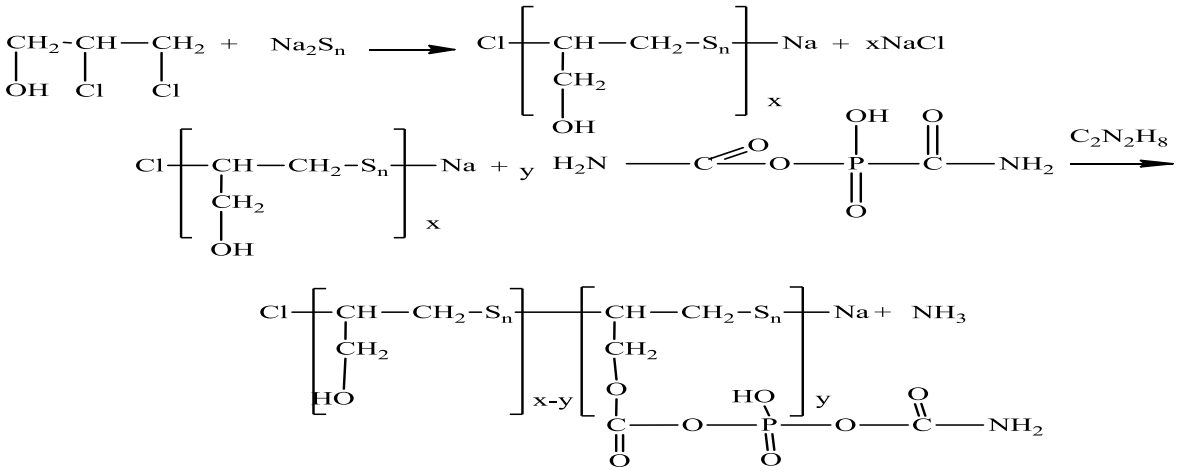


Fig.3. DSC of sulfur-, nitrogen- and phosphorus-containing oligomer grade DKA-4

From the results of the above analyzes and literature data [27–31], the reaction scheme for obtaining a modified thiokol oligomer of DKA-4 grade can be represented as follows:



The physicochemical properties were studied: density, melting point, solubility of the resulting thiokol oligomer. Data on the physicochemical characteristics of the synthesized thiokol oligomer brand DKA-4 are presented in Table 2.

Table 2. Physico-chemical parameters of thiokol oligomer

Indicators	Thiokol oligomer
	ДКА-4
Density, g/cm^3 GOST 15139-69	1,33
T_{Liq}, ^oC	223
$\eta_{хв}$, cm^3/g	0,061
Rastvorimost	Dimethylsulfoxide, dimethylformamide
Внешний вид и цвет	brown viscous substance

Conclusion.

Nitrogen-, phosphorus-, and sulfur-containing thiokol oligomer DKA-4 were synthesized. The influence of various factors on the synthesis of new thiokol oligomers during the synthesis, including temperature, the ratio of starting substances, and the possibility of obtaining thiokol oligomers with complex properties as a result of studying the physicochemical characteristics of oligomers using modern highly informative methods of analysis are shown. Reactions for the preparation of a thiokol oligomer based on sodium tetrasulfide, dichlorohydrin, and urea adduct according to IR spectroscopy and DSC data are proposed.

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