Synthesis and structure of sulfur-containing polymers based on polymer industrial waste applied for rail lubrication

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Abstract. Rail lubricants were produced using sulfur containing industrial waste. The study proved benefits of several methods for production of sulfur-containing polymers. The use of alkali polysulfides allows production of compounds with a high sulfur content which can be used in lubricating compositions.

1. Introduction
The first high-molecular compounds containing sulfur atoms in the polymer chain were obtained in the middle of the XIX century by dichloroethane condensation with potassium pentasulfide [1]. However, these polymers gained practical value only in the 1930s – 1940s. Since then, they have been produced on an industrial scale. The range of chlorine-containing monomers used for polycondensation and the range of industrially produced polymers (thiokols) expanded significantly. In addition to dichloroethane, bis(2-chloroethyl)formal (CICH₂CH₂OCH₂CH₂Cl), 1,2 – dichloropropane and symmetric glycerol dichlorohydrin (CICH₂CHOHCH₂Cl) were used as monomers [2, 3, 4]. Further studies on these polymers were carried out to improve their performance characteristics.

In the second half of the last century, after the method for producing halogenbenzenes with alkali sulfides or polysulfides based on high-temperature polycondensation has been developed, polyarylene sulfide chemistry gained momentum [5]. High thermal-oxidative stability and a number of other specific properties of polymers predetermined wide prospects for their industrial application.

Other types of sulfur-containing polymers have not found wide practical application. In 1998, the research [6] reviewed organic sulfur polymers and summarized results of more than three hundred papers devoted to this issue.

The present article analyzes data on production, structure and use of polysulfide polymers in terms of their use as components of lubricant compositions [7, 8]. In addition, the article summarizes the data on polysulfide polymers production in the aqueous hydrazine – alkali system.

2. Materials and methods
The method for production of polymeric monosulfides is polyaddition of thiols to unsaturated compounds which is presented by two schemes. Polycondensation methods were used for producing polymeric monosulphides.
3. Results and analysis

3.1. Key methods for production of sulfur containing polymers

Sulfur and its inorganic and organic compounds are capable of entering into polymerization reactions, thus ensuring a large variety of organic sulfur polymers [6].

The most important example of introduction of sulfur into the polymer chain by forming bridging polysulfide fragments is vulcanization of natural and synthetic rubbers [3, 9]. Although the chemistry of these processes has not been identified yet, most of intermediate stages of this complex process have been determined [9]. During the vulcanization, spatial structures with cyclic fragments containing several sulfur atoms in the cycle are formed [9].

Sulfur can copolymerize with unsaturated (styrene, butadiene, isoprene, chloroprene) and cyclic monomers (thiiranes, ethylene oxide) to form rubber-like products with wide molecular weight distribution [6]. For styrene, the process is presented in Figure 1.

![Figure 1. Styrenation of sulfur](image)

Thiiranes can polymerize and copolymerize with olefin oxides and form oligomeric products which can be used for producing synthetic oils [10, 11]. The use of catalysts in these processes (lithium or cadmium salts) allows production of polymers with propylene sulfide with di- and monosulphide fragments with a molecular weight of up to 270 thousand [12, 13].

Propylene sulfide (methyl thiirane) polymerizes much more easily than ethylene sulfide [11]. When heated with ethyl alcohol, a mixture of oligomeric products is formed: (Figure 2).

![Figure 2. Mixture of oligomeric products](image)

In the presence of complex cadmium compounds with optically active ligands, polymerization of the racemic mixture of methyl thiirane is stereoregular. It forms R-or S-centers depending on the ligand configuration [14].

Among other cyclic sulfides, ring opening polymerization of aromatic derivatives was described (phenothiazine [15]): (Figure 3).
The polymers are soluble in organic solvents and very promising as anti-corrosion protectors.

Important monomers for production of organic sulfur polymers are thiocarbonyl compounds containing the group $\text{> C == S}$. This is due to the fact that for sulfur, unlike oxygen, single bonds with carbon are energetically more favorable [16, 17]. Thioaldehydes and thioketones are particularly prone to polymerization, although dimers or trimers are often formed during their transformations [18, 19]. Thiocarbonyl compounds in which $\text{> C == S}$ group is connected with a heteroatom (thioamides, thiocarboxylic acids, etc.) are less polymerized. Some examples of copolymerization of thiocarbonyl compounds with vinyl monomers are described in [6].

An important method for production of polymeric monosulphides is polyaddition of thiols to unsaturated compounds which can be presented by two schemes [6]:

1. Homopolymerization of unsaturated thiols (e.g., allyl mercaptan) in the presence of peroxides:

   \[
   n \text{CH}_2=\text{CH}_2\text{SH} \rightarrow (\text{--CH}_2\text{--CH}_2\text{--S--})_n
   \]

2. Copolymerization of dithiols with diene or diine hydrocarbons:

   \[
   n \text{HS--R--SH} + n\text{CH}_2=\text{CH}_2\text{R'} \rightarrow (\text{--CH}_2\text{--CH}_2\text{--R'}\text{--CH}_2\text{--S--R--S--})_n
   \]

Non-conjugated dienes contributed to the process which is carried out in a solution or an emulsion in the presence of free radical initiators [20].

When using diacetylene compounds and aromatic or heteroaromatic dithiols, the method can be used to produce polymers with semiconducting properties [21]: (Figure 4).

Adding dithiols to maleic anhydride followed by interaction of products with aromatic diamines, thermoactive polymers with a molecular weight of up to 80 thousand were produced [22]: (Figure 5).
Other examples of similar reactions are described in [6].

However, all the above-mentioned methods for production of organic sulfur polymers based on polymerization reactions use problematic monomers — thioaldehydes, thioketones, thiranes, dithiols, etc. However, for production of sulfur-containing polymers, especially with polysulfide fragments, polycondensation methods have become more common. They are used for production of thiokols (based on aliphatic monomers) and polyarylene sulfides.

Although some of the polymers are produced on a semi-industrial or an industrial scale, polycondensation methods are widely used for production of sulfur-containing polymers, especially those with polysulfide fragments.

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3.2. Production of polysulfide polymers in the aqueous hydrazine-alkali system

The hydrazinehydrate alkali system can reduce the S – S bonds in polysulfides which made it possible to obtain asymmetrically substituted organic sulfides [23]:

$$2R_2S_2 + 4NaOH + NH_2NH_2 \rightarrow 4RSNa + N_2 + 4H_2O$$

$$RSNa + R^'X \rightarrow RSR^' + NaX$$

Over the last years, polyfunctional electrophiles (di- and trihalo derivatives of aliphatic hydrocarbons) have been involved in these reactions which allowed production of polysulfide polymers. The main focus of these studies is associated with subsequent reduction of the polymers produced by the hydrazine hydrazine-alkali system.

Dichloroethane reacts with all types of anions and forms a polymer in which di- and monosulfide fragments alternate at a rhythmic pace. (at x=2):

\[ \text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S}-\text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S} \rightarrow \text{SCH}_2\text{CH}_2\text{SCH}_2\text{CH}_2\text{S} \\]
4. Discussion
The reductive splitting by the hydrazine hydrate-alkali system presented in the diagram produces two types of dithiols with similar yield values.
3-Tianeptan-1,5-dithiol (HSCH₂CH₂SCH₂CH₂SH) was obtained irrespective of bis (chlorethyl)sulfide through intermediate Thiokol formation [24].
Trithioglycerol was obtained from 1,2,3-trichloropropane (yield 59%) [25, 26, 27, 28]:

\[
\text{SCH}_2\text{CH} - \text{CH}_2\text{S} \xrightarrow{\text{N}, \text{H}, \text{H}, \text{O} + \text{NaOH}} \text{SNaCH}_2\text{CH} (\text{SNa})\text{CH}_2\text{SNa} \xrightarrow{[\text{H}^+]} \text{HSCH}_2\text{CH(SH)CH}_2\text{SH}
\]

5. Conclusion
The analysis allows us to conclude that methods for production of sulfur-containing polymers are promising. The use of alkali polysulfides makes it possible to produce compounds with a high sulfur content. They can be used for producing lubricating compositions. Therefore, application of the methods for production of sulfur-containing polymers using polysulfides and industrial waste is promising.

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