Rapid Acetylation of Native Cellulose by TFAA and Characterization of the Products*

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Synopsis

Acetylation of cellulose (Whatman cellulose powder CF-11 and Egyptian cotton fiber) by the use of the TFAA "impelling" method was examined, and the decrease in the degree of polymerization (DP) during the reaction was determined. Cellulose triacetate can be readily prepared by the TFAA method. When Whatman cellulose powder was used, the degradation of cellulose during acetylation was not observed in reaction times up to 5 hr, and a slight decrease in the degree of polymerization was detected in samples after reaction for more than 12 hr. The number of chain scissions per cellulose molecule for Egyptian cotton fiber was similar in magnitude to that for Whatman cellulose at the reaction time of 8 hr, but the value for Egyptian cotton fiber was considerably larger compared with that for Whatman cellulose after 12 hr.

INTRODUCTION

Although various methods and techniques for the preparation of cellulose acetate have been reported, acetylation with acidic catalysts is the simplest and most convenient. A considerable decrease in the degree of polymerization of cellulose occurs during acetylation with acidic catalysts.[1] On the other hand, acetylation to cellulose triacetate, by means of a pyridine–acetic anhydride system without an acidic catalyst, causes a small degree of degradation.[2,3] However, the disadvantages of this latter method are first that peracetylation of native cellulose is extremely difficult (the cellulose derivatives up to cellulose diacetate can usually be obtained, whereas triacetylation can be realized only by utilizing regenerated cellulose) and, second that a rather long reaction period is required.

Bourne et al.[4] showed that cellulose triacetate can be prepared by reacting cellulose with an acetic acid–trifluoroacetic anhydride (TFAA) mixture for 1 hr at 60°C, where TFAA works as a condensing agent. Although they had no direct measure of the degree of degradation of the polysaccharide chain during this treatment, it did not appear extensive. Barclay et al.[5] acetylated a sample of bacterial cellulose using treatment with acetic acid–TFAA.

This article is concerned with the acetylation of two kinds of native cellulose by means of the acetic acid–TFAA method in which chloroform is used as a diluent. The relation between the conditions of acetylation, particularly the length of the reaction period, and the degree of number-average polymerization $\overline{DP}_n$, of the cellulose acetate was examined. Cellulose trinitrates were also prepared from corresponding cellulosic materials and the values of their $\overline{DP}_n$ were mea-

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sured and compared with those for cellulose acetates, because almost no degradation of the cellulose chains is considered to occur during nitration.

EXPERIMENTAL

Samples

Whatman cellulose powder CF-11 and Egyptian cotton fiber were used as native cellulose samples. Whatman cellulose powder CF-11 was first extracted with ethanol–benzene (1:1) mixture and then with acetone for 10 hr. It was then washed with distilled water, air dried, and vacuum dried at 40°C. Egyptian cotton fiber was successively extracted with ethanol and ether for 6 hr, boiled with 1% NaOH aqueous solution in an atmosphere of nitrogen, and washed with hot water and cold water, successively. Then, it was neutralized with 1% acetic acid, washed thoroughly with distilled water, and dried in air and in a vacuum.

Acetylation

TFAA (3 to 6.6 ml), acetic acid (1.5 to 4 ml), and chloroform (20 ml) were mixed together and stirred at a definite temperature (40 or 50°C) for about 20 min for solvation of acetic acid and TFAA. This solution was added to 0.3 g of dried cellulose, and placed in a 50-ml Erlenmyer flask equipped with a condenser. The reaction was continued for a definite period at 40 or 50°C with stirring. At the end of the reaction, the solution was poured into an excess of methanol and the precipitate was filtered. The crude product was extracted with deionized water for 48 hr in order to remove acids. The fibrous ester was thoroughly washed with distilled water, before being dried at 40°C in a vacuum.

Determination of Degree of Substitution (DS)

Sample acetate (0.1 g) was vacuum dried at 100°C, weighed, and transferred to a stoppered Erlenmyer flask containing 2 ml of 75% ethanol and 5 ml of 0.5N sodium hydroxide aqueous solution. After standing for 48 hr at room temperature, 5 ml of 0.5N sulfuric acid was added, and after an additional 4 hr, the solution was titrated with 0.5N sodium hydroxide aqueous solution. Bromothymol blue–phenol red was used as the indicator. From this procedure, the acetyl content (% Ac) and the value of DS were obtained [eqs. (1) and (2)]:

$$\% \text{ Ac} = [(A\,B - C\,D) \times 4.3]/W \tag{1}$$

where W is weight of cellulose acetate (g). A and B are titrating amount (ml) and normality of sodium hydroxide solution, respectively. C and D are amount (ml) and normality of sulfuric acid solution, respectively;

$$\text{DS} = 3.86 \times (\% \text{ Ac})/[102.4 - (\% \text{ Ac})] \tag{2}$$

Nitration

Phosphorus pentoxide (202 g) was added to fuming nitric acid (450 g) with mild stirring, and then 50 ml of distilled water sufficiently cooled by ice was slowly added in 2- to 3-ml portions. This nitrating agent was placed in a reagent bottle and was allowed to stand for about 2 hr in a freezer at −20°C.

To 1 g of dried cellulose, 100 ml of the nitrating agent was added. After reaction for 20 hr at −20°C, the product was filtered, washed with deionized water previously cooled with ice (2 liter), and distilled water (200 ml), successively. The cellulose nitrate thus obtained was immersed in methanol for about 2 hr, before being dried first in air and then in a vacuum at room temperature.

DS of the product was calculated by the following equation:

$$DS = 3.60 \times N/(3.11 - N) \tag{3}$$

where N is the content (%) of nitrogen found from elementary analysis.

Determination of $\overline{DP}_n$ for Cellulose Acetate and Cellulose Nitrate

The number-average molecular weights of cellulose acetate and nitrate determined by Knauer Electronic Membrane Osmometer were used to calculate the corresponding values of $\overline{DP}_n$. The molecular weight for cellulose acetate was measured at 25°C using chloroform (specially prepared reagent for spectrometric usage) as the solvent; for cellulose nitrate, the experiment was run at 27°C using tetrahydrofuran (specially prepared reagent for chromatographic usage). Regenerated cellulose film was used as the membrane in both cases.

RESULTS AND DISCUSSION

Figure 1 shows the results of acetylation of Whatman cellulose powder under various reaction conditions. When chloroform was not used as a diluent, that is, in the system of 6.6 ml TFAA–4.0 ml acetic acid, peracetylation is attained after 2 hr. When chloroform is used as a diluent, cellulose is converted to its acetate with a DS of only slightly less than 3 after 3 hr of reaction at 50°C. However, when the reaction temperature is 40°C, even after 48 hr of reaction, a part of the cellulose remains undissolved in the reaction solution and the DS realized is far less than the value of 3. In this case, values of DS obtained by use of the systems with reaction conditions of 5.0 ml TFAA–2.5 ml acetic acid–20

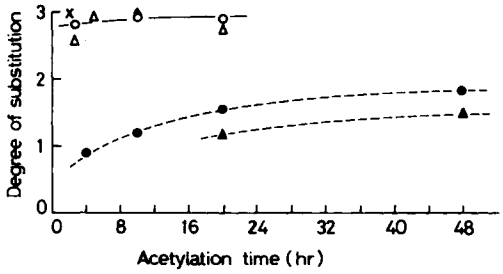

Fig. 1. Degree of substitution vs. acetylation time for Whatman cellulose powder. (×) TFAA 6.6 ml, acetic acid 4.0 ml, at 50°C, (○) TFAA 5.0 ml, acetic acid 2.5 ml, $CHCl_3$ 20 ml, at 50°C, (△) TFAA 4.0 ml, acetic acid 2.0 ml, $CHCl_3$ 20 ml, at 50°C, (●) TFAA 5.0 ml, acetic acid 2.5 ml, $CHCl_3$ 20 ml, at 40°C, (▲) TFAA 4.0 ml, acetic acid 2.0 ml, $CHCl_3$ 20 ml, at 40°C.

ml $CHCl_3$ and 4.0 ml TFAA–2.0 ml acetic acid–20 ml $CHCl_3$ are 1.83 and 1.52, respectively.

As noted above, peracetylation is readily attained at 50°C within a short reaction period utilizing the reaction system of TFAA (5.0 ml)–acetic acid (2.5 ml)–$CHCl_3$ (20 ml). The relation between the reaction time and the value of DS is shown (Fig. 2). A large difference in the acetylation reaction rate is found between the two cellulose species. In the case of Whatman cellulose powder, the reaction goes essentially to completion after 3 hr, while peracetylation of Egyptian cotton fiber is realized after 8 hr. This difference in reactivity between the two kinds of cellulose samples must be due to differences in specific surface areas and molecular weights of the samples. Whatman cellulose powder has a larger specific surface area than Egyptian cotton. This facilitates diffusion of the acetylating agent into the inner part of the cellulose, favoring the reaction and the dissolution of acetylated cellulose into the reaction solution from the surface of the solid cellulose sample. Whatman cellulose has the degree of polymerization $\overline{DP}_n$ of 228 which is one order less than that of Egyptian cotton ($\overline{DP}_n$ = 2100). This fact also enables the cellulose acetate to dissolve easily and rapidly into the reaction medium during acetylation.

Cellulose acetates obtained by the TFAA method do not show absorbance due to —$COCF_3$ group in their IR spectra and the IR spectra coincides quite well with those of cellulose acetates obtained acidic catalysts.

The reaction time dependence of the number average degree of polymerization $\overline{DP}_n$ of cellulose triacetate obtained by TFAA method was also examined. The relation between the acetylation period and $\overline{DP}_n$ for Whatman cellulose powder is shown (Fig. 3). In various acetylation trials the progress of acetylation was

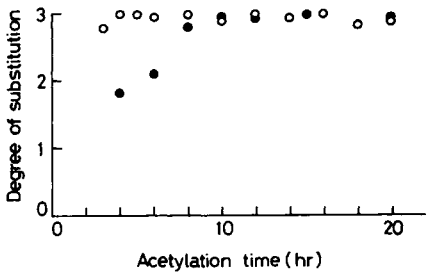

Fig. 2. Degree of substitution vs. acetylation time. Cellulose 0.3 g, TFAA 5.0 ml, acetic acid 2.5 ml, $CHCl_3$ 20 ml, at 50°C; (○) Whatman cellulose powder; (●) Egyptian cotton fiber.

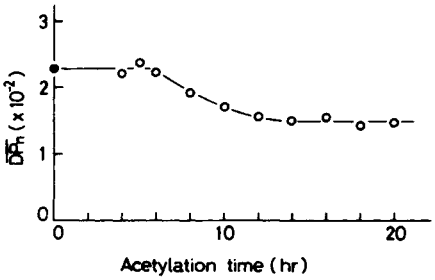

Fig. 3. $\overline{DP}_n$ vs. acetylation time for Whatman cellulose powder. The reaction condition is described (Fig. 2). (○) Cellulose triacetate; (●) cellulose trinitrate.

accompanied by a decrease in the molecular weight of cellulose. In order to get a comparative standard, cellulose trinitrate (nitrogen content 14.13%, DS = 3) was prepared using a modification of Staudinger's method[6] which minimizes the degradation of cellulose during the reaction, and $\overline{DP}_n$ of the nitrate was determined.

No alteration in the value of $\overline{DP}_n$ was observed in the reaction up to 6 hr (Fig. 3); no degradation of the cellulose chain occurs during this reaction period. The value of $\overline{DP}_n$ then decreases to about 150 between 6 and 12 hr reaction time, after which the value $\overline{DP}_n$ is kept constant. Barclay et al.[5] reported that the number of chain scissions per cellulose molecule is 1.4 during peracetylation by treatment with TFAA–acetic acid without any diluent. Although the reaction temperature in this experiment (40 or 50°C) is higher than Barclay's experiments at room temperature, the number of chain scissions per cellulose molecule found in this experiment are smaller than reported by Barclay. That is, the number of scissions per cellulose chain are 0.2 after 8 hr and 0.5 after more than 12 hr of acetylation. The low level of chain scission encountered in this experiment may be due to the use of chloroform as a diluent.

The relation between the acetylation period and $\overline{DP}_n$ for Egyptian cotton fiber is shown (Fig. 4). Because of the lower reactivity of the cellulose sample as well as the insoluble character of low-substituted cellulose acetate in chloroform, the value of $\overline{DP}_n$ can be determined by the Knauer Osmometer only for the samples acetylated for long periods. In the reaction period after 12 hr, the values of $\overline{DP}_n$ for cellulose triacetate are held constant at about 300 (Fig. 4). When this value is compared with the $\overline{DP}_n$ value for the corresponding cellulose nitrate (nitrogen content 13.08, DS = 2.61), the number of chain scissions per cellulose molecule becomes 6. This number of chain scissions is considerably larger than those obtained in Whatman cellulose powder. However, the value of $\overline{DP}_n$ for cellulose acetate prepared after 8 hr of acetylation is 1280, corresponding to 0.6 chain scission per cellulose molecule. This degree of chain breaking is the same as that with the Whatman cellulose powder. The values of DS found for cellulose acetate attained after 4- and 6-hr reactions are 1.83 and 2.08, respectively, and the corresponding acetates are insoluble in chloroform, making it impossible to measure the value of $\overline{DP}_n$. However, it can be expected from the results obtained for Whatman cellulose powder, that the number of chain scissions per cellulose molecule are less than 0.6 for Egyptian cotton fiber within the 6-hr reaction time. It is important to note the following as a possible explanation for the difference between two cellulose species in the degree of degradation during acetylation.

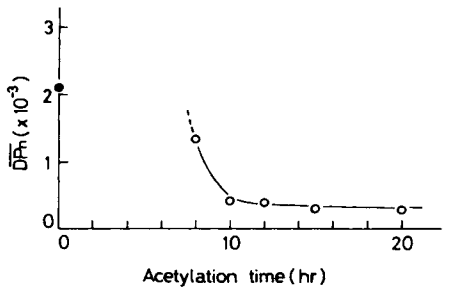

Fig. 4. $\overline{DP}_n$ vs. acetylation time for Egyptian cotton fiber. The reaction condition is described (Fig. 2). (○) Cellulose triacetate; (●) cellulose nitrate.

Whatman cellulose powder was previously purified and hydrolyzed in weak acid, while Egyptian cotton remained in a natural state. It is recognized that in natural cellulose a few weak bonds are contaminated in its chain linkage. This weak bond contamination has been removed from Whatman cellulose, while Egyptian cotton retains a few weak bonds in its chain bonding. This difference between the two cellulose species in chain formation can explain the difference in the number of chain scissions during acetylation.

TFAA is a convenient method for acetylating native cellulose without encountering serious degradation.

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