INVESTIGATION OF EXCHANGE REACTIONS IN LIQUID THIOKOLS

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Recently the attention of a number of researchers has been attracted to the problem of exchange reactions in liquid polysulfide polymers—Thiokols [1-4]. Liquid formal Thiokols, possessing the approximate structure

$$IIS-(C_2H_4-O-CH_2-O-C_2H_4-S-S)_n-C_2H_4-O-CH_2-O-C_2H_4-SH$$

are capable of exchange reactions. It is believed that there is a thiol—disulfide interaction; however, the rate of these reactions, according to the data of various authors, varies substantially. In some cases the process proceeded readily, while in others a substantial thermal activation was required [2, 4], and in a number of cases no exchange interaction was detected [3]. Such a difference is evidently explained not only by the influence of the impurities contained in the Thiokol, but also by structural peculiarities of the investigated Thiokols. According to [5], the first factor is extremely important: traces of mercaptans, elementary sulfur, bases, and ionic compounds of various types strongly influence the exchange reactions in Thiokols. As for the influence of structural differences, it is associated primarily with the degree of polysulfide character of the Thiokols. The presence of bonds with a sulfdite character greater than two facilitates the occurrence of exchange reactions, since these bonds are cleaved far more readily than disulfide bonds [5-7].

It is assumed that during the synthesis of liquid Thiokols, during cleavage and desulfuration, those compounds lose their polysulfide (bound and free) sulfur and cannot contain sulfide bonds with a degree higher than two. However, in the case of desulfuration of Thiokols in aqueous dispersions, not all the polysulfide of the polymer macromolecules are subjected to the action of the desulfurizing agent to equal degrees. As a result of the nonpolar hydrophobic character of the polymer, particles of the dispersion form dense, little-swelling globules, the internal chains of which are readily inaccessible to the influence of the agents dissolved in the aqueous phase. In accord with the aforementioned it might be thought that desulfuration will proceed more completely in the case of more profound cleavage of the dispersion and, consequently, in the same Thiokol sample the degree of desulfuration should decrease from low-molecular to high-molecular fractions. Moreover, with all conditions equal, a Thiokol produced by cleavage of a disulfide polymer

![Fig. 1. Curves of turbidimetric titration of Thiokol: 1) fraction 5000; 2) fraction 900; 3) mixture of fractions 1 and 2, 1:1, at room temperature; 4-13) the same mixtures after heating at 70° for 12, 24, 38, 44, 54, 63, 80, 92, 128, and 208 h, respectively.](image-url)
Fig. 2. Turbidimetric curves reflecting the action of bases on a 1:1 mixture of Thiokols 1830 and 4300 (curves 1–3 were obtained immediately after preparation of the mixtures): 1) mixture of Thiokols; 2) mixture with 0.5 part by weight triethylamine; 3) mixture with 0.5 part by weight DPG; 4) equilibrium mixture of Thiokols 300 h of heating at 50°C.

EXPERIMENTAL METHOD

A sample of liquid dichlorodiethylformal Thiokol (industrial product) with a viscosity of 420 P was purified by filtering a benzene solution and fractionated by the method of fractional precipitation from a benzene–methanol system into eight fractions. The fractions with mol. wt. 4300, 1830, and 940 were selected for the investigations. The sulfur content in these Thiokols was 37.6, 36.8, and 35.4%, respectively; these data agree with the above-mentioned hypothesis of the dependence of the desulfurization of Thiokols upon their molecular weight. For exchange reactions, the Thiokols, taken in a 1:1 ratio, were mixed with the ingredients and heated at the corresponding temperature.

The change in the polydispersion of the mixture during the occurrence of the exchange process was monitored by turbidimetric titration. It was shown earlier [4] that this method gives a graphic picture of the changes in the molecular weight distribution of the mixture of liquid Thiokols during the process of exchange. The change in the shape of the titration curves during the reaction is evident from Fig. 1. The displacement of the curves to the right along the scale characterizes the exchange reaction as a process of averaging of the molecular composition (polydispersion) of the polymer. When an equilibrium molecular weight distribution has been reached, the shift ceases. The turbidimetric curves were recorded on an automatic instrument [8]. The experimental procedure and conditions were analogous to those used in [4]. Absolute benzene and methanol were used as the solvent–precipitant system. The titration curves are presented as plots of V versus I, where V is the volume of the added precipitant, while I characterizes the turbidity of the titrated solution.

In the study of exchange reactions, in a number of cases we also used the methods of viscosimetry and IR spectroscopy. Measurements of the intrinsic viscosity of solutions of Thiokol mixtures were performed in an Ubbelohde viscosimeter at 20 ± 0.1°C; initial concentration of the solutions 2.5%. The IR spectra of the liquid Thiokols were taken on an UR-10 spectrophotometer in a KBr cuvette with a layer thickness of 0.220 mm. In the spectrophotometry of the Thiokol mixtures, the absorption of several types of bonds was monitored: the valence vibrations of the SH groups in the region of 2600–2500 cm⁻¹, the absorption of the –S–S– and –C–S– bonds in the regions of 800–600 and 500–400 cm⁻¹, respectively, and in the case of mixtures with organic bases, also the valence vibrations of the NH groups in the region of 3500–3200 cm⁻¹ [9].

DISCUSSION OF RESULTS

Influence of Temperature. Exchange reactions in liquid Thiokols with a minimum content of impurities are characterized by a strong dependence of the rate of exchange on the temperature. Although the...