

Review

Factors Involved in Reversible Disulfide Cross-Linking in Cellulose

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Works on the reversible disulfide-cross-linking in cellulose were reviewed. Reactions of tosylated cotton with potassium thioacetate followed by alkaline hydrolysis were found to yield products (M) containing both mercaptan and disulfide. The disulfide fraction of the total sulfur content in M depended much on the sort of solvent used for the thiolacetylation. It was found by polarographic and infrared analyses that a part of the acetylthio groups introduced in acetone or in dimethylformamide (DMF) underwent rearrangement to form mercaptocellulose acetate, and that acetylthio groups introduced in methanol underwent complete methanolysis to form mercaptocellulose, and most of the mercapto groups thus produced were oxidized before the hydrolysis treatment to yield the corresponding disulfide. Reactions of tosylated cotton with thiourea were also studied.

A new cross-linking reagent, bis- β -isocyanatoethyl disulfide (BIED) was synthesized from diethyl dithiodipropionate and its reaction with cotton in DMF was investigated. The sulfur content of the BIED-treated cotton (DTC) decreased by reduction with tri-*n*-butylphosphine. The polarographic and infrared analyses revealed that BIED reacted with cotton monofunctionally and bifunctionally to form branches and cross-links, respectively.

It is considered that the cross-linking reagent that contains disulfide bond seems valuable in studying factors controlling the cross-linking efficiency because the efficiency can be estimated easily in this system. Works on the cross-linking efficiencies of BIED for reactions with cotton, ramie, and viscose rayon in DMF under various conditions were described. In general, the cross-linking efficiency increased as the reaction progressed. In order to study the effect of size of cross-linking reagents, several disulfide-containing diisocyanates of different sizes have been prepared and their reactions with various kinds of cellulose are being studied.

The oxidation behaviors of mercaptocellulose (RM) made by the reduction of M with tri-*n*-butylphosphine and cellulose β -mercaptoethylaminocarboxylate (RDTC) made by the reduction of DTC were studied and factors controlling the oxidation of solid polymeric mercaptans were discussed. RDTC was converted quantitatively to the corresponding disulfide by oxidation under mild conditions. On the other hand, only a portion of the mercapto groups in RM could form disulfide groups by oxidation, and the rest of those was converted to sulfonic acid groups by oxidation with a severer reagent. It is considered that the mobility of the mercapto groups necessary for the oxidation coupling is restricted because they are attached directly to rigid cellulose chains. The oxidation of RM and RDTC with air in alkaline medium was studied kinetically. It was found that the oxidation of the mercapto groups in paired placement in the cellulose matrix proceeded more than tenfold faster than that of the randomly placed mercapto groups.

RDTC made from cotton was partially oxidized in various solvents of different swelling power followed by treatment with excess methyl iodide to yield disulfide cross-linked cotton containing sulfonium groups (MORDTC). The effect of the solvent in cross-linking on the equilibrium and kinetics of dyeing with three anionic dyes of different molecular size was investigated. The pore structure of the cross-linked cotton was discussed. The cross-linked cotton seemed to have a "memory" of the state

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Factors Involved in Reversible Disulfide Cross-linking

at the time of cross-linking and to have a tendency to come back close to that state when placed in a dye bath.

Reversible mechanical properties of cotton and rayon treated with BIED by repeated alternating reduction-oxidation treatments were demonstrated.

Related studies on disulfide-cross-linked polycaprolactam fibers, which were made by the spinning of N-mercaptomethyl polycaprolactam into aqueous hydrogen peroxide, were briefly summarized.

I. INTRODUCTION

Cystine linkages in proteins form inter- and intra-chain cross-links which stabilize the tertiary structure of the proteins. One of the significant features of the cystine linkages is their chemical reversibility: Cystine linkages can be cleaved by reduction to form cysteine residues and the cysteine residues can form cystine linkages again by mild oxidation. Wool, which contains a large amount of cystine linkages, has long served as a challenging model for making new valuable fibers. The treatment of wool fabrics with a reducing agent followed by mild oxidation in a desired shape is the basis of a commercial chemical setting process. It is considered that the newly formed cross-links stabilize the given shape.

The chemically reversible cross-linking in cotton and other cellulose fibers has been of interest from both theoretical and practical viewpoints. In this review we will briefly describe our works on the preparation of disulfide cross-linked cellulose and discuss factors important in polymer reactions in solid state.

II. MERCAPTOCELLULOSE

Several modified cellulose fibers containing disulfide cross-links have been prepared and the reactions have been studied by analogy with the reactions of wool fibers.¹⁻⁷ One of the methods to prepare disulfidecross-linked cotton is the oxidation of mercaptan-containing cotton derivatives. Schwenker *et al.*^{1,2} reported that mercapto cellulose was obtained by the reaction of tosylated cotton with potassium thiolacetate in acetone followed by alkaline hydrolysis.

Mercaptan (SH) and disulfide (SS) groups in modified cotton could be determined by application of Leach's polarographic method⁸) for intact wool, with a minor modification.^{9,10} The method is based on a specific reaction of methylmercuric iodide with SH groups. Concentrations of methylmercuric iodide solution before and after the reaction with a sample are determined polarographically, from which the amount of methylmercuric iodide consumed, that is equal to the amount of SH groups present in the sample, is calculated. The reaction of the sample with methylmercuric iodide is also carried out under alkaline conditions in the presence of sodium sulfite. Sulfitolysis of SS bonds occurs and one mole of those yields one mole of SH groups. The latter eventually reacts with methylmercuric iodide along with SH groups present originally. Thus the equilibrium uptake of methylmercuric iodide under alkaline conditions in the presence of sodium sulfite corresponds to the molar sum of SH and SS groups in the sample.

It was found^{9,11}) that the freshly hydrolyzed product (M) from the reaction product of tosylated cotton with thiolacetate, which had been supposed to be mercapto cellulose by Schwender *et al.*^{1,2}) contained considerable amounts of SS groups, in addition to SH groups. The SS fraction in the total sulfur content in M ($2SS/(SH+2SS)$) depended

much on the solvent used for the thiolacetylation.¹¹⁾ Infrared and polarographic analyses on the reaction product of tosylated cotton with thiolacetate revealed that some parts of the acetylthio groups produced in acetone or in dimethylformamide (DMF) underwent rearrangement to form mercaptocellulose acetate.



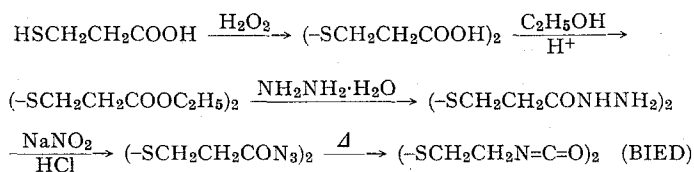
Adley and Owen¹²⁾ obtained a mixture of a thiolester and its rearrangement product, an O-acetate of 4-acetyl-5-deoxy-1,2-O-isopropylidene-5-mercapto-D-xylose, when 1,2-isopropylidene-5-O-tosyl-D-xylose was treated with potassium thiolacetate in boiling DMF.

It was found¹¹⁾ that acetylthio groups formed in methanol by the treatment of TS with thiolacetate underwent complete methanolysis simultaneously to form mercaptocellulose, and most of SH groups thus produced were oxidized before the hydrolysis treatment to yield the corresponding SS groups. This could account for the large disulfide fraction in the sample obtained through the reaction of tosylated cotton in methanol.

The reaction of the tosylated cotton with thiourea was also investigated in various solvent.¹³⁾ The product was subjected to alkaline hydrolysis to give both SH and SS residues. The substitution reaction proceeded more slowly than with potassium thiolacetate. In contrast to the results with thiolacetate, the disulfide fraction of the hydrolysis product became greater with increasing tosyloxy conversion, regardless of the solvent used for the treatment with thiourea.

III. MONO- AND BIFUNCTIONAL REACTIONS OF BIS- β -ISOCYANATOETHYL DISULFIDE (BIED) WITH CELLULOSE

A method to introduce SS cross-links into cellulose is to cross-link cellulose with a bifunctional reagent that contains a SS bond in the molecule. A new cross-linking agent, bis- β -isocyanatoethyl disulfide (BIED) was prepared from β -mercaptopropionic acid according to the following reaction scheme:¹⁴⁾

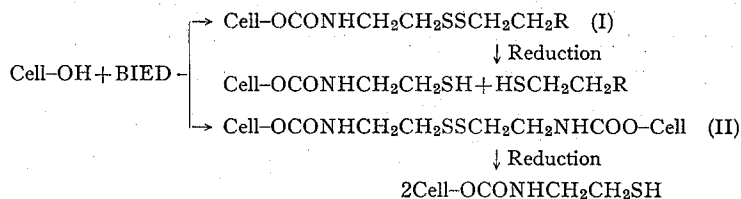


Cotton fabrics were allowed to react with BIED in dimethylformamide under various conditions. Tri-*n*-butylphosphine, which completely reduces cystine residues in wool,¹⁵⁾ was applied to the reaction product (DTC) to obtain cellulose β -mercaptoethylaminocarboxylate (RDTC). The SH and SS contents of DTC and RDTC were determined by polarography with methylmercuric iodide. The molar content of total sulfur (SH+2SS) of RDTC thus determined was much lower than that of the corresponding DTC. The sulfur content of RDTC obtained by elemental analysis agreed well with that calculated from the molar content of the total sulfur determined polarographically and was lower than the sulfur content of the parent DTC.

The results described above seem to indicate that DTC contained branches (I) formed by monofunctional reaction of BIED with cotton, in addition to cross-links (II) formed by

Factors Involved in Reversible Disulfide Cross-linking

bifunctional reaction of BIED. One of the sulfur atoms in the branch should then be removed from the cellulose molecule by reduction:



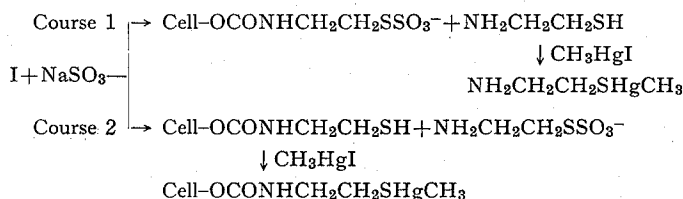
Hobart *et al.*⁴⁾ reported that the sulfur content of a cotton derivative made by the reaction of dialdehyde cotton and acetylhydrazide disulfide decreased by reduction with sodium borohydride and they suggested that this decrease was due to the presence of branches formed by monofunctional reaction of acetylhydrazide disulfide.

The quantitative infrared analysis with the absorption at 2900 cm^{-1} ($\nu\text{C-H}$) as an inner standard and the transmission at 1900 cm^{-1} as a base line indicated that the intensities of amide bands at 1710 and 1520 cm^{-1} of DTC did not change by reduction.¹⁶⁾ Evidently, the sulfur removed by the reduction was not accompanied by any carbonyl group.

The infrared spectrum of DTC did not show an absorption band around 2260 cm^{-1} , indicating the absence of terminal isocyanate groups. Probably the isocyanate in the original branch was hydrolyzed to an amine during aftertreatment and storage of RDTC samples. Cotton was not stained with 2,4-dinitrofluorobenzene, while DTC reacted with the reagent to produce a yellow dinitrobenzene derivative, indicating the presence of amino groups in DTC.

The presence of the branches in DTC was further demonstrated by investigating the polarogram of $\text{CH}_3\text{HgI-Na}_2\text{SO}_3$ solution after the treatment with DTC or RDTC.¹⁴⁾ A new wave was recorded at ca -0.8 V to a mercury electrode after the treatment with DTC, while no such a wave was observed when the solution was treated with RDTC. The current-voltage curves of $\text{CH}_3\text{HgI-Na}_2\text{SO}_3$ solution after the reaction with β -mercaptoethylamine showed a new wave at -0.73 V to the mercury electrode. It is likely that the new waves observed were due to the reductive fission of the S-Hg linkages.

The reaction of the branch in DTC with Na_2SO_3 may proceed in two ways under the conditions employed for the polarographic analysis:



Quantitative analysis indicated that sulfitolysis took place exclusively via course 1.

The cross-linking agent that contains a disulfide bond seems valuable in studying factors controlling the cross-linking efficiency (cross-links/total cross-linking agent combined) because the efficiency can be estimated easily in this system, *eg.*, from the sulfur contents of the treated sample and the corresponding reduction product.

It is expected that the molar ratio of bifunctional reagents to substrates is an important factor in the determination of the ratio of the monofunctional reaction to the bifunctional

one. Zahn¹⁷⁾ studied the reaction of *p,p'*-difluoro-*m,m'*-dinitrodiphenyl sulfone with wool and found that a low ratio of the cross-linking agent favored the bifunctional reaction and *vice versa*. The effect of reaction variables on the reaction of cotton with BIED in DMF was studied by the authors.¹⁰⁾ Contrary to the results of Zahn on wool, the high ratio of BIED to the substrate, cotton, favored the cross-linking when the reaction was carried out in DMF.¹⁰⁾ The reaction of BIED with cotton under the conditions studied seemed to be far from completion, while the reaction of the difluoro compound with wool was brought to completion. This difference may explain the contradictory results. Higher reaction temperatures and use of catalyst increased the amount of combined BIED and favored the bifunctional reaction. X-ray study indicated that the reaction took place mainly in the amorphous region of cotton.

It seems that microporous structure of cellulose in the reaction medium is one of the factors to determine the cross-linking efficiency. The reactions of BIED with ramie and viscose rayon were studied.^{16,18)} The reaction of ramie proceeded similarly to that with cotton. On the other hand, the reaction with viscose rayon proceeded more rapidly and the cross-linking efficiency was higher than those for cotton and ramie.

Another method to study the effect of the structure of cellulose on the cross-linking reaction is to compare the reactions of cross-linking reagents of different molecular size. Two new compounds, bis-isocyanatomethyl disulfide (BIMD)¹⁹⁾ and bis- γ -isocyanatopropyl disulfide (BIPD)²⁰⁾ were synthesized and their reactions with various kinds of cellulose in a more inert solvent, dimethylacetamide, were studied in comparison with that of BIED. Bis-*p*-isocyanatophenyl disulfide (BIPPD) was also prepared according to the literature²¹⁾ and its reaction with cotton was studied as well.²²⁾ Much work still remains to be done to draw any conclusion.

IV. SPATIAL AND OTHER FACTORS IN THE OXIDATION OF MERCAPTO GROUPS ATTACHED TO CELLULOSE CHAINS

Oxidation of SH to SS with iodine is often used for the quantitative analysis of mercaptans of low molecular weight. Schwenker *et al.*¹⁾ considered that the SH groups in mercaptocellulose were also converted to SS cross-links quantitatively by treatment with iodine in water. However, it was found that the iodometric titration of the hydrolysis product (M) from the reaction product of tosylated cotton with thiolacetate gave a higher SH content than that obtained by the polarographic method.⁹⁾

The analysis of the SH and SS contents together with the Methylene Blue uptake of the iodine-oxidation product (OM) suggested that some of the SH groups further underwent oxidation to acidic groups by the iodine-treatment. Tesoro *et al.*⁵⁾ prepared mercaptoacetamidomethylcellulose by the reaction of cotton with N-hydroxymethylacetylthioacetamide followed by hydrolysis and found that iodometry gave higher values than that expected theoretically.

Most of SS groups in M was reduced to SH groups with tri-*n*-butylphosphine, stoichiometrically. The reduced sample (mercaptocellulose, RM) was treated with air saturated in an alkaline buffer of pH 10.5 at 30°C.¹⁴⁾ Only a part of the SH groups in RM was converted to SS groups in about 10 hr, and the rest of the SH groups remained unchanged for a prolonged period of treatment. It was considered that some of the SH

Factors Involved in Reversible Disulfide Cross-linking

groups favorably arranged in cotton matrix were readily coupled under mild oxidation conditions to form SS groups, and the remaining SH groups unfavorably placed could not form the SS groups and were oxidized to other uncoupled groups when being treated with a strong oxidizing agent such as iodine. Fraenkel-Conrat²³⁾ reported that SH groups in undenatured tobacco mosaic virus yielded sulfenyl iodide intermediate and this did not produce SS groups when treated with iodine.

Judging from the wet crease recovery measurement, Mack *et al.*³⁾ and Hobart *et al.*⁴⁾ concluded that the reduced form of dialdehyde cotton treated with acetylhydrazide disulfide was very susceptible to oxidation.^{3,4)} It was supposed that two mercapto groups produced from a disulfide group easily coupled with each other and reproduced a disulfide group because those were thought to locate in an adjacent position even after the reduction. Contrary to the case of mercapto cellulose(RM) in which SH groups were placed randomly, SH groups in cellulose β -mercaptoethylaminocarboxylate(RDTC, *i.e.* the reduction product of BIED-treated cotton) converted almost quantitatively to SS groups in 3 days by the air oxidation in a buffer of pH 10.5. This means that SH groups even unpaired could form SS groups quantitatively in the case of RDTC. Such difference between the oxidation behaviors of unpaired SH groups of RM and of RDTC probably comes from difference in the mobilities of SH groups in the two cellulose derivatives. The SH groups in RM is directly attached to a rigid cellulose chain, thereby restricting its movement in the cellulose matrix to another to form a SS linkage. The SH groups in RDTC, on the other hand, is attached to the end of a long side chain, thereby enabling it to move around more easily in the matrix to link with another.

Figure 1 shows plots of logarithm of the SH concentration versus reaction time for the oxidation of various RDTC samples. A linear relationship was observed for RDTC-6, which happened to contain only unpaired SH groups. The plots for RDTC-7 and RDTC-8, which contained both paired (from cross-links) and unpaired (from branches) SH groups, were divided into two parts; an initial rapid decrease and the following slower decrease. A linear relationship was observed for the latter part of the plots. From the extrapolation of the straight line in the latter part to zero time, the initial concentration of SH groups

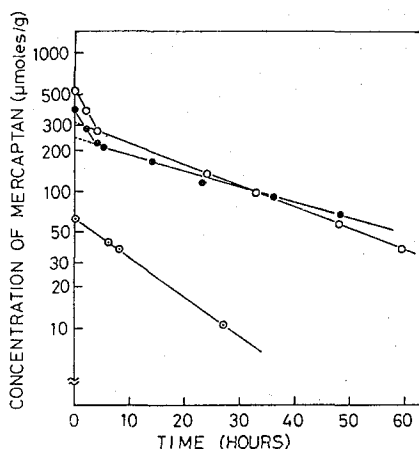


Fig. 1. Kinetics of the oxidation of mercapto groups in RDTC: (○), RDTC-6; (●), RDTC-7; (○), RDTC-8. (Reprinted from *J. Polymer Sci.*, A-1, 8, page 2147 with permission of John Wiley & Sons, INC.)

Table I. Apparent First-Order Reaction Rate Constants for the Oxidation of Mercaptans in RDTC with Air Saturated in an Alkaline Buffer of pH 10.5 at 30°C.

Sample	Initial concentration, $\mu\text{mole/g}$			Rate constants ^b	
	Total SH	Unpaired SH	SH of slower disappearance ^a	$k_1 \times 10^3 \text{ min}^{-1}$	$k_2 \times 10^3 \text{ min}^{-1}$
RDTC-6	64	64	64	—	1.1
RDTC-7	395	265	250	7.1	0.51
RDTC-8	547	325	320	7.6	0.59

a Estimated by extrapolation of the second part of the first-order kinetic plots.

b k_1 , rate constant for the paired mercaptan; k_2 , rate constant for the unpaired mercaptan.

of slower disappearance could be estimated. The values estimated for both RDTC-7 and RDTC-8 were nearly equal to the concentrations of unpaired SH groups, calculated from the contents of the SH and SS groups in RDTC and the corresponding parent DTC samples (reaction products of cotton with BIED). The apparent first-order rate constant (k_1) for the oxidation of the paired SH groups and that (k_2) of the unpaired SH groups calculated are shown in Table I. The oxidation of the paired SH groups proceeded more than tenfold faster than that of the unpaired SH groups.

The apparent rate constant ($5 \times 10^{-3} \text{ min}^{-1}$) for the air oxidation of a mercaptocellulose sample (RM-1) was close to k_1 for the oxidation of paired SH groups of RDTC. This suggests that only SH groups that happen to locate in a proximate position when introduced can form SS cross-links as rapidly as the paired SH groups in RDTC, while those considerably separated from one another cannot be combined to form SS cross-links under the conditions employed.

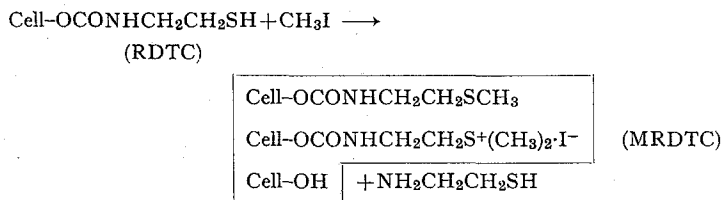
V. MEMORY EFFECT OF THE CROSS-LINKING MEDIUM IN THE DYEING OF CROSS-LINKED COTTON

Reeves, Perkins, and Chance²⁴) observed that cotton cross-linked in a collapsed state adsorbed a direct dye (Chlorantine Fast Blue 4GL) much less than control cotton, while cotton cross-linked in a swollen state adsorbed the dye as much as control cotton and considered that the cross-linking in a collapsed state occurred in a more accessible region to stabilize the collapsed structure and the cross-linking in a swollen state occurred in a hydrogen bonded fringe region to stabilize the swollen state. It can be considered that the cross-linked cotton has a "memory" of the state at the time of cross-linking. Iyer, Rao, and Chanekar²⁵) extensively examined the physicochemical properties of Form D- and Form W-cross-linked cotton fibers. From comparison of the surface area calculated from the isothermal adsorption of a direct dye (Chlorazol Sky Blue FF) with the BET nitrogen surface area of Form D-cross-linked cotton fibers, it was considered that larger pores in cotton were preferentially blocked off in the initial stage of cross-linking and smaller pores were lost in a more proportionate manner with further cross-linking. Blouin, Martin, and Rowland²⁶) obtained similar results in the reverse gel permeability study with sugars of different molecular weight on Form C- and Form W-cross-linked cotton gels.

Treatment of cellulose β -mercaptoethylaminocarboxylate (RDTC, *i.e.* the reduction

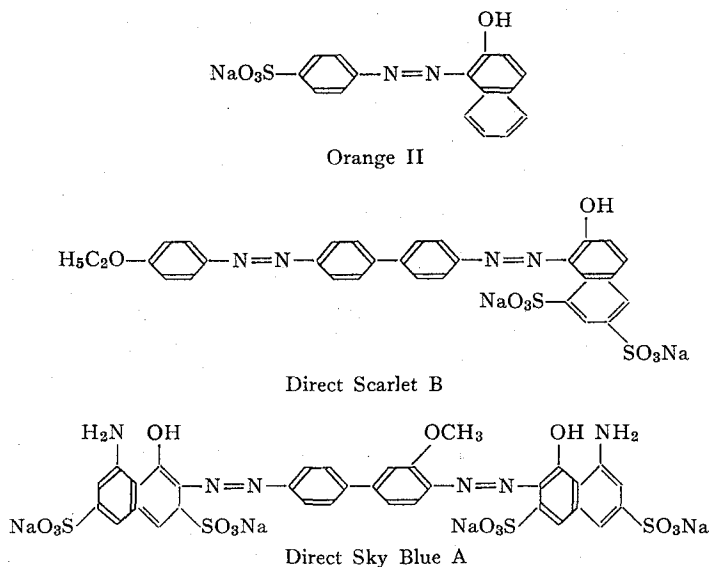
Factors Involved in Reversible Disulfide Cross-linking

product of BIED-treated cotton) with methyl iodide formed dimethyl sulfonium groups in addition to S-methyl groups, with accompanying hydrolytic cleavage of some of urethane linkages.²⁷⁾



RDTC was partially oxidized with iodine in various solvents of different swelling power followed by treatment with excess methyl iodide to yield partially SS-cross-linked cotton samples (MORDTC) containing sulfonium groups.²⁸⁾ The degrees of cross-linking of these MORDTC samples were almost equal to each other, and the degrees of sulfonium substitution also almost equal to each other. The subscripts to MORDTC indicate the solvent used for the preparation of the precursor ORDTC: d, DMF; m, methanol; and b, benzene. From the work of Minhas and Robertson²⁹⁾ on the hydroxy accessibility of cotton in different solvents, it is supposed that, among the solvents used in this work, cotton is swollen in DMF and collapsed in benzene, both to the highest extents.

The effect of the solvent in cross-linking on the equilibrium and kinetics of dyeing with the following three dyes of different molecular size was investigated (see Table II):



The 1 : 1 ionic bonding was observed at equilibrium between sulfonic acid groups in the dye molecules and sulfonium groups in MORDTC in cases of Orange II and Direct Scarlet B. The equilibrium uptake (M_∞) of the largest dye, Direct Sky Blue A, was much influenced by the solvent used in cross-linking; the higher the degree of swelling during cross-linking, the larger the equilibrium uptake. The apparent diffusion coefficient of

Table II. Dyeing Characteristics of Various Samples

Dye	Sample	M_{∞}^a $\mu\text{moles/g}$	$\frac{M_{\infty}}{\text{Sulfonium}}$	$D/r^{2b} \times 10^4 \text{ min}^{-1}$
Orange II	MORDTC _d	160	1.03	15
	MORDTC _m	151	1.05	12
	MORDTC _b	135	1.03	8.1
Direct Scarlet B	MORDTC _d	74.6	0.48	0.44
	MORDTC _m	74.1	0.52	0.093
	MORDTC _b	58.9	0.45	0.049
Direct Sky Blue A	MORDTC _d	18.0	0.12	0.26
	MORDTC _m	10.3	0.072	0.23
	MORDTC _b	8.9	0.068	0.16

a: Equilibrium uptake of the dye.

b: Apparent diffusion coefficient where D is the diffusion coefficient and r is the radius of cylindrical fibers.

Direct Scarlet B was much affected by the solvent used; the higher the degree of swelling, the higher the diffusion rate.

Some speculation is made on the pore structure of cross-linked cotton. The pores of all the three samples in the dye bath are large enough for the free penetration of the smallest Orange II molecules. The pores of the sample cross-linked even in the most collapsed state are large enough for penetration of the molecules, but the decreased pore size induced by cross-linking in a collapsed state leads to reduction in the rate of penetration. Only larger pores can admit the free penetration of the largest Direct Sky Blue A molecules. The number of such larger pores decreases during cross-linking in a collapsed state, and some sulfonium groups are entrapped in the smaller pores and the dye molecules can not reach there.

The cross-linked cotton seems to have a "memory" of degree of swelling at the time of cross-linking and to have a tendency to come back to this state when placed under appropriate conditions, even after collapse by drying. Takagishi and Klotz³⁰⁾ reported a similar memory effect of pore structure in cross-linking of polyethylenimine having SH side chains in solution. The pocket or pore produced and stabilized by cross-linking in the presence of Methyl Orange seemed to remain unchanged after removal of the dye by dialysis followed by lyophilization.

VI. REVERSIBLE MECHANICAL PROPERTIES OF COTTON AND RAYON TREATED WITH BIED

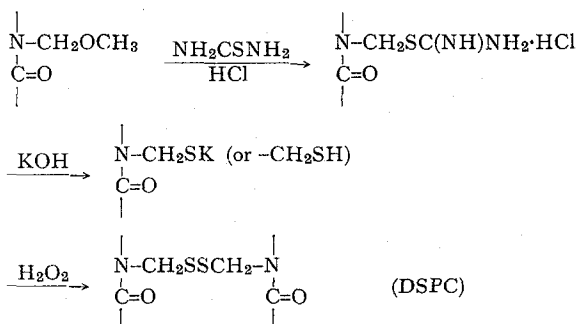
The mechanical properties of cotton fabrics treated with bis- β -isocyanatoethyl disulfide (BIED) and their derivatives prepared by repeated alternating reduction-oxidation treatments were studied.^{16,31)} Both dry and wet wrinkle recoveries were increased by the reaction with BIED, decreased by the reduction and increased again by the oxidation with iodine in methanol. This confirmed the earlier works on SS-cross-linked cotton fabrics made by Schwenker, Lifland, and Pacsu¹⁾ and Tesoro, Sello, and Willard.⁵⁾ The latter group⁵⁾ also reported that the tensile strength of their cotton derivatives decreased with

repetition of oxidation-reduction treatments. In the case of BIED-treated cotton, the tensile strength was decreased by introduction of SS bonds and increased by reduction even after repeated oxidation-reduction cycles, although the strength of reduced samples was still lower than that of untreated cotton. The flex abrasion resistance decreased gradually with repetition of the cyclic treatments, although the abrasion resistance of a reduced sample was higher than those of its cross-linked precursor and its oxidation product. Chemical durable pleats could be given to RDTC cotton fabrics by oxidizing in 1% aqueous hydrogen peroxide as being kept folded. The pleats given were reversible through repeated reduction-oxidation pleating treatments.

Reversible mechanical properties of rayon fibers treated with BIED through repeated reduction-oxidation cycles were demonstrated especially in water and in 50% aqueous urea.¹⁶⁾ The stress strain curve of RDTC rayon fibers prepared from BIED-treated fibers by reduction was very similar to that of untreated rayon fibers and the stress strain curve of the oxidation products of RDTC rayon fibers was similar to that of BIED-treated rayon fibers, in the hydrogen-bond breaking medium. The modulus of the fibers increased with increasing content of SS cross-links.

VII. RELATED STUDIES ON DISULFIDE-CROSS-LINKED POLYCAPROLACTAM FIBERS

Along with the studies on SS-cross-linked cellulose summarized above, we studied the preparation of elastic SS-cross-linked polycaprolactam (DSPC) fibers by the reaction of N-methoxymethyl polycaprolactam with thiourea, the hydrolysis with excess potassium hydroxide, and the spinning into aqueous hydrogen peroxide.³²⁾



DSPC fibers of high sulfur contents were amorphous and rubbery in water. They contained a small amount of SH groups in addition to SS groups and can serve as a simple wool model in this respect. Stress relaxation of DSPC fibers in hot water was found to proceed via SH/SS interchange mechanism.³³⁾ Kinetic study of the relaxation suggested that the newly formed SH as a result of SH/SS interchange might not always be able to come close to the next stressed SS bond due to steric arrangement.

The stress relaxation of DSPC fibers in aqueous potassium cyanide was also studied and the formation of stable monosulfide cross-links after the cleavage of the SS linkages was well demonstrated.³⁴⁾ The setting behaviors of DSPC fibers under various conditions were investigated.³⁵⁾ Potassium cyanide was the best setting agent.

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REFERENCES

- (1) R. F. Schwenker, Jr., L. Lifland, and E. Pacsu, *Textile Res. J.*, **32**, 797 (1962).
- (2) R. F. Schwenker, Jr. and L. Lifland, *Textile Res. J.*, **33**, 107 (1963).
- (3) C. H. Mack, H. H. McGregor, Jr., and S. R. Hobart, *Textile Res. J.*, **35**, 353 (1965).
- (4) S. R. Hobart, C. H. Mack, and C. P. Wade, *Textile Res. J.*, **36**, 30 (1966).
- (5) G. C. Tesoro, S. B. Sello, and J. J. Willard, *J. Appl. Polymer Sci.*, **12**, 683 (1968).
- (6) W. A. Mueller and R. Swindler, *Textile Res. J.*, **34**, 656 (1964).
- (7) W. Sauer, O. A. Stamm, and H. Zollinger, *Textilveredlung*, **1**, 4 (1966).
- (8) S. J. Leech, *Australian J. Chem.*, **13**, 547 (1960).
- (9) M. Sakamoto, Y. Yamada, and H. Tonami, *J. Appl. Polymer Sci.*, **13**, 1845 (1969).
- (10) M. Sakamoto, J. Takeda, Y. Yamada, and H. Tonami, *J. Appl. Polymer Sci.*, **14**, 865 (1970).
- (11) M. Sakamoto, Y. Yamada, N. Ojima, and H. Tonami, *J. Appl. Polymer Sci.*, **16**, 1495 (1972).
- (12) T. J. Adley and L. N. Owen, *Proc. Chem. Soc.*, 418 (1961).
- (13) M. Sakamoto, Y. Yamada, and H. Tonami, *Sen-i Gakkaishi*, **29**, T28 (1973).
- (14) M. Sakamoto, J. Takeda, Y. Yamada, and H. Tonami, *J. Polymer Sci.*, A-1, **8**, 2139 (1970).
- (15) B. J. Sweetman and J. A. Maclaren, *Australian J. Chem.*, **19**, 2347, 2355 (1966).
- (16) M. Sakamoto, H. Cho, Y. Yamada, and H. Tonami, *Colourage Annual*, **1971**, 90.
- (17) H. Zahn, *Lectures for the 25th Anniversary Meeting of the Society of Fiber Science and Technology, Japan*, Tokyo, April, 1969, p. 1.
- (18) M. Sakamoto, H. Cho, Y. Yamada, N. Ojima, and H. Tonami, *Sen-i Gakkaishi*, **30**, T17 (1974).
- (19) M. Sakamoto, Y.-M. Ngan, Y. Imai, N. Nagasawa, T. Sato, and T. Teshirogi, Unpublished.
- (20) M. Sakamoto, S.-C. Choi, J. Murakami, T. Sato, and T. Teshirogi, *Sen-i Gakkaishi*, **30**, T286 (1974).
- (21) Y. Kawamura, K. Takemoto, and M. Imoto, *Kobunshi Kagaku*, **26**, 148 (1969).
- (22) M. Sakamoto, Y. Imai, Y.-M. Ngan, and S.-C. Choi, Presented in part at the Annual Meeting of Society of Fiber Science and Technology, Tokyo, June, 1971, No. B1-05.
- (23) H. Fraenkel-Conrat, *J. Biol. Chem.*, **217**, 373 (1955).
- (24) W. A. Reeves, R. M. Perkins, and L. H. Chance, *Textile Res. J.*, **30**, 179 (1960).
- (25) S. R. S. Iyer, L. S. Rao, and A. S. Ghanekar, *Textilveredlung*, **5**, 345 (1970).
- (26) F. A. Blouin, L. F. Martin, and S. P. Rowland, *Textile Res. J.*, **40**, 959 (1970).
- (27) M. Sakamoto, Y. Yamada, N. Ojima, and H. Tonami, *J. Appl. Polymer Sci.*, **17**, 283 (1973).
- (28) M. Sakamoto, Y. Yamada, and H. Tonami, *J. Polymer Sci. Polymer Chem. Ed.*, **11**, 1961 (1973).
- (29) P. S. Minhas and A. A. Robertson, *Textile Res. J.*, **37**, 400 (1967).
- (30) T. Takagishi and I. M. Klotz, *Biopolymer*, **11**, 483 (1972).
- (31) M. Sakamoto, Y. Yamada, J. Takeda, and H. Tonami, Presented at the Annual Meeting of Society of Fiber Science and Technology, Japan, Tokyo, May, 1969, No. 15.
- (32) H. Tonami, S. Miyauchi, and M. Sakamoto, *J. Appl. Polymer Sci.*, **13**, 1595 (1969).
- (33) S. Miyauchi, M. Sakamoto, and H. Tonami, *J. Appl. Polymer Sci.*, **13**, 2169 (1969).
- (34) S. Miyauchi, K. Kajiyama, M. Sakamoto, and H. Tonami, *Appl. Polymer Symp.*, **18**, 925 (1971).
- (35) S. Miyauchi, M. Sakamoto, and H. Tonami, *Sen-i Gakkaishi*, **26**, 174 (1970).