# Characterization of Cellulose Acetate in Acetone Solution. Studies on Prehump II in GPC Pattern

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**SYNOPSIS**

Cellulose acetate in acetone solution is known to show some peaks in its chromatogram as measured by gel-permeation chromatography. These peaks are named from the shorter elution time as prehump I, prehump II, and main hump. In our previous paper, we characterized prehump I. In this study, the second peak, prehump II, was fractionated by using the large-scale GPC column and its molecular properties were investigated. The results have shown that the molecules of prehump II are not aggregated but molecularly dispersed with some anionic residues. These anionic groups may be sulfuric acid groups introduced during the acetylation process as a catalyst that interact repulsively with the anionic groups of the GPC column gel. This resulted in the phenomenon that the prehump II elutes earlier than the main hump in the GPC chromatogram. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

Cellulose acetate is one of the important cellulose derivatives used in the fiber and textile industries. Although it can be dissolved in some organic solvents, such as acetone and tetrahydrofuran (THF), cellulose acetate is known to exhibit the complicated solution conditions in these solvents. Gel permeation chromatography (GPC) has, therefore, been used by some investigators for characterizing its solution conditions. Tanghe et al.[1] and Kamide et al.[2] observed a small peak prior to the main peak in the GPC pattern of the cellulose acetate in THF. They termed this peak "prehump." Russo and Serad[3] also observed the same peak in their GPC patterns in the same solvent. However, in its acetone solution, a different GPC pattern was found by Kamide et al.[4] in which two distinguishable peaks named prehumps I and II were present prior to the main peak. Although they speculated prehump II was molecular aggregates of cellulose acetate with some anionic groups cross-linked by metal ions, they could not evaluate the molecular weight due to the failure in its complete separation.

In our previous papers,[5-7] we have studied the physical and chemical properties of prehump I in acetone and discussed its structure in detail. In this paper, the prehump II was fractionated by using a large-scale GPC column. Its properties were then studied to clarify the molecular structure and elucidate the mechanism of prehump II to appear in the GPC pattern in acetone solution.

## EXPERIMENTAL

### Materials and Methods

Cellulose acetate used in this study is the same as described in the previous paper,[5] which was prepared from a sulfite softwood pulp ($\alpha$-cellulose content, 97.5%) based on the conventional acetylation and ripening processes.[8] The degree of substitution (DS) of this cellulose acetate is 2.4. Gel permeation chromatography coupled with a low-angle laser light scattering (GPC-LALLS, Tosoh Co. Ltd., Japan) was used to investigate the solution conditions of

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cellulose acetate.[9] Experimental conditions for GPC-LALLS measurement were the same as mentioned previously.[5]

The following three types of GPC columns were used for the measurements of elution patterns of prehump II. TSK gel $GMPW_{XL}$ (Tosoh Co. Ltd.) specially packed with acetone was mainly used for investigating solution conditions and efficiency of fractionation, while CPG-10 (glass beads, Electro-Nucleonics Inc., USA) and Toyopearl-75HW (cross-linked polyvinylalcohol, Tosoh Co. Ltd.) were used for studying elution patterns of prehump II.

The prehump II and main hump were fractionated by using the large-scale GPC system whose column was packed with a mixture of FPG 2500S and 3000S (14 : 9) (Wako Chem., Japan).

In order to study the effect of metal ions on the elution pattern of a GPC chromatogram, an aqueous solution (0.125 mol/kg) of metal salts, $CaI_2$ and NaI, was prepared and each added to the acetone solution of cellulose acetate with the weight ratio of 8 : 92. The salt concentration obtained was thus $10^{-2}$ mol/kg. The control solution of cellulose acetate without any metal salt was also prepared. For studying the pH dependence of prehump II in chromatogram, a CPG-10 column was also used with acetone as a moving phase. Three kinds of hydrochloric acid solutions (0.125, $1.25 \times 10^{-2}$, $1.25 \times 10^{-3}$ mol/kg) were prepared and each was added to the acetone solution of cellulose acetate with the weight ratio of 8 : 92. The hydrochloric acid concentrations obtained were thus, respectively, $10^{-2}$, $10^{-3}$, and $10^{-4}$ mol/kg.

The intrinsic viscosity $[\eta]$ of the original cellulose acetate and fractionated samples of prehump II and main hump was measured in an Ubbelohde-type dilution viscometer in acetone at 25°C. From the obtained values, the number-average molecular weight $\bar{M}_n$ was evaluated by the following equation:[10]

$$[\eta] = 8.97 \times 10^{-5} \bar{M}_n^{0.9}.$$

The chemical composition was also determined by alditol–acetate method[11] for original cellulose acetate and its fractions.

For sulfur content determination, the film of 2.5 cm in diameter was prepared for original cellulose acetate and its fractions with thickness of 0.5–1.0 mm. For quantitative assay, sulfur-containing standards were also prepared. Sodium dodecyl sulfate that contained 11.1% sulfur was mixed in varying proportions with cellulose acetate. This cellulose acetate was prepared by the method in which perchloric acid is used as a catalyst, thus being free from sulfur. A calibration curve was established by plotting the counts of the S-$K_\alpha$ X-ray intensity measured by the following method against sulfur content estimated.

The determination of the S-$K_\alpha$ X-ray intensity of the standards, original cellulose acetate, and its fractions were made by Shimadzu X-ray Fluorescence Spectrometer (VF-310) at the accelerating voltage of 40 kV and emission current of 70 mA. Under these conditions, S-$K_\alpha$ X-ray counts at $2\theta$ of 110.9 degrees were measured by a 40-s analysis with the crystal of germanium (Ge). Background for the S-$K_\alpha$ was estimated from the $2\theta$ of 114 degrees and subtracted from the total counts at the $2\theta$ of 110.9 degrees to obtain the X-ray intensity of the S-$K_\alpha$. A preliminary examination of the film of 0.1, 0.2, and 0.3 mm thickness prepared from the same sample revealed basically the same intensity of S-$K_\alpha$, indicating that the site from which S-$K_\alpha$ X-rays are generated is less than 0.1 mm in depth from the film surface. Thus, prepared films with thickness of 0.5–1.0 mm must be thick enough for analysis.

## RESULTS AND DISCUSSION

### Separation of Prehump II

Figure 1(a) shows typical GPC-LALLS pattern of cellulose acetate. The complexity of the solution conditions of cellulose acetate is obvious as several peaks are present in its chromatogram.[4] Prehumps I and II appear in a shorter elution time than the main hump. Although a peak intensity of refractive index (RI) is less extensive in prehump I compared to prehump II, prehump I is highly extensive in the signal of light scattering (LS) with LS being negligibly small in prehump II. This result indicates that the prehump I is a substance with a high molecular weight in acetone whereas prehump II is not so large in its molecular weight.

In our previous paper,[5] prehump I was clarified to be molecular aggregates of some cellulose acetates forming a "microgel" in acetone. In this work, therefore, prehump I was first removed from the original cellulose acetate solution by ultracentrifugation to separate the molecules of prehump II. The GPC chromatogram of the obtained microgel-free solution was then studied by the GPC-LALLS measurement as shown in Figure 1(b). It is apparent

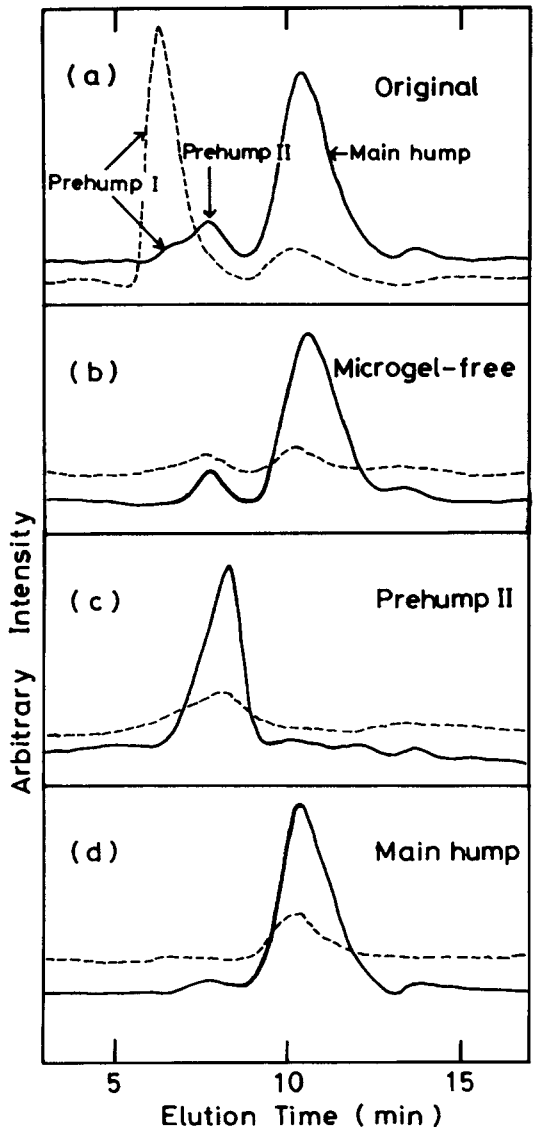


**Figure 1** GPC-LALLS patterns of original cellulose acetate (DS = 2.4) and its fractions in acetone solution. Solid and dashed lines indicate the refractive index (RI) and light scattering (LS), respectively.

in this figure that the prehump II and main hump are still present in the solution after removing prehump I. This solution was further separated into two fractions of prehump II and main hump with the large-scale GPC column. Figure 1(c) and (d) show the GPC-LALLS patterns of the fractionated samples of the prehump II and main hump, respectively. A complete separation is obvious.

## Characterization of Prehump II

### *Chemical Composition and Molecular Weight*

The chemical composition of the prehump II fraction is shown in Table I with the data of original cellulose acetate, prehump I, and main hump for comparison. Obviously, the main component of prehump II is glucose, indicating that the hemicelluloses are negligibly small.

For determination of the molecular weight, the specific viscosity of prehump II was measured in acetone solution. In comparison, that of the original cellulose acetate and main hump was also measured as shown in Figure 2. From the intrinsic viscosity $[\eta]$, which was obtained from the values of reduced viscosity at different concentrations extrapolated to the zero concentration, the number-average molecular weight $\bar{M}_n$ was calculated. It is apparent in Table I that the $\bar{M}_n$ of the prehump II is only about 20% larger than that of the original cellulose acetate or main hump.

### *Elution Patterns of Prehump II With Some GPC Columns*

In the gel permeation chromatography, the polymers with higher molecular weight are generally eluted earlier. However, the prehump II that was eluted earlier than the main hump was found to have a similar molecular weight by viscometric measure-

**Table I Chemical Composition, Intrinsic Viscosity, and Number-Average Molecular Weight of Original Cellulose Acetate and Its Fractions**

| | Chemical Composition (wt %) | | | | |
|---|---|---|---|---|---|
| Sample | Glucose | Xylose | Mannose | $[\eta]$ (dl $g^{-1}$) | $\bar{M}_n/10^4$ |
| Original | 99 | 0.3 | 0.5 | 1.7 | 5.6 |
| Prehump I | 87 | 7 | 7 | — | — |
| Prehump II | 99.6 | 0.2 | 0.2 | 1.9 | 6.4 |
| Main hump | 100 | 0 | 0 | 1.6 | 5.2 |

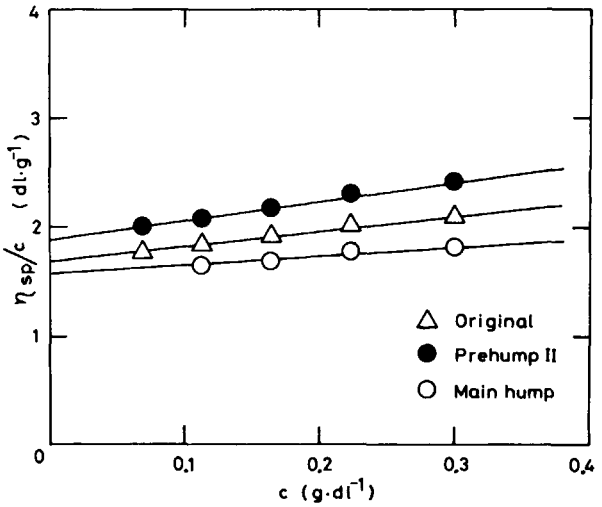


**Figure 2** Concentration dependence of the reduced viscosity of original cellulose acetate (DS = 2.4) and its fractions.

ments to that of the main hump (Table I). Therefore, we studied the elution mechanism of the prehump II by using some GPC columns packed with different types of column gels. In order to facilitate a comparison, microgel-free cellulose acetate as seen in Figure 1(b) was used in this study. The obtained elution patterns are shown in Figure 3. Interestingly, the peak of the prehump II was observed in both $GMPW_{XL}$ and CPG-10 columns, whereas that was not observed when the Toyopearl-75HW column was used. The column materials of the former have some weakly anionic groups in the column gels, while the latter is made of cross-linked polyvinylalcohol without any ionic groups on its beads. Therefore, it may be suggested that the molecules of the prehump II have some anionic groups on their glucose residues that would force these molecules of prehump II to elute earlier in the GPC pattern by electrostatic repulsive forces.

### *Effect of Metal Ions*

The effect of metal ions was studied on the elution pattern of prehump II by adding two kinds of metal salts, $CaI_2$ and NaI, to the microgel-free cellulose acetate solution. For comparison, the control solution without any metal salt added was also studied as shown in Figure 4. Although the large peak of solvent distorted the chromatogram curves at the end region of elution time, the peaks of both prehump II and main hump could be observed for the control solution. However, the peak of the prehump II no longer appeared prior to the main hump when $CaI_2$ or NaI was added to the solution. This result can provide additional evidence that the molecules of the prehump II have some anionic residues in cellulose acetate, because the metal salts added would have acted as counterions to reduce not only the repulsion of electrostatic forces by anionic residues, but also the expansion of the molecules in the solution. As a result, the prehump II would have disappeared into the elution region of the main

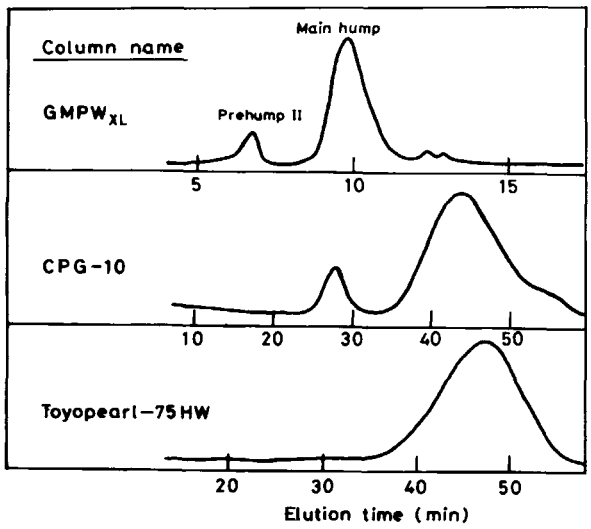


**Figure 3** Chromatograms of the microgel-free cellulose acetate in acetone as different types of GPC column materials were used.

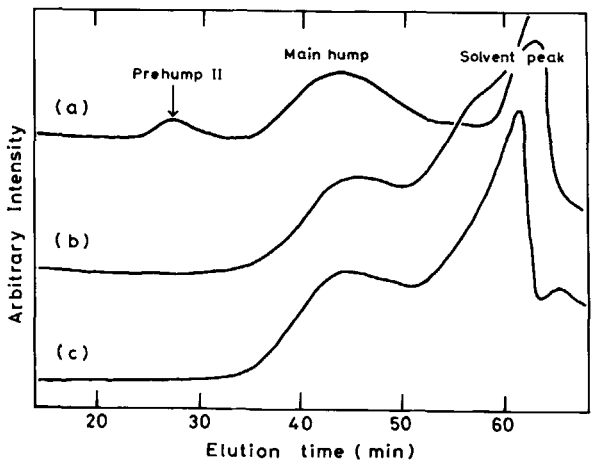


**Figure 4** *Effects of metal ions on occurrence of prehump* II in the GPC chromatograms: (a) control; (b) $CaI_2$; and (c) NaI.

hump. Consequently, the possibility can be ruled out that the prehump II is a molecular aggregate cross-linked with metal ions introduced.[4]

### *Effect of the pH*

The pH dependence of prehump II on the elution pattern of GPC was also studied by adding the hydrochloric acid to the acetone solution of cellulose acetate. The obtained results are shown in Figure 5. It seems apparent that as the concentration of hydrochloric acid increases, the prehump II gets smaller in its intensity compared with that of the control, and finally disappears [Fig. 5(c) and (d)].

Such an observed phenomenon would be explained in the following manner: the gels of CPG-10 column used in this study are made of glass beads. Therefore, as the acid was added, the syranol groups of the glass beads and anionic residues of the prehump II are likely to be protonated. Consequently, the electrostatic repulsive forces present between the molecules of prehump II and column gels would be diminished. Both the molecules of prehump II and main hump can thus enter into the pores of the column gel, eluted at the same position of the main hump. Therefore, once again the results could have supported the presence of the anionic residues in the cellulose acetate of the prehump II.

### *Sulfur Content*

The most probable anionic residues present in cellulose acetate would be sulfuric acid groups introduced during the acetylation process as a catalyst. Therefore, the sulfur content was determined for original cellulose acetate and its fractions. As expected, the obtained results in Table II indicated that the prehump II was six times higher in sulfur content than the main hump. With sulfur contents and known weight percentages of the fractions, the sulfur content of the original cellulose acetate was estimated to be 215 ppm ($=690 \times 0.046 + 800 \times 0.095 + 125 \times 0.859$). This value is slightly higher than that of 180 ppm obtained by the direct determination for cellulose acetate. However, considering the errors introduced by the fractionation, we can claim good agreement between these results. Therefore, the high content of sulfur in the prehump II fraction must be valid, indicating that cellulose acetate in the prehump II must have some residues of sulfuric acid groups.

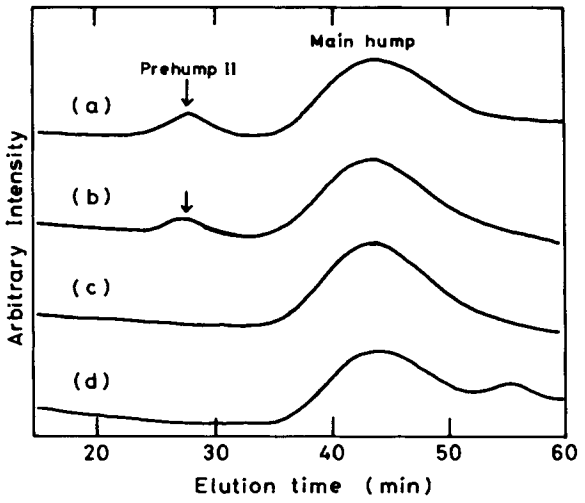


**Figure 5** The pH dependence of prehump II in the GPC chromatograms: (a) control; (b) HCl ($10^{-4}$ mol/kg); (c) HCl ($10^{-3}$ mol/kg); and (d) HCl ($10^{-2}$ mol/kg).

**Table II Sulfur Content of the Original Cellulose Acetate and Its Fractions**

| Fraction | Weight Percentage (%) | Sulfur Content (ppm) |
|---|---|---|
| Original | 100 | 180 |
| Prehump I | 4.6 | 690 |
| Prehump II | 9.5 | 800 |
| Main hump | 85.9 | 125 |

## CONCLUSION

Various lines of evidence obtained in this study clearly indicated that the molecules of the prehump II are cellulose acetates with anionic residues of sulfuric acid groups introduced during the acetylation process. It is apparent that such anionic groups on the cellulose acetates would repulsively interact with the column gels of glass beads and thus elute earlier than the main hump in the GPC chromatogram. Additionally, the molecules of the prehump II are not molecular aggregates cross-linked with metal ions as suggested in the literature,[4] but have a similar molecular weight to that of the original cellulose acetate.

The elution mechanism introduced in this study can be supported by the fact that the cellulose acetate prepared with the higher amount of sulfuric acid as a catalyst has the higher intensity of the prehump II in the GPC chromatogram (unpublished data).

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