

# Durable Press Finishing of Cotton with Polycarboxylic Acids. I. Preparation of Thiosuccinyl-*s*-triazine

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**ABSTRACT:** The preparation of an alternative polycarboxylic acid to replace the most promising, but expensive, crosslinking reagent 1,2,3,4-butanetetracarboxylic acid (BTCA) is reported. The reaction of mercaptosuccinic acid with 2,4,6-trichloro-*s*-triazine (cyanuric chloride) gave a dithiosuccinyl derivative. The preparation reaction was followed using horizontal ATR infrared spectroscopy and capillary electrophoresis. The final product was characterized by FTIR, capillary electrophoresis, and <sup>1</sup>H-NMR. © 1997 John Wiley & Sons, Inc. *J Appl Polym Sci* **66**: 1465–1474, 1997

**Key words:** poly(carboxylic acid); horizontal ATR infrared spectroscopy; capillary electrophoresis

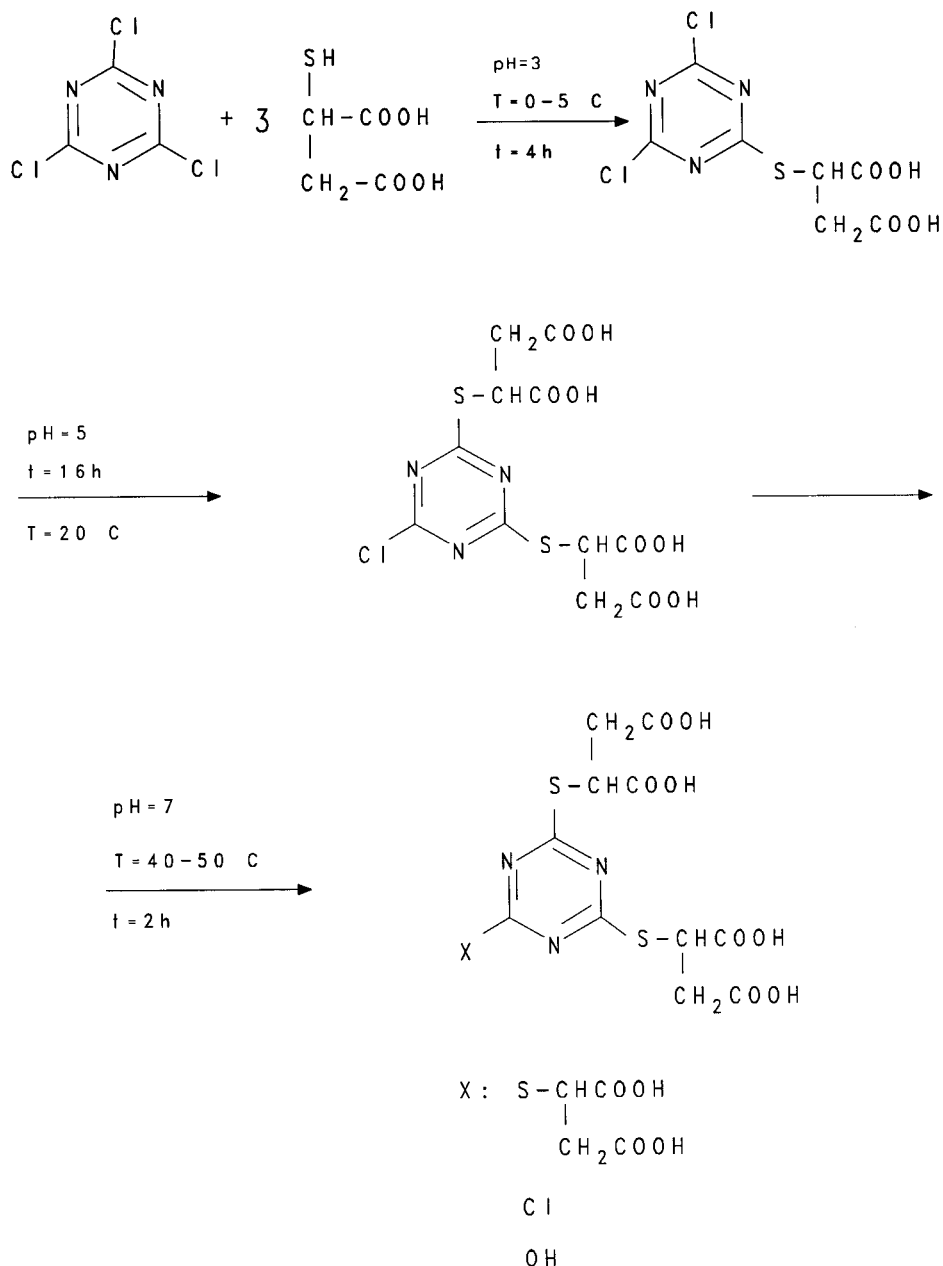
## INTRODUCTION

Gagliardi and Shippee<sup>1</sup> reported a new formaldehyde-free method for producing dimensional stability and crease resistance in cotton fabrics. This involves the direct esterification of the hydroxy groups in cotton cellulose with different polycarboxylic acids such as citric, diglycolic, 1,2,3,4-cyclopentanetetracarboxylic acid, and 1,2,3,4-butanetetracarboxylic acid (BTCA). Rowland and co-workers<sup>2</sup> studied in detail the reactions of polycarboxylic acids with cotton. A high level of cellulose crosslinking was obtained with a polycarboxylic acid having three or more carboxyl groups per molecule.<sup>2–7</sup> The most promising polycarboxylic acid, according to the durable press and wrinkle recovery angle values of the treated cotton, was BTCA. Welch<sup>8</sup> established that the phys-

ical properties of cotton fabric treated with BTCA were comparable with those obtained for cotton treated with the most effective *N*-methylol reagents such as dimethyloldihydroxyethyleneurea (DMDHEU).

The aim of this research was to prepare an alternative polycarboxylic acid to replace the most promising but expensive crosslinking agent, BTCA. The first attempt to prepare polycarboxylic acid involved the reaction of 1 mol of cyanuric chloride with 3 mol of aspartic acid. Unfortunately, aspartic acid is not a sufficiently reactive nucleophile for the ready preparation of a trisubstituted aspartyl derivative of cyanuric chloride or even a diaspartyl derivative with a high yield.<sup>9</sup> A more reactive nucleophile, mercaptosuccinic acid (MSA), was chosen, which when reacted with cyanuric chloride readily gave the dithiosuccinic acid derivative. Part I of this series describes the preparation and characterization of this material and Part II will describe its application as a durable press reagent.

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**Scheme 1** Reaction that was assumed to occur.

## EXPERIMENTAL

### Chemicals

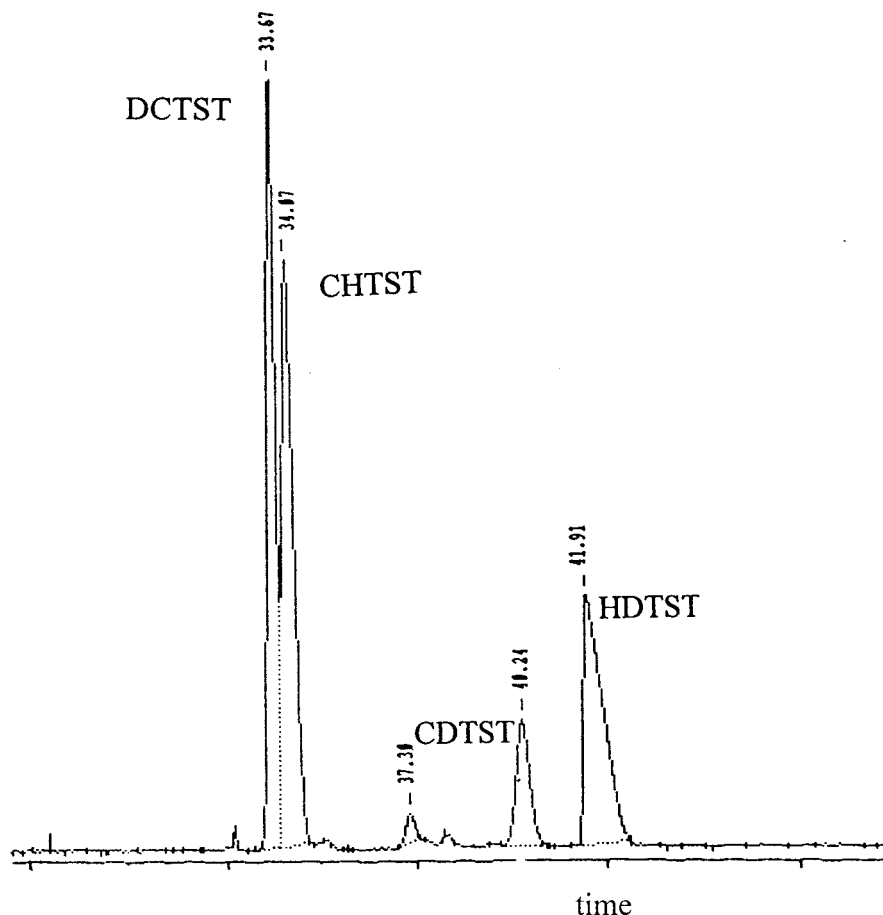
All chemicals were obtained from Aldrich Chemical Co.: cyanuric chloride, 97% pure; MSA, 98% pure; sodium hydroxide pellets, 99.99% pure; sodium carbonate, chemical laboratory grade; hydrochloric acid, 37 wt % in water, 99.99% pure; pyridine, chemical laboratory grade; sodium tetraborate, 99.99% pure; potassium dihydrogen phosphate, 99.99% pure. These chemicals were used without further purification.

### Fujiwara Test

Spot an aqueous solution of pyridine onto filter paper, spot with a 2M solution of NaOH, and then spot the reaction mixture onto the alkaline pyridine. In the presence of dichlorotriazine a yellow coloration is produced.<sup>10</sup>

### Preparation of Thiosuccinyl-s-triazine Derivative

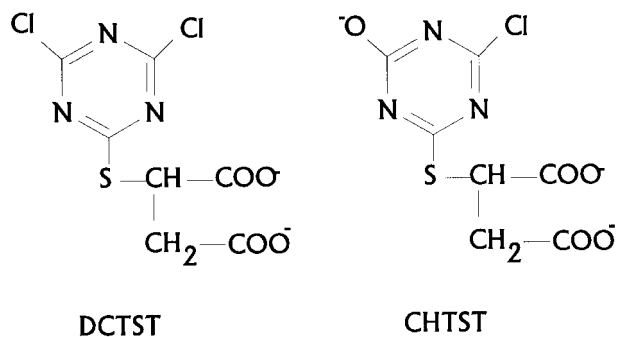
Cyanuric chloride (0.1 mol, 18.4 g) was stirred in the minimum amount of water (200 mL) at 0–



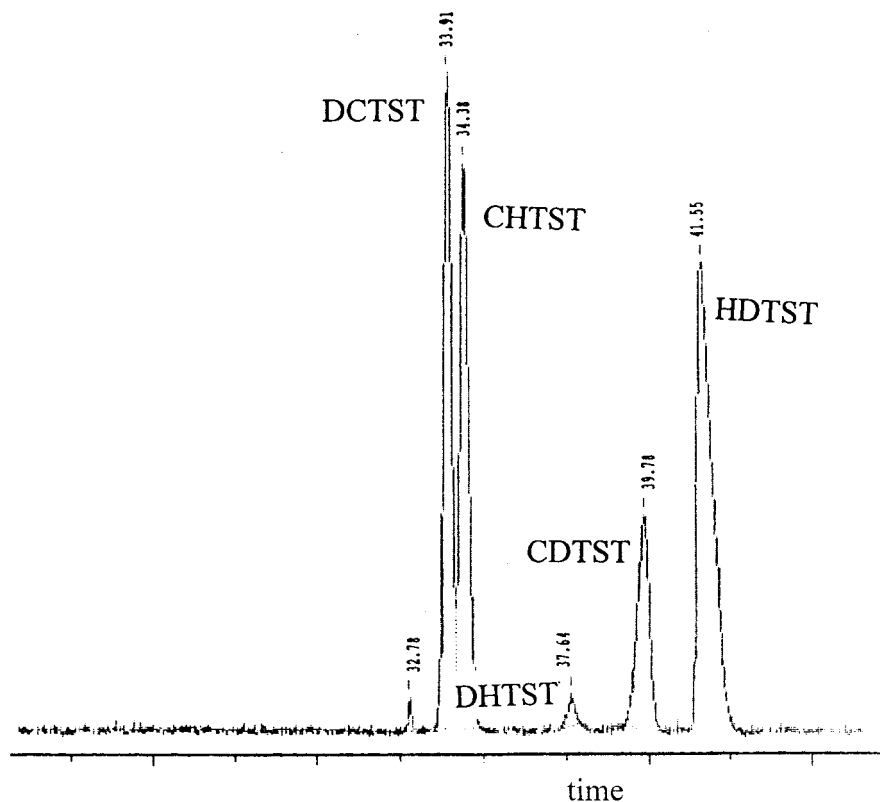
**Figure 1** Electropherogram of cyanuric chloride and MSA reaction mixture on ice for 2 h at pH 3 and at 20°C for 2 h at pH 5.

3°C for 1 h. MSA (60 g, 0.3 mol + 0.1 mol excess) was dissolved in ice-cold water at a pH of 3. This solution was added slowly (over 45 min) to the aqueous suspension of cyanuric chloride and the reaction mixture was left stirring at 5°C for 2 h. The pH was maintained at 3 by neutralizing the HCl released with 2*N* sodium carbonate. At this stage the Fujiwara test for dichlorotriazine was

positive. After increasing the temperature to 20°C the reaction mixture was left overnight at pH 5 (maintained with 2*N* sodium carbonate). When after about 16 h at 20°C the test for dichlorotriazine was negative, the temperature was increased to 40°C, the pH was raised to 7, and the reaction continued for 2 h. When the reaction was complete (pH stabilized) the reaction mixture was cooled



**Scheme 2** Chemical structures of DCTST and CHTST.



**Figure 2** Electropherogram of MSA and cyanuric chloride reaction mixture on ice for 2 h at pH 3 and at 20°C for 8 h at pH 5.

to 0°C and acidified with concentrated HCl to pH 3.<sup>11</sup> After excess water was evaporated under pressure, the mixture was cooled again and in 5 days white crystals precipitated. Scheme 1 shows the reaction that was assumed to occur.

#### Characterization of Prepared Compounds

Capillary zone electrophoresis (CZE) using the Dionex CS1 instrument was used to analyze the prepared compounds. The buffer electrolyte employed was 6 mM  $\text{KH}_2\text{PO}_4$  and 10 mM sodium tetraborate,<sup>12</sup> which gave a pH of 8.8 and the sample pH was adjusted to 9 with sodium hydroxide solution. CZE was carried out at a constant current of 30  $\mu\text{A}$  at 18.2 kV. The samples were introduced into the capillary (diameter 75  $\mu\text{m}$ ) with gravity injection at 50 mm high for 8 s. All separated species were detected with a UV-VIS detector set at 300 nm.

A Perkin-Elmer 1740 FTIR spectrophotometer coupled to an Elonex PC-433 with the Perkin-Elmer Data Manager System for data handling was used to characterize the triazine derivatives. IR spectroscopy measurements were carried out in so-

lution at room temperature using a Contact sampler<sup>TM</sup> (Spectra-Tech), which is a trough fitted with a ZnSe 60° crystal base. In all cases the spectrum of water was computer subtracted. Dry samples of the prepared compounds were analyzed by pressing them into disks with potassium bromide.

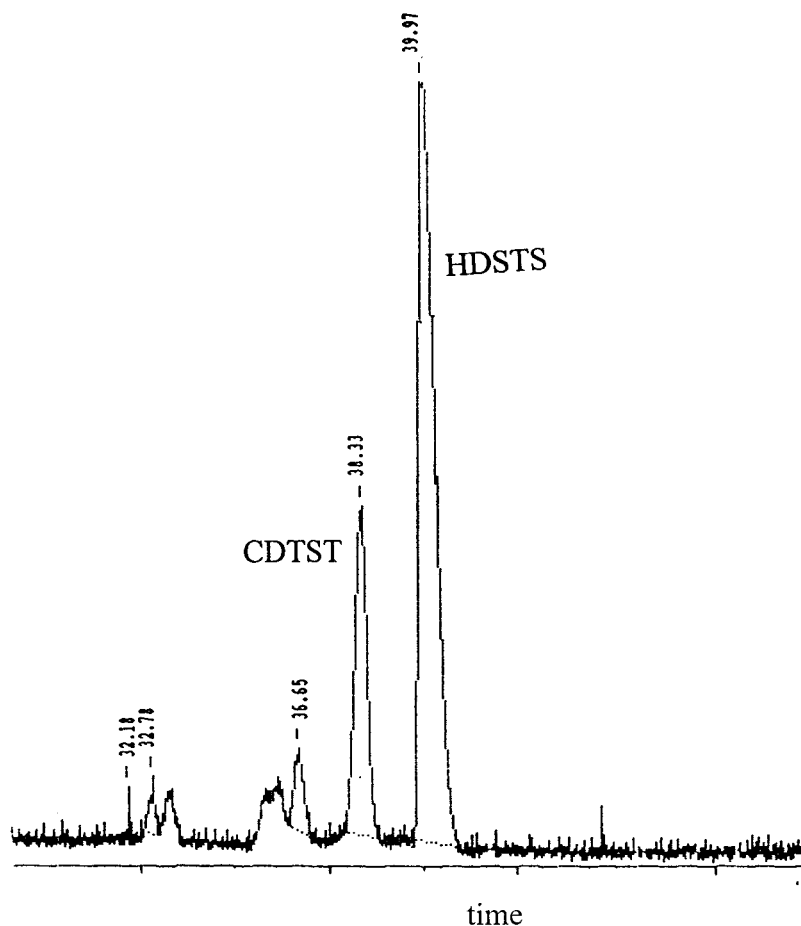
To obtain NMR data, JNM-FX200 equipment was used (JEOL).  $\text{D}_2\text{O}$  was used as a solvent and tetramethyl silane (TMS) as an internal standard.

## RESULTS AND DISCUSSION

In our research two chlorine atoms in 2,4,6-trichloro-*s*-triazine were readily substituted with MSA to obtain a polycarboxylic acid with four carboxylic acid groups; this derivative would be capable of reacting with the hydroxyl groups of cellulose to form ester crosslinks.

#### CZE Analysis

The initial electropherogram from the ice-cold reaction at pH 3 mainly revealed that hydrolysis of cyanuric chloride was the main feature, probably



**Figure 3** Electropherogram of cyanuric chloride and MSA reaction mixture on ice for 2 h at pH 3, at 20°C for 16 h at pH 5, and at 40°C for 2 h at pH 7.

because the analysis sample had to be adjusted to pH 9 prior to running the CZE analysis. It was likely that little reaction between cyanuric chloride and the MSA had actually occurred under ice-cold, acidic conditions (pH 3) and therefore it was decided to change the pH to 5 to enhance the nucleophilicity of the thiol and allow the temperature to rise to 20°C. The expected reaction did occur on raising the pH to 5 and allowing the temperature to rise to 20°C (Fig. 1).

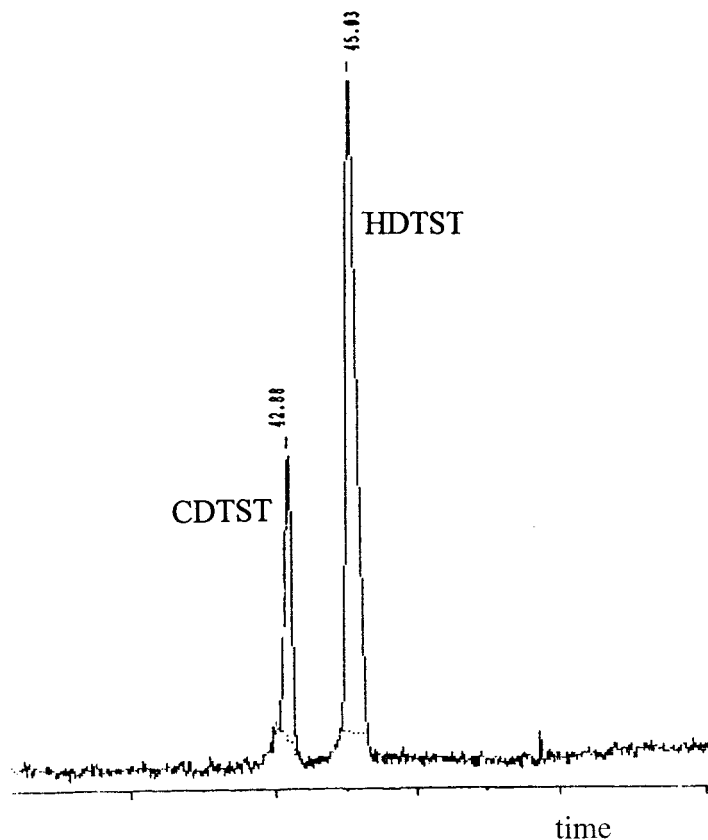
At this stage of reaction, the Fujiwara test was positive, which indicated some dichlorotriazine product was still present. The two main peaks at 33.7 and 34.1 min (Fig. 1) can be attributed to 2,4-dichloro-6-S-thiosuccinyl-*s*-triazine (DCTST) and 2-chloro-4-hydroxy-6-S-thiosuccinate-*s*-triazine (CHTST) (Scheme 2).

Two peaks with higher migration times (MT) but with lower intensity appear as well, and can be attributed to 2-chloro-4,6-di-S,S-thiosuccinyl-*s*-triazine (CDTST) at 40.2 min and to 2-

hydroxy-4,6-di-S,S-thiosuccinyl-*s*-triazine (HDTST) at 41.9 min. When the reaction was continued for a longer time (8 h) at 20°C (Fig. 2), peaks for DCTST and CHTST decrease in their intensity and the intensity of peaks at MTs of 40.0 min for CDTST and 41.6 min for HDTST increases. A small peak at 37.6-min MT may be attributed to 2,4-dihydroxy-6-S-thiosuccinyl-*s*-triazine (DHTST).

Following the reaction at 40°C for 2 h, the electropherogram shown in Figure 3 was obtained. Peaks for DCTST and CHTST almost completely disappear and just two main peaks at MTs of 38.3 min for CDTST and 40.0 min for HDSTS remain. At this stage the Fujiwara test for dichloro-*s*-triazine was negative.

Figure 4 shows the electropherogram of the final isolated compound. The DCTST and CHTST peaks completely disappear; the main peaks are probably MTs of 42.9 min for CDTST and 45.0 min for HDTST.



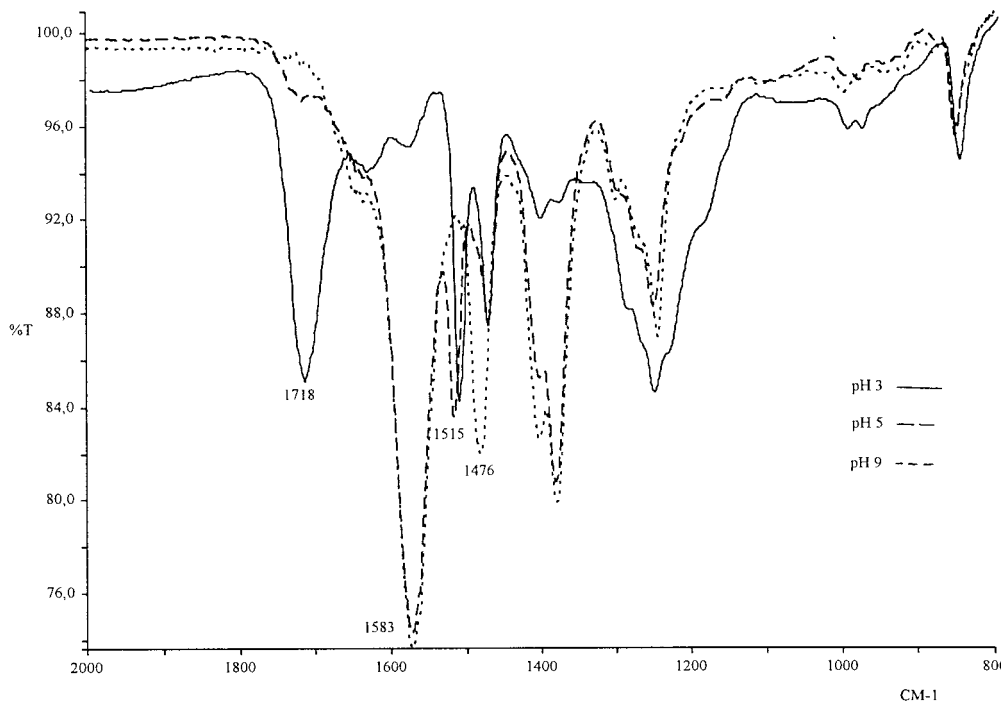
**Figure 4** Electropherogram of isolated final product from cyanuric chloride and MSA reaction.

#### FTIR-ATR Solution Analysis

One way to follow the hydrolysis of derivatives of cyanuric chloride is FTIR-ATR spectroscopy using the horizontal solution cell (Spectra-Tech). When the reaction of cyanuric chloride with MSA is carried out in water some hydrolyzed products can be formed. These products can be converted into keto forms in acid media and the aromatic structure of the triazine ring is thus disrupted.<sup>13</sup> This behavior permits the hydrolysis of MSA derivatives of cyanuric chloride to be followed by ATR (solution cell) IR spectroscopy; because the  $1476\text{ cm}^{-1}$  band intensity is due to the aromatic structure of *s*-triazine derivatives, it is a useful indicator of the extent of hydrolysis.<sup>13</sup> Figure 5 shows the changes in these aromatic *s*-triazine ring vibrations and carboxylic acid groups vibrations according to the pH of the media. In the spectra of the reaction mixture at pH 3, bands attributed to the free carboxylic acid group ( $1718\text{ cm}^{-1}$ ) and to the aromatic *s*-triazine structure ( $1476$  and  $1525\text{ cm}^{-1}$ ) are present. When the pH is increased, the intensity of the carboxylic acid band decreases and bands for the carboxylate anion appear ( $1583$

and  $1382\text{ cm}^{-1}$ ). In the spectra of the reaction mixture at pH 5 and 9, the band for the *s*-triazine aromatic structure at  $1578\text{ cm}^{-1}$  overlaps with the band for the carboxylate anion. However, the presence of the triazine aromatic structure is supported by the  $1476\text{ cm}^{-1}$  band; at pH 9 this band is strongest and weakens significantly at pH 3 and 5. In the case of hydrolyzed derivatives, Scheme 3 shows the tautomerism that may be expected, where MSA represents mercaptosuccinate. The electropherogram in Figure 2 indicates that this reaction mixture actually contains a mixture of products that are shown in Scheme 4.

Compounds 2, 3, and 5 in Scheme 4 will give the above tautomerism whereas compounds 1 and 4 will not; this explains why the  $1476\text{ cm}^{-1}$  band is not totally removed from the spectra at pH 3 and compounds 1 and 4 retain their aromatic triazine character. Lewis and Gillingham<sup>13</sup> showed that compared to dihydroxy-*s*-triazines the monohydroxy-*s*-triazine derivatives were less prone to total loss of aromaticity of the triazine due to the equilibrium of the triazine form with the cyclic urea, explaining the partial persistence of the  $1476\text{ cm}^{-1}$  band in the above case.



**Figure 5** Horizontal ATR IR spectra of MSA and cyanuric chloride reacted 4 h on ice at pH 3 and 16 h at 20°C at pH 5 (solution spectra measured at different pH and the spectrum of water subtracted).

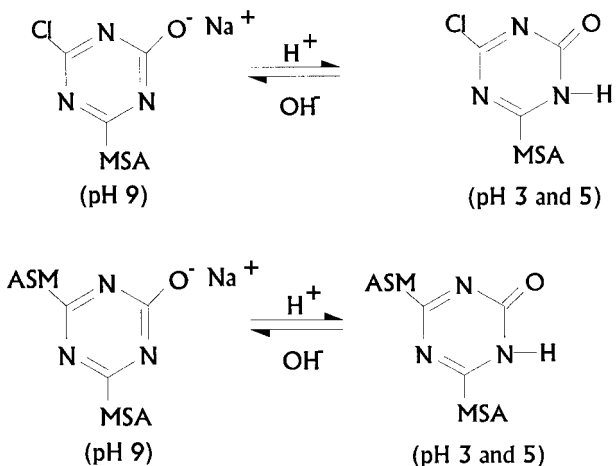
It is known from the literature<sup>14,15</sup> that sulfur, when bonded with carbon, stabilizes the negative charge of carbanions. It is possible that the band at 1515  $\text{cm}^{-1}$  in the solution IR spectra of the MSA triazine derivative at pH 3 and 5 represents protonated nitrogen in the *s*-triazine ring.

Following the reaction at room temperature, the reaction mixture was heated to 40°C to complete the reaction. Isolation at pH 3 gave crystals that were assumed to be mainly CDTST, but from

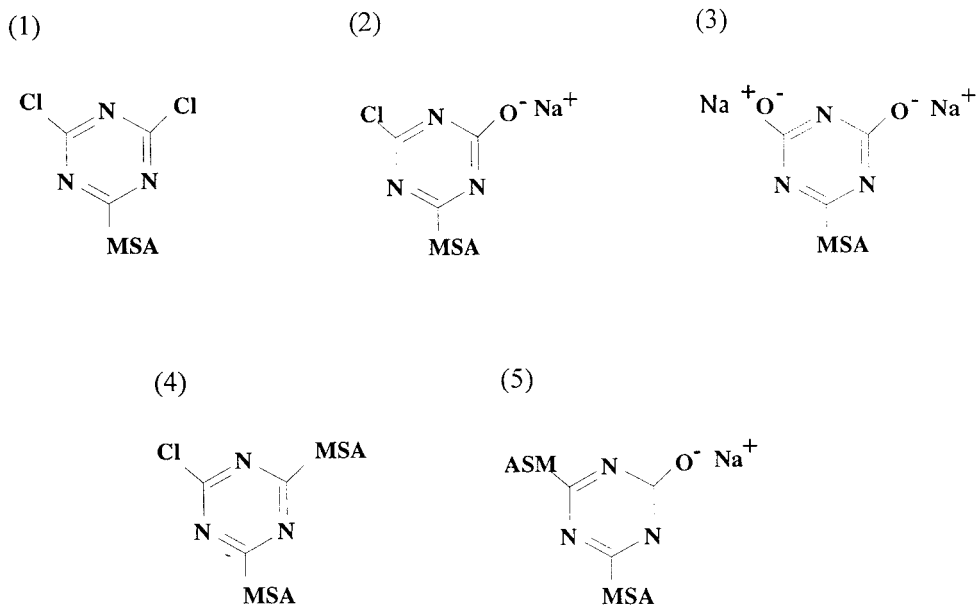
the electrophoresis pattern (Fig. 4) they were judged to be mainly monohydroxy-dimercaptosuccinyl-*s*-triazine. This solid sample was analyzed using transmission (KBr disk) FTIR, and its spectrum is reproduced in Figure 6. Table I gives the band frequencies and their intensities for the IR spectrum of isolated final product.

This compound exhibits a relatively strong 1485  $\text{cm}^{-1}$  band that indicates that the *s*-triazine aromatic structure is intact. The bands for the carboxylic acid groups appear near 1714, 1410, and 1200  $\text{cm}^{-1}$ . The band for the SH group (at 2565  $\text{cm}^{-1}$ ), clearly present in the spectrum of MSA, does not appear in the spectrum of the dimercaptosuccinic acid derivative of *s*-triazine. From Figure 6 it is possible to conclude that the reaction of MSA with cyanic chloride proceeds to a compound with a clearly defined aromatic triazine structure containing carboxylic acid groups. Carried out after heating the reaction mixture to 40°C, the Fujiwara test showed that no dichlorotriazine was present.

The six-membered heterocycles display characteristic patterns of bands between 910 and 665  $\text{cm}^{-1}$  according to their substituents. The second derivatives of the IR spectra at different stages in the reaction were obtained (Fig. 7). It is possible to see that the 819  $\text{cm}^{-1}$  band, which can be attrib-



**Scheme 3**

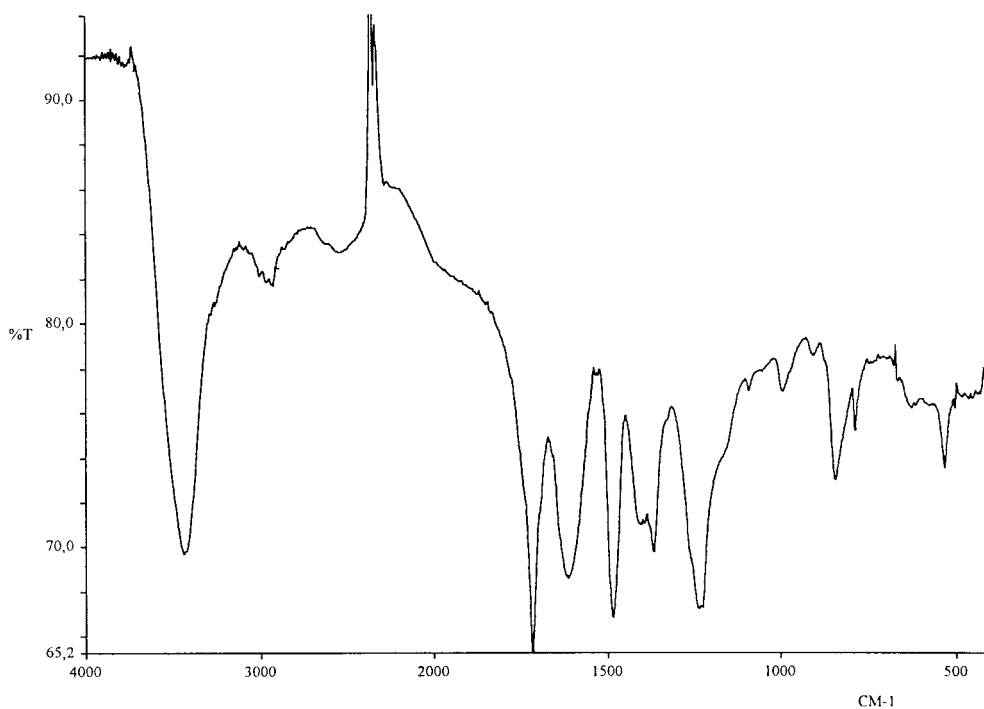


**Scheme 4** Product mixture in the reaction mixture.

uted to the second chlorine atom in the dichlorotriazine derivative, appears in the spectra from reactions carried out at 0–5°C and at 20°C. This band disappears in the spectrum of the products formed following heating to 40°C. Zero and second derivative IR spectra do not clarify the nature of the third substituent (Cl and thiosuccinyl acid group) on the prepared substituted thiotriazine.

To obtain the information of whether the final isolated product is the substituted dithio or trithio derivative of *s*-triazine, <sup>1</sup>H-NMR was carried out. The most important data obtained from <sup>1</sup>H-NMR regarding the number of thiosubstituents are shown in Table II.

<sup>1</sup>H-NMR gives evidence that the product of the cyanuric chloride and MSA reaction has



**Figure 6** Infrared spectrum of isolated final product.



**Table I Band Frequencies and Their Intensities for IR Spectrum of Isolated Final Product**

Frequency (cm <sup>-1</sup> )	Intensity (%T)
3441	69.7
2925	81.8
2349	90.7
1714	65.3
1614	68.6
1485	66.8
1366	69.8
1236	67.3
845	73.0
787	75.2
531	73.5

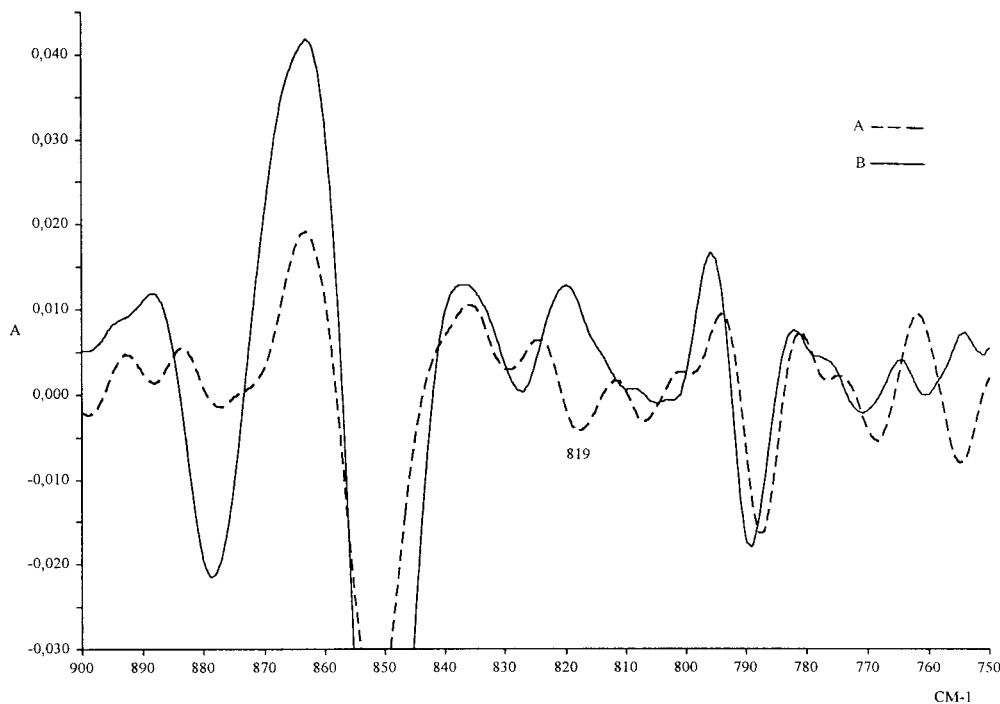
four carboxylic acid groups. This is proved by the appearance of a triplet for two protons of the CH group at 5.6 ppm that is coupled with a doublet for four protons in the CH<sub>2</sub> group (Table II). From the NMR spectra it was not possible to clarify the third substituent on the *s*-triazine ring, but the evidence is strong that a derivative of *s*-triazine with four carboxylic acid groups was obtained. Capillary electropho-

resis and IR spectra support the conclusions that the isolated product is 2-hydroxy-4,6-dimercaptosuccinyl-*s*-triazine (76%) and 2-chloro-4,6-dimercaptosuccinyl-*s*-triazine (24%).

## CONCLUSIONS

Cyanuric chloride reacts with MSA to produce a disubstituted derivative. The reaction was carried out under mild conditions to minimize the hydrolysis of cyanuric chloride and its derivatives. The final product was characterized by FTIR, CZE, and <sup>1</sup>H-NMR and was judged to be a mixture of two components, 2-hydroxy-4,6-dimercaptosuccinyl-*s*-triazine and 2-chloro-4,6-dimercaptosuccinyl-*s*-triazine. The above product was used further to crosslink cotton fabrics and these results will be reported in Part II.

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**Figure 7** Second derivative IR spectra, obtained at different stages of reaction, in the region of 900–750 cm<sup>-1</sup>. (A)  $T = 0-5^{\circ}\text{C}$ , pH 3,  $t = 4$  h; (B)  $T = 0-5^{\circ}\text{C}$ , pH 3,  $t = 4$  h;  $T = 20^{\circ}\text{C}$ , pH 5,  $t = 16$  h;  $T = 40^{\circ}\text{C}$ , pH 7,  $t = 2$  h.

**Table II**  $^1\text{H-NMR}$  Shifts, Their Intensity, Couplings, and Assumed Fragments

Shifts ( $\delta$ )	Number of H	Coupling	Assumed Structure
5.6	2	Triplet	S—CH—COOH
7.3	4	Doublet	CH <sub>2</sub> —COOH
5.5	4	Singlet	COOH

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