

Cyanoethylated Cellulose Prepared by Homogeneous Reaction in Paraformaldehyde-DMSO System

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Synopsis

A series of cyanoethylated celluloses with various degrees of substitution was prepared by homogeneous reaction of cellulose in PF/DMSO system. Their thermal deformation properties changed regularly with the degree of cyanoethylation. By comparing highly cyanoethylated cellulose in the series with that prepared by a traditional cyanoethylation method, it was seen that they were quite different in physical properties such as thermal deformation or tensile properties. Based on the results of dynamic mechanical measurements and infrared spectroscopy, cyanoethylated cellulose prepared in PF/DMSO system was found to be a new cellulose derivative, which includes oligo-oxymethylene groups at the position between the glucopyranose ring and the cyanoethyl group in the side chain. The maximum DS value of this cyanoethylated cellulose was estimated to be ca. 2.5.

INTRODUCTION

Cyanoethylation of cellulose can be traced back to the pioneering work of MacGregor et al. in the 1940s.¹ Since then, partial cyanoethylation of cotton cellulose has been extensively studied to improve its durability, such as thermal, chemical, and microbiological resistance. Other cellulosic materials have also been cyanoethylated to obtain a highly substituted product,² which was used as an electric material because of its high dielectric constant, although it is brittle in nature.

While these reactions proceed heterogeneously, a homogeneous cyanoethylation reaction of cellulose in viscose medium is also known.³ However, in this case, the degree of substitution seldom reaches 2.0, due to the steric hindrance of xanthate groups introduced to cellulose, and no notable products were expected from this method for practical use.

In relation to the homogeneous reaction of cellulose, recently, various types of organic cellulose solvents have been developed, and the chemical modifications of cellulose in these solvents have been investigated, including acetylation,⁴ trimethylsilylation,⁵ carboxymethylation,⁶ and hydroxyethylation.⁷

In our present work, the homogeneous cyanoethylation method of cellulose in PF/DMSO medium is presented. The physical properties of the resulting products differ substantially from those of the cyanoethylated cellulose prepared by the traditional method. For example, although the traditional products are not available for film application due to their brittle

nature, the products prepared in PF/DMSO medium give clear, transparent, and flexible films which suggests the possibility of these products being applicable to various new fields.

EXPERIMENTAL

Materials. The cellulose used is a Whatman cellulose powder CF-11. Paraformaldehyde(PF) is that for electron microscopy(98% purity) from Nakarai Chemicals (specifically prepared reagent EMS-80). Dimethyl sulfoxide (DMSO) used as a solvent, and acrylonitrile, sodium hydroxide, and sodium metal used as cyanoethylating agents, acetic anhydride, and triethylamine (TEA) used as acetylating agent are all guaranteed grade.

Preparation of cellulose solution. The detailed procedure for preparing cellulose solution was described in our previous paper.⁸ Dried cellulose powder (6 g) and PF(150 mL) dispersed in DMSO (150 mL) were stirred mildly at 120°C for 80 min. The resulting transparent solution was cooled to room temperature and left to stand.

Preparation of cyanoethylated cellulose. To the cellulose solution was added specified amount of Na/DMSO solution in which sodium metal (0.19 g) was dissolved in DMSO (50 mL), next acrylonitrile (30 mL) was added. The reaction mixture was kept at room temperature for 24 h with continuous stirring, after which it was poured into excess methanol to obtain the product. In some cases, the reaction mixture was divided into two parts, one of which was poured into excess methanol as described just above, while the other was followed by acetylation reaction described below.

In another case, an attempt was made to obtain a cyanoethylated sample by using a traditional method as a reference. Cellulose powder was immersed in a weak (3%) aqueous solution of sodium hydroxide, squeezed free of excess liquor, treated with excess acrylonitrile at 50°C for several hours, and then poured into excess water to yield the product.

Acetylation of cyanoethylated cellulose. To the resulting mixture reacted in PF/DMSO for 24 h as mentioned above, TEA (30 mL) and acetic anhydride (21 mL) were added. After mild stirring at room temperature for 2 h, it was poured into excess methanol to yield the products.

Infrared spectroscopy. Infrared absorption spectra were obtained with a Hitachi infrared spectrometer Model 260-30. Film specimens cast from DMSO, or KBr pellet specimens were used for measurements.

Measurements of thermal deformation. The thermal deformation of the sample was observed using a thermomechanical analyzer (Shinku Riko Co., Ltd., TM-1500), in which a column of the sample collapsed under a plunger which supported a constant load of 3 kg/cm², when heated at a uniform rate of 1°C/min.

Measurements of dynamic mechanical properties. Dynamic mechanical properties of the film specimens were measured with a direct reading viscoelastometer (Toyo Baldwin Co., Ltd., Rheovibron DDV-II-C) in the temperature range from -190°C to 200°C and at frequencies of 3.5,11,35, and 110 Hz.

Static tensile test. Static tensile tests for film specimens were carried out at room temperature using an Instron type testing instrument (Shinko Communication Industry Co., TOM-5000X).

RESULTS AND DISCUSSION

Figure 1 shows the infrared spectra of the products prepared by homogeneous reaction in PF/DMSO solvent system. From the absorption bands at 2950, 2250, 1480, 1420, 1370, 1330, 1270, and 1230 cm^{-1} , it appears that the cellulose is cyanoethylated. By increasing the amount of Na/DMSO added to the system, the intensity of these absorption bands due to cyanoethyl groups increases, while that of OH absorption at around 3450 cm^{-1} decreases. From this, it was found that the degree of cyanoethylation proceeds in the order of the amount of Na/DMSO. However, even if an additional amount of Na/DMSO (3.0 mL or more) is added, the intensity of above bands remains fairly constant. In this connection, it is known that the infrared spectra of cyanoethylated cellulose prepared by the conventional method often exhibit additional absorption bands due to carbamyl or carboxyethyl groups which are introduced by side reactions. However, since there is no such evidence in all spectra shown in Figure 1, our cyanoethylation method can be regarded as more effective than the conventional method.

For a qualitative analysis concerning the degree of cyanoethylation, one should note the absorbance ratio of A_{CH} at 2900 cm^{-1} to A_{OH} at 3450 cm^{-1} (i.e., $A_{\text{CH}}/A_{\text{OH}}$). Brown et al.⁹ studied infrared spectra of a series of cyanoethylated cellulose with various degrees of substitution (DS), which is prepared by homogeneous reaction in viscose, and reported that the product with DS=0.77 in the series is soluble in water. The $A_{\text{CH}}/A_{\text{OH}}$ value of this product was 0.5. It is noted that our cyanoethylated cellulose with $A_{\text{CH}}/A_{\text{OH}}=0.36$ obtained in case of Na/DMSO=1.32 mL is also water soluble.

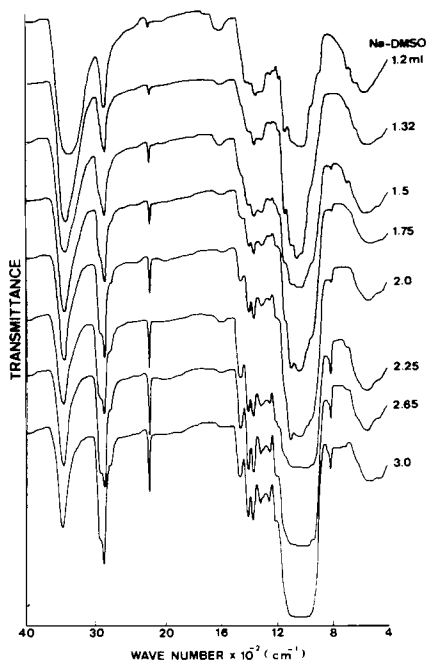


Fig. 1. Infrared spectra of the cyanoethylated cellulose prepared in PF/DMSO medium.

So far water-soluble cyanoethylated cellulose has been known to be prepared only by homogeneous reaction in viscose. Therefore, our method suggests a new way to prepare a water-soluble cyanoethylated cellulose. On the other hand, highly cyanoethylated cellulose ($\text{Na}/\text{DMSO}=3.0 \text{ mL}$) obtained by our method is soluble in dry acetone in the same manner as the conventional cyanoethylated cellulose whose DS value is 2.5 or more. Judging from high solubility in acetone and high $A_{\text{CH}}/A_{\text{OH}}$ value, DS value of the highly cyanoethylated cellulose prepared by our method is expected to be about 2.5. This will be discussed again and confirmed in the last paragraph.

The degree of reaction in cyanoethylated cellulose is usually expressed by nitrogen content. Figure 2 shows a relationship between the percentage of nitrogen contents (%N) and $A_{\text{CH}}/A_{\text{OH}}$ value for our cyanoethylated cellulose. In the figure, the result of cyanoethylated cellulose prepared by a reaction in aqueous medium (hereinafter termed as conventional CEC) is also included. It can be seen that, with increasing the value of $A_{\text{CH}}/A_{\text{OH}}$ up to ca. 1.2, nitrogen content increases, while it levels off for $A_{\text{CH}}/A_{\text{OH}}$ above 1.2. It should be noted here that the plot for conventional CEC greatly deviates from the regression curve shown in the figure: the nitrogen content of conventional CEC at $A_{\text{CH}}/A_{\text{OH}}=1.36$ is measured to be 11.3%, though 7.9% is expected from the curve. This discrepancy becomes clearer by converting the nitrogen contents of 7.9 and 11.3% into the corresponding DS value of 1.3 and 2.3, respectively, on the basis of a well-known conversion formula:

$$\text{DS}=(162 \times \%N)/(1400 - 53 \times \%N)$$

From these findings, it is suggested that a newly prepared cyanoethylated cellulose may be different in chemical composition from the conventional cyanoethylated cellulose, despite the similarity of their infrared spectra.

Figure 3 shows the diagrams of thermal deformation D in arbitrary scale against temperature with our cyanoethylated cellulose having various degrees of cyanoethylation, Whatman cellulose CF-11, and the regenerated cellulose from PF/DMSO system. The thermodiagrams labelled A to G

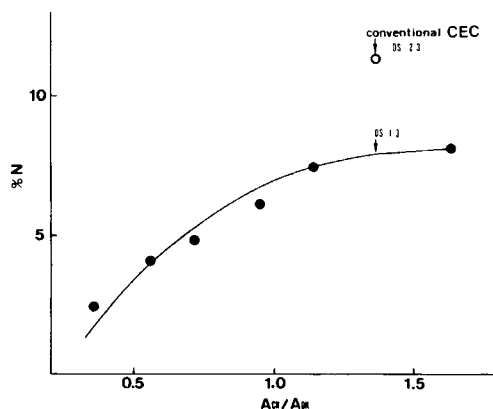


Fig. 2. Relationship between percentage of nitrogen contents (%N) in the cyanoethylated cellulose and the ratio of absorbance A_{CH} at 2900 cm^{-1} to A_{OH} at 3500 cm^{-1} ($A_{\text{CH}}/A_{\text{OH}}$).

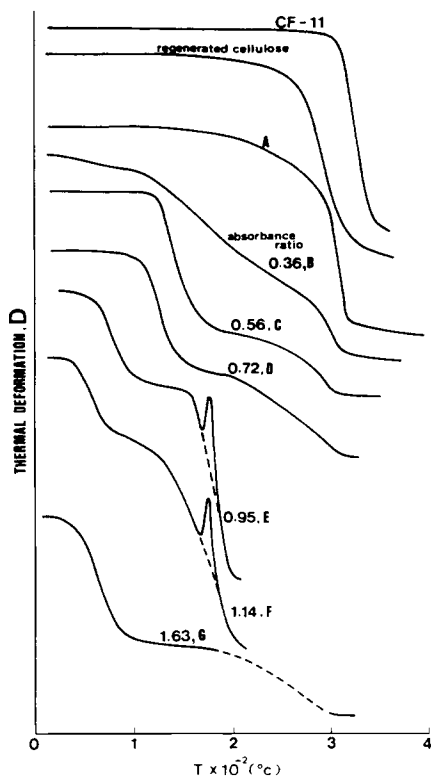


Fig. 3. Diagram of thermal deformation D in arbitrary scale versus temperature for Whatman cellulose CF-11, regenerated cellulose and cyanoethylated cellulose.

correspond to the infrared spectra in Figure 1 in case of $\text{Na}/\text{DMSO} = 1.2, 1.32, 1.75, 2.0, 2.25,$ and $3.0,$ respectively. The absorption ratio, $A_{\text{CH}}/A_{\text{OH}},$ is also shown in the figure for reference. For the Whatman cellulose, the deformation due to carbonization of the sample occurs at around $330^\circ\text{C},$ while for the regenerated cellulose it appears at a temperature 30°C lower than that for the Whatman cellulose. This lowering may be attributed to the decreased amount of the crystalline region in cellulose. The similar diagram to that of the regenerated cellulose was observed for the sample A, in which a trace amount of cyanoethyl groups was introduced in the side chain. Further cyanoethylation induced different thermal properties from those of cellulose. For the sample B which is soluble in water as mentioned before, two transition regions were recognized. The first region appeared at temperatures between 0 and $100^\circ\text{C},$ then the second region above $100^\circ\text{C},$ and finally the carbonization process occurred at about $300^\circ\text{C}.$ For the sample C, the deformation diagram exhibits a remarkable transition at around 120°C prior to the carbonization. Similar transitions were also seen for cyanoethylated cellulose from D to G. Since cyanoethylated cellulose is known to be amorphous in nature, this transition can be regarded as due to the glass-rubber transition of the sample. In this region, the temperature T_g is defined as the temperature corresponding to the dD/dT maximum. Apparently, T_g shifted to a lower temperature with increasing

A_{CH}/A_{OH} value in the range of 0.56 to 1.14, but it remained constant for $A_{CH}/A_{OH} = 1.14$ or more. T_s is considered as a rough measure of the glass transition point T_g .

If it is assumed that the chemical structure of cyanoethylated cellulose thus surveyed differs from that of conventional cyanoethylated cellulose as suggested before, then such differences may be reflected in its physical properties. Figure 4(a) shows D temperature curves for both the sample G and the conventional CEC whose A_{CH}/A_{OH} values are similar, being 1.6 and 1.3, respectively. In the Figure, D is normalized, that is unity at room temperature and zero at the temperature at which the plunger reached the bottom of the glass capillary, indicating completion of liquid flow of the sample. It can be seen that two diagrams are apparently quite different and the diagram for conventional CEC seems to correspond to what should be obtained for our sample with an intermediate degree of cyanoethylation between A and B in Figure 3, despite its highly cyanoethylated character.

Figure 4(b) shows the stress-strain diagrams for both the sample G and conventional CEC in tension measured at room temperature. In the figure, the values of Young's modulus E , ultimate strength σ and elongation ϵ for both samples are also included. Regarding conventional CEC, the diagram is that for brittle polymers. In contrast, for the sample G the diagram shows typical features for tough polymers which result in a flexible film.

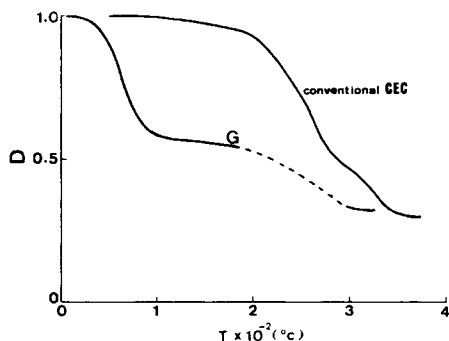


Fig. 4a. Diagram of thermal deformation D versus temperature for both G and conventional CEC

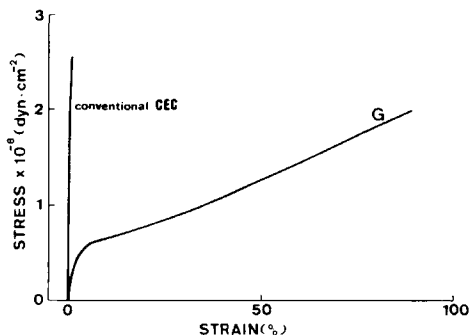


Fig. 4b. Stress-strain diagrams for both G and conventional CEC in tension measured at room temperature.

From these remarkable differences in physical properties as well as in DS mentioned before, cyanoethylated cellulose prepared in PF/DMSO medium can no longer be considered to be the same as conventional cyanoethylated cellulose in chemical structure. However, the difference should be limited to the side chain portion, because these polymers have the same cellulose backbone.

Since the difference in molecular structure in the side chain cause different molecular relaxation mechanisms, such differences must be reflected in their viscoelastic properties in the solid state. Figure 5 shows the variation of dynamic modulus E' , and loss modulus E'' with temperature for both the conventional CEC and the sample G in the range from -190 to 200°C at 110 Hz. With respect to E'' , three relaxation processes were observed for both samples within the experimental frequency and temperature ranges. They are labelled α_{CEC} , β_{CEC} , and γ_{CEC} for the conventional CEC, and α_G , β_G , and γ_G for the sample G, respectively, in order of decreasing temperature at which they were detected. Noting the conventional CEC first, the drop in E' in the α_{CEC} region was very large. On the other hand, it has been reported that the drop in Young's modulus for highly cyanoethylated cotton yarn at a corresponding temperature region is also very large, being regarded as due to the glass-rubber transition of the sample.¹⁰ Therefore, the α_{CEC} process is considered to result from the short-range diffusional motion of the segment along the main chain (i.e., the micro-Brownian motion).

The γ_{CEC} process is explained with the aid of the results of dielectric measurements for cyanoethylated cellulose after Mikhailov et al.¹¹ They reported that the orientational polarization of cyanoethyl groups present

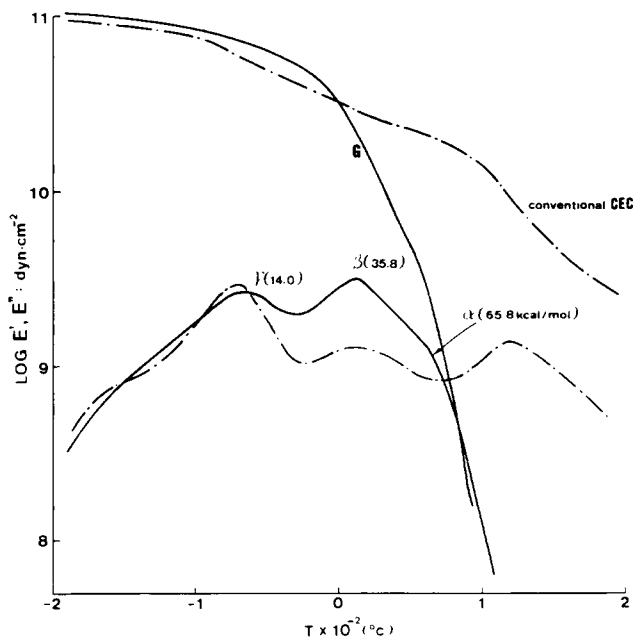


Fig. 5. Variation of dynamic modulus E' and loss modulus E'' with temperature for both G and conventional CEC at 110 Hz.

in cellulose side chain caused a dielectric relaxation in the temperature and frequency ranges comparable to those for γ_{CEC} process. From this evidence, the γ_{CEC} process can be attributed to the motion involving the cyanoethyl groups of the side chain. The cause of the β_{CEC} remains to be assigned. This process may be ascribed to a kind of complex motion of the conventional CEC and water contained.

Noting the sample G next, both E' and E'' temperature curves were again quite different from those for the conventional CEC as in the other physical properties mentioned above. Concerning E'' temperature curve, both the β_{G} and γ_{G} processes revealed a distinct peak, while the α_{G} process appears as a high temperature shoulder to the β_{G} peak. On the other hand, the $\tan \delta$ temperature plots in the α_{G} region exhibited a marked peak but those in the β_{G} and γ_{G} regions give a shoulder. Hence, the apparent activation energy, ΔE , for the α_{G} process was determined from $\tan \delta$ temperature curves and those for the β_{G} and γ_{G} processes were determined from E'' temperature curves. With respect to the α_{G} process, the maximum value of $\tan \delta$ exceeds unity and the ΔE value is calculated to be 65.8 kcal/mol, which is of the order of principle dispersions. In addition, the change in value of E' in this region is very large, extending from 5.0×10^9 to 1.3×10^8 dyn/cm⁻² at temperatures between 60 and 110°C. From this, the α_{G} process is considered to be due to the glass-rubber transition. Furthermore, the glass transition temperature of the sample G appeared considerably below that of the conventional CEC. This phenomenon seems intimately related to the molecular mechanism of the β_{G} process.

The β_{G} process exhibiting a marked peak in E'' temperature curve induces a remarkable change in E' , extending by one order in magnitude in the temperature range between -20°C and 80°C. The ΔE value for the process is calculated to be 35.8 kcal/mol, which is almost of the order of the principal dispersions. These quantities characterizing the β_{G} process seem to be unexpectedly large in magnitude, though they are observed in the glassy state.

In the following, an attempt was made to clarify the molecular relaxation mechanism of both the β_{G} and γ_{G} processes. In relation to this, the findings for the acetylated cellulose prepared by acetylation in PF/DMSO medium are worth reviewing.⁸ This acetylated cellulose is called cellulose oxymethylene ether acetate, CAcOM, whose chemical structure is different from conventional acetylated cellulose in that oxymethylene oligomer is introduced at the position between glucopyranose ring and acetyl group. The introduction of oxymethylene oligomer results from dissolving cellulose in PF/DMSO medium wherein cellulose is converted to the hydroxy oxymethylene ether of cellulose. For CAcOM, two relaxation processes were observed in the glassy state. One stems from micro-Brownian motion along the side chain independent of the micro-Brownian motion along the main chain, resulting in a large relaxation such as the β_{G} process. The other arises from the motion of the intervening oxymethylene group between glucopyranose ring and acetyl group, and it appears in the vicinity of the γ_{G} process. It should be noted that since the sample G is also obtained by the reaction of cellulose in PF/DMSO medium, it is most probable that the side chain of the sample G is not composed of cyanoethyl group, but instead,

it consists of $-(\text{CH}_2\text{O})_n-\text{CH}_2-\text{CH}_2-\text{CN}$ group. If this is the case, the micro-Brownian motion along the side chain as in CAcOM is responsible for the β_G process in the sample G.

However, cyanoethylation of cellulose oligo-oxymethylene ether in the presence of slight amount of strong basic catalyst such as NaOH or NaH results in rapid elimination of hydroxy oligo-oxymethylene side group because of its unstable hemiacetal structure. Therefore, it is necessary to clarify whether or not the introduced hydroxy oligo-oxymethylene group in the side chain is removed when Na/DMSO is used as a catalyst. Figure 6 shows E'' versus temperature curves at 110 Hz for the sample B, acetylated B and CAcOM below room temperature. For the sample B, a large relaxation process at around -50°C is observed, and the process can be attributed to the motion of methylol group in a similar manner as that in cellulose, since the sample B was not cyanoethylated to a great extent as shown in Figure 1. On the other hand, for the acetylated B the relaxation process due to $-\text{CH}_2\text{OH}$ motion disappears, and instead, two other processes appear at around -75°C and -5°C , respectively. It should be noted that these two processes correspond closely to those for CAcOM. In addition, the thermodiagram for acetylated B is also similar to that for CAcOM. Therefore, the acetylated B is regarded as almost the same as CAcOM, indicating that the process in higher temperatures is due to the micro-Brownian motion of the side chain and the process in lower temperature is due to the motion of oxymethylene groups which is located in the position between glucopyr-

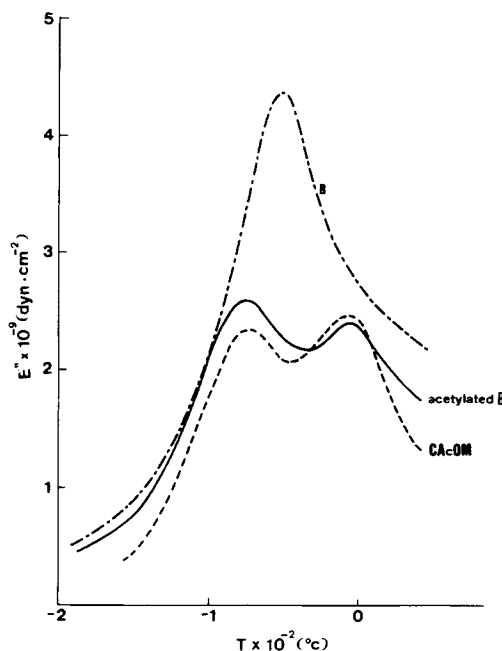


Fig. 6. Variation of loss modulus E'' with temperature for B, acetylated B and CAcOM at 110 Hz. Acetylated B was prepared by acetylation in the reaction mixture which gave B when it was poured into excess methanol. See also acetylation of cyanoethylated cellulose described in the experimental part.

anose ring and acetyl groups. From these findings, it was concluded that the formation of hydroxy oligo-oxymethylene group in PF/DMSO was little affected even if basic catalyst, Na/DMSO, is added to the system.

However, it is not yet clear whether or not oxymethylene oligomer is introduced at the intermediate position between glucopyranose ring and cyanoethyl groups. For the purpose of elucidating this point, E'' temperature curves at 110 Hz for the sample G, acetylated G and CAcOM are compared in Figure 7. For the sample G, the γ_G process may include the motion of methylol groups because the absorption band due to OH groups still remains in its infrared spectrum (Fig.1). On the other hand, for the acetylated G the γ_G process shifts somewhat to a lower temperature region, decreasing in height, but it still remains despite the absence of methylol groups. This slight change of the γ_G process can be considered to be due to the extinction of the contribution of CH_2OH motion to the γ_G process. It is of interest to note that the γ_G process in acetylated G corresponds closely to the process in CAcOM which is due to the motion of oxymethylene groups between glucopyranose ring and acetyl groups. However, acetyl contents in acetylated G is small because acetylated G is highly cyanoethylated prior to acetylation. Therefore, if the oxymethylene groups are responsible for the γ_G process, they are required to be situated in the position between glucopyranose ring and cyanoethyl groups as well as between glucopyranose ring and acetyl groups. From these reasonings, it is most probable that the γ_G process in the sample G is ascribed to the motion initiated by oxyme-

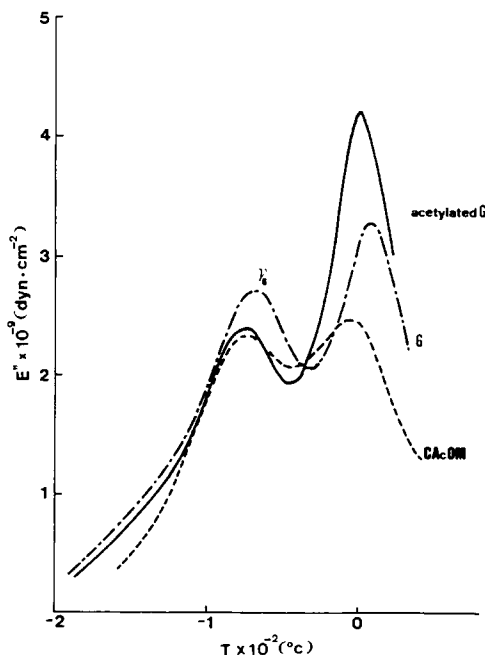


Fig. 7. Variation of loss modulus E'' with temperature for G, acetylated G and CAcOM at 110Hz. Acetylated G was prepared by acetylation in the reaction mixture which gave G when it was poured into excess methanol. See also acetylation of cyanoethylated cellulose described in the experimental part.

thylene groups in the side chain in addition to methylol groups. If such is the case, the micro-Brownian motion along the side chain (which consists of $-(\text{CH}_2\text{O})_n-\text{CH}_2-\text{CH}_2-\text{CN}$) is considered to cause the β_G process showing marked relaxation with a large ΔE value. In this connection, the release of micro-Brownian motion along the side chain induces a weakening of interchain cohesive force, facilitating chain backbone motion to lower the temperature region of the α_G process, as compared with that of α_{CEC} process.

With these considerations in mind, we should again investigate infrared spectra of the sample G. Figure 8 shows infrared spectra of the sample G, conventional CEC, and cyanoethylated xylan prepared in PF/DMSO medium. For conventional CEC, no absorption was observed at around 950 cm^{-1} . In contrast, the spectrum of the cyanoethylated xylan exhibit a distinct absorption at about 950 cm^{-1} . By noting these two spectra, it is clear that the spectrum of the sample G reveals absorption at the same band. On the other hand, it has been reported that the absorption band due to stretching vibration of methylene dioxy groups¹² appears at about 950 cm^{-1} . Consequently, it is concluded that the sample G has oxymethylene groups in the side chain as expected before, and thus cyanoethylated cellulose prepared in PF/DMSO medium is regarded as a novel cellulosic material.

It is worth remembering here, that the DS values of conventional CEC and sample G were calculated to be 2.3 and 1.3, respectively, though they seem similar in DS from their infrared spectra. The cause of this discrepancy stems from taking no account of difference in chemical structure between the sample G and conventional CEC, when their %N values are converted to the DS values. Therefore, the conversion formula usually used for cyanoethylated cellulose such as conventional CEC should be rewritten for the sample G, considering the introduction of $-(\text{CH}_2\text{O})_n$ -groups in the side chain. The result is expressed as follows:

$$\text{DS} = (162 \times \%N) / (1400 + \%N - (54 + 30n) \times \%N),$$

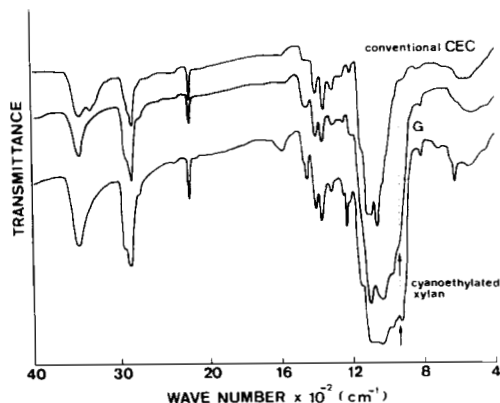


Fig. 8. Infrared spectra of conventional CEC, G, and cyanoethylated xylan. Cyanoethylated xylan was prepared from birch xylan supplied from Aldrich Co. The preparation procedure is almost the same as that for G. But, in this case, dissolution time of xylan in PF/DMSO is about 31 min, 50 min shorter than for G.

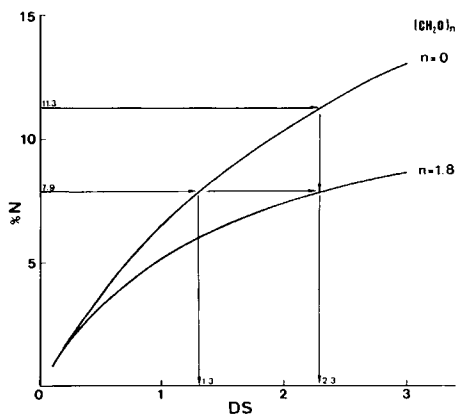


Fig. 9. Conversion diagrams of percentage of nitrogen contents (%N) to DS value for cyanoethylated cellulose with and without oxymethylene groups $-(CH_2)_n-$ in the side chain.

where n is determined as 1.8 from the corresponding NMR integral for CAcOM. In case of $n=0$, the formula agrees with conventional conversion formula for cyanoethylated cellulose. Figure 9 shows the relation between %N and DS for cyanoethylated cellulose whose n values are 0 and 1.8, respectively. From the figure, it is found that %N of 11.3 for conventional CEC and 7.9 on the curve in Figure 2 correspond to the same DS value of 2.3, when they are calculated from respective conversion formula. In the same manner, the DS value of the sample G with %N=8.3 is estimated to be about 2.5.

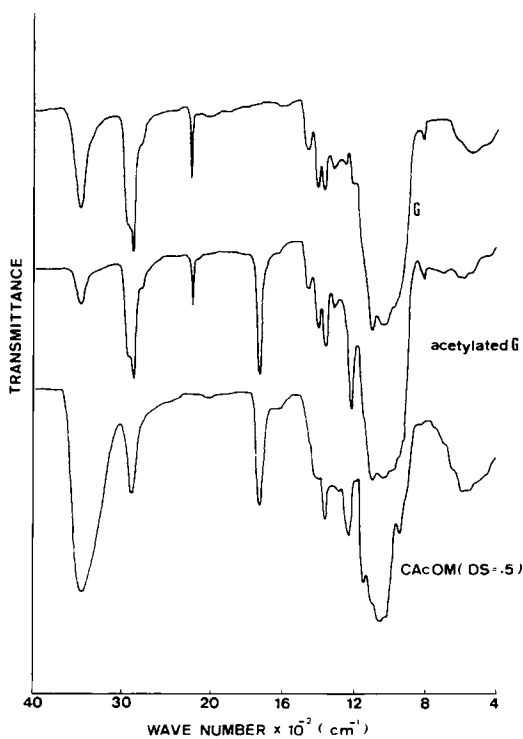


Fig. 10. Infrared spectra of G, acetylated G, and CAcOM with DS=0.5.

Further evidence for DS value of the sample G is given in Figure 10 by the comparison of infrared spectra of the sample G, acetylated G, and CACOM with DS=0.5. For the acetylated G, it is clear that there was little absorption band due to residual OH groups, while the absorption band due to C=O groups at 1750 cm^{-1} is recognized. It should be emphasized that when the absorption ratio of A_{1750}/A_{1100} is adopted as a measure of the degree of acetylation, the value of A_{1750}/A_{1100} for the acetylated G is similar to that of CACOM with DS=0.5. Therefore, it is concluded that the DS of the sample G is ca. 2.5.

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Received April 23, 1985

Accepted July 29, 1985