Reversible Crosslinking in Cellulose.   II.   Mono- and Bifunctional Reactions of Bis-β-isocyanatoethyl Disulfide with Cotton

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Synopsis

Bis-β-isocyanatoethyl disulfide (BIED) was synthesized from diethyl dithiodipropionate and its reaction with cotton in dimethylformamide was investigated.   The sulfur content of the treated cotton decreased by reduction with tri-n-butylphosphine.   The polarographic and infrared analyses revealed that BIED reacted with cotton both monofunctionally and bifunctionally to form branches and crosslinks, respectively.   The ratio of the crosslinks to the total amount of BIED combined increased in general as the reaction progressed.   X-Ray study indicated that the reaction took place mainly in the original amorphous region.

INTRODUCTION

The preparation of cotton derivatives containing disulfide crosslinks which can be ruptured and rebuilt by reduction and oxidation reactions has been of interest for studying the relationship between fiber properties and crosslinking.[1-6]   This report deals with the reaction of cotton with bis-β-isocyanatoethyl disulfide (BIED) synthesized from dithiodipropionyl dihydrazide.   It is often overlooked that bifunctional reagents may react with cotton either monofunctionally or bifunctionally.   Analytic methods to determine the extents of monofunctional and bifunctional reactions of BIED are presented.

EXPERIMENTAL

Materials and Reagents

Most samples were prepared from bleached, scoured, and unmercerized 140 × 70 cotton print cloth kindly provided by Fuji Spinning Co. Ltd., Japan.   A few samples were made from weakly mercerized cotton cloth.

Tri-n-butylphosphine and di-n-butyltin diacetate were of extra pure grade and were used without further purification.

β-Mercaptoethylamine hydrochloride was used after recrystallization from ethanol.

Dimethylformamide (DMF) and benzene were distilled and dried over a molecular sieve and sodium wire, respectively.

Dithiodipropionic acid was obtained by oxidation of β-mercaptopropionic acid according to Storner and Dougherty.[7] Diethyl dithiodipropionate was prepared by esterification of dithiodipropionic acid with ethanol: bp 132°C (0.6 mm); ir (liquid) 1720 cm^{-1} (ester C=O).

Bis-β-isocyanatoethyl Disulfide (BIED)

Diethyl dithiodipropionate (80 g) was mixed with 21 ml of ethanol and an excess of 80% hydrazine hydrate (45 g) and refluxed for 4 hr. A white precipitate obtained was recrystallized from ethanol giving dithiodipropionyl dihydrazide in 60% yield: mp 126°C; ir (KBr disk) 3300, 3200, 1670, and 1630 cm^{-1}.

Dithiodipropionyl dihydrazide (48 g) was dissolved in a mixture of 45 g of concentrated hydrochloric acid and 202 ml of water, and 28 g of sodium nitrite in 30 ml of water was added dropwise with vigorous stirring at 0–5°C. Then 200 ml of benzene was added into the reaction mixture and the temperature was kept at 5°C. The reaction mixture was filtered and the benzene layer separated. After the benzene solution was dried over calcium chloride, the mixture was filtered. The temperature of benzene solution was raised slowly and refluxed for 10 min to convert the acid hydrazide completely to isocyanate. BIED was obtained by distillation in 45%–50% yield: bp 148°C (0.8 mm); ir (liquid) 2240 cm^{-1} (N=C=O).

Dihydrazide should be used after complete purification, otherwise the resulting BIED cannot be purified by fractional distillation and shows a strong absorption at 1695 cm^{-1} (C=O) in its infrared spectrum.

o-Methylurethane of BIED was prepared by refluxing BIED in methanol for 2 hr and the product was recrystallized from benzene: mp 78°C; ir (KBr disk) 3300 (N—H), 1690 (C=O), 1530 (amide II), and 1260 cm^{-1} (amide III).

Anal. Calcd. for $C_8H_{16}O_4N_2S_2$: C, 35.80%; H, 6.02%; N, 10.44%; S, 23.89%. Found: C, 35.64%; H, 6.19%; N, 10.20%; S, 23.70%.

Reaction of Cotton with BIED

Most experiments were performed as follows. Conditioned cotton samples were rinsed with DMF and allowed to react with BIED in DMF under various conditions. The treated samples (DTC) were washed with DMF, extracted with acetone in a Soxhlet apparatus, and dried in vacuo.

Reduction of DTC. DTC samples were treated in 1% tri-n-butylphosphine in methanol containing 10% water at boiling temperature for 6 hr. The reduced samples (RDTC) were extracted with acetone in a Soxhlet apparatus for 5 hr and dried in vacuo.

Oxidation of RDTC. Oxidation of RDTC was carried out with 0.0125N iodine in methanol at room temperature.

Treatment of 2,4-Dinitrofluorobenzene. Samples were treated with $0.1M$ 2,4-dinitrofluorobenzene in methanol and refluxed for 2 hr and then extracted with methanol in a Soxhlet apparatus.

Analyses

Sulfur Analysis. Sulfur was determined by the standard oxygen combustion method with a Mitamura Micro Elementary Analyzer.

Polarographic Determination of Mercaptan and Disulfide. Solutions of methylmercuric iodide (CH_3HgI) were prepared as described in a preceding paper.[8] Reactions of modified cotton samples with CH_3HgI were performed under the conditions described in the results and discussion section. All polarograms were recorded on a Yokogawa Polarocorder Pol-12.

Crystallinity. X-Ray diffractograms of powdered modified cotton samples were obtained on a Rigaku Denki D-3F x-ray diffractometer with Cu $K\alpha$. The crystallinity index was calculated from the intensity of a peak due to the 002 plane (I_{002}, $2\theta = 22.6°$) and that of amorphous background (I_{am}, $2\theta = 19.0°$) by the method of Segal et al.[9] as follows:
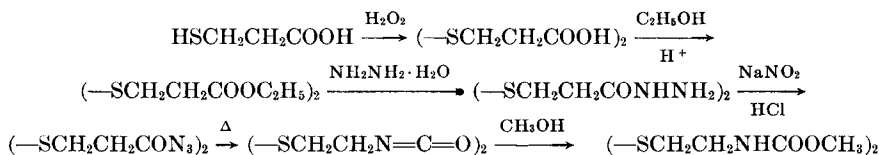
$$\text{crystallinity index} = \frac{I_{002} - I_{am}}{I_{002}} \times 100 \ (\%)$$

Infrared Spectra. Infrared spectra were obtained with a Shimazu IR 27-C spectrophotometer. KBr disks of modified cotton samples were made from mixtures of 350 mg of KBr and 2 mg of the samples finely cut with scissors (<200 mesh).

RESULTS AND DISCUSSION

General Scope and Analysis

Bis-β-isocyanatoethyl disulfide (BIED) was prepared from β-mercaptopropionic acid according to the following reaction scheme; BIED reacted with methanol to yield a bis-O-methylurethane derivative:

$$HSCH_2CH_2COOH \xrightarrow{H_2O_2} (-SCH_2CH_2COOH)_2 \xrightarrow[H^+]{C_2H_5OH}$$

$$(-SCH_2CH_2COOC_2H_5)_2 \xrightarrow{NH_2NH_2 \cdot H_2O} (-SCH_2CH_2CONHNH_2)_2 \xrightarrow[HCl]{NaNO_2}$$

$$(-SCH_2CH_2CON_3)_2 \xrightarrow{\Delta} (-SCH_2CH_2N=C=O)_2 \xrightarrow{CH_3OH} (-SCH_2CH_2NHCOOCH_3)_2$$

Cotton fabrics were allowed to react with BIED in DMF under various conditions. The differential infrared spectrum of the treated cotton (DTC) showed absorption bands due to urethane linkage at 1710, 1520, and 1260 cm^{-1}. The amount of combined BIED was estimated from the elemental sulfur analysis. Tri-n-butylphosphine, which reduces cystine residues in wool and disulfide in cellulose disulfide,[8] reduced DTC to yield cellulose β-mercaptoethylaminocarboxylate (RDTC).

The polarographic determination of mercaptan (SH) and disulfide (SS) in DTC and RDTC was investigated. DTC was treated with CH_3HgI in
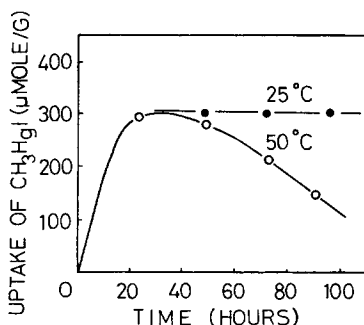
Fig. 1. Reaction of DTC with CH_3HgI at different temperatures in ammonium buffer (pH 9.3) containing $8M$ urea and $0.2M$ Na_2SO_3.

Sørensen buffer (pH 7.3) at 25°C according to the method reported previously,[8] which had been applied to the determination of SH and SS in mercaptocellulose prepared from tosyl cellulose. No CH_3HgI was taken up, indicating that SH groups were absent in DTC. When the treatment of DTC with CH_3HgI was repeated in ammonium buffer (pH 9.3) containing sodium sulfite at 50°C, some CH_3HgI was consumed. The uptake of CH_3HgI versus reaction time is shown in Figure 1. The uptake of CH_3HgI did not attain equilibrium but decreased gradually after the maximum value was obtained. As the decrease in the uptake of CH_3HgI appeared to be due to unidentified side reaction on prolonged treatment at 50°C, the reaction of DTC with CH_3HgI was carried out at a lower temperature. Figure 1 shows that the reaction proceeds to reach equilibrium at 25°C and the equilibrium uptake of CH_3HgI is equal to the maximum uptake of CH_3HgI obtained at 50°C. The equilibrium uptake of CH_3HgI was considered to correspond to SS in the present case because SH groups were absent in DTC. Table I shows that the sulfur content calculated from the SS content determined polarographically agrees well with that found by the elemental sulfur analysis.
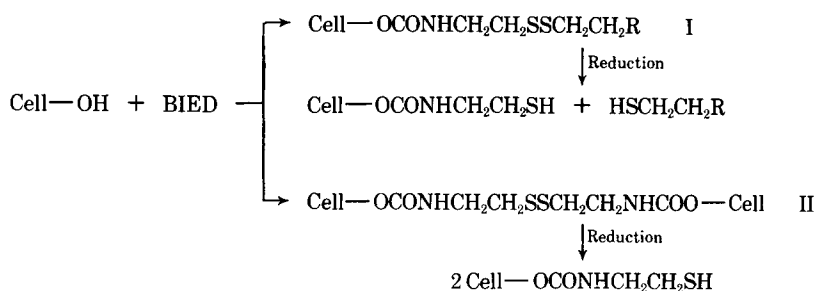
Figure 2 shows the course of the reaction of RDTC with CH_3HgI in Sørensen buffer at 25°C. The equilibrium uptake observed was considered to be equal to SH present in the sample. When the reaction of RDTC with

TABLE I

Analyses of SH, SS, and Sulfur Contents of DTC and the Corresponding RDTC

DTC				RDTC			
SH,	SS,	Sulfur, %		SH,	SS,	Sulfur, %	
μmoles/g	μmoles/g	calcd[a]	found	μmoles/g	μmoles/g	calcd[a]	found
0	94	0.61	0.56	139	9	0.50	0.49
0	309	1.93	1.92	336	4	1.07	1.06
0	377	2.41	2.40	—	—	—	—
0	485	3.10	3.28	733	0	2.35	2.52

[a] Calculated from SH and SS contents.

CH$_3$HgI was carried out in the presence of sodium sulfite at 25°C, the uptake of CH$_3$HgI also reached equilibrium, from which (SH + SS) in RDTC was obtained. The total sulfur (SH + 2SS) of RDTC was much lower than that of the corresponding DTC. The elemental sulfur analysis also indicated that a considerable amount of sulfur was removed from DTC by reduction with tri-n-butylphosphine. The sulfur content of RDTC calculated from SH and SS contents agreed well with that found by the elemental analysis. Evidently, no sulfur-containing group except SH and SS was present in RDTC. Analytic data discussed above are collected in Table I. The results described above seems to indicate that DTC contained branches (I) formed by monofunctional reaction of BIED with cotton, in addition to crosslinks (II) formed by bifunctional reaction of BIED. One of the two sulfur atoms in the branch should be removed from DTC by reduction:

$$\text{Cell—OH} + \text{BIED} \longrightarrow \begin{cases} \text{Cell—OCONHCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{R} \qquad \text{I} \\ \qquad\qquad \downarrow \text{Reduction} \\ \text{Cell—OCONHCH}_2\text{CH}_2\text{SH} + \text{HSCH}_2\text{CH}_2\text{R} \\ \\ \\ \text{Cell—OCONHCH}_2\text{CH}_2\text{SSCH}_2\text{CH}_2\text{NHCOO—Cell} \quad \text{II} \\ \qquad\qquad \downarrow \text{Reduction} \\ \qquad 2\,\text{Cell—OCONHCH}_2\text{CH}_2\text{SH} \end{cases}$$

Structures I and II may further react with BIED bifunctionally or monofunctionally under severe reaction conditions. The resulting allophanate crosslinks or branches would behave similarly to urethane crosslinks or branches, respectively, during the reduction. Hobart et al.[4] reported that the sulfur content of a cotton derivative made by the reaction of dialdehyde cotton and acethyrazide disulfide decreased by reduction with sodium borohydride and suggested that this decrease was due to the presence of branches formed by monofunctional reaction of acethydrazide disulfide.

Figure 3 compares the infrared spectra of DTC (B) and the corresponding RDTC (C) to prove the presence of the branches in DTC. B showed the amide I and II absorption peaks at 1710 and 1520 cm^{-1}, respectively. Both peaks did not change appreciably in intensity and position by reduction, although the sulfur content decreased considerably by the treatment. These results mean that the sulfur atoms which could not be removed by reduction were bound to cellulose with urethane linkages and the sulfur compound removed by reduction contained no urethane linkage. 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 amine during extraction and storage. Cotton exhibits a band assigned to adsorbed water at 1620 cm^{-1} (see Fig. 3A). The corresponding peak of B shifted to 1630 cm^{-1} and

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its intensity was stronger than that of control cotton. The reduced sample, C, showed the peak at 1620 cm^{-1} and its intensity was nearly equal to that of control cotton. This seems to indicate that a band due to amine overlapped that of adsorbed water in the spectrum of DTC.

To confirm the presence of amino groups in DTC, reactivities of untreated cotton, DTC, RDTC, and ORDTC (prepared by iodine oxidation of
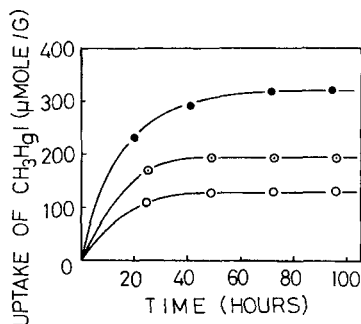

Fig. 2. Reaction of RDTC with CH$_3$HgI at 25°C in Sørensen buffer (pH 7.3) containing 8M urea. Sulfur content of samples: (○) 0.49%; (◉) 0.63%; (●) 1.03%.
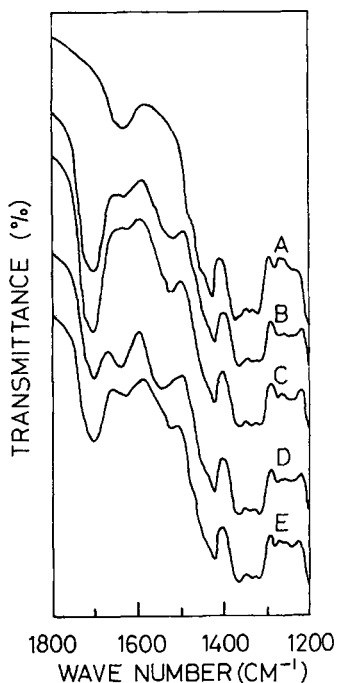

Fig. 3. Infrared spectra of DTC and RDTC: (A) untreated cotton; (B) DTC prepared in DMF (SS content, 267 μmoles/g); (C) RDTC prepared from B (SH content 428 μmoles/g); (D) DTC prepared in benzene (SS content 262 μmoles/g); (E) RDTC prepared from D (SH content 236 μmoles/g).
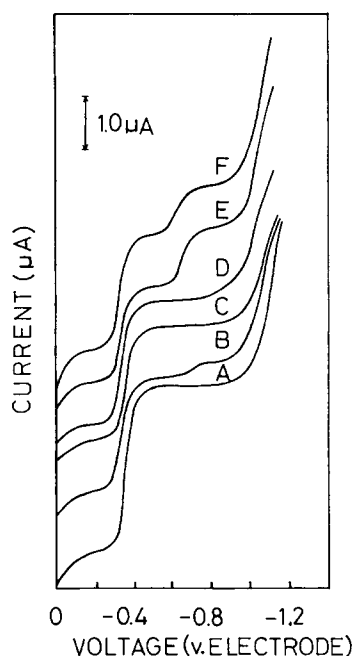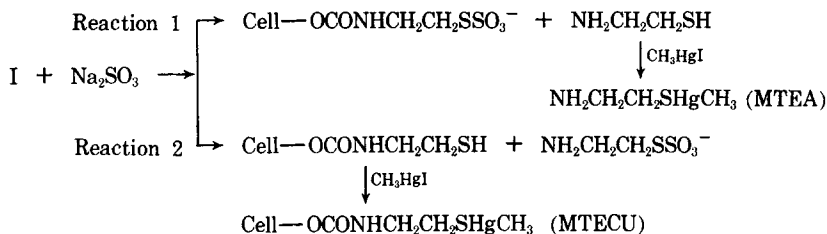
Fig. 4. Current–voltage curves of CH₃HgI solutions containing $8M$ urea and $0.2M$ Na₂SO₃ after treatment with various samples: (A) original CH₃HgI solution ($1.042 \times 10^{-3}M$); (B) treated with DTC; (C) treated with RDTC; (D) treated with ORDTC; (E) treated with dithiodipropionic acid; (F) treated with β-mercaptoethylamine.

RDTC), toward 2,4-dinitrofluorobenzene, which reacts with amine and mercaptan, were studied. Cotton was not stained with the reagent. DTC reacted with the reagent to produce yellow dinitrobenzene derivative, while ORDTC, that no longer contained any branches, was not stained with the reagent. All these behaviors suggest that DTC contained terminal amino groups. RDTC was also stained slightly with the reagent. The reactive groups in this sample were less reactive mercapto groups and not amino groups.

The presence of the branches in DTC was confirmed by investigating the polarogram of CH₃HgI–Na₂SO₃ solution after the treatment with DTC, RDTC, or ORDTC. A new wave was recorded at ca. −0.8 V to a mercury electrode after the treatment with DTC, while no such wave was observed when the solution was treated with RDTC or ORDTC (see Fig. 4). Therefore, the wave at −0.8 V appears to be closely related to the branches. Leach[11] reported that a new reduction wave was observed between two waves of CH₃HgI when β-mercaptoethylamine was titrated amperometrically with CH₃HgI. The current–voltage curve of CH₃HgI–Na₂SO₃ solution after the reaction with dithiodipropionic acid and β-mercaptoethylamine showed a new wave at −0.76 and −0.73 V to a mercury electrode, respectively (Fig. 4). It is likely that the new wave observed in the polaro-

gram of the CH₃HgI solution after treatment with DTC was due to the reductive fission of the S–Hg linkage of a compound produced from the branch in DTC by sulfitolysis, followed by the reaction with CH₃HgI.

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

Reaction 1 $\longrightarrow$ Cell—OCONHCH$_2$CH$_2$SSO$_3^-$ + NH$_2$CH$_2$CH$_2$SH

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ $\downarrow$CH$_3$HgI

I + Na$_2$SO$_3$ $\longrightarrow$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ NH$_2$CH$_2$CH$_2$SHgCH$_3$ (MTEA)

Reaction 2 $\longrightarrow$ Cell—OCONHCH$_2$CH$_2$SH + NH$_2$CH$_2$CH$_2$SSO$_3^-$

$\qquad\qquad\qquad$ $\downarrow$CH$_3$HgI

$\qquad\qquad$ Cell—OCONHCH$_2$CH$_2$SHgCH$_3$ (MTECU)

Reaction 1 produces soluble methylmercurithioethylamine (MTEA), resulting in the appearance of a reduction wave due to S–Hg linkages in the polarogram of the CH₃HgI–Na₂SO₃ solution, while reaction 2 produces insoluble N-methylmercurithioethyl cellulose urethane (MTECU), which does not give the reduction wave. The polarogram of CH₃HgI solution after the treatment with DTC indicated that reaction 1 proceeded at least to some extent. Polarograms discussed are illustrated in Figure 4.

MTEA formed could be estimated from the diffusion current at −0.8 V by the use of an authentic sample for calibration. The CH₃HgI–Na₂SO₃ solution was treated with pure β-mercaptoethylamine hydrochloride. The decrease in the diffusion current of CH₃HgI corresponded to β-mercaptoethylamine used, indicating that the reaction between them occurred quantitatively. The ratio of the decrease in the diffusion current of CH₃HgI to the diffusion current of the authentic MTEA was 1.46. Then the MTEA formed from DTC can be estimated from the polarogram of the CH₃HgI solution after the treatment of DTC, as follows:

$$\text{MTEA formed} = (\text{total SS}) \times \frac{1.46 \times I_{d2}}{I_{d1}}$$

where I_{d1} is the decrease in the diffusion current of CH₃HgI after the treatment with DTC and I_{d2} is the diffusion current at −0.8 V.

The amounts of branches and crosslinks in DTC can be estimated from the sulfur contents of DTC(S_1, %) and the corresponding RDTC (S_2, %) from the following equations:

$$\text{Branches } (\mu\text{moles/g}) = (S_1 - S_2)/0.0032$$
$$\text{Crosslinks } (\mu\text{moles/g}) = (2S_2 - S_1)/0.0064$$
$$\text{Total BIED combined } (\mu\text{moles/g}) = S_1/0.0064$$

In Table II are collected the amounts of branches calculated from the sulfur analyses and the amounts of MTEA formed during sulfitolysis. The amounts of MTEA were found to agree with the contents of the branches.
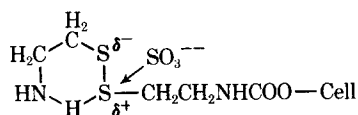
TABLE II
Branches and Crosslinks in DTC and Sulfitolysis of DTC

Sulfur, %		Total SS[a],	Branches[b],	Crosslinks[b],	MTEA produced from DTC,
DTC	RDTC	μmoles/g	μmoles/g	μmoles/g	μmoles/g
1.05	0.58	154	147	17	138
2.18	1.73	326	141	200	129
2.40	2.19	368	68	307	72
3.37	2.95	525	131	396	139

[a] From polarographic determination of SS in DTC.
[b] Calculated from sulfur contents of DTC and RDTC.

It was not expected for sulfitolysis to take place exclusively via reaction 1. It is evident that both the total amount of BIED combined and the amount of the branches can be determined in one procedure from the polarogram of the CH_3HgI–Na_2SO_3 solution after treatment with DTC. That reaction 1 was the preferred one may be explained by the formation of hydrogen bond between terminal amino hydrogen and sulfur atoms:

$$H_2C \overset{\overset{\displaystyle H_2}{C}}{\underset{HN}{\diagdown}} \overset{S^{\delta^-}}{\underset{\overset{S}{\underset{\delta^+}{\diagup}}}{\diagup}} \overset{SO_3^{--}}{\underset{CH_2CH_2NHCOO-Cell}{}}$$

Reaction of Cotton with BIED

Generally speaking, the extent of reaction of cotton depends on the pretreatment and the solvent used. Ellzey and Mack[12] reported that the reaction of cotton with phenyl isocyanate did not occur in toluene, which was a poor swelling agent for cotton. The reactivity of cotton in a non-swelling solvent increased if cotton was preswollen by the use of a suitable solvent such as water and the swelling agent replaced with a nonswelling solvent. Usmanov and Pilosov[13] reported that the reaction of cotton with hexamethylene diisocyanate in benzene or toluene increased as the moisture content of the sample increased.

Various cotton samples, conditioned, bone dried at 110°C for 2 hr, dried over phosphorous pentoxide for two days, or preswollen with DMF were allowed to react with 5% BIED in DMF or benzene at 60°C for 24 hr with a liquor ratio of 1:100. Results obtained are summarized in Table III. When the reaction was carried out in DMF, the effect of pretreatment of cotton fabrics on the amount of combined BIED was negligible. The crosslinking efficiency (100 × crosslinks/total BIED combined) was between 54% and 64%. On the other hand, the amount of combined BIED depended much on pretreatment when the reaction was carried out in benzene. The bone-dried cotton did not react with BIED in benzene while the cotton preswollen with DMF reacted with BIED as much as in DMF.

TABLE III
Effect of Pretreatment and Solvent on the Reaction of Cotton
(Unmercerized) with BIED

Reaction conditions[a]		SS in DTC, μmoles/g	SH in RDTC, μmoles/g	Branches in DTC, μmoles/g	Cross- links in DTC, μmoles/g	Cross- linking effi- ciency, %
pretreatment	solvent					
Conditioned	DMF	279	430	128	151	54
Conditioned	benzene	2	0	—	—	—
Dried at 110°C	DMF	267	428	106	161	60
Dried over P_2O_5	DMF	264	433	95	169	64
Preswollen in DMF	DMF	253	397	109	144	57
Preswollen in DMF	benzene	262	236	—	—	—

[a] Treated with 5% BIED at 60°C for 24 hr (liquor ratio 1:100).

TABLE IV
Effect of Pretreatment and Solvent on the Reaction of Cotton (Mercerized) with BIED

| Reaction conditions[a]		SS in DTC, μmoles/g	SH in RDTC, μmoles/g	Branches in DTC, μmoles/g	Cross- links in DTC, μmoles/g	Cross- linking effi- ciency, %
pretreatment	solvent					
Conditioned	DMF	274	459	89	185	68
Conditioned	benzene	15	11	—	—	—
Dried at 110°C	DMF	302	508	96	196	65
Dried over P_2O_5	DMF	315	513	117	198	63
Preswollen in DMF	DMF	309	513	105	204	66
Preswollen in DMF	benzene	294	249	—	—	—

[a] Treated with 5% BIED at 60°C for 24 hr (liquor ratio 1:100).

Similar results were obtained when weakly mercerized cotton samples were treated with BIED in DMF or in benzene (see Table IV). Generally, the extent of the reaction of mercerized cotton was slightly higher than that of unmercerized cotton.

The reaction of BIED in benzene seems to proceed differently from that in DMF. More than half the sulfur was removed when DTC prepared in benzene from preswollen cotton (D) was reduced. This large decrease in the sulfur content by reduction cannot be explained merely by the presence of branches. Figure 3 shows that the infrared spectrum of D differs much in the 1800–1300 cm^{-1} region from that of DTC prepared in DMF from bone-dried cotton (B) described in a previous section. Sample D showed the amide I absorption at 1710 cm^{-1} with much weaker intensity than B, although D contained as much SS as B. The absorption did not change in intensity and position by reduction. Sample D exhibited a peak at 1640 cm^{-1} and its intensity was stronger than that of the corresponding peak of B. The reduced sample (E) showed the peak at 1620 cm^{-1} with

an intensity nearly equal to that of control cotton. These results indicated that D contained fewer crosslinks than B.

Sample D exhibited a band at 1540 cm^{-1} and, contrary to B, its intensity was stronger than that of its amide I absorption. The amide II band appeared at 1520 cm^{-1} when D was reduced. The intensity became weaker than that of the amide I band. These results may indicate that D contained urea linkages to be eliminated by reduction, in addition to urethane linkages. The differential spectrum of D against E showed absorption bands at 1630 and 1555 cm^{-1}, which were tentatively assigned to amide I and II of urea linkages, respectively. It may be considered that the cotton sample used contained a trace of water which led to the formation of urea derivatives. Formation of urea derivatives and removal of them by reduction may account for the large decrease in the sulfur content by reduction, as seen in the example given below:

Cell—OCONHCH$_2$CH$_2$SSCH$_2$CH$_2$NHCONHCH$_2$CH$_2$SSCH$_2$CH$_2$NH$_2$ →

Cell—OCONHCH$_2$CH$_2$SH
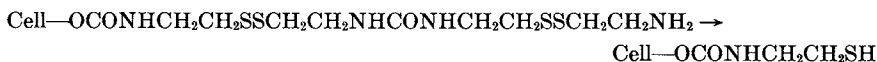
The effect of the reaction variables on the mono- and bifunctional reactions of BIED with cotton was investigated. The reaction was carried out in DMF with cotton preswollen with DMF. It is expected that the molar ratio of bifunctional reagents to substrates is an important factor in the determination of the ratio of the monofunctional reaction to the bifunctional one. Zahn[14] studied the reaction of p,p'-difluoro-m,m'-dinitrodiphenyl sulfone with wool and found that a low ratio of the crosslinking agent favored the bifunctional reaction and a high ratio favored the monofunctional reaction. Contrary to the results of Zahn, Table V indicates that the high ratio of BIED favored the crosslinking when the reaction was carried out in DMF at 60°C or 80°C for 24 hr. The reaction of BIED proceeded faster with increasing concentration of BIED with cotton under the conditions studied and 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.

Table VI shows the effect of reaction temperature on the reaction of BIED carried out in DMF for 5 hr. Both the total amount of combined

TABLE V
Effect of Molar Ratio of BIED to Cotton on the Reaction

Reaction conditions[a]		Total BIED combined, μmoles/g	Branches μmoles/g	Crosslinks, μmoles/g	Crosslinking efficiency, %
Temp., °C	BIED / AGU[b]				
60	2	179	122	57	32
60	4	279	128	151	54
80	2	303	153	150	49
80	4	410	151	259	63

[a] Treated in DMF for 24 hr.
[b] Anhydroglucose unit.

TABLE VI
Effect of Reaction Temperature on the Reaction of Cotton with BIED[a]

Temp., °C	Total BIED combined, μmoles/g	Branches, μmoles/g	Crosslinks, μmoles/g	Crosslinking efficiency, %
40	27	21	6	22
80	207	88	119	57
140	304	93	211	69

[a] Treated in DMF for 5 hr at different temperature (BIED/AGU 2; liquor ratio 1:75).

TABLE VII
Effect of Catalyst (Di-*n*-butyltin Diacetate) on the Reaction of Cotton with BIED[a]

Concentration of catalyst, %	Total BIED combined, μmoles/g	Branches, μmoles/g	Crosslinks, μmoles/g	Crosslinking efficiency, %
0	179	122	57	32
0.25	381	197	184	48
0.50	386	175	211	55
1.00	393	204	189	48

[a] Treated with 2.5% BIED in DMF at 60°C for 24 hr (liquor ratio 1:100) in the presence of di-*n*-butyltin diacetate.

TABLE VIII
Effect of Reaction Time on the Reaction of Cotton with BIED at 40°C[a]

Reaction time, hr	Total BIED combined, μmoles/g	Branches, μmoles/g	Crosslinks, μmoles/g	Crosslinking efficiency, %
5	27	21	6	22
48	141	52	89	63
72	162	33	129	80

[a] Treated in DMF (BIED/AGU 2; liquor ratio 1:75).

TABLE IX
Effect of Reaction Time on the Reaction of Cotton with BIED at 80°C[a]

Reaction time, hr	Total BIED combined, μmoles/g	Branches, μmoles/g	Crosslinks, μmoles/g	Crosslinking efficiency, %
1	110	55	55	50
5	207	88	119	57
10	267	110	157	58
24	303	153	150	49
48	404	209	195	48

[a] Treated in DMF (BIED/AGU 2; liquor ratio 1:75).

BIED and the crosslinking efficiency increased with increasing reaction temperature.   The reaction of BIED with cotton was carried out in DMF at 60°C for 24 hr in the presence of di-n-butyltin diacetate which was known to be a catalyst for the reaction of isocyanates with alcohols.   The results summarized in Table VII indicate that the reaction proceeds faster by the use of di-n-butyltin diacetate.   The catalyzed reaction resulted in a higher ratio of crosslinks.   The concentration (0.75% to 1.00%) of the catalyst did not affect the catalytic effect.

All the results described above suggest that the crosslinking efficiency increases with increasing total BIED combined.   The first reaction of BIED with cotton takes place monofunctionally and the reaction of terminal isocyanato group in the resulting branch has to compete with uncombined BIED present.   Therefore, in the initial stage of the treatment, the formation of branches occurs predominantly and the crosslinking occurs more significantly as the number of branches increases as the reaction proceeds.   The above consideration is supported from the results in Table VIII, which shows that the crosslinking efficiency increases profoundly with

TABLE X
X-Ray Crystallinity of DTC Prepared in DMF at 80°C[a]

Sample	Reaction time, hr	Sulfur, %	Crystallinity index, %
Untreated cotton		0	78
Control[b]		0	74
DTC	18	1.60	74
DTC	24	2.40	74
DTC	48	3.31	71

[a] Treated with 5% BIED in DMF (liquor ratio 1:20).
[b] Treated with pure DMF at 80°C for 48 hr.

increasing reaction time when cotton is treated with BIED at 40°C.   The reaction of BIED at 80°C, however, proceeded differently.   Table IX shows that the crosslinking efficiency keeps fairly constant for a wide range of reaction time.   The formation of allophanate-type branches and the rapid diffusion of BIED at this temperature may explain the observation.

X-Ray crystallinity indices of DTC prepared in DMF at 80°C for different times were determined according to the method of Segal et al.[9] (see Table X).   The crystallinity of cotton decreased slightly after the treatment with DMF at 80°C for 48 hr.   DTC samples exhibited the same crystallinity to that of the DMF-treated control cotton.   All samples mentioned were highly crystalline cellulose I.   These results indicate that the reaction of cotton with BIED took place mainly in the amorphous region of original cotton with no change in the crystal lattice under the conditions employed.

A study of repeated reduction–oxidation cycles on DTC is under way and will be reported in future.

CONCLUSION

Bis-β-isocyanatoethyl disulfide (BIED) was synthesized from diethyl dithiodipropionate. BIED reacted with cotton both monofunctionally and bifunctionally to form branches and crosslinks, respectively. The sulfur content of cotton treated with BIED decreased by reduction with tri-n-butylphosphine, for one of two sulfur atoms in the branch was removed from cotton by reductive fission of the disulfide linkage. The presence of branches in cotton treated with BIED was confirmed by polarographic and infrared analyses. The terminal groups of the branch appeared to be amino groups.

The effect of reaction variables on the reaction of cotton with BIED was studied. Higher concentration of BIED, higher reaction temperature, and addition of catalyst increased the amount of combined BIED and favored the bifunctional reaction. Bone-dried cotton did not react with BIED in benzene, while preswollen cotton reacted with BIED as much as in DMF. X-Ray study indicated that the reaction of BIED in DMF took place mainly in the amorphous region of the original cotton.

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