

## Cleavage of Disulfide Polymers. III. By Disulfides\*

E. M. FETTES† and H. MARK, *Polytechnic Institute of Brooklyn,  
Brooklyn, New York*

### Synopsis

A study was made of the cleavage of polymeric disulfide by organic disulfides of different structures in the presence and absence of sodium disulfide. While aliphatic disulfides will cleave polymeric disulfides only in the presence of sodium disulfide, hydroxyethyl disulfide and aromatic disulfides will cause partial cleavage in the absence of inorganic disulfide. It is believed that cleavage results not from a disulfide-disulfide interchange, but from cleavage of the organic disulfide by water to form a  $RS^-$  anion. Other salts known to cleave disulfide groups promote the cleavage of polymer by butyl disulfide, sodium sulfoxylateformaldehyde being particularly active. Benzothiazyl disulfide and tetraalkylthiuram disulfides reacted to cleave in the absence of sodium disulfide but had no effect when sodium disulfide was present. By carrying out the reaction stepwise, it was found that sodium disulfide reversed the softening action of the disulfide reforming the cleaved linkages. When the disulfide polymer contained terminal thiol groups, tetramethylthiuram disulfide would reform the high polymer by converting thiol terminals to disulfide links. In spite of the known ability of these complex disulfides to dissociate homolytically into radicals and initiate vinyl polymerization, no evidence was found that the cleavage of polymeric disulfides involved  $RS\cdot$  radicals.

### INTRODUCTION

Although thiol-disulfide interchange has received emphasis in the chemical literature and has been recently reviewed,<sup>1-4</sup> the interchange between two disulfides has received little attention. Smiles and Gibson<sup>5</sup> found the expected unsymmetrical disulfide formed from the reaction of a mercaptide and a thiol-sulfonate ester ( $RSSO_2R'$ ) to be contaminated with the two possible symmetrical disulfides, but attributed this to the reaction of disulfide with mercaptide discovered by Lecher.<sup>6</sup> Stern and Tobolsky<sup>7</sup> postulated the occurrence of a disulfide-disulfide reaction to explain the stress relaxation of polysulfide rubbers, but later Mochulsky and Tobolsky<sup>8</sup> concluded that the mechanism of relaxation of stress was probably a thiol-disulfide exchange.

A number of patents by Kleiman claimed that halogens and halogen halides,<sup>9</sup> organic peroxides,<sup>10</sup> heat,<sup>11</sup> and light<sup>12</sup> would all catalyze the reaction of one disulfide with another to effect exchange. Proell in a patent<sup>13</sup>

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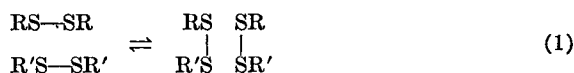
† Present address: Research Department, Koppers Co., Inc., Monroeville, Pa.

claimed that a mixture of two organic disulfides can be redistributed to the unsymmetrical disulfide by heating with an alcoholic solution of both sodium sulfide and potassium hydroxide. As sodium sulfide has already been shown to cleave organic disulfides to form mercaptides,<sup>4</sup> and as mercaptides do react with disulfides,<sup>6</sup> this is probably not a true disulfide-disulfide reaction. The later patent by Proell and Adams<sup>14</sup> described the formation of symmetrical from unsymmetrical disulfides by heating with sodium sulfide in an alkanolamine solution, but here too a mercaptide-disulfide reaction is likely to be occurring. The reaction of butyl disulfide with polysulfide polymers occurs readily,<sup>4</sup> but sodium polysulfide is necessary for the reaction. As sodium polysulfide can convert organic disulfides to mercaptides,<sup>15</sup> this is probably not really a disulfide-disulfide interchange.

The homolytic cleavage of disulfides by radiation, both visible and ultraviolet, has been well established. The redistribution of two disulfides in the presence of ultraviolet radiation to produce the unsymmetrical disulfide in low yields has been described.<sup>16</sup> Asymmetrical aliphatic disulfides such as ethyl *n*-propyl disulfide were found<sup>17</sup> partially to disproportionate into the corresponding two symmetrical disulfides upon standing at room temperature for long periods of time. Irradiation with ultraviolet light produced the same results quickly, and even visible light had a pronounced accelerating effect on the reaction. Disulfides with other aliphatic groups behaved in the same manner with the exception of those containing even one *tert*-butyl group. The radical cleavage of disulfide links postulated by these authors to account for the exchange was substantiated by finding that acrylonitrile in the presence of methyl ethyl disulfide was stable in the dark but polymerized upon exposure to sunlight. The ability of disulfides to initiate upon radiation the polymerization of vinyl monomers has been described.<sup>18-24</sup> The polymerization of the cyclic trimethylene disulfide by light has been carried out even at extremely low temperatures.<sup>25</sup>

The thermal dissociation of aromatic disulfides to form free radicals has been advocated as an explanation of the color developed on heating in solution,<sup>26</sup> but Lecher<sup>27</sup> has presented evidence against the dissociation of phenyl disulfide into long-lived sulfenyl radicals. He found no interchange in aromatic disulfides in boiling xylene or benzene at 200°C.,<sup>28</sup> although interchange was found<sup>19</sup> in dioxane at 170°C. Otsu<sup>22</sup> found that phenyl, tolyl, benzyl, and benzoyl disulfides would not cleave thermally at 60, 80, or 120°C. to initiate polymerization of styrene but did so at 30°C. by sunlight. The influence of radiation, even sunlight, is so pronounced<sup>17</sup> that one must suspect that the thermal cleavages postulated in some cases may well be photochemical cleavages. The disulfides containing a nitrogen on the carbon atom bonded to the sulfur such as tetramethylthiuram disulfide or benzothiazyl disulfide do cleave thermally and thereby initiate polymerization.<sup>22-24</sup>

In summarizing the published work, it seems evident that a disulfide-disulfide exchange is not a simple bimolecular rearrangement.



Instead the reaction is initiated by cleavage of a disulfide group to form, depending on the cleaving agent, a radical (RS·) or an ion (RS<sup>-</sup>). Light and possibly heat can produce the radical; base, thiol, and possibly water can produce the ion. The radical or ion can react with another disulfide group regenerating the radical or ion. The initiation by RS<sup>-</sup> is actually the thiol-disulfide reaction discussed in the previous paper. It should be noted that extremely small amounts of thiol are capable of bringing about a disulfide-disulfide interchange. It is extremely difficult to be sure that disulfides are sufficiently free of thiol so that the reaction can be assuredly disulfide interchange instead of actually a thiol-disulfide reaction.

## EXPERIMENTAL

### Polymer Preparation

The polymeric disulfides used in all of these experiments were prepared by the reaction of an aqueous solution of sodium disulfide with 98 mole-% bis(2-chloroethyl)formal and 2 mole-% 1,2,3-trichloropropane by the polymerization process previously described.<sup>4</sup>

### Cleavage of Polymer with Disulfide

The treatment of the aqueous dispersion of polymeric disulfide was carried out by addition of the desired disulfide, 0.05 mole/mole of polymer (segment weight), as previously described.<sup>4</sup> When sodium disulfide was present, 0.10 mole/mole of polymer (segment weight) was used, and the reaction carried out for 60 min. at 82.2°C. The effect of the disulfides on the polymer was determined by measurement of the hardness of a sample of dried polymer by a Shore Durometer A (ASTM D676-55T). When the elastomer was substantially cleaved, it was too soft to give a reading on the instrument and a qualitative observation was made. The method of preparation of suitable samples of dried polymer has also been described.

When alkaline salts other than sodium disulfide were used in conjunction with dibutyl disulfide, the same number of moles (0.05) was used, all other reaction conditions being the same.

## DISCUSSION

### Aliphatic and Aromatic Disulfides

It has been shown<sup>4</sup> that 5% (mole) of dibutyl disulfide will convert an aqueous dispersion of a polymeric disulfide of high molecular weight to liquid polymer of low molecular weight if a small amount (5-10%) of sodium disulfide is present. No decrease in the molecular weight of the polymer was found if the inorganic disulfide was absent.

The effect of a number of aliphatic and aromatic disulfides on a polymeric disulfide was investigated in the presence and absence of sodium disulfide. The results obtained are shown in Table I. The polymer in the form of an aqueous dispersion had a Shore hardness of 50 which was not increased by an additional treatment with sodium disulfide. A value of 50 corresponds to a tough elastomer, much too high in molecular weight to be capable of handling on a rubber mill. The dibutyl disulfide reduced this high polymer to a liquid as expected when sodium polysulfide was present, but contrary to previous work,<sup>4</sup> had a softening effect even in the absence of sodium disulfide. This behavior was so unexpected that a reinvestigation was made. It was found that the dibutyl disulfide contained traces of thiol as an impurity. Treatment of an aqueous dispersion of polymer with butyl disulfide, first treated with iodine to oxidize the thiol content, yielded products only slightly lower in Shore hardness than the untreated polymer rather than the soft rubber shown in Table I. It is felt, in view of these results as well as previous work,<sup>4</sup> that traces of unoxidized thiol were responsible for the slight softening still obtained. This experiment points up the difficulty in being assured a reaction is really disulfide interchange rather than a thiol-disulfide reaction.

TABLE I  
Effect of Disulfides on Cleavage of Disulfide Polymers

Disulfide	Hardness, Shore A	
	Without sodium disulfide	With sodium disulfide
None	50	50
Dibutyl disulfide	Soft rubber	Liquid
Di- <i>tert</i> -butyl disulfide	50	36
Bis(2-mercaptoethyl)disulfide	30	45
Dibenzyl disulfide	Very soft rubber	Soft rubber
Diphenyl disulfide	Very soft rubber	Soft rubber
Di- <i>p</i> -nitrophenyl disulfide	Soft rubber	Soft rubber

The di-*tert*-butyl disulfide had no effect on the polymer in the presence and only a slight effect in the absence of sodium disulfide. *tert*-Butyl mercaptan, unlike other thiols,<sup>1</sup> was not found effective in cleaving a disulfide polymer. This anomalous behavior of *tert*-butyl groups was also noted in photochemical cleavage.<sup>17</sup>

The bis(2-mercaptoethyl)disulfide had a slight softening effect in the absence of sodium polysulfide and almost no effect in the presence of sodium disulfide. These results agree with previous work<sup>1</sup> with the corresponding thiol, 2-mercaptoethanol, wherein the efficiency was much less in cleaving than was *n*-butyl thiol. This effect was attributed to the water solubility of the thiol. It is probable that the HOCH<sub>2</sub>CH<sub>2</sub>SNa formed by the action of sodium disulfide on the bis(2-mercaptoethyl)disulfide is partitioned so that it remains mostly in the aqueous phase and is

not in the polymer to react with it. The glycol disulfide does cleave the polymer in the absence of sodium disulfide, as does dibenzyl, diphenyl, and dinitrophenyl disulfides. This cleavage must be a true disulfide-disulfide reaction unless water (in the presence of the magnesium hydroxide remaining in the polymer) can have a sufficient hydroxyl ion concentration to cleave the disulfide linkage. Cleavage of disulfides by water has indeed been postulated by Fromm<sup>29</sup> and by Schoberl<sup>30-32</sup> to produce the thiol which can effect cleavage.



Evidence of such a reaction has been claimed for aromatic disulfides, combined cystine, and dithiodiglycolic acid, although mechanisms for the cleavage not involving the sulfenic acid have also been postulated.<sup>33,34</sup> Whatever the mechanism, it is evident that aromatic disulfides and bis(2-mercaptoethyl) disulfide can cleave aliphatic polymeric disulfides in the absence of thiol impurities and sodium disulfide. The amount of cleavage is slight as the amount of disulfide used was sufficient, if fully utilized, to reduce the high polymer to a liquid of low molecular weight. Aliphatic disulfides such as propyl, butyl, or amyl, when free from residual thiol, have no effect on a polymeric disulfide unless sodium disulfide is present.

A number of other alkaline salts were tried in place of sodium disulfide to see if they would effect cleavage of a polymeric disulfide by dibutyl disulfide which was treated with iodine to oxidize any traces of thiol present. The results in Table II show that sodium monosulfide and sodium hydroxide were equivalent in producing a very soft polymer. Sodium sulfite had a slight effect while sodium thiosulfate had almost none. Sodium sulfoxylate-formaldehyde was equivalent to sodium disulfide and was used because of its known cleavage of the disulfide linkage in wool.<sup>35</sup>

The salts which promote interchange of butyl disulfide with polysulfide polymers are those which have already been shown or would be expected to have a cleaving action upon disulfides. Indeed, all of the experiments described lead to the conclusion that disulfide interchange in polysulfide polymers occurs by way of a heterolytic cleavage of the disulfide. For aliphatic disulfides, sulfide ions, or an ion of similar nature is needed to

TABLE II  
Effect of Various Salts on Cleavage of a  
Disulfide Polymer with Dibutyl Disulfide

Salt	Hardness of product, Shore A
None	50
Sodium disulfide	Liquid
Sodium monosulfide	Very soft rubber
Sodium hydroxide	Very soft rubber
Sodium sulfite	35
Sodium thiosulfate	44
Sodium sulfoxylate-formaldehyde	Liquid

initiate the ionic cleavage to mercaptide ion which then reacts with the disulfide group in the polymer. For disulfides known to cleave readily (aromatic), water is apparently sufficient to cause cleavage and thus initiate the exchange reaction.

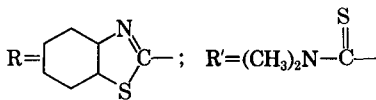
### Thiazyl and Thiuram Disulfides

Thiuram disulfides and benzothiazyl disulfides have long been used in the processing of polysulfide polymers to soften the material on the mill. This action has been shown<sup>36,37</sup> to be a chemical scission of the polymer and presumably involves disulfide-disulfide interchange. Unlike aliphatic and aromatic disulfides, these complex disulfides are known to undergo homolytic cleavage to form active radicals by heat or light. Tetramethylthiuram<sup>22-24</sup> and benzothiazyl disulfide<sup>22</sup> will thermally dissociate even at 70°C. to initiate polymerization of vinyl monomers.

The action of tetramethylthiuram disulfide and benzothiazyl disulfide on polymeric disulfides in aqueous suspension was examined in the same manner as was done with aliphatic and aromatic disulfides. As tetramethylthiuram monosulfide will thermally dissociate to initiate polymerization of vinyl compounds,<sup>22</sup> it was included along with metallic derivatives. The results are presented in Table III.

TABLE III  
Effect of Complex Disulfides on Cleavage of Disulfide Polymers

Cleavage agent	Structure*	Hardness, Shore A	
		Without sodium disulfide	With sodium disulfide
Benzothiazyl disulfide	RSSR	Liquid	50
Mercaptobenzothiazole (MBT)	RSH	37	50
Zinc salt of MBT	RSZnSR	50	52
Tetramethylthiuram disulfide	R'SSR'	Liquid	50
Tetramethylthiuram monosulfide	R'SR	Liquid	42
Zinc dimethyldithiocarbamate	R'SZnSR'	44	55
Lead dimethyldithiocarbamate	R'SPbSR'	45	42
Sodium diethyldithiocarbamate	R'SNa	47	50
None	—	50	50

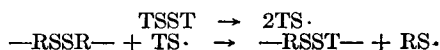


While the metallic derivatives of benzothiazyl and tetramethylthiuram disulfide had little effect in cleaving, the disulfides themselves, as anticipated, and also tetramethylthiuram monosulfide reduced the high polymer to a liquid when used alone. Surprisingly no cleavage at all was found with these two disulfides when sodium disulfide was present. This behavior is the opposite of that encountered with dibutyl disulfide which reacts with

the polymer only in the presence of sodium disulfide. A possible explanation would be the conversion of tetramethylthiuram disulfide by sodium disulfide into the sodium salt of the dithiocarbamic acid already shown in Table III to be ineffective in cleavage. It was found that tetramethylthiuram disulfide was virtually unchanged by treatment with aqueous sodium disulfide for 60 min. at 82.2°C. Another possibility was that the complex disulfides did cleave the polymer and the sodium disulfide then converted the cleaved polymer back to a high molecular weight. Aqueous dispersions of high polymer were cleaved to liquid polymers by treatment with benzothiazyl disulfide, tetramethylthiuram disulfide or tetramethylthiuram monosulfide and then treated in a second step with sodium disulfide. All three liquid polymers were converted back to tough elastomers, showing that indeed the sodium disulfide reversed the cleavage of the polymer by the complex disulfides. This action of sodium disulfide is similar in action to that of zinc oxide in removing, during vulcanization, the effect of the benzothiazyl disulfide used for cleaving the elastomer to facilitate processing.<sup>37</sup>

Further examination of the reaction of thiuram disulfides with aliphatic disulfide polymers was made with an aqueous dispersion of a liquid polymer with terminal thiol groups<sup>15,36</sup> prepared by treatment of the high polymer with sodium hydrosulfide plus sodium sulfide. It was found that tetraethylthiuram disulfide alone in this case did not lower, but on the contrary, increased the molecular weight. An amine odor was noticed during the reaction. The same reaction was carried out with the use of butyl mercaptan as a model compound instead of the polymeric dithiol. It was found that butyl mercaptan was oxidized to dibutyl disulfide and quantities of the diethylamine salt of diethyldithiocarbamic acid were isolated. The reaction of thiuram disulfide with a simple dithiol, bis(2-mercaptoethyl)-sulfide, was carried out. The dithiol was oxidized to a waxlike polymer, and the amine salt could be volatilized out of the mass. It is evident that when a disulfide polymer contains thiol groups, the thiuram disulfide does not react to cleave the disulfide groups in the polymer but instead reacts with the terminal thiol groups. A search revealed that tetramethylthiuram disulfide had been already shown<sup>38,39</sup> to convert *n*-dodecylmercaptan to the disulfide with liberation of the dimethylamine salt of dimethyldithiocarbamic acid.

The conclusion reached that ordinary aliphatic and aromatic disulfides cleave heterolytically to form RS<sup>-</sup> which then reacts with the polymeric disulfide might not necessarily be true for these complex disulfides which can readily cleave homolytically to form RS· radicals. These radicals produced by thermal dissociation of the complex disulfide may be capable of reacting with a disulfide group in the polymer regenerating a radical from that disulfide group even though the disulfide group in the polymer could not of itself cleave homolytically to form radicals.



If this could happen, a small amount of thiuram disulfide should be able to initiate complete interchange between an aliphatic disulfide polymer and an aliphatic disulfide such as dibutyl disulfide in the absence of sodium disulfide. The amount of cleavage of the polymer would then be determined by the total of reactive disulfide, tetramethylthiuram disulfide, and inactive disulfide, dibutyl disulfide. The cleaving effect on a polymeric disulfide of 5 mole-% dibutyl disulfide, plus 0.5% tetraethylthiuram and also plus 0.5% of azobisisobutyronitrile as an alternate source of radicals, was examined. The hardness of the polymer was unchanged by the dibutyl disulfide plus AIBN. The polymer was slightly softened by the dibutyl disulfide plus tetramethylthiuram disulfide, but to an extent attributable to the 0.5% of thiuram disulfide. Complete reaction with the 5% dibutyl disulfide would have produced a viscous liquid.

It has been shown that thiuram disulfides will react with aliphatic disulfide polymers to rearrange, lower the molecular weight, and place dithiocarbamate groups on the chain as terminals which can be removed by the action of sodium disulfide. In spite of the knowledge that these complex disulfides can readily form radicals at these reaction temperatures, it seems evident that the reaction with aliphatic polymeric disulfides in an aqueous medium proceeds by an ionic mechanism.

### References

1. Fettes, E. M., and H. Mark, paper presented at 136th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 13-18, 1959. Part II in this series.
2. Parker, A. J., and N. Kharasch, *Chem. Revs.*, **59**, 583 (1959).
3. Jensen, E. V., *Science*, **130**, 1319 (1959).
4. Bertozzi, E. R., F. O. Davis, and E. M. Fettes, *J. Polymer Sci.*, **19**, 17 (1956).
5. Smiles, S., and D. T. Gibson, *J. Chem. Soc.*, **1924**, 176.
6. Lecher, H. Z., *Ber.*, **53B**, 591 (1920).
7. Stern, M. D., and A. V. Tobolsky, *J. Chem. Phys.*, **14**, 93 (1946).
8. Mochulsky, M., and A. V. Tobolsky, *Ind. Eng. Chem.*, **40**, 2155 (1948).
9. Kleiman, M. (to Velsicol Corp.), U. S. Pat. 2,510,894 (June 6, 1950).
10. Kleiman, M. (to Velsicol Corp.), U. S. Pat. 2,610,968 (Sept. 16, 1952).
11. Kleiman, M. (to Velsicol Corp.), U. S. Pat. 2,610,967 (Sept. 16, 1952).
12. Kleiman, M. (to Velsicol Corp.), U. S. Pat. 2,474,849 (July 5, 1949).
13. Proell, W. A. (to Standard Oil of Indiana), U. S. Pat. 2,521,870 (Sept. 12, 1950).
14. Proell, W. A., and C. E. Adams (to Standard Oil of Indiana), U. S. Pat. 2,557,312 (June 19, 1951).
15. Fettes, E. M., and H. Mark, *J. Appl. Polymer Sci.*, **5**, 7 (1961).
16. Harris, J. F. (to E. I. duPont de Nemours & Co., Inc.), U. S. Pat. 2,719,170 (Sept. 27, 1955).
17. Birch, S. F., T. V. Cullum, and R. A. Dean, *J. Inst. Petrol.*, **39**, 206 (1953).
18. Kharasch, M. S., W. Nudenberg, and T. H. Meltzer, *J. Org. Chem.*, **18**, 1233 (1953).
19. Leandri, G., and A. Tundo, *Ricerca Sci.*, **23**, 1646 (1953).
20. Russell, K. E., and A. V. Tobolsky, *J. Am. Chem. Soc.*, **76**, 395 (1954).
21. Crawshaw, G. H., and J. B. Speakman, *J. Soc. Dyers Colourists*, **70**, 81 (1954).
22. Otsu, T., *J. Polymer Sci.*, **21**, 559 (1956).
23. Kern, R. J., *J. Am. Chem. Soc.*, **77**, 1382 (1955).



24. Ferington, T. E., and A. V. Tobolsky, *J. Am. Chem. Soc.*, **77**, 4510 (1955).
25. Barltrop, J. A., P. M. Hayes, and M. Calvin, *J. Am. Chem. Soc.*, **76**, 4348 (1954).
26. Schonberg, A., E. Rupp, and W. Gumlich, *Ber.*, **66**, 1932 (1933).
27. Lecher, H. Z., *Science*, **120**, 220 (1954).
28. Lecher, H. Z., *Ber.*, **53**, 577 (1920).
29. Fromm, E., *Ber.*, **41**, 3397 (1908).
30. Schoberl, A., and H. Eck, *Ann. Chem.*, **522**, 97 (1936).
31. Schoberl, A., E. Berninger, and F. Harren, *Ber.*, **67B**, 1545 (1934).
32. Schoberl, A., *Ber.*, **70**, 1186 (1937).
33. Tarbell, D. S., and D. P. Harnish, *Chem. Revs.*, **49**, 1 (1951).
34. Rosenthal, N. A., and G. Oster, *J. Soc. Cosmetic Chemists*, **5**, 286 (1954).
35. Brown, A. E., and M. Harris, *Ind. Eng. Chem.*, **40**, 316 (1948).
36. Fettes, E. M., and J. S. Jorczak, *Ind. Eng. Chem.*, **42**, 2217 (1950).
37. Fettes, E. M., J. S. Jorczak, and J. R. Panek, *Ind. Eng. Chem.*, **46**, 1539 (1954).
38. Craig, D., W. L. Davidson, A. E. Juve, and I. Geib, *J. Polymer Sci.*, **6**, 1 (1951).
39. Scheele, W., O. Lorenz, and W. Dummer, *Kautschuk Gummi*, **7**, WT273 (1954).

### Résumé

On a étudié la rupture du disulfure polymérique par des disulfures de différentes structures en présence et en absence de disulfure de sodium. Alors que des disulfures aliphatiques rompent les disulfures polymériques uniquement en présence de disulfure de sodium, le disulfure d'hydroxyéthyle et les disulfures aromatiques provoquent un clivage partiel en absence de disulfures inorganiques. On croit que la rupture résulte non d'un échange disulfure-disulfure mais de la rupture du disulfure organique par l'eau pour former un anion  $RS^-$ . D'autres sels connus pour leur pouvoir de rupture des groupes disulfures favorisent le clivage de polymères par le disulfure de butyle avec le sulfoxylate de sodium-formaldéhyde qui est particulièrement actif. Le disulfure de benzothiazyle et les sulfures de tétraalcoyl-thiurame réagissent dans le clivage en absence de disulfure de sodium mais n'ont pas d'effet lorsque le disulfure de sodium est présent. On trouve en effectuant la réaction étape par étape que le disulfure de sodium renverse l'action adoucissante du disulfure et reforme les liens rompus. Lorsque le polymère disulfure contient des groupes thiols terminaux, le disulfure de tétraméthyl-thiurame reforme le haut polymère par conversion des thiols terminaux en liens disulfures. Bien que l'on sache que ces disulfures complexes peuvent se dissocier homolytiquement en radicaux et initier la polymérisation vinylique, on n'a pas trouvé de preuve que le clivage des sulfures polymériques implique des radicaux  $RS\cdot$ .

### Zusammenfassung

Die Spaltung polymerer Disulfide durch organische Disulfide verschiedener Struktur in Gegenwart und Abwesenheit von Natriumdisulfid wurde untersucht. Während aliphatische Disulfide polymere Disulfide nur bei Gegenwart von Natriumdisulfid spalten, bewirken Hydroxyäthylsulfid und aromatische Disulfide auch in Abwesenheit anorganischer Disulfide eine teilweise Spaltung. Es wird angenommen, dass die Spaltung nicht durch einen Disulfid-Disulfidaustausch, sondern durch Spaltung des organischen Disulfides durch Wasser unter Bildung eines  $RS^-$ -Anions zustande kommt. Andere Salze mit bekannter Spaltungswirkung auf Disulfidgruppen begünstigen die Spaltung des Polymeren durch Butylsulfid, wobei Natriumsulfoxylat-Formaldehyd besonders wirksam ist. Benzothiazylsulfid und Tetraalkylthiuramdisulfide reagierten bei Abwesenheit von Natriumdisulfid unter Spaltung, hatten jedoch bei Gegenwart von Natriumdisulfid keine Wirkung. Durch schrittweise Durchführung der Reaktion konnte festgestellt werden, dass Natriumdisulfid die weichmachende Wirkung des Disulfids durch Neubildung der gespaltenen Bindungen aufhob. Bei einem Gehalt des Disulfidpolymeren an endständigen Thiolgruppen kann Tetramethylthiuramdisulfid

das Hochpolymere durch Umwandlung von Thiolendgruppen zu Disulfidbindungen zurückbilden. Trotz der bekannten Fähigkeit dieser komplexen Disulfide zur homolytischen Zerfall in Radikale mit Fähigkeit zum Start der Vinylpolymerisation, konnte kein Hinweis dafür gefunden werden, dass die Spaltung von polymeren Disulfiden über RS-Radikale verläuft.

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