

## Internal Catalysis of Reactions of Activated Vinyl Compounds Via Tertiary Amino Substituents in Cotton Cellulose

STANLEY P. ROWLAND and MARY ANN F. BRANNAN,  
*Southern Regional Research Laboratory, Southern Utilization  
Research and Development Division, Agricultural Research Service,  
U. S. Department of Agriculture, New Orleans, Louisiana 70119*

### Synopsis

The tertiary amino groups of 2-diethylaminoethyl substituents in cotton cellulose have been found to be effective catalysts for reactions of activated vinyl compounds with cellulosic hydroxyl groups. These reactions proceed more slowly and to lesser extents at equilibrium than the corresponding reactions catalyzed by quaternary ammonium substituents. The crosslinking of cotton cellulose with divinyl sulfone is catalyzed by  $(C_2H_5)_2NCH_2CH_2$ —substituents and by  $(C_2H_5)_2NCH_2CH(OH)CH_2$ —substituents, with the development of moderate levels of wrinkle recovery. On the other hand, only the former substituents catalyze the reorganization of the crosslinkages during reure (160°C, 10 min), with substantial increases (40°) in wrinkle recovery angles. These same 2-diethylaminoethyl substituents are effective in catalyzing the reorganization of crosslinkages from divinyl sulfone which are introduced into the cotton by conventional external catalysis (i.e., NaOH); this effectiveness can be overcome by the introduction of excessive crosslinkages into the cellulosic composition.

### INTRODUCTION

The reactions of activated vinyl compounds with cellulose are of considerable interest, for example, in cyanoethylation, in crosslinking with divinyl sulfone, and in dyeing with certain reactive dyes. Recently, activated vinyl compounds have been reacted with cellulose through the internal catalysis provided by quaternary ammonium substituents previously introduced into the cotton cellulose.<sup>1,2</sup> Internal catalysis offers interesting possibilities for delayed curing of cotton fabrics<sup>1,2</sup> and for thermally creasable (and uncreasable) wrinkle-resistant cotton fabrics.<sup>3</sup> Internal catalysis also offers intriguing means for clarifying certain aspects of the course of chemical reactions of crystalline polymers such as fibrous cotton cellulose.<sup>4</sup>

It is the purpose of this paper to report and describe the catalytic activity of tertiary amino groups upon the reaction of activated vinyl compounds with cellulose; the specific tertiary amino groups under consideration are those which are introduced into cotton cellulose as a part of substituent units, such as those in 2-diethylaminoethyl cellulose.

## EXPERIMENTAL

### Materials

The fabric employed in this study was 80×80 desized, scoured, bleached cotton print cloth weighing approximately 3.2 oz/yd<sup>2</sup>.

The following reagents were used without further purification: 2-chloroethyl-diethylamine hydrochloride (practical grade), epichlorohydrin, diethylamine, and acrylamide from Eastman Organic Chemicals; divinyl sulfone and methyl vinyl ketone from Monomer-Polymer Laboratories, Borden Chemical Co.; acrylonitrile (practical) and fumaronitrile (Baker grade) from J. T. Baker Chemical Company; and methyl vinyl sulfone from K & K Laboratories.

Glycidyl-diethylamine was prepared from diethylamine and epichlorohydrin according to the method of Gilman et al.<sup>5</sup>

### Procedures

**2-Diethylaminoethyl Cellulose (Amine I).** 2-Diethylaminoethyl cotton cellulose (designated Amine I), 1.10% nitrogen content, was prepared according to the method of Soignet and Benerito<sup>6</sup> by two 10-min treatments of printcloth impregnated with a 20% aqueous solution of 2-chloroethyl-diethylamine hydrochloride in hot aqueous 8% NaOH. The Amine I fabric of 0.4% nitrogen content was prepared in a similar manner from a single treatment of the cotton printcloth.<sup>7</sup>

**3-Diethylamino-2-hydroxypropyl Cellulose (Amine II).** This tertiary amino cotton cellulose (designated Amine II) was prepared by treating approximately 17 g of cotton printcloth containing 8% NaOH (120% wet pickup) for 3.5 hr, with periodic agitation, in a loosely stoppered tube containing 21 ml of glycidyl-diethylamine at 95°C. The fabric was rinsed 20 min in cool running tap water, 5 min in 1% acetic acid, and finally in distilled water. The resulting fabric contained 1.10% nitrogen.

**Reactions of Amine I with Activated Vinyl Compounds.** Samples of Amine I fabric, 0.4% nitrogen content, 2 in. × 3 in.; weighing 0.4–0.5 g each, were put into the base form by an overnight soak in 0.05*N* NaOH. The fabrics were rinsed in deionized water until free of NaOH. While still retaining approximately 100% wet pickup of the deionized water, each sample of fabric was immersed in a measured quantity of reagent solution preheated to 30.0 ± 0.1°C. The reagent solution was four times the weight of the dry Amine I fabric. Original concentrations of the vinyl compounds in the reagent solutions were 12.5% and 100%. (Acrylamide, which is a solid, was used as a 52% aqueous solution for reaction in the concentrated medium. This concentration dropped to approximately 42% upon introduction of the damp fabric.) The dilute solutions contained 12.5% of vinyl monomer dissolved in water–dimethylsulfoxide prior to contact with the wet fabric; during contact with the fabric, the concentrations of vinyl monomers were reduced to 10% and the concentrations of water–dimethylsulfoxide mixtures were 36%:54% for methyl vinyl ketone,

26%:64% for fumaronitrile, 90%:0% for methyl vinyl sulfone, 80%:10% for divinyl sulfone, 52%:38% for acrylonitrile, and 90%:0% for acrylamide. The weight ratio of solution to fabric was 5:1 in each case. This is little more solution than required to wet the fabric.

Addition of the wet Amine I fabric to the vinyl compounds in the absence of diluent caused the effective solution concentrations to drop to 80%; again, the weight ratio of solution to fabric was 5:1. Reactions were conducted for a total of 16 hr at  $30.0 \pm 0.1^\circ\text{C}$ . At the appropriate time intervals, reactions were halted by rinsing the fabric samples in tap water. The fabrics were soaked 5 min in 1% acetic acid, rinsed in distilled water, and air-equilibrated 16–24 hr prior to analyses.

#### **Crosslinking of *tert*-Amino Cotton Celluloses with Divinyl Sulfone.**

To insure that the *tert*-amino cotton celluloses were in the base form prior to reaction with divinyl sulfone, the fabrics were soaked overnight in 0.05*N* NaOH, rinsed in deionized water until free of NaOH, and subjected to further chemical modification without drying.

The *tert*-amino cottons, retaining approximately 100% wet pickup of deionized water, were padded through solutions of divinyl sulfone (12% in water, 33% in water–dimethylsulfoxide, or neat) to 95–110% wet pickup and stored for 1 hr at room temperature in a polyethylene bag. The fabrics were rinsed in tap water, 1% acetic acid, and finally distilled water.

**Crosslinking of *tert*-Amino Cotton Celluloses with Bis(2-hydroxyethyl)-Sulfone.** The *tert*-amino cotton fabrics, freshly converted to the base form as described above and retaining approximately 100% wet pickup of deionized water, were reacted with bis(2-hydroxyethyl) sulfone by padding the fabrics with either 20% or 65% solutions of the sulfone (approximately 100% wet pickup with the dilute solutions, 125% with the more concentrated solution) and curing 5 min at  $140^\circ\text{C}$ . The fabrics were rinsed in tap water, 1% acetic acid, and distilled water.

**Crosslinking Reactions of Amine I with Divinyl Sulfone Via External Catalyst.** Amine I fabric, 1.10% nitrogen content, was crosslinked with divinyl sulfone by the conventional wet cure method, i.e., the fabric was padded with a 10% solution of NaOH followed by the reagent (7.5% concentration, saturated solution, or neat) and allowed to react for 1 hr at room temperature in a polyethylene bag. All samples were rinsed in tap water, 1% acetic acid, and distilled water.

**Recurring Reactions for Crosslinked *tert*-Amino Cottons.** Samples of fabric were clamped between glass plates (primarily to support the small samples in a flat state), placed in a forced-draft oven, raised to a temperature of  $158\text{--}162^\circ\text{C}$  (as measured by a thermocouple between the glass plates), and maintained at this temperature for 10 min.

#### **Analyses**

The sulfur and nitrogen contents of the fabrics were determined by conventional microanalysis and by micro-Kjeldahl, respectively. Infrared spectra (to confirm incorporation of residues of methyl vinyl ketone into

the cellulose) were obtained from KBr discs using a Perkin Elmer 21 spectrophotometer equipped with NaCl optics.

### Physical Test Methods

Breaking strength and elongation were determined by the strip method, ASTM D1682-64; tearing strength, by the Elmendorf method, ASTM D1424.63. Conditioned and wet wrinkle-recovery angles were determined with the Monsanto tester, ASTM 1295-60T.

## RESULTS AND DISCUSSION

### Reaction of Activated Vinyl Compounds with 2-Diethylaminoethyl Cellulose

A variety of activated vinyl compounds in 10% semiaqueous solution reacted readily with 2-diethylaminoethyl cotton cellulose (Amine I) in the form of printcloth, as shown in Figure 1. These reactions required that the Amine I fabric be in the base form, which was obtained by soaking the fabric in 0.05*N* NaOH followed by extensive rinsing. The reactions shown in Figure 1 characterize an Amine I fabric containing 0.40% nitrogen, which is equivalent to 0.0285 mole of amino groups per 100 g of Amine I, or a degree of substitution of 0.048.

The course of the reactions of the vinyl compounds, in 10% semiaqueous solutions, with Amine I fabric is generally similar to that observed for the corresponding reactions with the quaternary ammonium cotton cellulose derived from Amine I by quaternization.<sup>1,4</sup> Amine I quaternized with methyl iodide and converted to the base form has been referred to as Quat I. The reactions of Amine I fabric that are reported here were conducted

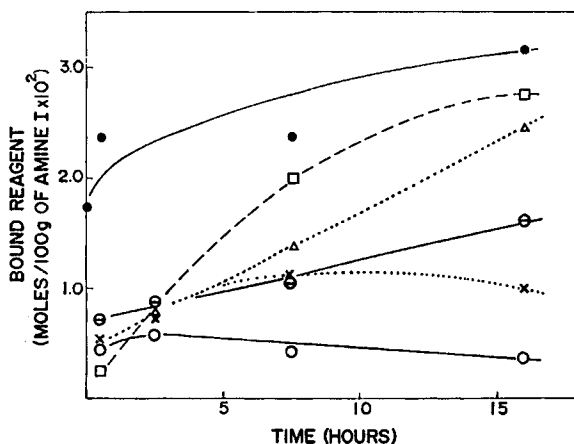


Fig. 1. Reactions of activated vinyl compounds with Amine I fabric (0.40% nitrogen): (●) methyl vinyl ketone; (□) fumaronitrile; (△) methyl vinyl sulfone; (×) divinyl sulfone; (⊙) acrylonitrile; (○) acrylamide.

under conditions identical to those of Quat I fabric which were reported previously.<sup>4</sup> There is, however, a small difference in the nitrogen contents of the two compositions, i.e., Amine I, see preceding paragraph; Quat I, 0.45% nitrogen, corresponding to 0.0322 mole of quaternary ammonium group per 100 g of Quat I and a degree of substitution of 0.055.

The extent of reaction of a vinyl compound with Amine I was only a fraction of that of the corresponding reaction with Quat I, i.e., ca. 5% for methyl vinyl ketone and acrylonitrile, ca. 10% for methyl vinyl sulfone, divinyl sulfone, and acrylamide, and ca. 30% for fumaronitrile. It is evident from the lower slopes of the curves in Figure 1 compared to those for the corresponding reactions of Quat I<sup>4</sup> that the former reactions are generally slower as well as less extensive.

When the Amine I fabric (containing its own weight of water) was brought into contact with the neat (or more concentrated) reagent, there was obtained the same extent of reaction at the end of 16 hr as already observed for the dilute reagent in the case of methyl vinyl ketone, acrylonitrile, and acrylamide. In preceding studies, methyl vinyl ketone and acrylonitrile showed pronounced increases in reaction under these conditions in the case of Quat I fabric. For both Amine I fabric and Quat I fabric, divinyl sulfone in neat form reacted to a lesser extent than in the dilute solution.

### Crosslinking with Divinyl Sulfone Via Internal Catalysis of *tert*-Amino Groups in Cotton Cellulose

In this portion of the study, two different substituents, each bearing a tertiary amino group, in the cotton cellulose were examined for catalytic activity on the reaction of divinyl sulfone with the cellulosic hydroxyl groups. The sample of Amine I fabric employed in this portion of the study had a nitrogen content of 1.1%. Amine II (the *tert*-amino cotton fabric having  $(C_2H_5)_2NCH_2CH(OH)CH_2-$  substituents) also had a nitrogen content of 1.1%.

The hydroxyl groups of the cellulose, catalyzed by the *tert*-amino substituents, reacted quite readily with DVS, as summarized in Table I. In each case, however, the DVS reacted with the cellulose to a substantially lesser extent with *tert*-amine catalysis than with the corresponding quaternary ammonium catalysis under the same conditions, i.e., ca. 45% in the case of Amine I<sup>1</sup> and 13% in the case of Amine II<sup>2</sup> (and the Quat II employed in the comparison contained only 0.56% nitrogen).<sup>\*</sup> The wrinkle-recovery angles (WRA) developed in the Amine I fabric that reacted with DVS to the extent of 0.68% of sulfur were comparable to those of Quat I-DVS fabric at 1.76% sulfur<sup>1</sup> (conditioned WRA = 246°, wet WRA = 261°). This suggests that the proportion of crosslinkages, substituents groups, etc., was probably quite similar in both cases.

\* The substituents in Amine I and Quat I are  $(C_2H_5)_2NCH_2CH_2-$  and  $(C_2H_5)_2(CH_3)N^+CH_2CH_2-$ , respectively, and those in Amine II and Quat II are  $(C_2H_5)_2NCH_2CH(OH)CH_2-$  and  $(CH_3)_3N^+CH_2CH(OH)CH_2-$ , respectively.

TABLE I  
Cotton Cellulose Fabric Crosslinked by in situ *tert*-Amine Catalysis

Fabric composition	Crosslinking reaction	S, % <sup>a</sup>	S/N <sup>b</sup>	Wrinkle-recovery angle (W + F), degrees		Breaking strength, lb	Elongation, %	Tear strength, g
				Conditioned	Wet			
Cotton print cloth	—	—	—	185	155	51.8	8.0	1048
Amine I (1.1% N)	—	—	—	150	138	45.0	29.6	640
Amine I (1.1% N)	neat DVS	0.45	0.18	178	213	44.4	33.1	710
Amine I (1.1% N)	12% DVS	1.60	0.68	247	257	38.0	32.2	600
Amine II (1.1% N)	—	—	—	202	185	32.0	19.5	450
Amine II (1.1% N)	33% DVS	0.53	0.21	212	240	—	—	410
Amine II (1.1% N)	12% DVS	0.52	0.20	247	219	—	—	410

<sup>a</sup> The bound sulfur in the product.

<sup>b</sup> The ratio of gram atoms of sulfur to nitrogen in the product, i.e., moles of reagent introduced into the fabric per *tert*-amine substituent.

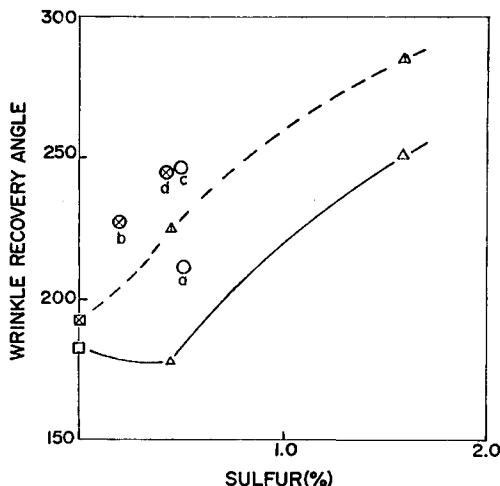


Fig. 2. Changes as a result of recure effected in conditioned WRA of fabrics crosslinked by the wet cure reaction: open symbols, original WRA; special symbols, WRA following recure; triangles, internally catalyzed fabric from Amine I; circles, internally catalyzed fabric from Amine II; squares unmodified cotton. Symbols labeled (a) and (b) refer to one Amine II fabric before and after recure, and symbols labeled (c) and (d) refer to the second set.

The low reactivity of Amine II fabrics with DVS is quite surprising in view of the substantially higher reactivity of Quat II fabric compared to Quat I fabric. At a given level of quaternary substituents, Quat II reacted with 1.5–2.0 times the amount of DVS bound by the Quat I.

The reactivities of Amine I and Amine II are notably different from those of the corresponding quaternary ammonium cottons in behavior toward bis(2-hydroxyethyl) sulfone at elevated temperature. Under conditions of bake cure (140°C, 5 min), which incorporated approximately 1% and 1.5% of sulfur in Quat I and Quat II, respectively, low to negligible reactions occurred with Amine I and Amine II fabrics. It was suspected that the lack of reaction in these cases was due to the relative ineffectiveness of the *tert*-amino groups in catalyzing the dehydration of the bis(2-hydroxyethyl) sulfone to DVS. A confirmation of this was indicated by the observation that Amine I and Amine II fabrics reacted with DVS under the bake cure conditions of reaction to introduce 0.68% and 0.53% of sulfur, respectively.

In earlier studies,<sup>1,2</sup> the effects of recure were particularly interesting. The recure involved subjecting the crosslinked fabric to a 10-min period at 160°C. It is pertinent to note that the *tert*-amino groups (or the quaternary ammonium groups) are in the form of acetate salts at the beginning of this recure, since the rinsing treatment following the crosslinking reaction involves acetic acid.

As a result of the recure, Amine I–DVS fabrics underwent approximately 40° increases in conditioned WRA (Fig. 2); this level of change is comparable to the lowest increases exhibited by Quat I–DVS and Quat II–DVS

fabrics as a result of recure. Amine II-DVS fabrics showed little response in WRA to the recure; at most, this was comparable to the increases shown in unmodified cotton printcloth (ca.  $+10^\circ$ ) and cotton crosslinked with DVS but containing no internal catalyst groups ( $+3-16^\circ$ ). Amine II-DVS fabrics were unique also in showing measurable losses in sulfur after the recure.

In a preceding study<sup>1</sup> it was observed that an Amine I fabric (1.1% nitrogen content) which was crosslinked with DVS by conventional external catalyst (i.e., 10% NaOH) to introduce 1.82% sulfur underwent a  $50^\circ$  increase in conditioned WRA as a result of the recure. On the other hand, samples of this fabric crosslinked to higher levels of sulfur (3.4% and 9.7%) exhibited only  $12-20^\circ$  increases in conditioned WRA. It is evident that at the low level of crosslinking, the *tert*-amine groups of Amine I are effective in catalyzing reorganization of the crosslinkages during the recure. It is interpreted that crosslinkages must be in the same general regions of the cotton fiber and within the range of the catalytic activity of the *tert*-amino groups in this composition. However, at the higher levels of crosslinking, it is clear that the catalytic activity of the *tert*-amino groups is inadequate to cause reorganization of sufficient crosslinkages to effect a substantial increase in WRA during the recure. It is believed that in the latter cases, the *tert*-amino groups are essentially inactivated by being surrounded by several "layers" of crosslinkages, any one of which would be accessible and responsive to the *tert*-amino catalysis in the absence of the other crosslinkages.

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