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Abstract

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Thiol-Disulfide Exchange in Polysulfide Polymers

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Reactions associated with the cleavage of disulfide bonds in organosulfur compounds have recently attracted the attention of many researchers both in organic chemistry and in biochemistry. This type of reaction includes, for example, exchange reactions of substances in proteins, which are accompanied by the conversion of cystine into cysteine (thiol-disulfide exchange). Numerous studies of the interaction of thiols with disulfides, carried out with the aid of labeled sulfur atoms, have shown that these reactions proceed chiefly by an ionic mechanism of nucleophilic substitution according to the following scheme (1,2)

$$\mathrm{R{-}S{-}S{-}R + R'S^- \rightleftharpoons R{-}S{-}S{-}R' + RS^-},$$

$$\mathrm{R{-}S{-}S{-}R' + R'S^- \rightleftharpoons R'{-}S{-}S{-}R' + RS'},$$

where R' denotes any groups capable of forming the anion $R'S^-$.

There are indications in the literature that similar reactions between disulfides and thiols also proceed by a free-radical mechanism (3,4). However, the ease with which most thiol-disulfide exchange reactions proceed is a strong argument in favor of nucleophilic substitution.

As a typical example one may cite reactions involving cleavage of disulfide bonds in high-molecular-weight polysulfides by means of such ions as HS^-, SO_3^-, CN^-, OH^-, etc. It is known that in the United States the plasticity of the rubber-like thiokol of the "ST" grade, obtained from di-(β-chloroethyl)-formal, is regulated in this way by treating high-molecular–

Table 1

Characteristics of polysulfide polymers

Sample No.	Method of preparation	Viscosity at 25°, poise	Mol. wt.	Number-average mol. wt. according to fractionation results	Weight-average mol. wt. according to fractionation results	Polydispersity coefficient
1	Individual	780	3200	3680	4280	1.15
2	Individual	57	1235	1225	1577	1.27
3	Mixture of 1 and 2 in a ratio of 1 : 1 by wt.	227	1925	2290	3258	1.35
4	Individual	221	1900	2410	3323	1.38
5	Individual	390	3000	3650	4308	1.17
6	Individual	6	660	593	821	1.39
7	Mixture of 5 and 6 in a ratio of 3 : 2 by wt.	76	1220	1360	1684	1.25
8	Individual	73	1600	1617	2240	1.39

high-molecular thiol with sodium sulfhydrate and thereby introducing terminal sulfhydryl groups into the polymer (5). The synthesis of low-molecular polysulfides is carried out according to the same scheme (6, 7); in this way similar polymers have been obtained with terminal groups such as SH, NH_2, OH (8, 9).

Table 2

Fractional composition of individual polymers and their mixtures (in weight percent)

Sample No.	>3000	3000	3000–2000	2000–1000	1000–500	<500
Experiment No. 1						
1	60.7	–	37.3	1.6	0.4	–
2	22.4	–	15.6	29.8	32.2	–

Fig. 1. Differential MWD curves of polymers Nos. 1, 2, 3

Figure 1: Fig. 1. Differential MWD curves of polymers Nos. 1, 2, 3

Sample No.	>3000	3000	3000-2000	2000-1000	1000-500	<500
3	28.9	–	29.9	39.4	1.8	–
4	43.7	–	21.7	32.8	1.8	–
Experiment No. 2						
5	35.5	55.5	7.5	1.5	–	–
6	–	1.1	4.5	22.9	31.0	40.5
7	12.3	2.7	14.6	47.9	20.9	1.6
8	11.0	11.6	10.3	53.9	12.0	1.2

Thiol-disulfide exchange occurs in polysulfide polymers not only at the synthesis stage, but also during ordinary mixing of polymers differing in molecular weight. This phenomenon was studied by us by determining the molecular-weight distribution (MWD) of polysulfides with terminal mercaptan groups, the schematic structure of which may be represented by the following formula:

$$\mathrm{HS}-[\mathrm{R}-\mathrm{S}-\mathrm{S}]_n-\mathrm{R}-\mathrm{SH}.$$

The MWD of the polymers was determined by eluent sorption chromatography, previously developed by us jointly with A. N. Genkin and T. P. Poddubnyi (11). To study thiol-disulfide exchange, polysulfides with molecular weights from 600 to 3000 were synthesized and their MWD was studied (Table 1). The polymers were mixed at room temperature for one hour, and the MWD of the mixture was determined. The fractional composition of the mixture of polymers shows that, upon mixing, a process of thiol-disulfide exchange takes place; at the same time the amount of fractions with the lowest molecular weight (up to 1000) sharply decreases, the amount of high-molecular fractions (above 3000) decreases considerably, and the amount of fractions with intermediate molecular weights (1000-2000) increases (Table 2). The differential MWD curves of the individual polymers and of their mixture also show that, upon mixing, reactions of chemical interaction occur which lead to the formation of polymers with a narrow molecular-weight distribution (Fig. 1).

Fig. 1. Differential MWD curves of polymers Nos. 1, 2, 3

Comparison of the fractional composition of polymers with the same viscosity, obtained by mixing samples differing in viscosity and molecu-

···molecular weight, with the fractional composition of the individual polymers, shows that their fractional composition is practically identical.

Consequently, the thiol-disulfide exchange that occurs both in the process of thiokol synthesis and when they are mixed leads to a narrow molecular-weight distribution of these polymers. It should be noted that the data obtained by us contradict the assertion of the American investigators Davis, Fettes, and Bertozzi that thiol-disulfide exchange leads to a broad MWD in liquid polymers [8].

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