

Preparation of water-soluble sodium deoxycellulosesulfonate from homogeneously prepared tosylcellulose

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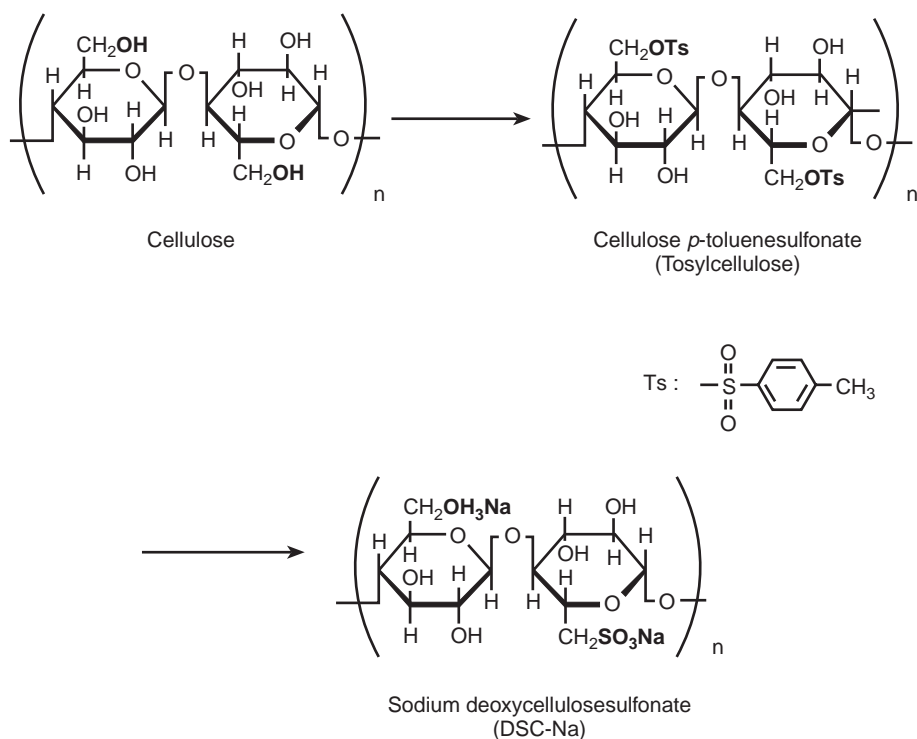
Water-soluble sodium deoxycellulosesulfonate (DCS-Na) was prepared by nucleophilic substitution of the *p*-toluenesulfonyl (tosyl) groups of cellulose *p*-toluenesulfonate (tosylcellulose) by a sulfonate group in aqueous Na₂SO₃ solution. In the substitution, the yield and degree of substitution (DS) by the sulfonate group (DS_{sul}) were found to increase with increasing reaction temperature and with reaction time, and reached up to 80% and 0.28, respectively, at 100 °C for 72 h. Although the DS of the tosyl group (DS_{tosyl}) decreased with increasing reaction temperature and with reaction time, a respectable amount of tosyl group still remained even at 100 °C for 72 h. Furthermore, the intrinsic viscosity, $[\eta]$, of the DCS-Na obtained decreased considerably with increasing reaction temperature and with reaction time. The decreases in DS_{tosyl} and $[\eta]$ were very similar to each other in that increasing DS_{sul} was independent of the reaction temperature and the reaction time. The similarity of the decreases suggests that the mechanisms of scission of the cellulose backbone and the leaving of the tosyl groups (from tosylcellulose) in the nucleophilic substitution were closely related to each other. The partial conversion of the tosyl group in the tosylcellulose to the sulfonate group, by the nucleophilic substitution, was also confirmed by the change in the IR absorption spectrum. The product could be considered to be a ter-polymer from the point of view of the AGU (anhydro glucose unit). Thus, we have AGU-co-DAGUS-Na-tosyl AGU as possible options.

KEYWORDS: sodium deoxycellulosesulfonate, cellulose *p*-toluenesulfonate, LiCl/dimethylacetamide system, intrinsic viscosity, degree of substitution

INTRODUCTION

In the previous paper (Arai and Aoki, 1994), we successfully prepared a new cellulose derivative, sodium deoxycellulosesulfonate (DCS-Na) by a nucleophilic substitution of cellulose *p*-toluenesulfonate (tosylcellulose). The (Scheme. 1) cellulose *p*-toluene sulphonate had been heterogeneously derived from microcrystalline cellulose, using a sodium hydrogen sulfite aqueous solution as a sulfonating agent under reflux in water. This approach arose as a combination of Rogovin's work (Rogovin, 1971) and the Strecker reaction (Zuffanti, 1940). Preparation of cellulosic sulfonic acids has not been reported with the exception of cellulose 2-oxyethanesulfonic acid ether (Karrer *et al.*, 1943;

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SCHEME 1. Preparation of sodium deoxycellulose sulfonate from cellulose.

Timell, 1948). The insoluble DCS-Na obtained had a degree of substitution (DS) of up to 0.22 and was identified by dyeing with Methylene Blue, which attaches to acidic groups, micro combustion tests for sulfur, incineration tests for the sulfonate and the sulfate groups, and hydrolysis–incineration tests for sulfonate groups, as well as infrared spectroscopy. In the present paper, we report the preparation of water-soluble DCS-Na derivatives having a higher degree of polymerization (DP). This was prepared from tosylcellulose which in turn had been homogeneously prepared from pulp.

MATERIALS AND METHODS

Materials

Dissolving pulp with an average DP of 960 was used as a cellulose sample. *N,N*-dimethylacetamide (DMAc) was dehydrated by the addition of Molecular Sieves 3A1/8 (Wako Pure Chemical Ind.) and distilled. All other reagent grade chemicals were used without further purification.

Preparation of tosylcellulose

Tosylcellulose was prepared according to the method reported by McCormick (McCormick and Callais 1987; McCormick *et al.*, 1990) with minor modifications. Cellulose [2.0 g; 0.0123 moles as anhydroglucose unit (AGU)] was dissolved in 100 ml of 9.0% LiCl DMAc solution and 7.7 ml (0.055 moles) triethylamine in 25 ml DMAc

was added slowly. To this solution, a solution of 10.6 g (0.055 moles) *p*-toluenesulfonyl (tosyl) chloride in 75 ml DMAc was added dropwise over a period of 1 h. The stirring was continued for 3 h at 0 °C. The reaction mixture was poured into an excess volume of methanol and the precipitate filtered and washed with methanol. It was then Soxhlet-extracted with methanol for 24 h and dried under vacuum. The product was soluble in DMAc. Elemental analysis: C, 47.2; H, 5.9, O, 43.1 S, 3.8 [calculated degree of substitution (DS) = 0.7]. Yield and intrinsic viscosity (DMAc solution) of the obtained tosylcellulose were 95 mol % (based on AGU) and 2.60 dl g⁻¹, respectively.

Preparation of DCS-Na

Tosylcellulose (1.0 g) was suspended in 100 ml of 1.9 M aqueous of sodium sulfite/sodium hydrogen sulfite (pH 7.0) and the reaction mixture heated to a given temperature, with stirring, for a given time. The reaction mixture was subjected to dialysis against running water for 1 week and then filtered. The filtrate was concentrated and mixed with a 10× vol. methanol to precipitate the water-soluble DCS-Na. The precipitate was filtered, washed with methanol, and dried under vacuum.

Determination of DS

The DS, by tosyl and by sulfonate groups (DS_{tosyl} and DS_{sul}) of the DCS-Na were determined by a combination of a microcombustion method (Schöniger, 1955, 1956) (for estimation of the total tosyl groups remaining after substitution and of total sulfonate groups) and an incineration method (Pregl-Roth, 1958) (for sulfonate group alone). Example: S%, 6.84 by microcombustion method and 2.94 by incineration method; DS_{sul} = 0.20 and DS_{tosyl} = 0.27.

Measurement of viscosity

The viscosity of DCS-Na aqueous solutions containing 0.1 M NaCl was measured with an Ubbelohde-type capillary viscometer at 25 °C. Values of $[\eta]$ were determined by extrapolation of the plot of the reduced viscosity against the polymer concentration to the concentration of zero.

IR absorption spectrum

IR absorption spectra were obtained using a double beam grating spectrometer (JASCO FT/IR-5300) using the KBr disc technique.

RESULTS AND DISCUSSION

Water-soluble DCS-Na was prepared by the nucleophilic substitution of the tosylcellulose with 1.9 M aqueous sodium sulfite sodium hydrogen sulfite (pH 7.0) as a sulfonating agent at various temperatures. In the present experiment, the tosylcellulose with DS_{tosyl} of 0.70 was used because in a preliminary experiment further increase in DS_{tosyl} of tosylcellulose in the homogeneous tosylation of cellulose, either by increase in the amount of reagents used or with longer reaction time, was confirmed to make $[\eta]$ of the tosylcellulose obtained considerably lower. Furthermore, the present substitution is an S_N2 type reaction and the tosyl group at C6 carbon is replaced solely by a sulfonate group.

Fig. 1 shows changes in the yield of water-soluble DCS-Na obtained by the

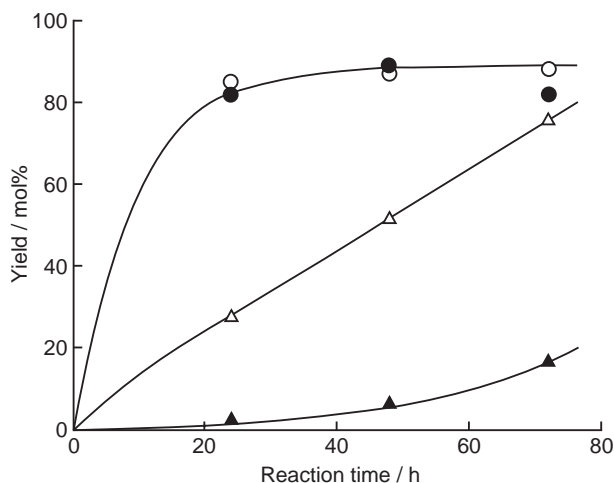


FIGURE 1. Changes in yield of water-soluble sodium deoxycellulosesulfonate (DCS-Na) obtained by nucleophilic substitution of cellulose *p*-toluenesulfonate (tosylcellulose) in 1.9 M aqueous sodium sulfite sodium hydrogensulfite (pH 7.0) as a sulfonating agent at various temperatures, with reaction time. Intrinsic viscosity ($[\eta]$) in *N,N*-dimethylacetamide and degree of substitution (DS) by tosyl group (DS_{tosyl}) of tosylcellulose used are 2.6 dl g^{-1} and 0.70, respectively. Reaction temperature ($^{\circ}\text{C}$): \circ , 100; \bullet , 90; \triangle , 80; \blacktriangle , 70.

sulfonation of tosylcellulose at various temperatures. It is found that although the yield at 70 $^{\circ}\text{C}$ is very low due to a large amount of residual insoluble fraction, it increases with increasing reaction temperature up to 90 $^{\circ}\text{C}$ and then shows a tendency to plateau. The yield increases with reaction time, considerably at lower reaction temperatures, and only slightly at temperatures above 90 $^{\circ}\text{C}$ over 24 h. The yields are up to about 80 mol% (based on AGU).

Fig. 2 shows changes in DS_{sul} of water-soluble DCS-Na obtained at various reaction temperatures versus reaction time. DS_{sul} increases with increasing reaction temperature and with reaction time in the manner similar to that of the yield. The increase in DS_{sul} becomes smaller at higher temperatures and for longer reaction times. Thus DS_{sul} is limited up to 0.28, even at 100 $^{\circ}\text{C}$ for 72 h.

Fig. 3 shows changes in DS_{tosyl} of water-soluble DCS-Na obtained at various temperatures versus reaction time. DS_{tosyl} decreases with increasing reaction temperature and with reaction time. However, the DS_{tosyl} remains at about 0.22 even after reaction at 100 $^{\circ}\text{C}$ for 72 h. This value of DS_{tosyl} (0.22) corresponds to about 30% of that of DS_{tosyl} of the original tosylcellulose. In the present nucleophilic substitution, the tosyl groups are substituted by sulfonate groups and by the hydroxyl group competitively. Respectable amounts of the tosyl group are inferred to be substituted by hydroxyl groups. The conversion of tosyl groups to hydroxyl groups (calculated by subtraction of the values of DS_{sul} and DS_{tosyl} of DCS-Na from that of DS_{tosyl} of the original tosylcellulose) is about 20%. The value shows a tendency to increase slightly with increasing reaction temperature. This result might imply that the tosyl group is not so good a leaving group in the present reaction.

Fig. 4 shows changes in $[\eta]$ of water-soluble DCS-Na, obtained at various reaction

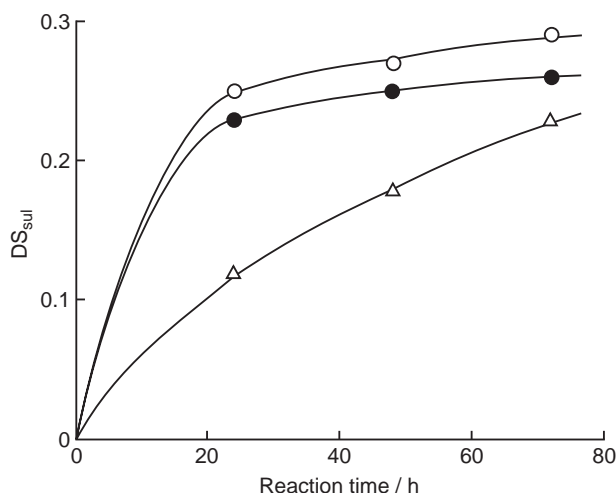


FIGURE 2. Changes in DS by sulfonate group (DS_{sul}) of water-soluble DCS-Na obtained at various reaction temperatures with reaction time. For symbols see Fig. 1.

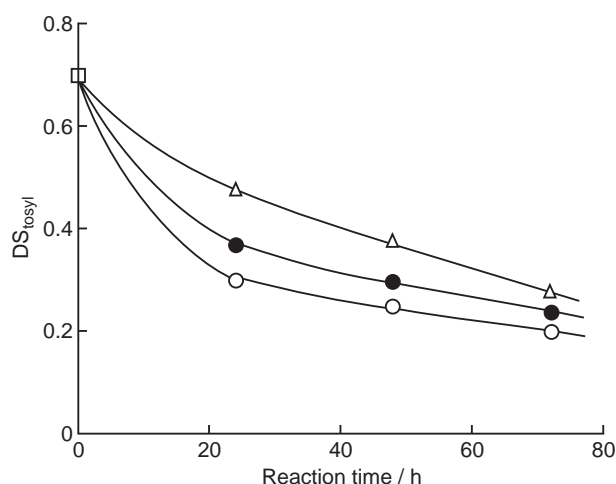


FIGURE 3. Changes in DS_{tosyl} of water-soluble DCS-Na obtained at various reaction temperatures with reaction time. For symbols see Fig. 1.

temperatures with reaction time. $[\eta]$ are found to decrease considerably with increasing reaction temperature and with reaction time. In general, $[\eta]$ of a polymer solution is not only influenced by the DP of the polymer but is also influenced by other factors, especially by interactions between the polymer chain and the solvent. In the present experiment, increases in DS_{sul} may enhance the interaction between DCS-Na and the solvent, thereby making $[\eta]$ increase whereas a decrease in the DP of the cellulose backbone makes $[\eta]$ lower. Therefore, the decrease in the $[\eta]$ of the DCS-Na solution, shown in the figure, may suggest that the DP of the cellulose backbone decreases

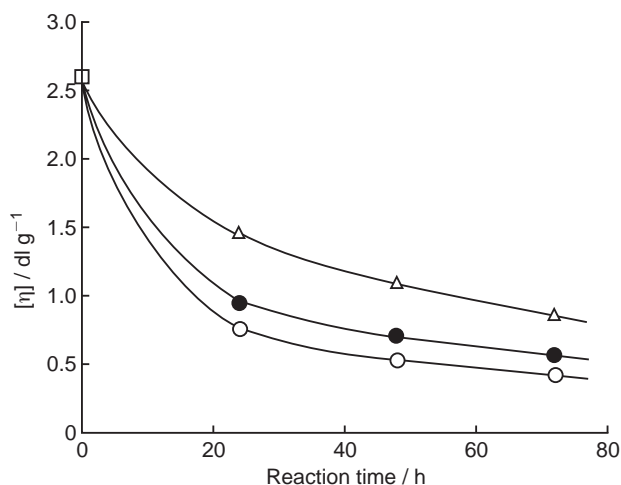


FIGURE 4. Changes in $[\eta]$ of water-soluble DCS-Na obtained at various reaction temperatures with reaction time. Solvent and temperature for viscosity measurement are 0.1 M NaCl aqueous solution and 25 °C. For symbols see Fig. 1.

during the nucleophilic substitution. This result suggests that a lower reaction temperature and a short reaction time are desirable in order to obtain DCS-Na with higher DP, although the yield and the DS_{sul} are lower. In some applications of DCS-Na, such as highly absorbent materials, polymers with higher DP might be necessary (Osada and Takase, 1983).

Fig. 5 shows the plots of all the values of $[\eta]$ and of DS_{tosyl} against that of DS_{sul} of DCS-Na obtained in the present experiment. DS_{tosyl} and $[\eta]$ of the DCS-Na decrease in a similar way to each other with increasing DS_{sul} ; they show steep decreases at about

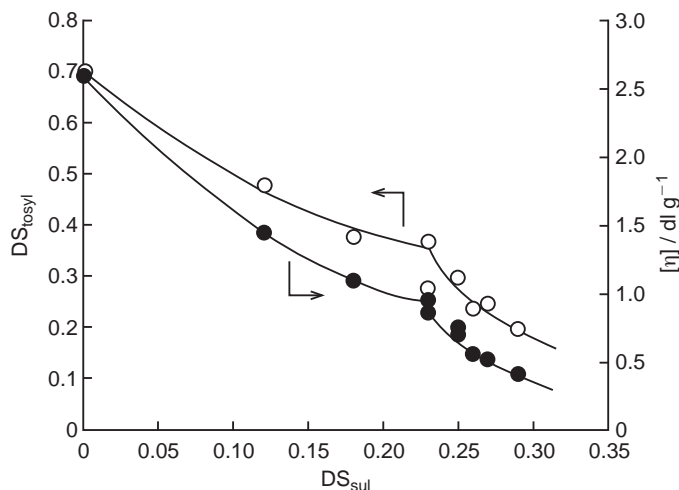


FIGURE 5. Plots of all values of DS_{tosyl} and $[\eta]$ against DS_{sul} of obtained DCS-Na. ○, DS_{tosyl} ; ●, $[\eta]$.

0.25 DS_{sul} . These decreases are independent of the reaction temperature and the reaction time. This tendency suggests that the mechanism of scission of the cellulose backbone and the mechanism of the leaving of the tosyl group from tosylcellulose in the nucleophilic substitution are closely related to each other.

Fig. 6 shows IR absorption spectra of the original cellulose, the tosylcellulose and the DCS-Na. The absorption peaks at about 1600 (aromatic C = C), 1350 (sulfonate) and 1170 (sulfonate) cm^{-1} in the spectrum of tosylcellulose decrease on the substitution of the tosyl group by the sulfonate group. A new peak appears at about 1030 cm^{-1} in the spectrum of DCS-Na. This may be assigned to a sulfonate group which is directly bound to carbon atom. The absorption peak height at 1030 cm^{-1} was found to increase with increasing DS_{sul} . These changes in the spectrum suggest the conversion of sections of the tosylcellulose to DCS-Na, although a proportion of the tosyl groups remains.

CONCLUSION

A water-soluble 'copolymer' of DCS-Na-co-tosylcellulose (DCS-Na) has been successfully prepared by a two-step reaction consisting of the homogeneous tosylation of cellulose and the subsequent nucleophilic substitution of some of the tosyl units of the

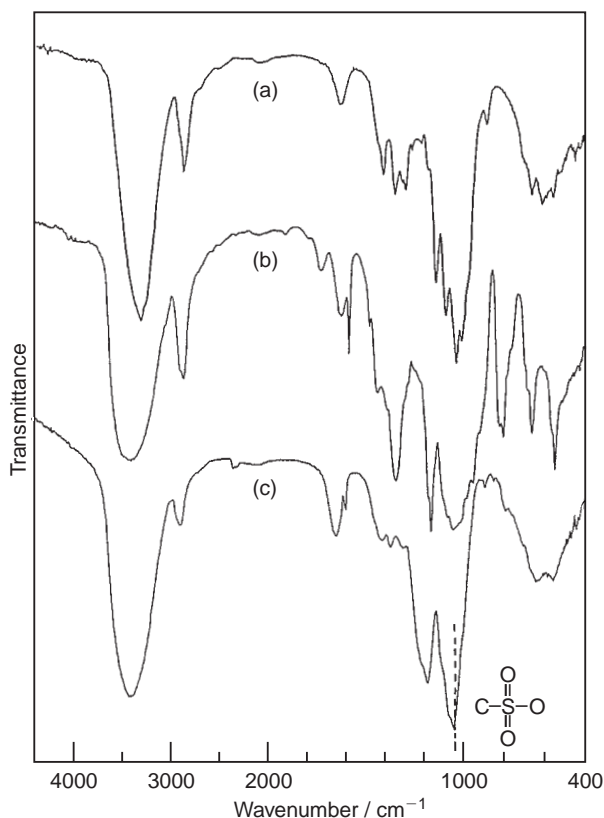


FIGURE 6. IR absorption spectra of original cellulose [(a)], tosylcellulose [$DS_{tosyl} = 0.7$, (b)] and DCS-Na [$DS_{sul} = 0.23$, $DS_{tosyl} = 0.37$, (c)].

tosylcellulose. In the substitution of tosylcellulose, soluble DCS-Na with DS_{sul} up to 0.28 was obtained with a yield up to 80%. Considerable amounts of the tosyl group still remained in obtained DCS-Na. The $[\eta]$ of the obtained DCS-Na 'copolymer' decreased considerably with increasing DS_{sul} , independent of the reaction temperature and the reaction time. The decrease in $[\eta]$ resulted from the decrease in DP of the cellulose backbone. The decrease might limit the utilization of the DCS-Na 'copolymer' to some applications such as highly absorbent materials. Furthermore, the DS_{tosyl} and $[\eta]$ showed similar decreases, at about 0.25 of DS_{sul} , with increasing DS_{sul} . This tendency suggests that the mechanism of scission of the cellulose backbone and the mechanism of the leaving of tosyl group from tosylcellulose in the nucleophilic substitution are closely related each other.

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