Note

Crosslinked, heterocyclic esters of cellulose. The reaction of bromo-substituted heterocyclic (furan and thiophene) acid chlorides with cotton cellulose in the presence of 1,3-bis(4-pyridyl)propane

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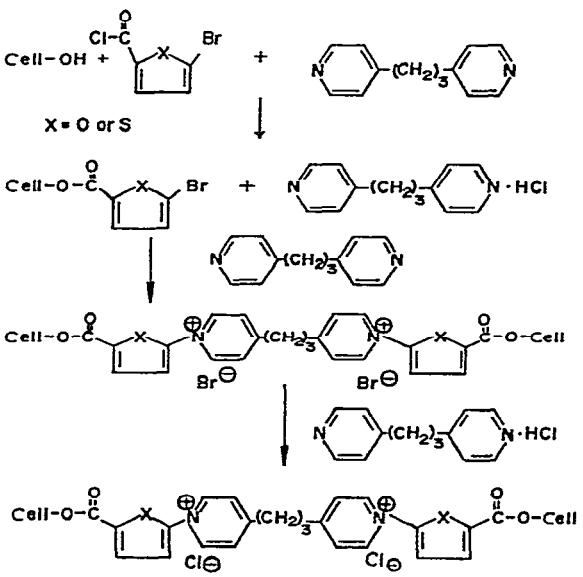
We have recently reported the synthesis and the properties of cellulose furoates[1] and thenoates[2] and also the nucleophilic displacement reactions of bromo-substituted furoates and thenoates of cellulose with tertiary amines, such as pyridine, triethylamine, and *N,N*-dimethylcyclohexylamine. We have extended these investigations to obtain crosslinked heterocyclic esters of cellulose by the reaction of 5-bromo-2-furoyl chloride, 5-bromo-2-thenoyl chloride, and 5-bromo-2-thiopheneacryloyl chloride with purified cotton cellulose in the presence of 1,3-bis(4-pyridyl)propane and dry *N,N*-dimethylformamide (DMF) at 80–85°. The crosslinking reaction may be explained by the sequence of reactions shown in Scheme A.



SCHEME A

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The conditions for reaction of 5-bromo-2-furoyl chloride with purified cotton cellulose yarns in 1,3-bis(4-pyridyl)propane, and the properties of the products, are given in Table I. The crosslinked polymeric products, obtained after reaction for 16 h, had

TABLE I

CONDITIONS[a] FOR FORMATION, AND PROPERTIES, OF CROSSLINKED HETEROCYCLIC ESTERS OF CELLULOSE

Cellulose treated with	*Reaction time, h*	*Add-on, %*	*Breaking strength, g, X 10^{-3}*	*Solubility in cuene*[b]
[Control[c]	—	0.0	4.73	soluble]
5-Bromo-2-furoyl chloride	16	35.5	3.18	insoluble
5-Bromo-2-thenoyl chloride	20	31.3	3.65	insoluble
5-Bromo-2-thiopheneacryloyl chloride	20	11.5	3.19	slight ballooning, partially soluble

[a]Molar ratios of D-glucose residue:acid chloride:1,3-bis(4-pyridyl)propane were 1:4:8; reaction temperature, 80–85°; DMF diluent. [b]Crosslinking indicated by insolubility of products in 0.5M cupriethylenediamine at 25°. [c]Cellulose having crystal lattice type I, in yarn form, recorded for control and products.

35.5% "add-on" (increase in weight); contained Br 10.98, Cl 0.29, N 0.22, and H_2O 2.78%; and had λ_{max}^{KBr} 5.85 (ester) and 6.40 μm (C=C). Assuming crosslinked products, this composition corresponds to a mixed derivative of cellulose, as in Fig. 1, line 1.

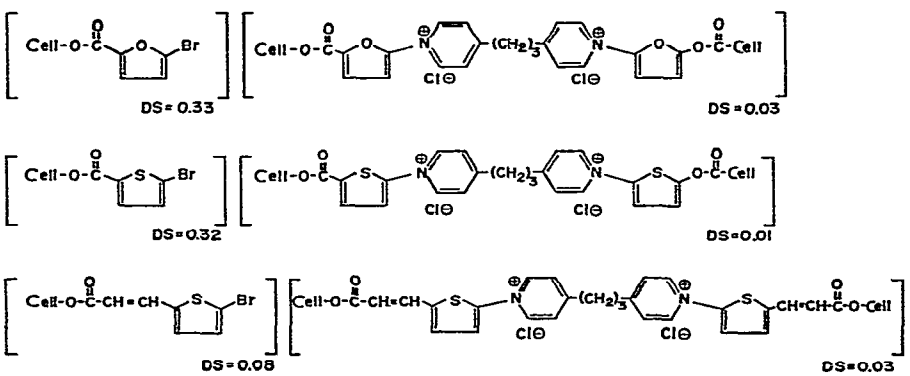

Fig. 1. Composition of heterocyclic cellulose esters crosslinked with 1,3-bis(4-pyridyl)propane.

The conditions for reaction of 5-bromo-2-thenoyl chloride with cellulose in 1,3-bis(4-pyridyl)propane, and the properties of the products, are given in Table I. The products, obtained after reaction for 20 h, had 31.3% "add-on"; contained Br 10.42, N 0.07, S 5.26, Cl 2.08, and H_2O 2.20%; and had λ_{max}^{KBr} 5.90 (ester) and 6.60 6.60 μm (C=C and/or aromatic). This composition corresponds to a mixed derivative of cellulose, as in Fig. 1, line 2.

The conditions for reaction of 5-bromo-2-thiopheneacryloyl chloride with cellulose in 1,3-bis(4-pyridyl)propane, and the properties of the products, are given in Table I. The products, obtained after reaction for 24 h, had 11.5% "add-on"; contained Br 3.24, Cl 0.57, N 0.23, S 1.45, and H_2O 4.21%; and had λ_{max}^{KBr} 5.85 (ester) and 6.20 μm (C=C). This composition corresponds to a mixed derivative of cellulose as in Fig. 1, line 3.

A conjugate, addition–elimination mechanism has been proposed for the nucleophilic displacement reactions[1,2]. The higher density of crosslinkages in the case of the 5-bromo-2-thiopheneacryloyl derivative of cellulose, as compared with that of the 5-bromo-2-thenoyl cellulose derivative reported here, may be due to extended conjugation.

Some of the physical properties of cotton cellulose fabrics, treated with heterocyclic acid chlorides in the presence of 1,3-bis(4-pyridyl)propane and dry DMF at 80–85°, to yield uniformly treated products as indicated by the dye test[8], are shown in Table II. The increases in wrinkle-recovery angles of the products, as compared

TABLE II

SOME PHYSICAL PROPERTIES OF COTTON CELLULOSE FABRICS TREATED WITH HETEROCYCLIC ACID CHLORIDES IN 1,3-BIS(4-PYRIDYL)PROPANE

Cellulose treated with	*Add-on, %*	*Wrinkle-recovery angles, degrees (warp+fill)*		*Spray rating*
		conditioned	*wet*	
5-Bromo-2-furoyl chloride	21.7	242	216	50
[Control	0.0	188	193	0]
5-Bromo-2-thenoyl chloride	19.7	234	225	70
[Control	0.0	167	183	0]
5-Bromo-2-thiopheneacryloyl chloride	5.0	192	197	50
[Control	0.0	159	135	0]

with those of unmodified fabrics, are interpreted as further evidence of the introduction of crosslinkages in the cellulosic products by reaction with 1,3-bis(4-pyridyl)-propane. The increases in spray ratings[7] indicate that the cover factors of the product fabrics are higher than those of the unmodified fabrics. Further investigations of the effects of these reactions of cellulose on the physical properties of cotton cellulose products are in progress.

EXPERIMENTAL

Materials. — Deltapine cotton in the form of 7s/3 yarn was purified[3] to yield cellulose (mol. wt.[4] 700,000). The fabric used was 80 × 80 cotton print cloth (about 3.50 oz/yd^2) which had been desized, scoured, and bleached.

1,3-Bis-(4-pyridyl)propane was obtained from Reilly Tar and Chemical Corporation*, New York, and was used as received. *N,N*-Dimethylformamide (analytical grade) was purified by distillation from calcium hydride. 5-Bromo-2-furoyl chloride, 5-bromo-2-thenoyl chloride, and 5-bromo-2-thiopheneacryloyl chloride were prepared by the methods described by Singh and Arthur[1,2].

Methods. — Physical tests were performed by ASTM methods[5]. Wrinkle-recovery angles were determined by the Monsanto method[6]. Spray ratings were determined by the AATCC method[7]. I.r. spectra of materials in potassium bromide discs [1:300 (w/w)] were recorded with a Perkin–Elmer double-beam spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tennessee. The degree and uniformity of the esterification were determined by a dye test that uses mixed Acetate Yellow and Direct Cotton Blue[8].

Reaction conditions. — Dry DMF (200 ml) was placed in a wide-mouthed, round-bottomed flask (500 ml), and the desired amount of the acid chloride was added. 1,3-Bis(4-pyridyl)propane (two moles per mole of acid chloride) was added rapidly, and the mixture was shaken thoroughly until a homogeneous solution was obtained. Cotton cellulose, in the form of yarn or fabric (4–8 g) predried in air for 2 h at 60°, was then added to the solution, and the mixture was heated, with continuous stirring, in an oil bath at 80–85°, ingress of moisture being excluded by use of a drying tube. After completion of the reaction, the mixture was cooled, and the yarn or fabric was removed, washed with two 100-ml portions of DMF, immersed for 30 min in methanol at 50–60°, kept in 10% potassium hydrogen carbonate solution for 30 min, and washed thoroughly with distilled water. The yarn or fabric was then stretched, overnight at 25°, to 80–85% of its original length, and equilibrated for 24 h at 50% relative humidity at 25°. The extent of reaction was ascertained by determining the increase in weight ("add-on") of the sample over the weight of the control yarn or fabric.

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*Trade names are given as part of the exact experimental conditions, and not as an endorsement of the products over those of other manufacturers.