

## Cleavage of Disulfide Polymers. II. By Thiols\*

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### Introduction

The reaction of a thiol (in the form of its sodium salt) with a disulfide was first reported by Lecher<sup>1</sup> in 1920.

Later studies on the reaction between thiols and disulfides have dealt chiefly with the combined cystine in proteins<sup>2-5</sup> and the disulfide elastomers.<sup>6-8</sup> The literature on the subject of thiol/disulfide interchange has recently been reviewed.<sup>8-10</sup>

The rapid reaction of *n*-butyl mercaptan with aqueous dispersions of aliphatic polysulfide polymers has been described.<sup>8</sup> The objective of the present study was to examine the reaction of various thiols with aliphatic polysulfide polymers in aqueous suspension, in bulk, and in solution.

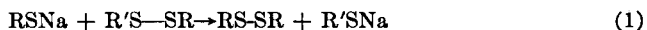
### Experimental Methods

#### *Polymer Preparation*

The polymeric polysulfide used in all of the experiments was prepared by the reaction of sodium disulfide and bis(2-chloroethyl)formal by the polymerization procedure previously described.<sup>8</sup> Crosslinked polymers were prepared in the same way, with 98 mole% bis(2-chloroethyl)formal and 2% 1,2,3-trichloropropane.

#### *Cleavage of Polymer with Thiols*

The treatment of the aqueous dispersion of polymeric disulfides was carried out by addition of 0.05 mole of the desired thiol per mole of polymer (segment weight) as previously described.<sup>8</sup> When sodium disulfide was present, 0.10 mole per mole of polymer (segment weight) was used and the reaction was run for 60 min. at 82.2°C. The effect of the thiols on the



\* Paper presented at the 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 13-18, 1959; based on a portion of the dissertation submitted by E. M. Fettes to the Graduate Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Doctor of Philosophy, June, 1957.

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polymer was determined by measurement of the hardness of a sample of dried polymer by a Shore Durometer A (ASTM D676-55T). The method of preparation of dried polymer has also been described.<sup>8</sup>

#### *Cleavage of Polymers with Sodium Hydrosulfide*

The cleavage of aqueous dispersions of polymeric disulfides by a mixture of sodium hydrosulfite and sodium sulfite was carried out as previously described,<sup>11</sup> with 1.10 moles of sodium sulfite per mole of polymer (segment weight) and varying amounts of sodium hydrosulfide.

#### *Molecular Weights*

Number-average molecular weights of the polymers containing terminal thiol groups were determined by treatment of a solution of the polymer in benzene-methanol with an excess of an aqueous solution of silver nitrate, and back-titration with ammonium thiocyanate.

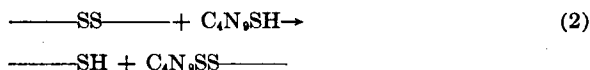
Weight-average molecular weights were determined by measurement of light scattering of solutions in dioxane with the Brice-Phoenix photometer.

Specific viscosities of solutions in dioxane were measured in an Ubbelohde viscosimeter and extrapolated to zero concentration to yield intrinsic viscosity.

### Discussion

#### *Aqueous Media*

When an aqueous dispersion of a polysulfide polymer, prepared by the reaction of bis(2-chloroethyl)formal with sodium disulfide is treated with small amounts (5 mole-%) of *n*-butyl mercaptan, a chemical reaction ensues, as in eq. (1). The characteristic odor of the thiol disappears and the polymer is converted from a tough elastomer to a viscous liquid.<sup>8</sup> The pH of the aqueous medium is about 8 because of the continued presence in the latex of the magnesium hydroxide customarily used as the dispersing agent for the polymerization. The reaction between the thiol and the disulfide groups in the polymeric molecule reduced markedly the length of the chain and introduces terminal butyl and thiol groups, as in eq. (2).



Subsequent oxidation should double the number-average molecular weight of the low polymer but have no effect on the terminal butyl groups.

Instead of *n*-butyl mercaptan, which is insoluble in water, 2-mercaptoethanol, which is completely miscible with water, was used in an attempted cleavage of the same disulfide polymer. The use of 5 mole-% thiol converted the high polymer to a rubber of a millable consistency, 10%, a very soft rubber; 15%, a soft stick mass; and 20%, a viscous liquid. As only 5% of *n*-butyl mercaptan was needed to convert the same polymer to a

viscous liquid, it is seen that the water-insoluble thiol is much more efficient in cleaving the polymer. The logical explanation is that the 2-mercaptoethanol tends to remain in the aqueous phase rather than enter the particle of polymer, there to react with the disulfide linkages of the polymer. It has been already established<sup>11,12</sup> that the process of preparing high polymers by the reactions of dihalides with sodium polysulfide depends upon reversible cleavage of disulfide linkages with sodium disulfide and the preferential solubilizing in the aqueous phase of terminal fragments containing hydroxyl groups. When the aqueous dispersion of low polymer produced by the treatment with 2-mercaptoethanol was treated with sodium disulfide, the hydroxyl terminals were solubilized in the aqueous polysulfide phase and a high polymer was again obtained. When the low polymer was treated either with air or with hydrogen peroxide, the molecular weight was increased (presumably doubled) by the oxidation of the terminal thiol groups introduced by the added 2-mercaptoethanol, but the polymer was far from restored to its original state.

The effect of a number of thiols of widely different structures was studied both in the presence and absence of sodium disulfide. The results in Table I show that the softening effect varies widely and depends on the precise thiol used. Thiourea, ethylene thiourea, cysteine, and the sodium salt of diethyldithiocarbamic acid had only a small cleaving action in the absence of sodium disulfide. The tertiary butyl mercaptan had less effect than the primary butyl mercaptan. The presence of sodium disulfide is not necessary for cleavage with butyl mercaptan.<sup>8</sup> Indeed, the hardness of the polymer is increased owing to an elimination by solubilization of some of the terminal hydroxyl groups present in the polymer.<sup>12</sup> With the various thiophenols used, as well as 2-mercaptobenzothiazole, the sodium disulfide prevented cleavage to various extents. There is at present no explanation for this unless it is the greater insolubility, and thus the slower reaction, of the corresponding disulfides that can be formed from the thiols in the presence of the sodium disulfide.

As the difference between the various thiols could, conceivably, result from varying rates of reaction, an experiment was run to examine the rate of cleavage of a polymer by butyl mercaptan in aqueous media.

The data in Table II shows the cleavage in aqueous media to be complex. In the case of the uncrosslinked latex the molecular weight quickly diminishes and then increases slightly, in that of the crosslinked latex the drop and rise are both even more pronounced. It is felt that this behavior is due to the heterogeneous conditions of the reaction. In the early stages the thiol attacks the outside of the polymer particle cleaving short sections of chains, and thus forms comparatively low molecular weight material and substantially unattacked polymer. Only the lower molecular fraction is soluble in dioxane and the higher molecular weight fraction is left behind in filtering the dioxane solution. The net result measured thus indicates a low molecular weight. The significantly lower molecular weights found in the cleaving of the crosslinked polymer substantiated this belief. The

TABLE I  
 Effect of Thiols on Cleavage of Disulfide Polymers

Thiol	Sodium disulfide <sup>a</sup>	
	Absent	Present
None	32	40
<i>n</i> -Butyl mercaptan	Liquid	Liquid
<i>t</i> -Butyl mercaptan	15	Soft gum
Lauryl mercaptan	Liquid	Liquid
Benzyl mercaptan	Liquid	Liquid
Thiophenol	Liquid	Soft gum
<i>p</i> -Chlorothiophenol	Liquid	Soft gum
Pentachlorothiophenol	Soft gum	39
<i>p</i> -Aminothiophenol	Liquid	9
Thiourea	27	42
Ethylene thiourea	30	40
<i>l</i> (-)-cysteine	30	37
2-Mercaptobenzothiazole	12	34
Diethyldithiocarbamic acid (Na)	33	37

<sup>a</sup> Numbers are hardnesses measured with Shore Durometer A.

crosslinks tie the polymer together more tightly so that only very short sections of the chains are rendered soluble in dioxane. As the reaction progresses and more links are cleaved, the average molecular weight of the soluble portion increases. This phenomenon is similar in principle to the results found in the Vistex method<sup>13</sup> for determining the intrinsic viscosity of GR-S prepared in emulsion. In this method a sample of the emulsion is added to benzene and the viscosity of the benzene layer which extracts and dissolves the polymer is then measured. As the per cent conversion of the monomer to polymer increases, the specific viscosity increases but then decreases at fairly high conversions. This effect is caused by the crosslinking reaction occurring at high conversions. The crosslinked poly-

 TABLE II  
 Rate of Cleavage of Crosslinked and Uncrosslinked Polymer with Butyl Mercaptan in Aqueous Suspension

Time, min.	Crosslinked		Uncrosslinked	
	[ $\eta$ ]	$\bar{M}_w$	[ $\eta$ ]	$\bar{M}_w$
0	0.188	27,800	0.1665	20,600
5	0.115	15,300	0.1115	10,400
10	0.091	6,220	0.1175	11,100
15	0.087	6,530	0.1145	10,300
30	—	—	0.0940	7,460
45	0.100	7,400	0.1155	10,000
60	0.128	14,500	0.0865	5,080
90	0.140	14,500	0.1110	8,580
180	—	—	0.1035	7,140
10,080	0.122	—	0.1110	8,580

mer formed a microgel which dispersed but did not really dissolve in the benzene and hence made no contribution to the viscosity of the solvent. The apparent molecular weight was low but, actually, only the lower molecular weight polymer was being measured. The higher molecular weight fractions were more likely to crosslink to form microgel and thus be eliminated from the molecular weight determination by viscosity measurement.

#### *Self-Redistribution*

The cleavage of disulfide polymers by a mixture of sodium sulfite and sodium hydrosulfide<sup>11,14</sup> results in a polymer of lower molecular weight with thiol terminals. These thiol terminals under suitable conditions should be capable of an interchange reaction with the disulfide groups present in the polymer. The net result should be redistribution to yield a random distribution of molecular weights. Flory<sup>15</sup> has examined the implications of such an interchange which would also occur in polyesters because of the known reaction of ester interchange. For such a random distribution of molecular weight species, the ratio of the weight-average molecular weight  $\bar{M}_w$  to the number-average molecular weight  $\bar{M}_n$  should be 2.00. Liquid polymers with varying molecular weight were prepared and the weight and number-average molecular weights were measured to determine the actual heterogeneity ( $\bar{M}_w/\bar{M}_n$ ).

The results in Table III show that the ratio of molecular weight averages is well above 2, especially as the amount of sodium hydrosulfide and thus the amount of cleavage is increased. The splitting of disulfide links to form thiol terminals is a heterogeneous reaction in that the insoluble polymeric particle is suspended in an aqueous solution containing the dissolved inorganic salts. The measured heterogeneity is thus not surprising and further indicates that redistribution is not appreciably occurring in the washing and drying of the coagulated liquid polymer.

TABLE III  
Effect of Amount of Cleavage of Polymers on Heterogeneity

Sodium hydrosulfide, mole	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0.084	3,730	10,526	2.8
0.100	3,550	8,930	2.5
0.145	2,300	6,900	3.0
0.250	892	3,676	4.1
0.500	600	2,700	4.5

In view of the heterogeneous reaction conditions, an experiment was run to determine the effect of reaction time on the distribution of molecular weights. The results given in Table IV show that the heterogeneity was still high even though the time of reaction was sixteen times that normally sufficient to effect cleavage. It was realized that the presence of cross-linkage would affect the theoretical ratio  $\bar{M}_w/\bar{M}_n$ , but the increase in func-

tionality of the polymer from 2.00 to 2.02 is so slight that it was considered negligible.

TABLE IV  
Effect of Time of Cleavage<sup>a</sup> of Disulfide on Heterogeneity

Reaction time at 82.2°C., hr.	Viscosity, poise <sup>b</sup>	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0.5	33	1180	6850	5.81
1.0	35	1210	7500	6.20
4.0	52	1620	8200	5.06
8.0	80	1890	8500	4.50

<sup>a</sup> 0.20 mole NaSH and 0.65 mole Na<sub>2</sub>SO<sub>3</sub> per mole of polymer (segment weight).

<sup>b</sup> Brookfield viscosimeter.

To overcome the heterogeneity implicit when an aqueous solution is used to produce the terminal thiol groups capable of redistributing with the uncleaved disulfide groups, self-redistribution of a liquid polymer in bulk was attempted. The liquid polymer selected had a heterogeneity index ( $\bar{M}_w/\bar{M}_n$ ) of 4.42. The polymer was heated at 100°C. under nitrogen.

The results in Table V indicate no change in molecular weight distribution. Under these conditions no reaction between thiol groups and disulfide links occurs.

In an attempt to provide conditions under which the reaction between thiol and disulfide would occur, various catalysts suggested in the literature

TABLE V  
Effect of Reaction Time on Heterogeneity

Heating time at 100°C., hr.	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0	629	2,778	4.42
6	681	2,817	4.14
24	656	3,030	4.62
53.5	661	3,125	4.73
72	656	2,857	4.36
168	674	2,985	4.43

TABLE VI  
Effect of Ultraviolet Irradiation on Molecular Weight Distribution

Heating time at 100°C., hr.	$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
0	1,055	4,545	4.3
4	1,058	4,000	3.8
76	1,022	4,650	4.6
124	1,042	4,444	4.3

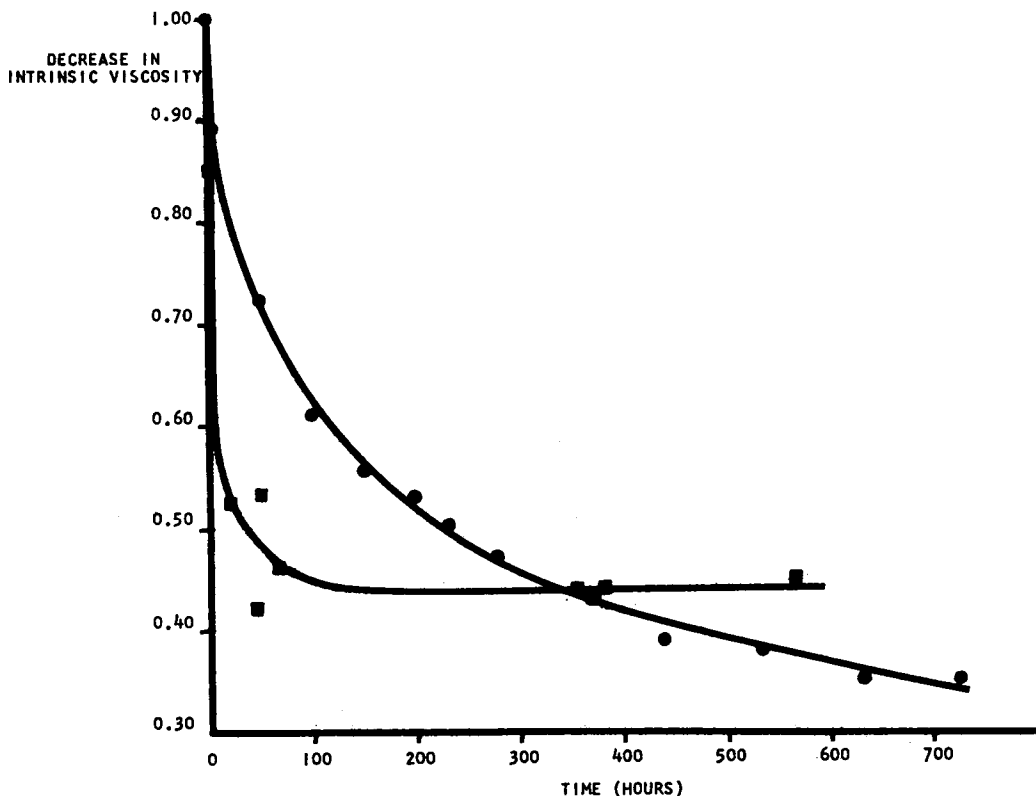


Fig. 1. Rate of reaction of butyl mercaptan with a disulfide polymer at 85°C.: (●) uncatalyzed; (■) catalyzed.

were tried. Ultraviolet light has been shown to promote the reaction,<sup>16</sup> so the reaction of a blend of two liquid polymers was studied at 100°C. under nitrogen with constant irradiation by ultraviolet light. The results shown in Table VI do not indicate any evidence of a reaction.

The results of Fava and Illiceto<sup>17</sup> showed that interchange between butyl mercaptan and butyl disulfide did not occur unless water was present. They further showed that alkali plus water was a much faster catalyst than water alone. Addition of 2% water to the liquid polymer before heating at 100°C. did not lower the heterogeneity. Addition of 3.3% *N*-ethyl morpholine lowered the ratio of molecular weights from 3.73 to 3.03 after 94 hr. at 100°C.

In summarizing the results obtained in the attempts to bring about self-redistribution of an aliphatic disulfide polymer with thiol terminals, it does not seem that much success was attained. Use of heat, water, or ultraviolet light had no significant effect in randomizing the dispersion of molecular weights. The best results appeared to be with the tertiary amine, *N*-ethyl morpholine, but even here the theoretical ratio of 2 was not reached in almost 100 hr. at 100°C. The lack of apparent reaction at 100°C., as contrasted with the relatively fast reaction of butyl mercaptan

with an aqueous dispersion of high polymers at 82.2°C., makes it evident that there must be fundamental differences between the two systems. This same marked difference was also found in the work of Fava and Iliceto,<sup>17</sup> who postulated an ionic mechanism for the thiol-disulfide reaction and Guryanova et al.,<sup>18</sup> who claimed the exchange to have a radical mechanism. There can be little doubt that the reaction of thiols with aqueous dispersions of polymer proceeds by an ionic mechanism.

### *Homogeneous Solution*

The reaction of a disulfide polymer with a thiol (butyl mercaptan) was studied in solution in dioxane. The reaction was carried out uncatalyzed and with sodium phenolate as a basic catalyst. The intrinsic viscosity of the solution was measured as a function of reaction time at 85°C. The results in Figure 1 show the reaction to be exceedingly slow in the absence of an alkaline catalyst (sodium phenolate) and far faster when catalyzed. The continued decrease of viscosity of the uncatalyzed thiol-disulfide reaction, even after 350 hr., when the flat portion of the curve for the catalyzed reaction is crossed, is believed due to slow cleavage of the formal linkage also present in the polymer. It has been shown in a study of the thermal stability of polysulfide polymers<sup>19</sup> that the formal linkage can be cleaved. This cleavage is prevented by alkaline materials, so the curve for the catalyzed reaction should and does reach a constant value. The profound effect on the rate of reaction by a basic material strongly indicates that the reaction of a thiol with the disulfide linkage in polysulfide polymers in solution is also ionic in nature.

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### Synopsis

The study of the interchange reaction of thiols with disulfides is extended to include additional thiols and conditions for redistribution. In aqueous suspension, polymeric disulfides are reduced in molecular weight to widely different extents by thiols of varying structures. Water-soluble thiols as mercaptoethanol, and tertiary thiols as *t*-butyl mercaptan, are relatively ineffective in cleaving. The presence of sodium disulfide with some of the thiols, particularly the thiophenols and 2-mercaptobenzothiazole, retarded cleavage by the thiols. A study of the molecular weight of the polymer as the cleavage by thiols proceeded indicated that short chain lengths were gradually removed from the surface of the polymeric particles. The partial cleavage of a disulfide polymer by a mixture of sodium sulfite and sodium hydrosulfite produces a disulfide polymer of lower molecular weight and terminal thiol groups. This product should be capable of self-redistribution to a random distribution. The liquid polymer resulting from the cleavage had a high heterogeneity index ( $\overline{M}_w/\overline{M}_n$ ). Efforts to randomize in bulk to the theoretical index of 2.0 by heat, ultraviolet light, water, and amines were not successful. It was found possible to effect the reaction of the disulfide polymer with butyl mercaptan in solution in dioxane with sodium phenolate as catalyst. The conclusion is drawn that the reaction of a thiol with a disulfide, both in aqueous suspension and in dioxane, is ionic rather than radical.

### Résumé

L'étude de la réaction d'échange de thiols avec les disulfures, décrite antérieurement en employant des polymères disulfurés et du butylmercaptan en milieu aqueux, a été étendue à d'autres thiols et à autres conditions de redistribution. En suspension aqueuse, les poids moléculaires de disulfures polymériques sont diminués à des degrés variables suivant les thiols et leurs structures. Des thiols solubles dans l'eau comme le mercapto-éthanol et les thiols tertiaires comme le *t*-butylmercaptan sont relativement inefficaces pour le clivage. La présence de disulfure de sodium avec la plupart des thiols, en particulier les thiophénols et le 2-mercaptobenzothiazol, retardent le clivage par les thiols. Une étude du poids moléculaire du polymère à mesure que progresse la rupture par les thiols, montre que de courtes chaînes sont graduellement déplacées de la surface des particules polymériques. Le clivage partiel d'un polymère disulfuré par un mélange de sulfite de sodium et d'hydrosulfite de sodium produit un polymère disulfuré de plus bas poids moléculaire et des groupes thiols terminaux. Ce produit sera capable d'une auto-redistribution statistique. Le polymère liquide qui résulte du clivage possède un index ( $\overline{M}_w/\overline{M}_n$ ) élevé d'hétérogénéité. Des efforts pour obtenir une distribution statistique correspondant à un indice théorique de 2.0 sous l'influence de la température, de la lumière ultraviolette, de l'eau et des amines ont été infructueux. Il s'est révélé possible d'effectuer la réaction du polymère disulfuré avec le butylmercaptan en solution dans le dioxanne en utilisant du phénolate de sodium comme catalyseur. On en conclut que la réaction d'un thiol avec un disulfure, aussi bien en suspension aqueuse que dans de dioxanne est une réaction ionique plutôt que radicalaire.

### Zusammenfassung

Die Untersuchung der früher beschriebenen Austauschreaktion von Thiolen und Disulfiden an Disulfidpolymeren und Butylmercaptan in wässrigem Medium wurde auf zusätzliche Thiole und Bedingungen für die Ausbildung einer neuen Verteilung ausgedehnt. In wässriger Suspension wird das Molekulargewicht polymerer Disulfide durch Thiole verschiedener Struktur in sehr verschieden weitem Ausmass herabgesetzt. Wasserlösliche Thiole, wie Merkaptoäthanol, und tertiäre Thiole, wie *t*-Butylmercaptan, sind bei der Spaltung verhältnismässig unwirksam. Die Anwesenheit von Natriumdisulfid verzögerte bei einigen Thiolen, besonders den Thiophenolen und 2-Merkapto-benzthiazol, die Spaltung durch die Thiole. Eine Untersuchung des Molekulargewichts

der Polymeren bei fortschreitender Spaltung durch Thiole zeigte, dass von der Oberfläche der Polymerpartikel stetig kurze Kettenstücke abgespalten wurden. Die partielle Spaltung eines Disulfidpolymeren durch eine Mischung von Natriumsulfit und Natriumhydrosulfit liefert ein Disulfidpolymeres von niedrigem Molekulargewicht und endständige Thiolgruppen. Dieses Produkt sollte von selbst einer Umwandlung seiner Verteilung in eine statistische fähig sein. Das bei der Spaltung entstehende flüssige Polymere besass einen hohen Heterogenitätsindex ( $\bar{M}_w/\bar{M}_n$ ). Versuche, die Verteilung durch Anwendung von Wärme, Ultraviolettlicht, Wasser und Amine in Substanz auf die statistische Form mit dem theoretischen Index von 2,0 zu bringen, hatten keinen Erfolg. Es war möglich, die Reaktion des Disulfidpolymeren mit Butylmerkaptan in Dioxanlösung mit Natriumphenolat als Katalysator durchzuführen. Man kommt zu dem Schluss, dass die Reaktion zwischen einem Thiol und einem Disulfid sowohl in wässriger Suspension als auch in Dioxan nicht eine Radikalreaktion sondern eine ionische Reaktion ist.

Received September 14, 1962