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### Reaction of Lithium Cellulosate with Episulfides

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## Reaction of Lithium Cellulosate with Episulfides

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### SUMMARY

The reactions of propylene, ethylene, and styrene sulfide with cotton fabrics in the form of their lithium cellulosate derivative, obtained by metallation with lithium methoxide, were studied. Both graft and homopolymerization took place and in the reaction with propylene and ethylene sulfide, cotton fabrics with high polysulfide content were obtained. With propylene sulfide 50% of the monomer polymerized was grafted. The effects of monomer concentration, cellulosate degree of substitution, reaction time, and solvent on the polymerization were investigated. In contrast with propylene and ethylene sulfide, only small conversions were obtained in the reaction with styrene sulfide. The results were attributed to steric effects.

### INTRODUCTION

Anionic graft polymerizations of episulfides were recently reported. Champetier and Hennequin-Lucas [1] reported the grafting of ethylene and propylene sulfide on alkali cellulose. The grafting of ethylene sulfide on cellulose in the gas phase and in solution was also reported [2, 3].

Mercaptopropane sulfide was reacted with alkali cellulose, rayon, polystyrene, polyamides, and copolymers of styrene-butadiene [4]. The graft polymerization of propylene sulfide on cellophane film was recently studied in this laboratory [5]. The graft polymers of the episulfides showed interesting adsorption properties for halogens and heavy metal salts [1, 5].

The present work deals with the reactions of propylene, ethylene, and styrene sulfide with the lithium cellulosate derivative of cotton fabrics. Alkali metal cellulosates were used successfully for initiation of graft polymerization [6-8], and therefore graft polymers of the polysulfides were expected to be formed in this reaction. The effects of monomer concentration, cellulosate degree of substitution (D.S.), reaction time, and solvent on the reaction were investigated.

## EXPERIMENTAL

Scoured and bleached cotton fabric was used and it was cleaned according to a known procedure [9]. Styrene sulfide was prepared according to Guss and Chamberlain [10]. Propylene and ethylene sulfide (Fluka) were dried over calcium hydride and were freshly fractionally distilled under dry argon. Dimethyl sulfoxide (DMSO) (Fluka) was dried by vacuo distillation over calcium hydride under dry argon. Tetrahydrofuran (THF) (Frutarom) was dried by distillation from sodium benzophenone solution [11]. Benzene (Frutarom) was dried over sodium wire. Lithium methoxide solution was prepared by dissolving lithium metal in a calculated amount of dry methanol, and its concentration was determined by titration with 0.1 N HCl.

### Preparation of Lithium Cellulosate

The reaction was carried in a closed glass cylinder equipped with a self-sealing rubber cap through which reagents can be added with a syringe.

Cotton fabric (0.97 g) was swelled by being soaked in 20% sodium hydroxide solution for 20 min. The fabric was neutralized with 2% acetic acid solution, washed with distilled water, sucked dry between filter papers, and transferred to the reaction cylinder. Water in the fabric was exchanged with methanol. Dry methanol (50 ml) was added and was exchanged six times within 6 hr. Lithium methoxide solution (50 ml) of a desired concentration was added. The reaction mixture was mechanically shaken for 10 min, and the methoxide solution was decanted. Excess of lithium methoxide was removed from the fabric by extraction with dry

DMSO (4 exchanges of dry DMSO within 2 hr). The lithium cellulosate D.S. was determined by a known procedure [12].

### Reaction of Episulfides with Cotton Fabrics

The reaction was carried out in a glass cylinder at room temperature under argon under anhydrous conditions. Cotton fabric (0.97 g) was swelled in 20% sodium hydroxide solution and was solvent exchanged with dry methanol. The fabric was soaked in lithium methoxide solution (250 ml) for 10 min, pressed between filter papers, and transferred without extraction of the lithium methoxide to the reaction cylinder which contained the monomer. The reaction mixture was mechanically shaken for 24 hr at room temperature. The fabric was neutralized by 2% acetic acid, washed with distilled water, dried in vacuo at 60°C over phosphorus pentoxide for 24 hr, and weighed. Fabrics containing polypropylene and styrene sulfides were extracted with benzene for 48 hr in order to remove any homopolymer present. The amount of homopolymer formed was determined from weight loss after extraction.

Reactions in different solvents were carried out similarly, using lithium cellulosate which was extracted by dry DMSO and then solvent exchanged with the required solvent. At the end of the reaction the solvent was poured into methanol (1.5 liter) in order to precipitate any polysulfide present.

## RESULTS

The reactions of propylene, ethylene, and styrene sulfide with lithium cellulosate were investigated. The lithium cellulosate was prepared by exchange reaction of cellulose with lithium methoxide solution in methanol using preswollen fabric. The cellulosate D.S. was controlled by the lithium methoxide concentration [12]. In most of the reactions the lithium cellulosate was pressed dry between filter paper and no attempt was made to remove any excess absorbed lithium methoxide. Thus, polymerization could be initiated by lithium cellulosate and by the lithium methoxide present in the fabric leading to graft and homopolymerization.

### Reaction with Propylene Sulfide

The effect of time on the reaction of propylene sulfide with lithium cellulosate was studied (Table 1). The reaction was completed within 8 hr,

**Table 1.** Reaction of Lithium Cellulosate with Propylene Sulfide<sup>a</sup>  
(Time Dependence)

Time (hr)	Monomer polymerized in fabric <sup>b</sup>		Monomer conversion (%)	Polypropylene sulfide in graft <sup>b,c</sup> (%)
	Graft <sup>c</sup> (%)	Homo (%)		
0.1	15.7	22.3	38.0	31.2
2	26.6	49.4	76.0	43.8
4	35.6	50.4	86.0	50.9
8	38.2	50.7	88.9	52.3
24	40.3	51.2	91.5	53.5

<sup>a</sup>Cotton fabric (0.97 g, containing 18 mmole OH groups), previously swollen in 20% sodium hydroxide, was reacted with 2.05 N lithium methoxide solution (250 ml) for 10 min at 23°C to give lithium cellulosate, D.S. = 0.54, and then added to monomer (2.82 g, 38.1 mmole) at room temperature.

<sup>b</sup>Determined from weight increase.

<sup>c</sup>Determined after extraction of the homopolymer.

leading to high monomer conversion and to high polypropylene sulfide-containing fabrics. The fabrics were extracted with benzene in order to remove the soluble homopolypropylene sulfide. About 40-50% of the monomer polymerized were grafted. Increasing the reaction time led to a relative equal increase in graft and homopolymerization.

The influence of the amount of monomer on the reaction is reported in Table 2. It was found that on increasing the monomer amount there was a decrease in the percentage yield of the graft polymerization, but nevertheless there was an absolute increase in the polypropylene sulfide content of the graft. Monomer conversion was high and about 45-55% of the monomer polymerized were grafted. The effect of lithium cellulosate D.S. on the reaction was studied (Table 3). High monomer conversions, as well as high polypropylene sulfide-containing fabrics, were obtained even at low lithium cellulosate D.S. In the D.S. range examined, it was found that increasing the D.S. led to a small increase in the graft polymerization yield and to a corresponding increase in the polypropylene sulfide content of the graft.

**Table 2.** Reaction of Lithium Cellulosate with Propylene Sulfide<sup>a</sup>

Monomer (mmole)	Monomer polymerized in fabric <sup>b</sup>		Monomer conversion (%)	Polypropylene sulfide in graft <sup>b,c</sup> (%)
	Graft <sup>c</sup> (%)	Homo (%)		
25.4	46.8	39.1	85.9	47.6
38.1	42.6	43.9	86.5	55.2
50.8	41.2	46.3	87.5	61.5
64.5	39.4	49.0	88.4	65.6

<sup>a</sup>Cotton fabric (0.97 g containing 18 mmole OH groups), previously swollen in 20% sodium hydroxide, was reacted with 2.05 N lithium methoxide solution (250 ml) for 10 min at 23°C to give lithium cellulosate, D.S. = 0.54, and then added to monomer. The reaction was carried out for 24 hr at room temperature.

<sup>b</sup>Determined from weight increase.

<sup>c</sup>Determined after extraction of the homopolymer.

### Reaction with Ethylene Sulfide

Since polyethylene sulfide is insoluble in common organic solvents, any homopolymer formed within the fabric could not be extracted. Homopolymer formed out of the fabric was physically removed.

The time dependence of the reaction of lithium cellulosate with ethylene sulfide was studied (Table 4). The reaction was almost completed within 4 hr, leading to high monomer conversion and to high polyethylene sulfide content in the fabric. Most of the monomer polymerized within the fabric.

The influence of monomer amount on the reaction was studied (Table 5). Monomer conversion was always high and most of the monomer polymerized within the fabric. Increasing the monomer amount led to an increase in the polyethylene sulfide content of the fabric and to a small increase in monomer conversion. A slight decrease in the monomer polymerized within the fabric accompanied by an increase in the amount of polymer formed out of the fabric was found.

The effect of the lithium cellulosate D.S. on the reaction was studied (Table 6). Cotton fabrics of high polyethylene sulfide content, as well as high monomer conversions, were obtained even at low D.S. In the D.S. range examined it was found that above D.S. = 0.29 monomer conversion reached its maximum value and there were no significant changes in the polyethylene sulfide content of the fabric.

Table 3. Reaction of Lithium Cellulosate with Propylene Sulfide<sup>a</sup> (D.S. Dependence)

Lithium methoxide solution (N)	Lithium cellulosate (D.S.)	Monomer polymerized in fabric <sup>b</sup>		Monomer conversion (%)	Polypropylene sulfide in graft <sup>b,c</sup> (%)
		Graft <sup>c</sup> (%)	Homo (%)		
0.105	0.06	34.5	42.0	76.5	49.7
1.15	0.31	36.0	49.3	85.3	51.2
2.05	0.54	41.7	39.5	81.2	54.6
2.55	0.66	44.0	41.4	85.4	55.9

<sup>a</sup>Cotton fabric (0.97 g containing 18 mmole OH groups), previously swollen in 20% sodium hydroxide, was reacted with lithium methoxide solution (250 ml) for 10 min at 23°C and then added to monomer (2.82 g, 38.1 mmole). The reaction was carried out for 24 hr at room temperature.

<sup>b</sup>Determined from weight increase.

<sup>c</sup>Determined after extraction of the homopolymer.

**Table 4.** Reaction of Lithium Cellulosate with Ethylene Sulfide<sup>a</sup>  
(Time Dependence)

Time (hr)	Monomer polymerized in fabric <sup>b</sup> (%)	Monomer conversion (%)	Polyethylene sulfide content in fabric <sup>b</sup> (%)
0.1	41.4	48.4	57.0
2	61.3	67.1	66.1
4	87.4	94.3	73.7
8	89.6	96.2	74.0
24	90.4	96.6	74.3

<sup>a</sup>Cotton fabric (0.97 g, containing 18 mmole OH groups), swollen in 20% sodium hydroxide, was treated with 2.15 N lithium methoxide solution (250 ml) for 10 min at 23°C to give lithium cellulosate, D.S. = 0.56, and then added to ethylene sulfide (3.11 g, 51.8 mmole) at room temperature.

<sup>b</sup>Determined from weight increase.

Since reactions were carried out without solvent, it was interesting to examine the effect of solvent on monomer conversion and on polyethylene sulfide content of the fabric. Excess of lithium methoxide was removed from the fabric by extraction with DMSO, and the reactions were performed in benzene, THF, or DMSO under anhydrous conditions (Table 7). In the former two solvents all the monomer polymerized within the fabric while in DMSO only 70% of it did. In general, similar results were obtained in the reactions carried out without solvent (Tables 4-6) or in THF or benzene (Table 7). It was also found that polyethylene sulfide-containing fabrics could be obtained even in the presence of water (using THF-water as solvent) though in low yield.

#### Reaction with Styrene Sulfide

The reaction with styrene sulfide was carried out either without solvent (in the presence of lithium methoxide absorbed by the fabric) or in DMSO. Homopolystyrene sulfide was removed from the fabric by extraction with benzene.

The reaction without solvent was performed under similar conditions as those used with propylene and ethylene sulfide. On reacting lithium



**Table 5.** Reaction of Lithium Cellulosate with Ethylene Sulfide<sup>a</sup>

Monomer (mmole)	Monomer polymerized in fabric <sup>b</sup> (%)	Monomer conversion (%)	Polyethylene sulfide in fabric <sup>b</sup> (%)
34.5	89.0	93.2	65.4
51.8	87.3	94.4	73.7
69.2	86.0	96.4	78.3
86.5	84.0	97.2	81.8

<sup>a</sup>Cotton fabric (0.97 g, 18 mmole OH groups), swollen in 20% sodium hydroxide, was treated with 2.15 N lithium methoxide solution (250 ml) for 10 min at 23°C to give lithium cellulosate, D.S. = 0.56, and then added to monomer at room temperature; reaction time 24 hr.

<sup>b</sup>Determined from weight increase.

cellulosate, D.S. = 0.55, with styrene sulfide (3.25 g, 23.9 mmole), only low monomer conversion (3%) was obtained. After extraction of homopolystyrene sulfide from the fabric, the polystyrene sulfide content of the graft was 6% corresponding to 2% monomer conversion. Increasing the monomer amount did not lead to better results.

The reaction was repeated in DMSO after extraction of the lithium methoxide present in the fabric. Here also the monomer conversion was low (7%). After extraction with benzene it was found that 5% of the monomer were grafted, corresponding to 5% polystyrene sulfide content of the graft. Repeating the reaction with sodium and potassium cellulosates and higher monomer concentrations led to similar results.

In a control experiment it was found that the homopolymerization of styrene sulfide in DMSO using lithium methoxide as initiator was very fast, leading to high conversions (85%). Now mercaptan end groups or their oxidation products, the corresponding disulfides, are expected to be present in the fabric after termination of the polymerization. However, no such groups were found using the N-ethyl maleimide procedure [13] for the detection of mercaptan groups, or using 1,4-dithiothreitol (Celand's Reagent) [14], recommended for the determination of disulfide bonds in wool [15], for the detection of disulfide linkages.

Table 6. Reaction of Lithium Cellulosate with Ethylene Sulfide<sup>a</sup> (D.S. Dependence)

Lithium methoxide solution (N)	Lithium cellulosate (D.S.)	Monomer polymerized in fabric <sup>b</sup> (%)	Monomer conversion (%)	Polyethylene sulfide in fabric <sup>b</sup> (%)
0.12	0.06	71.3	75.0	69.1
1.04	0.29	90.6	93.9	74.2
2.05	0.54	83.3	90.2	72.4
2.05	0.54	91.6	96.5	73.8
2.05	0.54	87.6	93.8	73.6
2.15	0.56	90.9	94.8	76.5
2.64	0.67	91.8	95.1	77.4

<sup>a</sup>Cotton fabric (0.97 g, 18 mmole OH groups), swollen in 20% sodium hydroxide, was reacted with lithium methoxide solution (250 ml) for 10 min at 23°C and then added to monomer (3.11 g, 51.8 mmole) at room temperature; reaction time 24 hr.

<sup>b</sup>Determined from weight increase.

**Table 7.** Reaction of Lithium Cellulosate with Ethylene Sulfide<sup>a</sup>  
(Solvent Dependence)

Solvent	Monomer polymerized in fabric <sup>b</sup> (%)	Monomer conversion (%)	Polyethylene sulfide in fabric <sup>b</sup> (%)
Benzene	87.0	87.0	48.0
Benzene	91.2	91.2	49.0
THF	82.4	82.4	46.8
THF	86.3	86.3	47.9
DMSO	60.0	87.3	39.3
DMSO	66.1	91.6	41.3
THF-H <sub>2</sub> O(1:1)	10.2	29.6	9.6
THF-H <sub>2</sub> O(1:1)	11.0	30.8	10.4

<sup>a</sup>Cotton fabric (0.97 g, 18 mmole OH groups), swollen in 20% sodium hydroxide, was reacted with 2.05 N lithium methoxide solution (50 ml) for 10 min at 23°C to give lithium cellulosate, D.S. = 0.54. The reaction with ethylene sulfide (1.04 g, 17.4 mmole) was carried out in the appropriate solvent (50 ml) for 24 hr at room temperature.

<sup>b</sup>Determined from weight increase.

## DISCUSSION

The reaction of the lithium cellulosate derivative of cotton fabrics with propylene, ethylene, and styrene sulfide led to graft and homopolymerization within the fabric. Though the reaction is heterogeneous, fabrics of high polysulfide content were obtained in good yields using propylene sulfide (up to 65.6%) and ethylene sulfide (up to 81.8%).

In the reactions carried out without solvent in the presence of lithium methoxide absorbed by the fabric, two initiation species are present. Initiation could be started by lithium cellulosate leading to graft polymer formation and by lithium methoxide leading to homopolymer formation. It was interesting to find in the case of propylene sulfide that even under

these conditions almost 50% of the monomer polymerized was grafted. The fact that the anionic polymerization of propylene sulfide is a "living one" with no termination, and that it is devoid of chain transfer reactions to monomer [16, 17], makes it possible for the graft polymerization to compete favorably with the homopolymerization. Though no attempts to remove the homopolyethylene sulfide formed in the fabric were made, most probably the polyethylene sulfide-containing fabrics consist of graft and homopolyethylene sulfide.

After termination with acetic acid the propagating centers — the mercaptide ions formed in the initiation reaction — were converted to mercaptan groups. Since no mercaptan groups or their oxidation products — disulfide groups — were detected, it can be concluded that the polymers obtained were of high molecular weight. The molar ratio of monomer to initiator (lithium cellulosate and lithium methoxide) was always less than 10. The formation of high molecular weight polymers therefore indicates that most of the alkoxide groups on the cellulose did not participate in initiation.

It was found that polymerization of ethylene sulfide by lithium cellulosate could be initiated even in the presence of water. This should be attributed to the relative stability of the mercaptide ion in the presence of water [18]. The low yields obtained, nevertheless, indicate that reaction of the mercaptide ion with water can occur, thus leading to termination of the graft polymerization.

The reaction of styrene sulfide with alkali cellulosate led to very low yields of graft polymer and monomer conversion was less than 7%. Performing the reaction with or without solvent, using lithium, sodium, or potassium cellulosates and excess of styrene sulfide, did not lead to better results. It may be mentioned that in the reaction of styrene oxide with potassium starch alkoxide in DMSO [19], it was found that no graft polymerization occurred and the reaction stopped at the initiation stage. On the other hand, homopolymerization of styrene oxide under similar conditions in DMSO was successful. The results were attributed to steric hindrance of the anhydroglucose units in the starch and of the phenyl group in the product formed in the initiation step towards addition of a further molecule of styrene oxide (propagation). Since polymerization of styrene sulfide with lithium methoxide led to formation of polystyrene sulfide in high yield, it seems that the same explanation is valid here. The even lower conversion of styrene sulfide as compared with that of styrene oxide [19] can be attributed to the heterogeneous nature of the present reaction.

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