Periodate Oxidation of Cellulose by Homogeneous Reaction

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Synopsis

Homogeneous periodate oxidation of cellulose was achieved through methylol cellulose. The dissolution of methylol cellulose into aqueous periodate solution was followed by the gradual decomposition of methylol groups at random sites along the methylol cellulose chain. The recovery of glycol hydroxyl groups at the C_2 and C_3 positions on the glucopyranose ring during the above decomposition process caused uniform cleavage of C_2—C_3 bonds by the periodate ion. The oxidation level reached nearly 100% in 10 h. The reduced product of the resulting dialdehyde cellulose, i.e., dialcohol cellulose, resulted in mechanical properties quite different from those of conventional dialcohol cellulose. Examination of the thermal deformation and tensile properties revealed that no notable cellulose degradation occurred during the reaction. Our dialcohol cellulose gave a clear and transparent film with a flexible nature.

INTRODUCTION

Periodate oxidation of cellulose is characterized by inducing the selective cleavage of the C_2—C_3 bond of the glucopyranose ring.[1] The reaction is accompanied by the formation of reactive dialdehyde units at the C_2 and C_3 sites. The resulting product (henceforth called dialdehyde cellulose) has the potential for preparing new cellulose derivatives which are composed of a nonglucopyranose ring backbone. It is well known, however, that cellulose is not soluble in water, though its presence is essential to periodate oxidation; the oxidation of cellulose cannot take place uniformly, but occurs first in its accessible regions, and then more slowly in the rest of the material as its crystalline structure gradually breaks down. Because of this heterogeneous reaction, a period of 1 week or more is required for the preparation of high oxidized dialdehyde cellulose.[2] Prolonged reaction causes further notable cellulose degradation due to the side reaction occurring at the reducing end groups, even if conditions are chosen in such a way that the side reaction is minimized. Thus, little attention has been paid to periodate oxidation as a derivatization method of cellulose, although partial periodate oxidation of cellulosic materials such as cotton and paper has been studied for improving their physical properties.[3-6]

In recent years fiber production using DMSO solution of methylol cellulose in place of viscose has been attempted. In this case, methylol cellulose promptly decomposes to regenerated cellulose in the presence of excess water. However, if the decomposition rate of methylol cellulose in water is slowed enough compared to the above, then the methylol cellulose is thought to maintain the solution state for several hours.

The present article describes the homogeneous periodate oxidation method of cellulose using methylol cellulose. For the resulting dialdehyde and its borohydride-reduced product, dialcohol cellulose, thermomechanical properties were investigated.

EXPERIMENTAL

Preparation of Methylol Cellulose

Eight grams of dried cellulose powder (Whatman cellulose CF-11) and 14 g of paraformaldehyde well dispersed in DMSO (200 mL) were stirred gently at 120°C for 180 min. After the resulting transparent solution was cooled to room temperature, it was poured into excess methanol to obtain precipitates. The precipitates were filtered, and the crude product was repeatedly washed with methanol.

Preparation of Dialdehyde Cellulose

The freshly prepared methylol cellulose (equivalent to 10 g of cellulose) was dissolved in a solution of sodium metaperiodate (17.15 g) in water (500 mL). It was stirred at 20°C for a definite period (60–700 min) in the dark. After the excess periodate was decomposed with ethylene glycol, the solution was poured into excess methanol. The product was filtered, and repeatedly washed with methanol.

Dialdehyde cellulose was also prepared by the conventional method.[2] Cellulose powder (10 g) was dispersed in a solution of sodium metaperiodate (17.15 g) in water (500 mL). It was continuously stirred mildly at 20°C for about 1 week. The subsequent procedures to obtain samples were similar to the above.

Preparation of Dialcohol Cellulose

A freshly prepared aqueous solution of sodium borohydride (160 mL) (NaBH$_4$/water = 8 g/200 mL) was added dropwise to the dialdehyde cellulose (equivalent to 10 g of cellulose) suspended in 400 mL of water. It was then stirred gently at about 3°C for 2 h. In order to terminate the reduction, dilute acetic acid was added to the reaction mixture. This solution was then poured into cold methanol. The precipitates were washed with cold methanol repeatedly. Different variables of time and NaBH$_4$ quantity were also applied to examine various reduction conditions.

Determination of Oxidation and Cleavage Levels

We have defined the oxidation level of dialdehyde cellulose as the amount of periodate, expressed in the quantity of periodate per 100 anhydroglucose units, consumed in the preparation of dialdehyde cellulose. Periodate consumption was determined by measuring the absorbance at 290 nm of supernatant liquid, which is similar to that reported by Maekawa and Koshijima.[2] Instead of the oxidation level, the cleavage level is also used for dialcohol cellulose prepared by the reduction of corresponding dialdehyde cellulose.

Both values are identical, and they indicate the measure of the number of open ring units due to oxidative cleavage.

Measurement of Thermal Deformation

A thermomechanical analyzer (Shinku Riko Co. Ltd., TM-1500) was used for measurements of thermal deformation. A 25-mg powdered sample was compressed in a glass capillary by a plunger, 1.4 mm radius, which was driven by a weight of 200 g. As the temperature was raised, the sample softened and the plunger moved downward. The deformation of the sample was measured automatically as a function of temperature *in vacuo*. The measurements were conducted over a temperature range from 20 to 150°C at a programmed heating rate of 1°C/min.

Static Tensile Test

Static tensile tests for film specimens (26.5 × 1.26 × 0.17 mm), which were molded to film in a laboratory press at their fluid temperatures, were carried out in a conditioned room (20°C, 65% RH) using an Instron type testing instrument (Shinkoh Communication Industry Co., TOM-5000X). Elongation was applied to the specimen at a constant speed of 1 mm/min.

RESULTS AND DISCUSSION

In accordance with the conventional periodate oxidation procedure, we prepared dialdehyde cellulose with a high oxidation level (80% or higher) over 1 week reaction. Figure 1 shows the thermal deformation diagrams for this dialdehyde cellulose, its reduced product [dialcohol cellulose(I)], and cellulose itself. These diagrams exhibit normalized deformation D: D is zero at room temperature, and unity at the temperature at which the plunger in TMA reached the bottom of the glass capillary, indicating completion of liquid flow of the sample. Although cellulose itself does not exhibit any deformation in the diagram except for the apparent deformation due to carbonization at around 300°C, it is observed that the dialdehyde cellulose reveals a remarkable transition at around 220°C. Because the cleavage of $C_2 - C_3$ bonds of the glucopyranose ring in dialdehyde cellulose is considered to facilitate cellulose chain mobility (see formula I in Fig. 2), this transition can be regarded as having been due to the glass transition of the dialdehyde cellulose examined. In general, however, the aldehyde groups at C_2 or C_3 sites are believed to form intra- or interchain crosslinks to a certain extent as shown in formula II in Figure 2. It is, therefore, plausible that dialdehyde cellulose does not melt, but shows apparent deformation due to the carbonization at around 300°C.

On the other hand, since the reduction to the hydroxyls of all the aldehydes present in dialdehyde cellulose destroys such crosslinks, the dialcohol cellulose reveals a fluid state at around 200°C. Dialcohol cellulose exhibits another transition appearing just before the flow. This transition can be ascribed to the glass transition of the sample examined. It should be noted that since the side reaction causes remarkable decomposition of the cellulose chain during extended oxidation and/or subsequent reduction reaction, we resulted in obtaining the dialcohol cellulose whose glass transition and melting tempera-
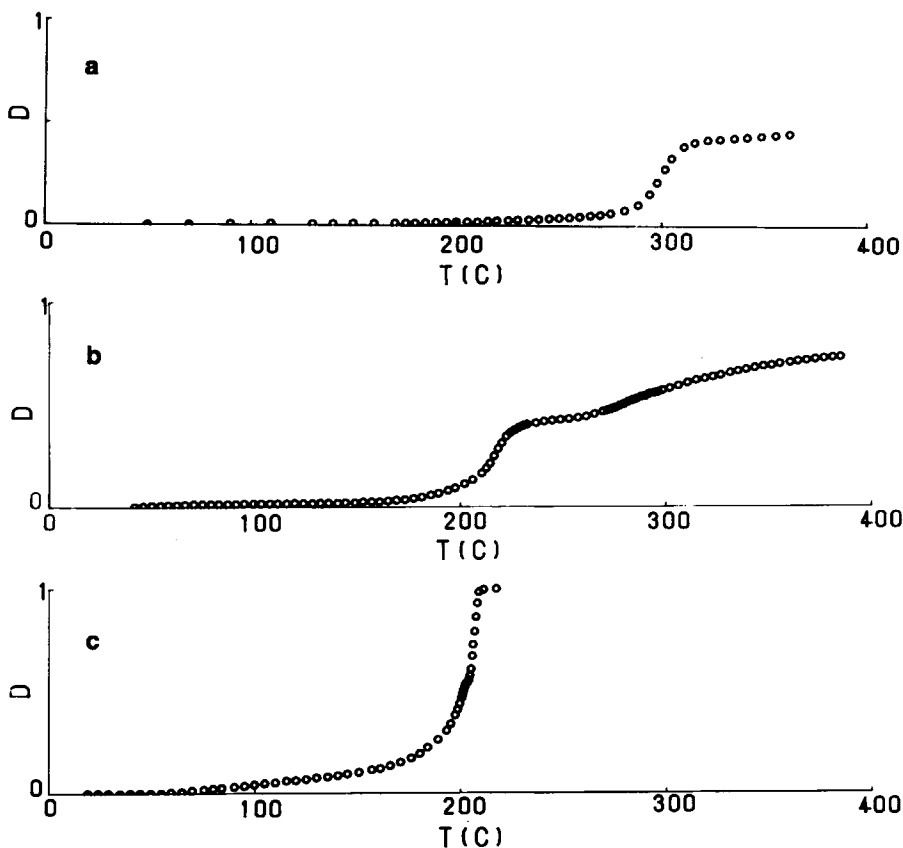
Fig. 1.   Diagram of thermal deformation D vs. temperature for dialdehyde and dialcohol cellulose prepared by conventional method, along with cellulose: (a) cellulose; (b) dialdehyde cellulose; (c) dialcohol cellulose(I).
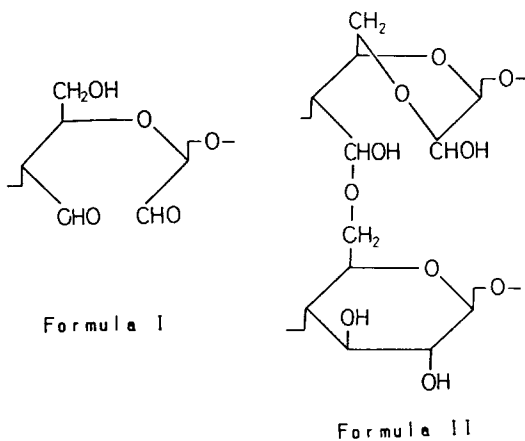
Formula I

Formula II

Fig. 2.   Chemical structures of dialdehyde cellulose.

tures were too close for clear distinction. As a result, this dialcohol cellulose was not appropriate for film application because of its brittle nature.

In order to avoid or suppress the chain scission during the reaction process, it seems effective to introduce the periodate oxidation reaction in aqueous solution of cellulose, since the reaction in solution is expected to proceed homogeneously and rapidly enough to avoid chain scission. As mentioned above, however, cellulose is not soluble in water because of its high interchain cohesive force due to the presence of hydrogen bonds which result in the crystalline nature of cellulose. This difficulty may be avoided by using trisubstituted methylol cellulose[7] as a starting material rather than cellulose itself.

It is well known that in a basic aqueous medium methylol cellulose decomposes rapidly to regenerated cellulose, because of its unstable hemiacetal structure. However, as long as it does not decompose, methylol cellulose itself is essentially soluble in water. In fact, when the decomposition rate is suppressed by acidic aqueous medium, methylol cellulose maintains solution state in water for a certain time (Δt) prior to the decomposition. Δt can be regarded as a rough measure of the decomposition rate, and is defined as the time interval between the time when clear aqueous solution of trimethylol cellulose is freshly prepared and the time when the precipitates of regenerated cellulose due to the decomposition arise. The appearance of precipitates can be detected by observing that the clear solution becomes unclear. Figure 3 displays the variation of Δt as defined above, against the pH values of the aqueous methylol cellulose solution. The pH values are adjusted by the
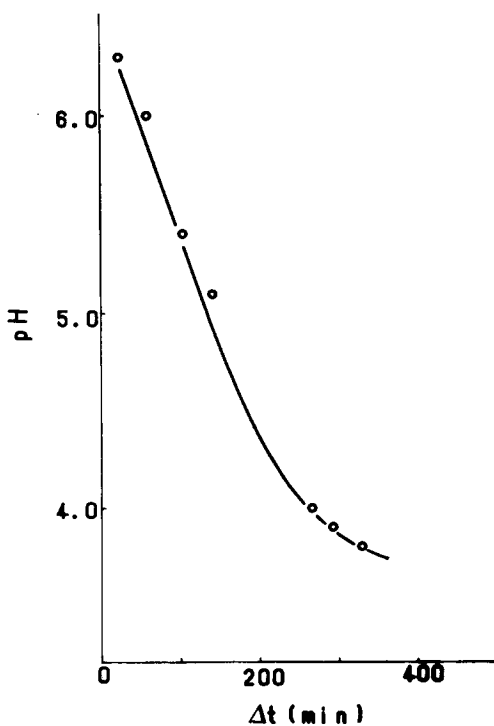

Fig. 3. Variation of decomposition rate of methylol cellulose in water with pH value.

addition of dilute acetic acid to the solution. It is apparent from the figure that at pH 6.2 methylol cellulose decomposes rapidly, and precipitates appear in 10 min. However, the decomposition rate becomes slower with decreasing pH values, and finally at pH 3.8 the solution state continues for 320 min. It should be noted that the oxidation in our study is carried out at pH 4. Thus, methylol cellulose is expected to remain soluble in water long enough to realize homogeneous periodate oxidation.

Since the decomposition of methylol groups is considered to occur at random positions along the methylol cellulose chain, glycol hydroxyl groups at C_2 and C_3 positions are therefore recovered at random sites. Accordingly, if periodate ions coexist in this system, the recovered sites of glycol units should receive oxidative cleavage in solution. Successive recovery and oxidation of glycol units results in periodate oxidation in solution. This process is illustrated schematically in Figure 4.

In the following, the results for periodate oxidation of the methylol cellulose in aqueous solution are discussed. Figure 5 represents the relationship between the oxidation level and the reaction time for methylol cellulose. In the figure the results for cellulose, at a time corresponding to that for methylol cellulose, are also included for reference. In contrast to the results for cellulose, the oxidation level for methylol cellulose increases markedly with the passage of time, reaching 80% in about 600 min. Further reaction time (ca. 1200 min) leads to a product with an over 100% oxidation level. It should be emphasized here that the reaction continues in the solution state not only in the initial stage but also throughout the entire course. This indicates that the dialdehyde cellulose produced is also soluble in water; though once water is removed, it becomes water-insoluble because of the formation of interchain crosslinks. In this connection, the dialdehyde cellulose produced conventionally did not become soluble in water, even when the oxidation level reached 80% or higher. This suggests that even though the apparent oxidation level is
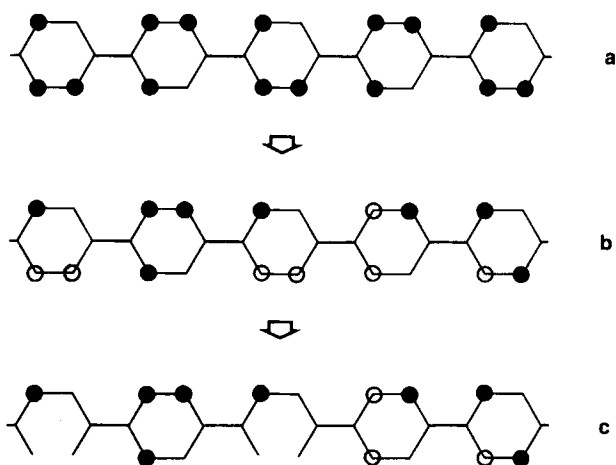

Fig. 4.   Mechanism of homogeneous periodate oxidation of methylol cellulose in solution: ($\bullet$) —O—CH$_2$—OH; (O) —OH; (a) methylol cellulose (DS = 3); (b) partial decomposition of methylol groups (DS = 1.6), and the recovery of glycol hydroxyl groups; (c) oxidative cleavage of recovered glycol portion.
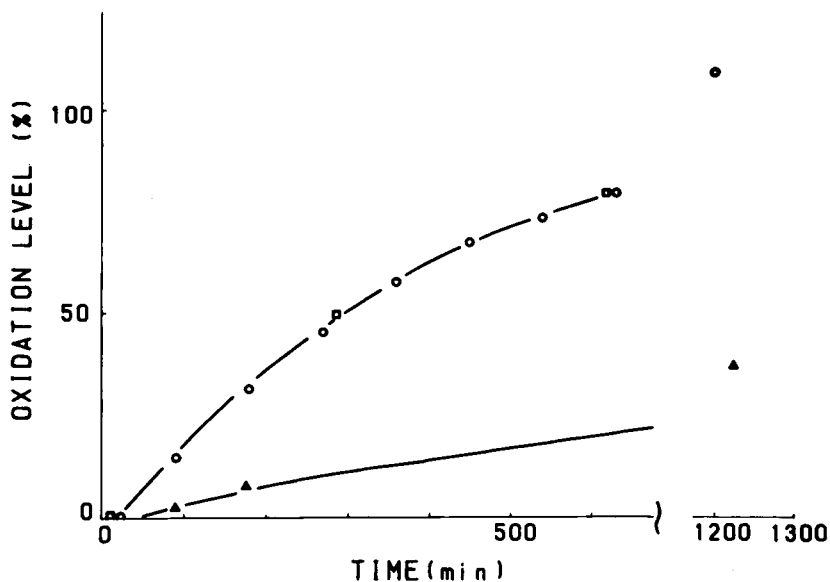
Fig. 5.   Oxidation rate for methylol cellulose (O, □) and cellulose (△).

high, the reaction of cellulose is still heterogeneous and a large amount of periodate is consumed in the side reaction. Therefore, the periodate oxidation method employed in this study can be regarded as being more effective than the conventional method.

Figure 6 shows thermal deformation diagrams for dialdehyde and dialcohol cellulose(II) (oxidation or cleavage levels of 80% or more) we obtained. With respect to dialdehyde cellulose, the deformation process is similar to that of dialdehyde cellulose in Figure 1. This is thought to arise from the formation
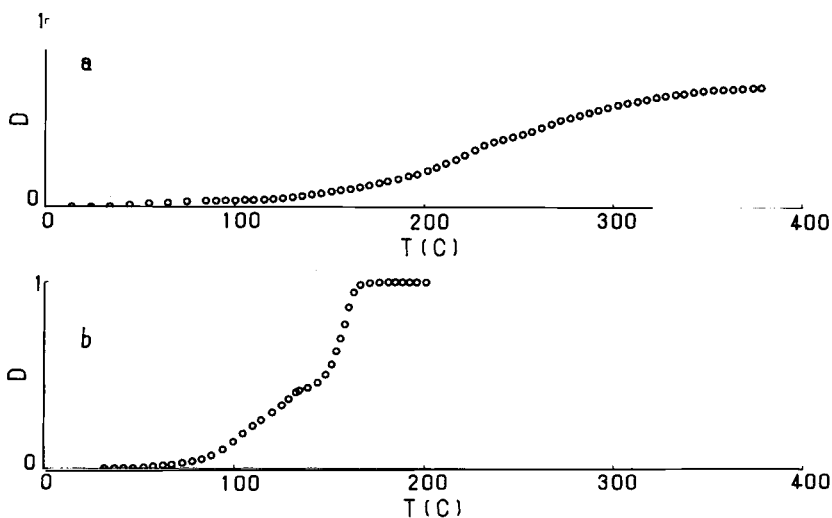

Fig. 6.   Diagram of thermal deformation D vs. temperature for dialdehyde and dialcohol cellulose prepared from methylol cellulose: (a) dialdehyde cellulose; (b) dialcohol cellulose(II).

of interchain crosslinks which cause a network structure similar to that of dialdehyde cellulose in Figure 1. On the other hand, dialcohol cellulose(II) shows a quite different deformation pattern from that for dialcohol cellulose(I) in Figure 1. Although the dialcohol cellulose(II) exhibits both the glass transition and flow regions in the diagram, these regions appear at considerably lower temperatures than those of the dialcohol cellulose(I). It can be further observed that in dialcohol cellulose(II) the glass transition region appears removed from the flow region. These two facts are respectively considered to be a result of the higher actual cleavage level and the lower chain degradation for the dialcohol cellulose(II), though the apparent cleavage level for both products are similar.

The above consideration is supported by the difference in tensile properties between the dialcohol cellulose(I) and (II). Figure 7 demonstrates a typical load elongation diagram for the dialcohol cellulose(I) and (II). As the diagram shows, while the dialcohol cellulose(I) is hard and brittle, the dialcohol cellulose(II) is almost in a fluid state at 20°C and 65% RH. Furthermore, the dialcohol cellulose(II) exhibits surprisingly great elongation, reaching ca. 600%.

In relation to the above deformation pattern for dialcohol cellulose, we have to examine the reduction condition of dialdehyde cellulose for obtaining dialcohol cellulose. Table I summarizes amounts of $NaBH_4$ and reaction times employed for reducing dialdehyde cellulose with 80% or more oxidation level. All the reaction conditions employed here are chosen so as to reduce dialdehyde cellulose enough to dissolve in water. The thermodiagrams for the products corresponding to the respective conditions in Table I are shown in Figure 8. From the figure, we may observe that both the onset of fluid state and glass transition regions move to lower temperatures as the amount of
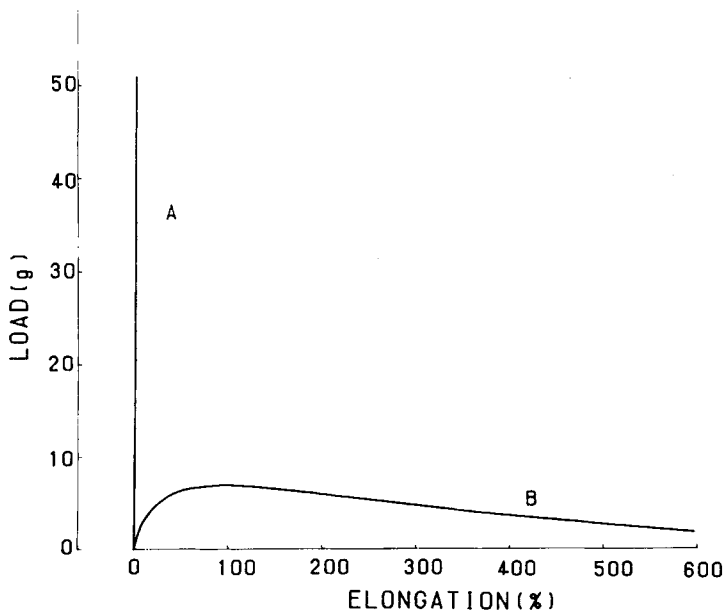

Fig. 7. Typical load elongation curve of both dialcohol cellulose(I) (A) and (II) (B) measured at 20°C and 65% RH.

TABLE I
Relationship Between Reduction Time and the Amount of NaBH$_4$ (mol) Used
for Reducing 0.1 mol of Dialdehyde Cellulose

NaBH$_4$ (mol)	Reduction time (min)	Symbol
0.053	52	○
0.053	140	■
0.105	140	□
0.105	480	◻
0.173	40	□
0.173	100	●
0.350	40	△
0.350	100	△
0.350	470	△

NaBH$_4$ and reduction times increase. This is considered a result of the increased flexibility of the chain. The flexibility arises from the increase in dialcohol portion, since the conversion of dialdehyde to dialcohol is accompanied by the breaking of crosslinks formed at the aldehyde portions. However, the diagram reaches stasis in the case of NaBH$_4$, 0.35 mol, and 100 min, indicating completion of reduction of all dialdehyde groups in the sample. Accordingly, this condition proves sufficient for the reduction of dialdehyde cellulose. Our reduction condition used in this article has satisfied this condition.

Homogeneous oxidation of cellulose through methylol cellulose should also result in systematic change in the thermal properties of dialcohol cellulose according to its cleavage levels. Figure 9 illustrates thermodiagrams for dialcohol cellulose with different cleavage levels. It is clear that with increasing cleavage level both the glass transition and flow regions shift to lower temperatures. This can be interpreted as follows: Since the products are regarded as random copolymers composed of glucopyranose units and open
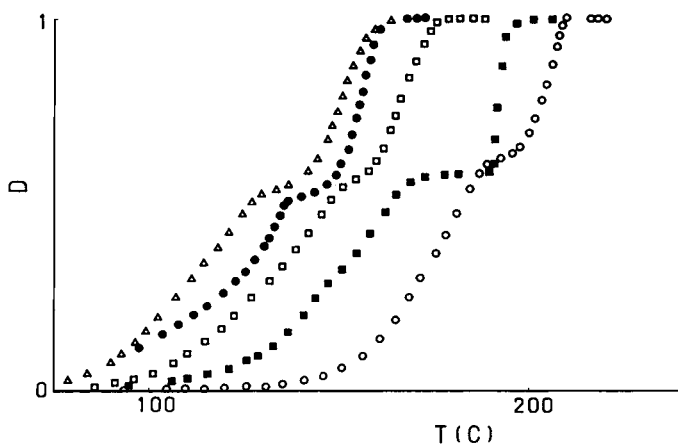

Fig. 8.   Diagram of thermal deformation D vs. temperature for partially reduced dialdehyde cellulose. The symbols used here are the same as those in Table I.
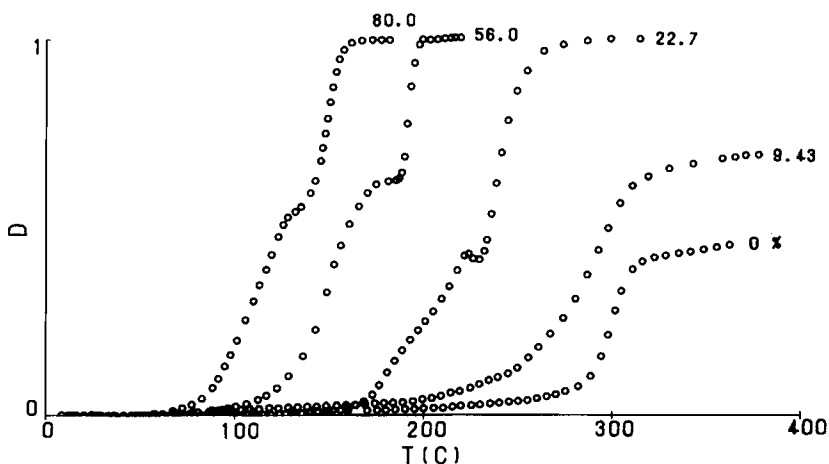
Fig. 9. Variation of thermal deformation properties of dialcohol cellulose with cleavage level.

ring units (linear chain units) due to oxidation, the increase in open ring units causes further flexibility of the main chain, which decreases both glass transition and flow temperatures. In this connection, we have studied thermal deformation properties of both acetylated[8] and cyanoethylated[9] cellulose series substituted to different degrees by homogeneous reactions. Varying the amount of substitutent induced changes in deformation similar to those described above. Hence, such a picture of the change in deformation properties is considered to be characteristic of polymers prepared by homogeneous reaction.

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