

Effects of Substitution of Triphenylmethyl Groups into Cellulose on the Fine Structure and Thermal Properties of the Products*

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Synopsis

Mercerized cellulose in the form of 7/2 yarn was reactivated with 17.5% sodium hydroxide and then heated at 100°C. with 5 moles of trityl chloride, in pyridine, per anhydroglucose unit. The time of reaction was varied, giving ether derivatives of the cellulose containing 0.31-0.79 triphenylmethyl groups (DS) per anhydroglucose unit. Controls consisted of (1) the untreated cellulose yarn and (2) a portion subjected to all the reaction conditions except the reactant. The density of the product decreased hyperbolically with increasing substitution. The mixed x-ray pattern of the untreated control cellulose (35% cellulose I, 43% cellulose II) was largely converted by the activation treatment (10% cellulose I, 53% cellulose II). As reaction proceeded the crystal structure largely disappeared. The assumption is that substitution was confined almost exclusively to the primary hydroxyl position. The behavior of tensile stiffness, elastic recovery, and work recovery was explored at temperatures from about 25 to 225°C. Considerable improvement, which generally increased with increasing substitution, was observed in both elastic and work recovery at all temperatures studied.

INTRODUCTION

In a continuing program to determine the influence of the chemical nature of substituents on the physical and thermal properties of cotton cellulose derivatives, certain products have been studied by Conrad et al.^{1,2} Recently, certain properties of cotton yarns chemically modified with diphenylmethyl groups have been studied by Stanonis et al.³ It is the purpose of the present paper to report the results of a similar study of the influence of an additional phenyl in the methyl group in triphenylmethyl cellulose with several degrees of substitution (DS). The chemical reaction has already been discussed by Stanonis.⁴

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MATERIALS AND METHODS

The cotton yarn used in the present study was from the same supply of commercially mercerized nominally 7/2 (200 tex) product as that used in the study of benzhydrylated cotton yarns described by Stanonis et al.³ It was reacted heterogeneously under controlled tension for different periods of time in a specially constructed reactor described by Stanonis et al.,⁵ designed to minimize corrosion problems, and eliminate contamination of the resulting yarns. The method of reactivation with 17.5% sodium hydroxide, washing with dilute acetic acid (5%) and water, and exchanging into pyridine, has also been described.⁵

Briefly, approximately 50 g. (0.3 mole anhydroglucose units) of yarn was reacted at 100°C. with 403 g. (1.45 moles) of trityl chloride dissolved in 235 ml. of pyridine. It proved impracticable to substitute beyond DS = 0.79 due to excessive damage to the fiber structure. This is much lower than was obtained with the somewhat less bulky benzhydryl group,³ where substitutions as high as DS = 1.22 were obtained readily.

In addition to the completely unreacted control, a second control was prepared with the same pretreatment and heating for 4 hr. at the same temperature and with the same reagents, exclusive of the trityl chloride. The time of reaction, degrees of substitution obtained, and yarn tex are given in Table I. The Sakurada relationship between extent of reaction and reaction time⁶ was followed approximately.

TABLE I
Details of Tritylation of Cotton Yarn

Type of sample	Length of reaction, hr.	Yarn number, tex.	Degree of substitution, <i>S</i>
Control,O(I) ^a	0	200	0
Control,O(II) ^b	4	203	0
Reacted	1	341	0.31
Reacted	2	407	0.53
Reacted ^c	5.6	518	0.58
Reacted	4	413	0.69
Reacted	8	476	0.79

^a Unmodified commercially mercerized 7/2 yarn.

^b Control exposed to all conditions of reacted samples except trityl chloride for 240 minutes.

^c Due to pump failures there were two interruptions of reaction totaling 1 hr. 25 min.; time shown is accumulated time.

Methods for evaluation of the reacted yarns, including determination of density, crystalline structure, tensile properties, thermal behavior, and elastic and work recovery at various temperatures, have been described previously.^{1,7,8} Helium was used for differential thermal analysis (DTA) and thermogravimetric analysis (TGA). The latter was conducted at 3°C./min., the DTA at 7.5°C./min. The tensile measurements at

elevated temperatures were conducted within the temperature range of 25–225°C., nitrogen being used as inert medium to minimize any oxidative tendencies. The temperature was raised and lowered at the rate of 2°C./min. The readings were recorded through two cycles of heating and cooling. Only the second cycles are presented, however, since, as observed in this and earlier studies,^{1,3} mechanical adaptations of the yarn takes place during the heating phase of the first cycle. Thereafter, during the cooling phase and both phases of subsequent cycles the curves are reproducible.

RESULTS

Density

The density of the cellulose decreases progressively with substitution, as is seen by reference to Figure 1. The hyperbolic equation relating density d to degree of substitution S was found to be

$$d = 1.316 + 0.093/(S + 0.434) \quad (1)$$

in general agreement with the effect of introducing other substituents^{1,2} into the cellulose molecules. It will be noted that the density of the untreated control (1.536 g./cc. Table II) is somewhat less than that of native cellulose (ca. 1.55 g./cc.) and at theoretical maximum substitution would, according to eq. (1), approach 1.343 g./cc. The density at maximum substitution appears to be slightly greater than that (1.333 g./cc.) computed for benzhydryl cellulose³ at the same DS.

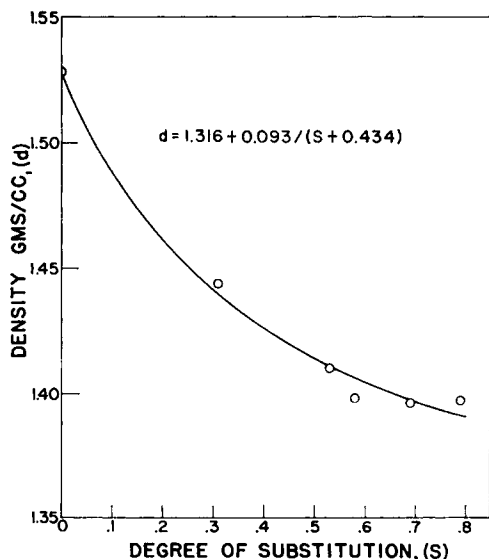


Fig. 1. Density of mercerized cotton cellulose and of products of different degrees of trityl substitution.

Crystallinity

The x-ray diffractograms of the control samples and of the chemically reacted samples are shown in Figure 2.

By reference to the figure it is evident that the untreated, commercially mercerized sample O(I) contains a considerable portion of native cellulose. The peaks of the native cellulose at $2\theta = 14.7^\circ$, 16.3° , and 22.6° are largely replaced in the activation treatment by the corresponding cellulose II peaks at $2\theta = 12.0^\circ$, 20.0° , and 22.0° . Incomplete conversion of the native x-ray pattern of cellulose to that of the regenerated pattern has been observed, repeatedly, in commercial practice. Crystallinity estimation by the modification of Patil et al.⁹ of the Wakelin method¹⁰ for the untreated control gave 35% cellulose I and 43% cellulose II, with 22% amorphous. The corresponding figures for the treated control were 10% cellulose I, 53% cellulose II, and 37% amorphous.

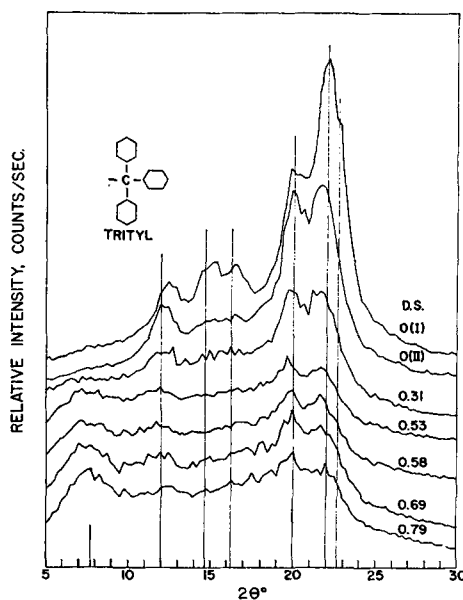


Fig. 2. X-ray diffractograms of commercially mercerized cotton cellulose O(I) and remergerized cellulose O(II) and of the latter reacted to different degrees of trityl substitution (figures at right end of curve).

Reaction of the activated cellulose with the trityl chloride leads to further rapid loss of crystalline structure so that at a substitution of $DS = 0.53$ the original lattice diffraction peaks are largely lost. At the same time, a peak begins to develop at $2\theta = 7.70$, corresponding to the 101 lattice spacing of the tritylated cellulose. It appears that the cellulose cannot accommodate more than one bulky triphenylmethyl group⁴ per anhydroglucose unit and that such introduction disrupts the crystalline structure. This disruption occurs at a much lower substitution than in the case of benz-

hydryl groups³ where the diffraction peaks were still evident at DS greater than 1.

Thermal Behavior

The thermal stability of the several samples is indicated in Figures 3 and 4.

By reference to the panels for the two control samples [Fig. 3, O(I) and O(II)] it will be observed that the DTA curve proceeds exothermically throughout the heating range. All of the panels corresponding to tritylated cellulose, however, show an endotherm beginning at about 300°C. with minima at 323–327°C. It is concluded that these endotherms are associated with the scission or loss of triphenylmethane, which begins at about 285°C. and apparently becomes rapid at these temperatures ending at about 310°C. According to Stanonis,⁴ degradation would begin already at 180°C., but at this temperature a long (12 hr.) induction period is required. Figure 3 also shows that the rapid loss of weight of cellulose alone or of the substituted cellulose begins at a temperature below 300°C. and that

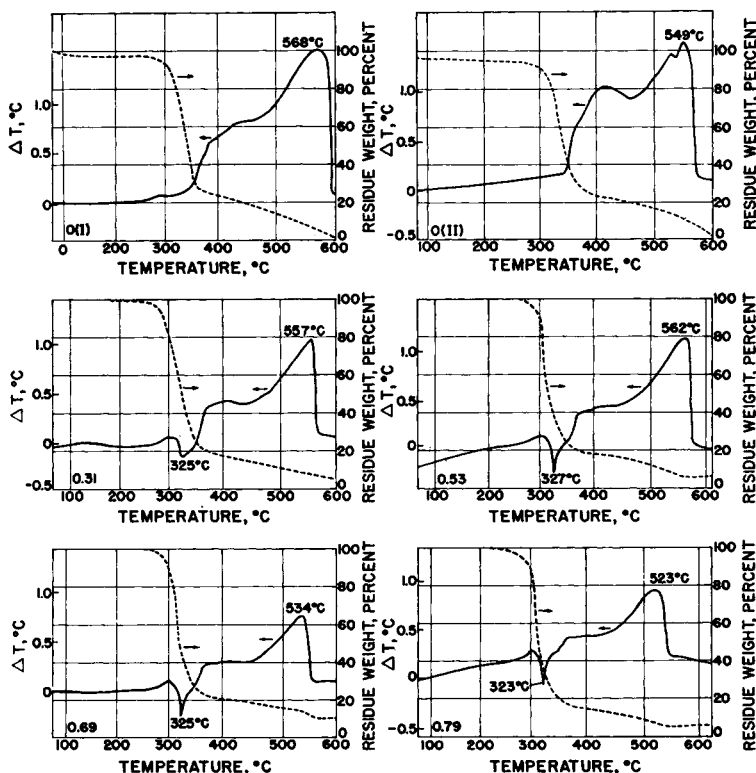


Fig. 3. Differential thermal (—) and thermogravimetric (---) curves for the control samples O(I) and O(II) and the reacted samples (DS) shown in lower left corner of each panel.

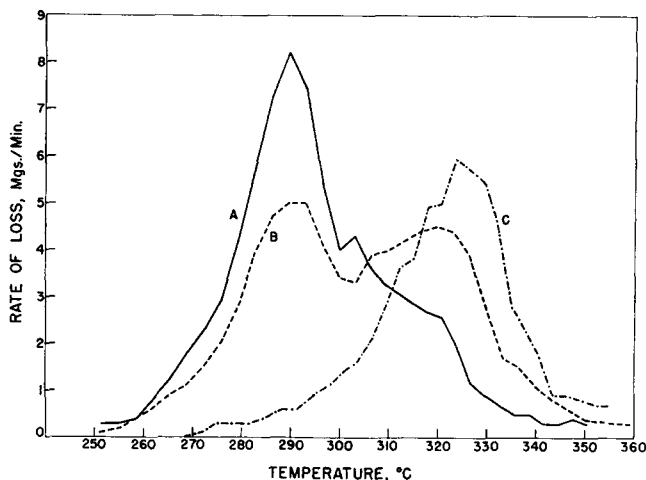


Fig. 4. Thermogravimetric rate curves: (A) trityl cellulose, DS = 0.69; (B) trityl cellulose, DS = 0.31; and (C) treated control, O(II).

approximately 75–80% of the weight disappears when the temperature reaches 350°C. This is in line with the parallel behavior of benzhydrylated celluloses in helium.³ By careful inspection of Figures 3 and 4 it can be concluded that the weight loss in the substituted samples occurs at a lower temperature than does that of the controls.

A clearer picture of the weight loss can be obtained from Figure 4. Curve A for a tritylated sample with DS = 0.69 shows a maximum rate of weight loss at 290°C. This corresponds with the left peak of curve B for the tritylated sample with DS = 0.31. Curve C for the treated control begins decomposition at about 270°C. and has its maximum at 325°C. It is deduced that the high peak of curve A is due largely to scission and loss of triphenylmethane. This sample contains over 50% by weight of triphenylmethyl. Presumably, the shoulder in the rate loss at the high temperature side of this curve is due to residual unsubstituted anhydroglucose units of the cellulose. In the case of curve B, there seem to be two distinct stages in the weight loss, the first due to triphenylmethane and the second to unsubstituted portions of the cellulose. It was ascertained experimentally that liberated triphenylmethane would disappear completely below 250°C. It may be concluded, therefore, that scission of the triphenylmethyl group which occurs at a considerably higher temperature is strongly restricted by its attachment to the cellulose.

Tensile Properties

Results of tensile tests on the samples are presented in Table II, in order of increasing degree of substitution. The breaking strength is expressed both on the basis of the tex of the untreated control (adjusted breaking load) and as tenacity, which takes into account the added

TABLE II
Properties of Tritylated Cotton Yarns

DS	Strength		Elongation, %	Stiffness, g./tex	Work of rupture, g./tex	Density, g./cc.	Mois- ture, %
	Breaking, g./tex ^a	Tenacity, g./tex ^b					
O(I) ^c	25.1	25.1	6.3	398	0.79	1.536	—
O(II) ^d	27.0	26.8	18.9	142	2.67	1.528	6.8
0.31	26.8	15.7	16.3	96	1.28	1.444	4.6
0.53	19.0	9.4	15.3	61	0.72	1.410	2.8
0.58	20.0	7.8	12.8	61	0.50	1.398	2.3
0.69	14.8	7.2	11.8	61	0.42	1.396	2.0
0.79	3.3	1.4	17.3	8	0.12	1.397	1.7

^a Breaking load expressed in tex of untreated control.

^b Strength expressed in terms of tex of treated control, O(II).

^c Untreated control, commercially mercerized.

^d Control exposed to all conditions of reacted samples except trityl chloride for 240 min.

substituent weight. The column of breaking strength shows that remercerizing of the commercially mercerized yarn leads to about 8% increase in breaking load. This increase is associated with nearly complete loss (90%) of the native crystalline structure of the cellulose (see Fig. 2). The increase is nearly all retained upon trityl substitution of DS = 0.31. Above that substitution and extending to about DS = 0.58 tensile loss amounts to about 20% of the original control. Further substitution is associated with additional loss of breaking load which becomes very damaging at the highest substitution.

The strength losses are much more significant when weight increases are included in the expression of tenacity. Thus, on a weight basis all substitution is attended with substantial losses.

Especially interesting is the increase of elongation at break. It is evident that the original control yarn was mercerized with tension, since otherwise the breaking elongation would have been much larger. The remercerization, which forms a part of the present treatment, results in high elongation values which gradually decline with progressive substitution with the exception of the most highly substituted sample. No doubt these values are to a considerable extent the result of contractions and the tensions applied during treatment and during rewinding when employed.

The tensile stiffness calculated from the tenacity value decreased as a result of the remercerizing step, and further, though somewhat irregularly, with progressive substitution. These values are comparable with those observed in other chemical treatments.¹⁻³

The work of rupture undergoes relatively large changes with treatment. Relatively normal in the original control, the value increases greatly as a result of remercerization, influenced perhaps by considerable contraction during this step. Part of this increase is retained still at the lowest substitution, but thereafter the work of rupture decreases rapidly below the

control with progressive chemical reaction, becoming negligible at the highest substitution.

Stiffness at Elevated Temperatures

The course of tensile stiffness of the unreacted control and of the products of reaction within the range of 25–225°C. is shown for the second cycle in Figure 5. The control undergoes only minor fluctuations with heating. Introduction of a small amount of trityl groups (DS = 0.31) results in a major reduction of tensile stiffness at all temperatures, with the possible exception of about 200°C., where a type of discontinuity seems to occur. Samples of other substitutions (with the exception of DS = 0.58) also show reductions of stiffness generally, although, here too, there appear to be discontinuities at the higher temperatures. The behavior is approximately comparable to that of benzhydrylated yarns³ at a similar DS and cycle of heating.

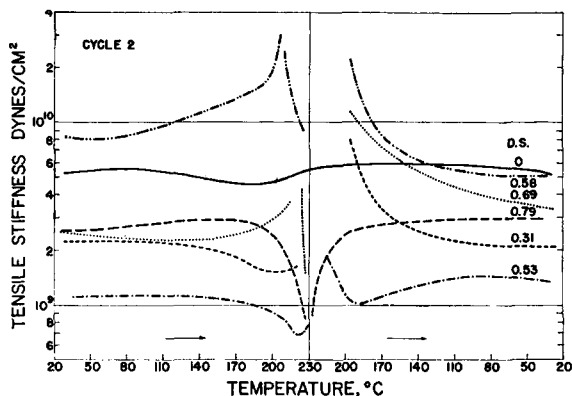


Fig. 5. Tensile stiffness of the control yarn O(I) and of the reacted yarns as a function of temperature (DS shown at right of curves).

Elastic Recovery at Elevated Temperatures

Elastic recovery of the yarns within the range 25–225°C. is shown in Figure 6. As can be seen, the elastic recoveries undergo relatively symmetrical changes with temperature. The substituted samples generally show considerably improved elastic recovery relative to that of the control at temperatures up to about 150°C. Above this temperature elastic recovery of the yarns deteriorates greatly as they approach their flow temperature. There is evidence for a second-order response in one of the yarns at about 150°C.

Comparison of the curves of Figure 6 with those of Figure 5 of a previous paper³ suggests that elastic recovery of tritylated celluloses is generally better than that of benzhydrylated celluloses of similar substitutions. It is approximately comparable to that of the acetylated celluloses,¹ though at much lower DS.

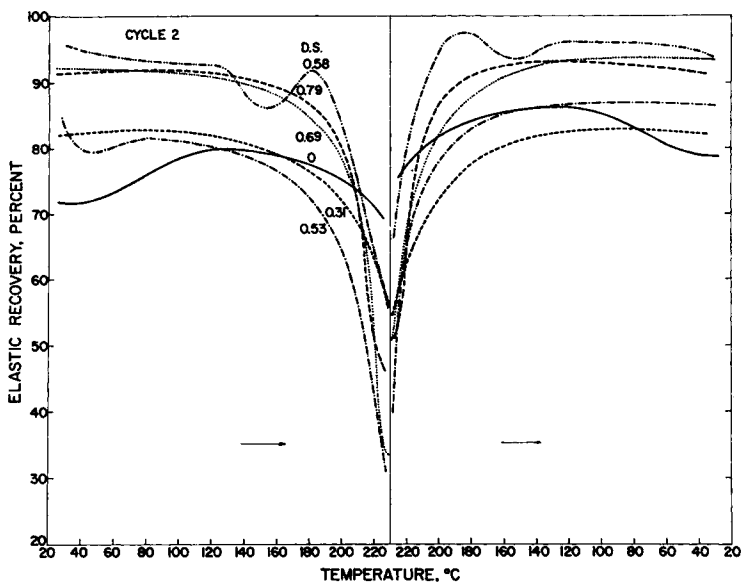


Fig. 6. Elastic recovery of the control yarn O(I) and of the reacted yarns as a function of temperature (DS of yarns shown at center).

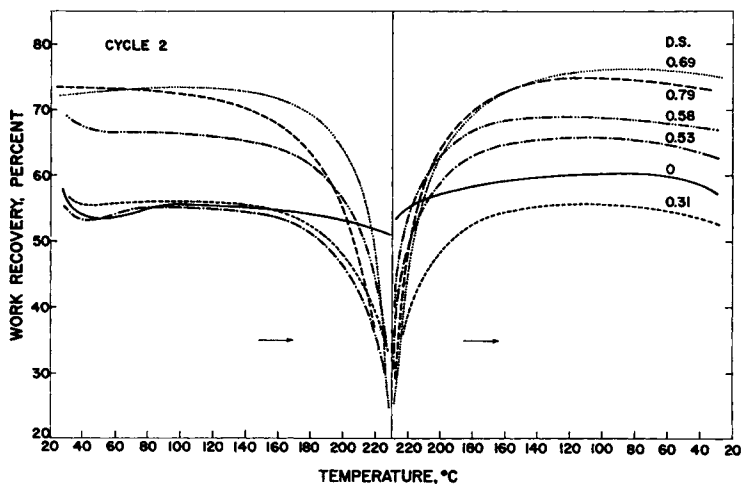


Fig. 7. Work recovery of the control yarn O(I) and of the reacted yarns as a function of temperature (DS shown at right end of curves).

Work Recovery at Elevated Temperatures

The work recovery of the different yarns during the second cycle is shown in Figure 7. Although these represent total energy expended and recovered (rather than dimensional changes), these curves largely reproduce those of elastic recovery. Work recoveries during both heating and cooling cycles are distinctly improved over those of benzhydrylated celluloses³ of

comparable substitution. Also, they were much superior to those of the acetylated celluloses of comparable DS.¹

DISCUSSION

The results described above indicate that celluloses in the form of commercially mercerized yarn can be etherified with trityl chloride in pyridine, though to a considerably lower substitution than in the reaction with benzhydryl bromide,³ the maximum substitution being limited to about 26% of the hydroxyl groups. The products retain satisfactory tensile properties up to a substitution of DS = 0.6, after which considerable loss of strength occurs. The decrease of density as substitution increases is quite comparable to that observed with benzhydrylated cotton yarns³ and is indicative of decreasing crystallinity. If anything, for comparable substitution, the tritylated yarns have higher densities, but the difference is less than 1%. Interestingly, too, the separation of the 101 lattice plane of the unit cell of the partially etherified celluloses is almost identical for benzhydryl and trityl groups, indicating that the phenyl groups are strongly flattened in both derivatives.¹¹ Perhaps considerable straining of the trityl group occurs during the reaction as suggested by the inability to obtain substitutions equal to those of benzhydryl derivatives.

The products could be heated somewhat higher than the corresponding benzhydryl derivatives without loss of textile quality. In spite of the somewhat restricted substitution, as compared to the benzhydrylated yarns, they showed somewhat better elastic and work recoveries at comparable substitutions. This may be due to the repulsive effects of the electrons in the neighboring phenyl groups, which are accommodated in approximately the same space confines as the two phenyl groups in the benzhydrylated celluloses. On the other hand, the trityl celluloses show better elastic and work recovery than do acetylated yarns of the same degree of substitution. It is probable that the bulkiness of the trityl group, compared to the small volume required by the acetyl group, is the principal factor here.

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