Thiokol-Like Polymers Based on By-Products of Epichlorohydrin Production

YU. K. DMITRIEV[1], N. A. LOKTIONOV[1], YU. A. SANGALOV[2], S. G. KARCHEVSKIY[3], I. O. MAIDANOVA[3] and S. N. LAKEEV[3]

[1]"Caustic» Company,
Ul. Tekhnicheskaya 32, Sterlitamak 453110 (Russia)

E-mail: irina_m@anrb.ru

[2]Institute of Petrochemistry and Catalysis, Russian Academy of Sciences,
Pr. Oktyabrya 141, Ufa 450075 (Russia)

[3]"Sodeystviye» Bashkir Innovation Centre,
Pr. Oktyabrya 69, Ufa 450054 (Russia)

Abstract

The issue of the use of mixtures of organochlorine products from epichlorohydrin production wastes to yield the commercially valuable sulphur-containing polymers, thiokols, is considered. It has been demonstrated that carrying out the reactions of mixtures of organochlorine compounds of various composition with sodium polysulphide in non-aqueous media (methanol) allows one to obtain powdered solid polymers, namely, polyorgano polysulphides, with 66–90 % yield and with high content of sulphur, up to 82 %. The analysis of possible ways of formation of polymers is performed; their physicochemical and structural properties are studied; suggestions are given concerning the ways of putting to work.

INTRODUCTION

The problem of creating non-waste or low-waste chemical processes can be solved both by the improvement of the basic technologies and by the development of the rational ways of reclamation of waste materials being formed. The second line is more promising and frequently has no alternative. Thus, for example in epichlorohydrin production, the wide spectrum of organochlorine by-products is produced, the recovery of which is not a simple problem. Presently, the disposal of the main body of organochlorine waste is made through combustion that requires the big volume of fuel, gives rise to highly toxic products like dioxins, phosgene, *etc.*, and results in short lifetime of the equipment.

One of the possible ways of salvaging the organochlorine waste of epichlorohydrin production may be the procedure based on chemical interaction of wastes with available polysulphides of alkaline and alkali-earth metals to obtain sulphur-containing products valuable from the practical point of view (diorganyl polysulphides, thiokols, thiols, sulphides, *etc.*) [1–3]. It is of no little significance that this approach also involves elemental sulphur (in the form of polysulphides) into the practical field, the accumulation of which at the plants of chemical and power industry creates a serious environmental problem [4]. Known commercial methods to obtain thiokols, the S-containing polymeric products that possess valuable properties (high oil and petrol resistance, gas and moisture impermeability, *etc.*), are characterized by the big water consumption and formation of the significant amount of sewage. In going from individual chlorine-containing monomers to mixtures (epichlorohydrin production wastes), the situation can be aggravated because of the various organic and

inorganic compounds of sulphur and chlorine, including yprite-like toxic agents, available in the aqueous drains. Processing of drains like that presents significant difficulties and may put into question the expediency of the ways suggested for salvaging [1−3] the chlorine-containing mix products by means of thiokols synthesising.

We suggest the procedure of salvaging the wastes of epichlorohydrin production that eliminates the use of water as the reaction medium at the stage of synthesis of sodium polysulphide (Na_2S_x) and its subsequent polycondensation with organochlorine products to yield thiokol-like polymers. The advisability of performing the commercial runs, specifically, the synthesis of small-tonnage polymers, in non-aqueous environments at all stages of technological process has been substantiated previously as regards the production of polyisobutylenes of low molecular weight [5].

Among the known commercial ways of Na_2S_x synthesis, the most widespread is the procedure based on the interaction of concentrated NaOH water solutions with sulphur at 100 °C [6]. The significant amount of sodium thiosulphate $Na_2S_2O_3$, which pollutes the sewage, is formed as a by-product. To eliminate $Na_2S_2O_3$ formation, the process is conducted under more severe conditions (70 % NaOH, 120 °C) or a reducer, highly toxic hydrazine (in the form of hydrazine hydrate), is introduced into the reaction medium [6]. Sodium polysulphide may also be obtained without solvent by careful heating the appropriate quantity of alkali and sulphur at 135−140 °C with the subsequent transfer of the product into methanol solution. In our opinion, the synthesis of Na_2S_x in methanol medium is more practically feasible at 72−74 °C. The process can be controlled by gradual addition of sulphur to alcohol solution of NaOH. Resulting Na_2S_x remains in the solution, and $Na_2S_2O_3$, slightly soluble in alcohol, precipitates and thus can be easily removed from the solution. The solution of Na_2S_x produced (with a mass fraction of 30−40 %) is stable with time (within a month) and can be used to advantage later on in the reaction of polycondensation

TABLE 1

Composition of epichlorohydrin production wastes

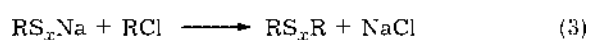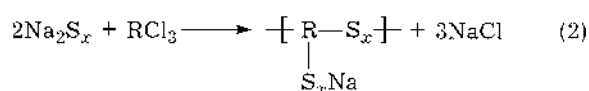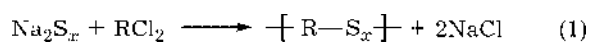| Compounds	Composition, mass %			Conventional group
	I	II	III	
2,2-Dichloropropane	0.70	0.12	−	A
1,2-Dichloropropane	41.20	63.87	0.69	A
1,3-Dichloropropane	1.19	0.68	−	A
cis-1,3,3-Trichloropropene	2.40	0.35	−	A (D)
trans-1,3,3-Trichloropropene	4.03	0.57	−	A (D)
Tetrachloropropenes	0.23	0.01	−	A (C)
1,2,2-Trichloropropane	0.25	0.15	0.29	B
1,2,3-Trichloropropane	1.14	0.11	0.60	B (A)
Tetrachloromethane	0.11	0.01	−	B
Tetrachloropropanes	3.16	0.17	−	B
Pentachloropropanes	0.22	−	−	B
Chloroallyl	0.12	0.15	−	C
cis-1,2,3-Trichloropropene	−	−	0.24	C
2-Chloropropane	0.02	0.01	−	C
cis-1,3-Dichloropropene	18.60	16.41	36.24	C (A)
trans-1,3-Dichloropropene	25.13	13.44	60.88	C (A)
1,5-Hexadiene	0.01	0.04	−	D
1,1+1,2-Dichloropropenes	1.18	3.76	1.06	D
Tetrachloroethylene	0.25	0.15	−	D

with organochlorine compounds in the non-aqueous environment.

The degree of polysulphidity x in Na_2S_x, as in the case of water solutions, varies on the average from 1 to 5. This fact is indirectly verified by melting point (mp) of Na_2S_x samples, the composition of which was varied by the ratio between NaOH and S in the course of synthesis. In all cases, the mp of the samples was within the interval of mp for individual Na_2S_2 (445 °C) and Na_2S_5 (255 °C) and was characterized not by a point, but by an interval of melting (from 5 to 30 °C). In addition, the reactions of Na_2S_x with hexylchloride (60−70 °C) proceed to form the set of polysulphide products, which also counts in favour of mixed composition of Na_2S_x.

Because of the complex and variable composition of organochlorine wastes of epichlorohydrin production (the ratio between the basic monomers, 1,2-dichloropropane and 1,3-dichloropropenes, may vary over a wide range), it is difficult to calculate the requisite ratio of components and the yield of target products. Therefore, it is necessary to analyse chlorine-containing compounds of various degrees of substitution with relation to the part they play in the reaction of polycondensation.
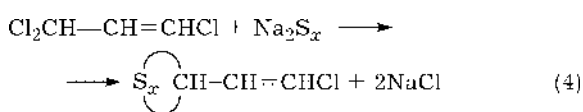
EXPERIMENTAL

The wastes of epichlorohydrin production from "Caustic" Company with a various content of mono-, di-, tri-, and tetraorganyl chlorides (I and II in Table 1), and expressly purified 1,3-dicloropropene for carrying out the model experiments (97.8 % pure, the mixture of *cis*- and *trans*-isomers) (III, see Table 1) have been taken for investigation.

The assignment of compounds to one or another of groups (A, B, C) was defined by their function in the process of polycondensation, namely, chain growth (1), branching (2), or breaking (3), respectively:

$$Na_2S_x + RCl_2 \longrightarrow \text{---}[R\text{---}S_x]\text{---} + 2NaCl \qquad (1)$$

$$2Na_2S_x + RCl_3 \longrightarrow \text{---}[R\text{---}S_x]\text{---} + 3NaCl \qquad (2)$$
$$\underset{S_xNa}{|}$$

$$RS_xNa + RCl \longrightarrow RS_xR + NaCl \qquad (3)$$

The compounds inactive during the process of polycondensation are related to group D. Some monomers could be related to several groups: tetrachloropropenes to A or C depending on position of Cl atoms; 1,2,3-trichloropropane to tri- and bifunctional monomers (B and A); 1,3,3-trichloropropene can miss its function of monomer (A→D) in the reaction of cyclization:

$$Cl_2CH\text{---}CH{=}CHCl + Na_2S_x \longrightarrow$$
$$\longrightarrow \overset{\frown}{\underset{\smile}{S_x}}\ CH\text{--}CH{=}CHCl + 2NaCl \qquad (4)$$

As will be shown in what follows, 1,3-dichloropropenes along with the expected involvement in the reaction of chain breaking can also play the part of comonomer (C and A).

Besides the main reactions (1)−(3), side reactions of an interchain exchange, of macrocycles formation, *etc.* may proceed during synthesis of thiokols. In addition, nonsaturated character of compounds taken into consideration, an involvement of olefinic bonds in chemical interactions and in cross-linking of polymer chains is likely too. However, in view of potential applications of the polymers being synthesized, this is but a detail.

Table 2 generalizes the data on synthesis and some properties of polymers.

Selection of organochlorine products of various group content, including the combinations between them and with trichloropropane as a dopant, affords the total content of active components ($\Sigma A,B,C$) to reach 96−98 % with the variable, over the definite range, concentration of components of specific groups.

To calculate the amount of Na_2S_x necessary for the reactions and, accordingly, a theoretically expected yield of products (the set of all solid and liquid substances, soluble and insoluble in alcohol, arising during the interaction of organochlorine compounds with Na_2S_x), some assumptions were made: molecular weights of compounds from A, B, and C groups for experiments Nos. 1−9 comprise 112.0, 147.5, and 76.5 (predominantly chloroallyl and monochloropropanes) respectively, and the ones for experiments Nos. 10−12 comprise 111.0, 147.5, and 145.5 (predominantly 1,3-dichloropropenes) respectively. In addition, no allowance was made for the chain branching. Then, based on molecular weights of the

possible chain links, which for $R^A–S_4$, $R^B ClS_4$, $R^C–S_4–R^C$, as an example, are equal to 170.0, 204.5, and 281.0 (exp. Nos. 1–9), respectively, we will have the following equations for calculation of the Na_2S_x weight and the expected yields:

$N = 1.52A + 1.39B + 1.37C$ (exp. Nos. 1–9)

$N = 1.52A + 1.39B + 1.20C$ (exp. Nos. 10, 11)

$N = 0.95A + 0.95B + 0.98C$ (exp. No. 12)

$m = 1.55A + 1.18B + 1.14C$ (exp. Nos. 1–9)

$m = 1.57A + 1.18B + 0.60C$ (exp. Nos. 10, 11)

$m = 0.99A + 0.78B + 0.38C$ (exp. Nos. 12)

where N is the yield, g; m is the mass of Na_2S_4 (exp. Nos. 1–11) and Na_2S_2 (exp. No. 12), g; A, B, C are the mass fractions of appropriate groups in the mixture, %.

The use of excessive or deficient Na_2S_x (in relation to the calculated one) was intended to produce the greatest possible yield of polymers.

The process of polycondensation was performed through gradual addition of organochlorine compounds to 25–30 % methanol solution of Na_2S_x under stirring (the reaction is exothermic) at initial temperature 50–60 °C. The temperature of the reaction was maintained at a level of ~65 °C. Upon mixing of the components, reaction time comprised from 1 to 4 h. By means of special experiments, it has been shown that this time is long enough for the optimum yield of the product to be achieved under the test conditions. The polymer filtered off from the mother solution coloured in red was washed out by methanol and then by water to separate from salts, and then it was dried at 90–95 °C.

RESULTS AND DISCUSSION

The data of Table 2 suggest that irrespective of the quantity of Na_2S_x applied, the yield of solid powdered polymers is high enough and amounts to 66–90 %. Unexpected was the highest yield of polymer (up to 89.2 %) in the case of 1,3-dichloropropene (raw material III). As it is commonly supposed, chlorine of vinyl group is not involved in the reaction, thus implying the function of chain stopping, instead of its growth (as it turned out in the experiment). The result obtained stems supposedly from the fact that during 1,3-dichloropropene interaction with Na_2S_x, nucleophilic substitution of allylic chlorine occurs first, and then Na_2S_x adds to the olefinic bond to form a transient state involving the polysulphide sulphur at the allylic position [schematic diagram (5)].

Producing the polymers from raw material III significantly expands the range of raw materials used for synthesis of thiokols, in particular, thiokols containing olefinic bonds in hydrocarbon fragments.

As regards the structure and properties of obtained polymers, the use of composite component as one of the monomers does not enable one to synthesize thiokols individual in composition, *i. e.* with alternated units of the same type. Organic fragments of thiokols may contain olefinic bonds (absorption at ~1600 cm^{-1} in IR spectra) and halogen atoms (see Table 2). Sulphur content of the product (from 68 to 82 %) is testimony to a high degree of polysulphidity of initial Na_2S_4. End groups are presented for the most part by SNa and hydroxyl group (wide absorption in the region of 3200–3600 cm^{-1} of IR spectra).

Apparently, the higher ash content of polymers (~0.5 mass %, see Table 2) is related to mercaptide groups present. On the other hand, SNa end groups can cause an effect of "internal stabilization of polymers": the products of thermal decomposition are free from H_2S and HCl, and the presence of S^{2-}
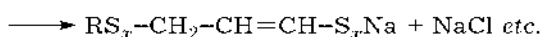
$$2ClCH=CH-CH_2Cl + Na_2S_x \longrightarrow (ClCH=CH-CH_2)_2S_x + 2NaCl$$

$$\text{(generally } R–S_x–CH_2–CH=CHCl)$$

$$R–S_x–CH_2–CH=CHCl + Na_2S_x \longrightarrow \left[\begin{matrix} CH_2—\overset{-\delta}{C}H—CHCl \\ \diagdown \diagup \quad | \\ RS_x^{-\delta} \quad S_xNa \end{matrix} \right]^- Na^+ \tag{5}$$

$$\longrightarrow RS_x–CH_2–CH=CH–S_xNa + NaCl \text{ } etc.$$
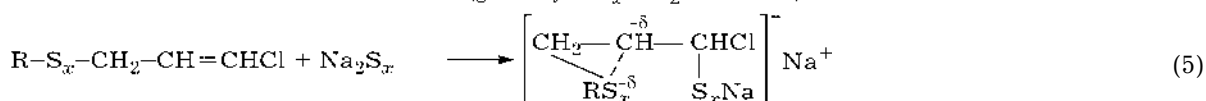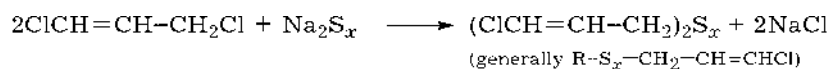
TABLE 2

Conditions of synthesis and the properties of the obtained polymers

Exp. No.	Organochlorine products Type	Group content (A : B : C / ΣA,B,C)	Quantity of Na_2S_x*, %	Polymers Yield, % of theor.	Elemental composition, % C	H	S	Cl	Ash content, %	Density, kg/m³	Structure
1	I	93.36 : 4.98 : 0.31/98.65	+10.8	67.0	18.3	3.3	74.0	4.1	0.39	1330	X-ray amorphous
2			−15.4	66.1					0.53		
3	II	95.45 : 0.44 : 0.16/96.05	+10.6	70.4	19.1	2.9	73.2	3.6	0.54	1360	»
4			−7.2	72.2							
5	I + II (50/50)	94.41 : 2.71 : 0.24/97.35	+10.7	70.0	18.1	3.1	75.5	2.7			
6	I + TCP (95/5)	88.69 : 9.73 : 0.29/98.71	+10.8	71.3	21.9	2.8	68.1	5.6		1380	
7			−13.1	71.7							
8	II + TCP (95/5)	90.68 : 5.42 : 0.15/96.25	+10.3	73.3	17.1	3.6	76.9	1.7	0.19	1310	
9			−5.1	76.0	19.8	2.7	75.0	1.9			
10	III	97.81 : 0.89 : 0.24/98.94	+16.4	87.7	16.4	2.6	80.5	0.4			
11			+1.3	89.2	15.6	1.7	82.3	—	0.29	1300	»
12			+1.4	75.4							

Note. TCP denotes 1,2,3-trichloropropane.

*An excess (+) or deficit (−) relative to equimolar quantity.

and Cl⁻ ions in aqueous extracts of destruction products gives evidence for binding of H-acids by sodium.

Elevated values of products density (1300 kg/m³ and higher) and insolubility in organic solvents (ethylene dichloride, benzene, toluene, benzene chloride, dimethyl sulfoxide, hydrocarbons, *etc.*) are intrinsic to solid powdered thiokols [1]. The amorphous structure of thiokols (from X-ray diffraction data) is related to their high polarity and irregular structure (the variable nature of organic fragments, chain branchings). In parallel with this, the elements of structural regularity (paracrystallinity) can be caused by polysulphide fragments available in the polymer.

Owing to the high sulphur content and low range of softening points (150 °C and higher), the synthesized thiokols are compatible with elemental sulphur. Besides apparent dissolving of thiokol in the melted sulphur, a lowering of S_8 melting point upon introduction of 2−10 % of thiokol additives is worth to be noted. Observable values (112−114 °C) are close to "the natural melting point" of sulphur (114.5 contra 119.2 °C that is the ideal melting point of S_8), this melting point being typical for melting of S_8 contaminated by sulphur-containing impurities [7].

On the other hand, the amorphous structure and a relatively low range of softening temperatures for thiokols motivate their operational compatibility with a variety of organic substrates, for example, with sulphurized polyolefins (polymeric factices), bitumens, *etc.*, which is of practical interest for modification of their properties. In so doing, thiokol acts not only as an independent component of compositions, but also as a kind of preparative form of elemental sulphur that makes easy its introduction into the compositions.

REFERENCES

1 N. A. Korchevin, N. V. Russavskaya, Ya. N. Silinskaya *et al.*, *Khim. Tekhnol.*, 4 (2001) 30.

2 M. G. Voronkov, N. A. Korchevin, N. V. Russavskaya *et al.*, *Khimiya v interesakh ustoichivogo razvitiya*, 1 (2001) 4.

3 N. V. Russavskaya, Ya. N. Silinskaya, G. A. Yakimov *et al.*, *Zh. Prikl. Khim.*, 75 (2002) 270.

4 Yu. A. Sangalov, *Vestn. Akad. Nauk RB*, 6 (2001) 26.

5 Yu. A. Sangalov, K. S. Minsker, Polimery i sopolimery izobutilena. Fundamentalnye problemy i prikladnye aspekty, Gilem, Ufa, 2000.

6 I. V. Garmonov, Sinteticheskiy kauchuk, Khimiya, Leningrad, 1983.

7 Inorganic polymers, in F. Stone and W. Grahem (Eds.), Wiley, New York, 1963.