# Characterization of Polymer-Brush-Type Polysaccharide β-Ketoesters

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**ABSTRACT:** Polyvinyl alcohol (PVA) and four glucans, cellulose, curdlan, amylase, and pullulan, were dissolved in 8% lithium chloride/1,3-dimethyl-2-imidazolodinone, and reacted with ketene dimers with long alkyl or alkenyl chains under homogeneous conditions. The corresponding polysaccharide β-ketoesters with degrees of substitution (DS) of 2.1–2.9 and the PVA β-ketoester with DS 0.9 were prepared in the yields of 80–90%. Solution-state ^{1}H- and ^{13}C-NMR spectra of the polysaccharide and PVA β-ketoesters revealed that the polymer chains behaved like solid even in solutions. However, size-exclusion chromatographic analysis showed that the polysaccharide and PVA β-ketoesters prepared had random-coil conformations in tetrahydrofuran, which could not explain the anomalous NMR patterns. The specific chemical structures of the substituents having long and branched alkyl or alkenyl chains may have brought about such specific solution-state NMR patterns, irrespective of the chemical structures of the polymer backbones. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 109: 1667–1674, 2008

**Key words:** lithium chloride; 1,3-dimethyl-2-imidazolodinone; nonaqueous cellulose solvent; ketene dimer; homogeneous reaction; β-ketoester; SEC-MALLS; biopolymers; esterification; NMR; polysaccharides; solution properties

## INTRODUCTION

Esterification is one of the most typical derivatizations of polysaccharides. Organic solvent-soluble and other new properties can be added to polysaccharides by esterifications, depending on the chemical structures of the substituents, degrees of substitution (DS), DS distribution and degrees of polymerization (DP).[1–4] Various cellulose esters such as cellulose acetate, nitrate, propionate, phthalate and mixed esters have been produced at industrial level, and used in various fields. Ketene dimers are included in the esterification reagents of hydroxyl groups, and long two alkyl or alkenyl chains can be introduced at once into one hydroxyl group by β-ketoesterification. Preparation and characterization of ketene dimers were reviewed in detail.[5]

Cellulose β-ketoesters with two alkenyl chains in one substituent were prepared using *cis*-9-octadecenyl ketene dimer (OKD) and LiCl/1,3-dimethyl-2-imidazolidinone (DMI)[6,7] as the esterifying reagent and cellulose solvent, respectively. Relationships between degree of substitution (DS) of the cellulose/OKD β-ketoesters and reaction conditions were studied in detail.[8] DS values of the products were controllable up to 2.1 by selecting the reaction conditions. Solution- and solid-state ^{13}C-NMR analyses revealed that cellulose backbones of the β-ketoesters with DS 2.1 behaved like solid in chloroform owing to strong restriction on movement of cellulose chains by the long and branched alkenyl substituents introduced. Thus, cellulose β-ketoesters with dense substituents like polymer brushes or comb-shaped polymers could be prepared.[8]

When cellulose and alkyl ketene dimers (AKDs) prepared from C8–C18 fatty acids were reacted under homogeneous conditions using the same cellulose solvent, cellulose/AKD β-ketoesters with DS 1.9–2.9 were obtained.[9] ^{13}C-NMR spectra of the cellulose/AKD β-ketoesters showed also that cellulose carbons and substituent carbons close to cellulose chains were restricted in motion and behaved like solid in solutions. In contrast, cellulose/C8–C18 fatty acid esters with DS 2.5–2.9 did not demonstrate such anomalous ^{13}C-NMR spectra.[9] Thus, the unique ^{13}C-NMR patterns are characteristic for the cellulose/AKD β-ketoesters, which have long and branched alkyl substituents in each anhydroglucose unit.

The cellulose β-ketoesters prepared were gummy solid at room temperature and had birefringence due to liquid crystalline structures in wide temperature range.[10] The liquid crystalline/isotropic phase

transition points were 150–175°C, depending on the DS and substituents introduced into cellulose hydroxyls. X-ray diffraction patterns indicated that cellulose backbones had disordered structures at room temperature, whereas long alkyl chains in the substituents formed ordered or crystalline domains in the cellulose β-ketoesters.[10] Films of the cellulose/AKD β-ketoesters prepared by casting their chloroform solutions on glass plates had highly hydrophobic nature, and contact angles of water droplet on the films were more than 90°.

In this article, the method of homogeneous β-ketoesterifications reported previously[8–10] was applied to polyvinyl alcohol (PVA) and various glucans consisting of α- and β-type glycoside bonds. Reaction products thus obtained were analyzed by FTIR, NMR and size-exclusion chromatography attached with a multi-angle laser light-scattering (MALLS) detector to characterize their chemical structures and conformations in solutions. The influence of chemical structures of the polymer backbones on the solution-state properties of the corresponding β-ketoesters was studied in comparison with cellulose β-ketoesters.

## EXPERIMENTAL

### Materials

All polysaccharide samples used were glucans having α- or β-glycoside bonds. A microcrystalline cellulose powder originating from cotton linters was used as the cellulose sample (Advantec Toyo, Japan). Curdlan, pullulan and amylose originating from cornstarch were supplied by Wako Pure Chemicals, Japan. The curdlan was hydrolyzed in $1M$ hydrochloric acid at 80°C for 3 h to reduce its weight average degree of polymerization ($DP_w$) from ∼ 4,000 to 270 before use. These polysaccharides were used after vacuum drying at room temperature for more than 1 day. PVA with 98.7% saponification (GOH-SENOL $N$-300) was supplied by Nippon Synthetic Chemical Industry, Japan.

Oleic ketene dimer (*cis*-9-octadecenyl ketene dimer: OKD) and octyl ketene dimer (C8-KD), which were prepared from oleic acid chloride and octanoic acid chloride, respectively, and triethylamine by the conventional method of preparing AKDs,[11] were kindly provided by NOF, Japan. Both OKD and C8-KD were liquid at room temperature. Purities of OKD and C8-KD determined by ^{1}H-NMR were more than 90%. Anhydrous lithium chloride (LiCl), 1,3-dimethyl-2-imidazolidinone (DMI), 1-methylimidazole (MEI) and other reagents and solvents were of laboratory grade (Wako Pure Chemicals, Japan), and used without further purification. Tetrahydrofuran (THF) of liquid chromatographic grade (Wako

Pure Chemicals, Japan) was used as an eluent of size exclusion chromatography (SEC).

### Preparation of polysaccharide solutions

A 2 mass % cellulose solution in 8 mass % LiCl/DMI was prepared according to the reported method for preparation of cellulose/LiCl/DMAc solutions.[12,13] Cellulose (10 g) was suspended in DMI (450.8 g), and this suspension was heated at 150°C for 30 min followed by the addition of LiCl (39.2 g) at about 100°C during the course of natural cooling. A clear cellulose solution was obtained by stirring the mixture at room temperature for one day. Other polysaccharide/LiCl/DMI and PVA/LiCl/DMI solutions were prepared in a similar manner to that of the cellulose solution. The 2% polysaccharide and PVA solutions in 8% LiCl/DMI were then diluted with fresh DMI to prepare 1% and 0.25% solutions in 4 and 1% LiCl/DMI for reactions with ketene dimers and SEC analysis, respectively.

### Preparation of polysaccharide β-ketoesters

The reaction between the polysaccharide and either OKD or C8-KD was carried out in accordance with the reported method.[8,9] OKD or C8-KD and MEI used as a promoter (10 mol per anhydroglucose unit of the polysaccharide for each reagent) were added to the 1% polysaccharide solution in 4% LiCl/DMI with continuous stirring at ambient temperature. The mixture was stirred at the same temperature for 3 h, where homogeneous solution was maintained in every case. Then, the mixture was poured into a large volume of 1-propanol. Precipitates thus formed were then filtered, rinsed with fresh 1-propanol and then acetone, and dried in a vacuum oven at room temperature for more than 1 day. PVA was reacted with OKD in 4% LiCl/DMI, and the reaction product was isolated and purified in a similar manner to those of the other products prepared from polysaccharides.

### Determination of molecular mass parameters by SEC

Weight and number average molecular mass values ($M_w$ and $M_n$, respectively) and other molecular mass parameters of the original polysaccharides and their β-ketoesters were obtained by means of a size-exclusion chromatograph equipped with a multi-angle laser light-scattering detector (SEC-MALLS). The 0.25% polysaccharide or PVA solution in 1% LiCl/DMI was subjected to the SEC-MALLS analysis using 1% LiCl/DMI as the eluent. In the case of polysaccharide and PVA β-ketoesters, they were dissolved in THF and analyzed by SEC-MALLS using

**TABLE I**
**Molecular Mass Parameters of Polysaccharides and PVA Used in This Study[a]**

| Polymer | Glycoside bond | $M_w$ | $DP_w$ | $M_n$ | $DP_n$ | $M_w/M_n$ | Slope of conformation plot |
|---------|---------------|-------|--------|-------|--------|-----------|---------------------------|
| Cellulose | β-(1→4) | 38,900 | 240 | 27,400 | 170 | 1.4 | 0.59 |
| Curdlan | β-(1→3) | 42,800 | 260 | 27,500 | 170 | 1.6 | 0.54 |
| Amylose | α-(1→4) | 499,000 | 3,100 | 239,000 | 1,500 | 1.9 | 0.42 |
| Pullulan | α-(1→4) + α-(1→6) | 114,000 | 700 | 75,800 | 470 | 1.5 | 0.58 |
| PVA | – | 88,200 | 2,100 | 66,100 | 1,500 | 1.3 | 0.53 |

[a] 1% LiCl/DMI was used as the eluent for the SEC-MALLS analysis.

THF as the eluent. The SEC columns used were KD-806M and KF-806M HQ (both from Shodex, Japan) for 1% LiCl/DMI and THF, respectively. The MALLS (DAWN EOS, λ = 690 nm; Wyatt Technologies, USA) and RI (RID-10A; Shimadzu, Japan) detectors were attached to the SEC system. The detailed SEC system used and operation conditions were described elsewhere.[14,15] Data acquisition and processing were performed with the ASTRA software (Wyatt Technologies, USA). The *dn/dc* value of 0.087 mL/g was adopted to calculation of molecular mass parameters of the polysaccharides dissolved in 1% LiCl/DMI,[16] because all of them consisted of anhydroglucose unit alone. The *dn/dc* values of the polysaccharide β-ketoesters in THF were obtained by the SEC analysis on the assumption of 100% mass recovery. The polymer/OKD β-ketoesters prepared from cellulose, curdlan, amylose, pullulan and PVA had *dn/dc* values of 0.080 mL/g (DS 2.1), 0.062 mL/g (DS 2.3), 0.062 mL/g (DS 2.6), 0.062 mL/g (DS 2.6) and 0.100 mL/g (DS 0.9), respectively. The polysaccharide/C8-KD β-ketoesters prepared from cellulose, curdlan, amylase, and pullulan had *dn/dc* values of 0.077 mL/g (DS 2.9), 0.065 mL/g (DS 2.9), 0.060 mL/g (DS 2.9), and 0.066 mL/g (DS 2.8), respectively. A polystyrene standard (molecular mass 30,000; Pressure Chemical, USA) was used for the MALLS and RI calibration and normalization.

**Other analyses**

Infrared spectra of the polysaccharide β-ketoesters were obtained using a Nicolet Magna 860 (Madison, WI) by the thin film method formed on a KRS-5 plate from the polysaccharide β-ketoester/chloroform solutions. The DS of the polysaccharide β-ketoesters were calculated from hydrogen and carbon contents determined by elementary analysis, and expressed as average values of three measurements for each sample. ^{1}H- and ^{13}C-NMR spectra of the polysaccharide β-ketoesters were collected on a JEOL ALPHA 500 spectrometer (JEOL, Japan), where CDCl3 and tetramethylsilane (both from Wako Pure Chemicals, Japan) were used as a solvent and an internal standard, respectively.

## RESULTS AND DISCUSSION

### SEC-malls analysis of polysaccharides and PVA used as starting materials

The polysaccharides used in this study were all glucans, and their molecular mass parameters as well as those of PVA were measured by SEC-MALLS using 1% LiCl/DMI as the eluent (Table I). DP data calculated using *dn/dc* values, which are obtained by the SEC-MALLS analysis on the assumption of 100% mass recovery, may bring about significant errors when filtration losses occur. However, because the SEC elution peak areas were almost equal to one another, no significant filtration losses might take place for particular samples and thus the DP data in Table I are enough to be reliable. The values of ''slope of conformation plot'' in Table I were obtained from the double logarithmic plots between root-mean-square (RMS) radius and molecular mass of SEC-MALLS data via the following equations;

$$\langle S^2 \rangle^{1/2} = kM^a$$

$\langle S^2 \rangle^{1/2}$, RMS radius or radius of gyration; $k$, constant; $M$, molecular mass; $a$, slope of conformation plot.

Because the commercial curdlan had a high DP of ~ 4000, partially acid-hydrolyzed curdlan was prepared and used as the starting material. Cellulose and curdlan, both of which have β-type glycoside bonds, had similar slope values in the conformation plots, 0.59 and 0.50, respectively, showing that both polysaccharides have flexible or random-coil conformations in the good solvent. Although both amylose and pullulan have α-type glycoside bonds, their slope values were quite different to each other, 0.42 and 0.58, respectively. Because the commercial amylose originating from cornstarch used in this study has some branched structures due to the residual amylopectin component, it may have such a small slope value of 0.42 in 1% LiCl/DMI. On the other hand, pullulan consisting of both α-(1→4) and α-(1→6) glycoside bonds had in turn a more flexible chain conformation in 1% LiCl/DMI. Literature data also show that pullulan has the slope values of 0.62–
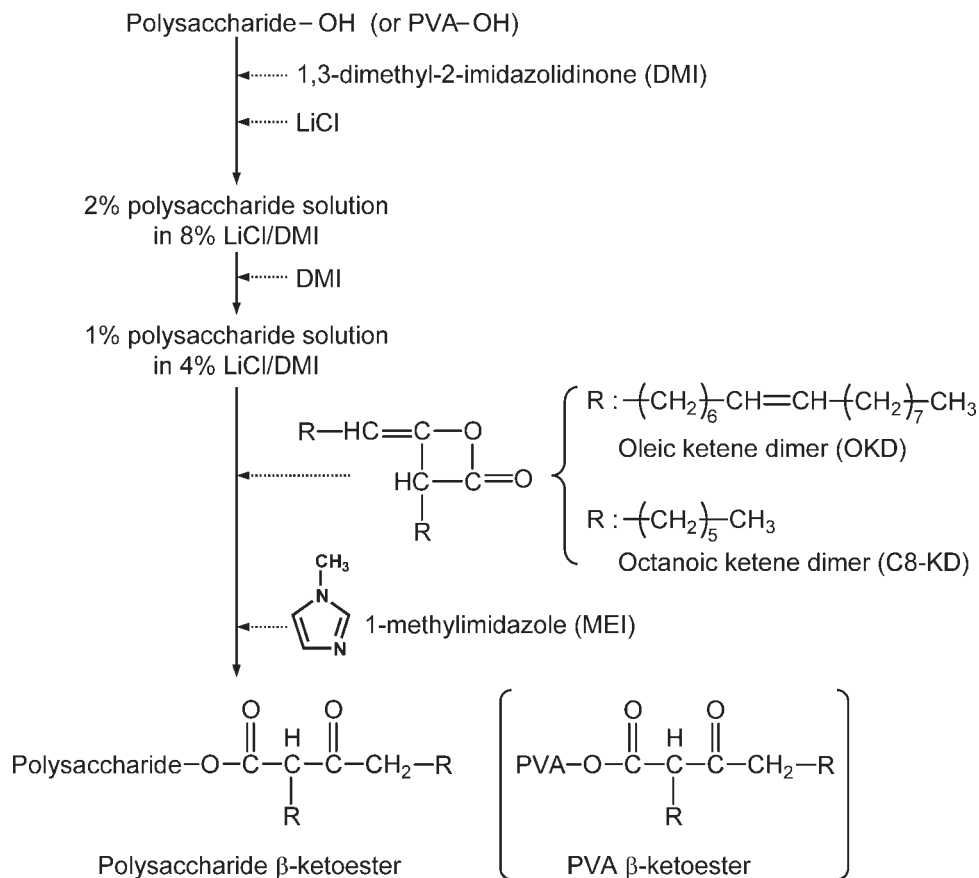
**Figure 1** Reactions between polysaccharide hydroxyls and ketene dimer in LiCl/DMI with 1-methylimidazole.

0.64 in aqueous solutions. PVA had a typical random-coil conformation in the solution.

### FTIR and NMR analyses of polysaccharide β-ketoesters

The polysaccharide/OKD and polysaccharide/C8-KD β-ketoesters were prepared using the LiCl/DMI as the homogeneous reaction medium. The original commercial curdlan with $DP_w$ of $\sim 4000$ could not be converted to organic solvent-soluble products, when the reaction conditions described in the Experimental section were adopted. Thus, partially acid-hydrolyzed curdlan was prepared and used as the starting material.

All polysaccharide and PVA β-ketoesters obtained were white gummy solid, and soluble in THF, chloroform, etc. Yields were in the range of 80–90%, and the yield losses were primarily caused by handling during the isolation and purification procedure. Figure 2 shows FTIR spectra of the polysaccharide and PVA β-ketoesters. Two absorption bands at 1740 cm$^{-1}$ and 1710 cm$^{-1}$ are due to C=O stretching vibrations typical for β-ketoesters.[8,9] The polysaccharide/OKD β-ketoesters had DS values of 2.1–2.6,

whereas the polysaccharide/C8-KD β-ketoesters had DS values of 2.8–2.9 (Table II); the shorter the alkyl chains of ketene dimers used, the higher the DS of the polysaccharide β-ketoesters, probably because of steric hindrance.

Solution-state ^{1}H- and ^{13}C-NMR spectra of the polysaccharide and PVA β-ketoesters are shown in Figures 3 and 4, respectively. Because the polysaccharide/OKD and PVA/OKD β-ketoesters have double bonds in the substituents, methine protons of the double bonds and methylene protons adjacent to the double bonds were clearly detected at 5.3 and 2.0 ppm, respectively, whereas no such signals were present in ^{1}H-NMR spectra of the polysaccharide/C8-KD β-ketoesters. The methine and methylene protons (*b* and *d*, respectively, in Fig. 3) had only broad signals for all β-ketoesters. Nearly no signals due to C—H protons of polysaccharide skeletons were detected for any β-ketoesters. It was confirmed from the ^{1}H-NMR spectra that neither DMI, by-products nor 1-propanol remained in the polysaccharide and PVA β-ketoesters, showing that the isolation and purification procedure adopted in this study using 1-propanol was sufficient to remove these nonpolysaccharide components.
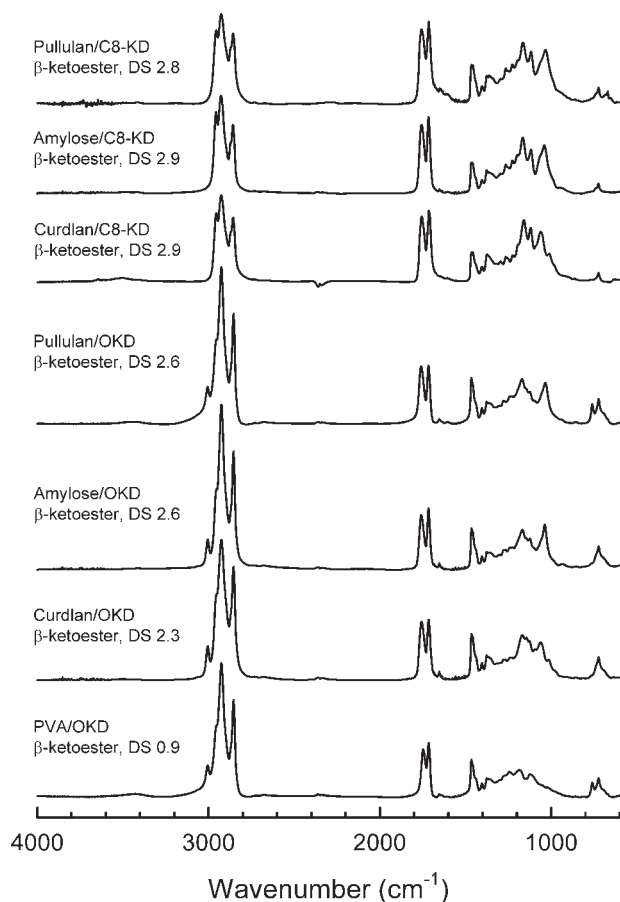
**Figure 2** FTIR spectra of polysaccharide and PVA β-ketoesters.

Although sharp signals due to methyl and methylene carbons of substituents were detected in the range from 13 to 32 ppm in Figure 4, polysaccharide carbons as well as substituent carbons close to the polysaccharide chains had nearly no or quite small signals. A similar ^{13}C-NMR spectrum was observed also for the PVA β-ketoester. Thus, ^{13}C-NMR spectra of all β-ketoesters look like those of simple alkanes

or alkenes. These anomalous ^{1}H- and ^{13}C-NMR spectra were also observed for cellulose/OKD and cellulose/C8-KD β-ketoesters with DS 2.1 and 2.9, respectively.[8,9] Thus, irrespective of the chemical structures of the backbone polymers, the polymer carbons and protons and those of substituents close to the polymer chains in the β-ketoesters behave like solid in $CDCl_3$ solutions, whereas carbons and protons of substituents distantly positioned from the polymer chains do like normal alkanes or alkenes in the solutions. Because two alkyl chains are introduced at once into one hydroxyl group of polysaccharides and PVA via β-ketoesterifications (Fig. 1), the characteristic polymer-brush-type chemical structures of the β-ketoesters may have brought about such unique solution-state ^{1}H- and ^{13}C-NMR spectra in Figures 3 and 4.
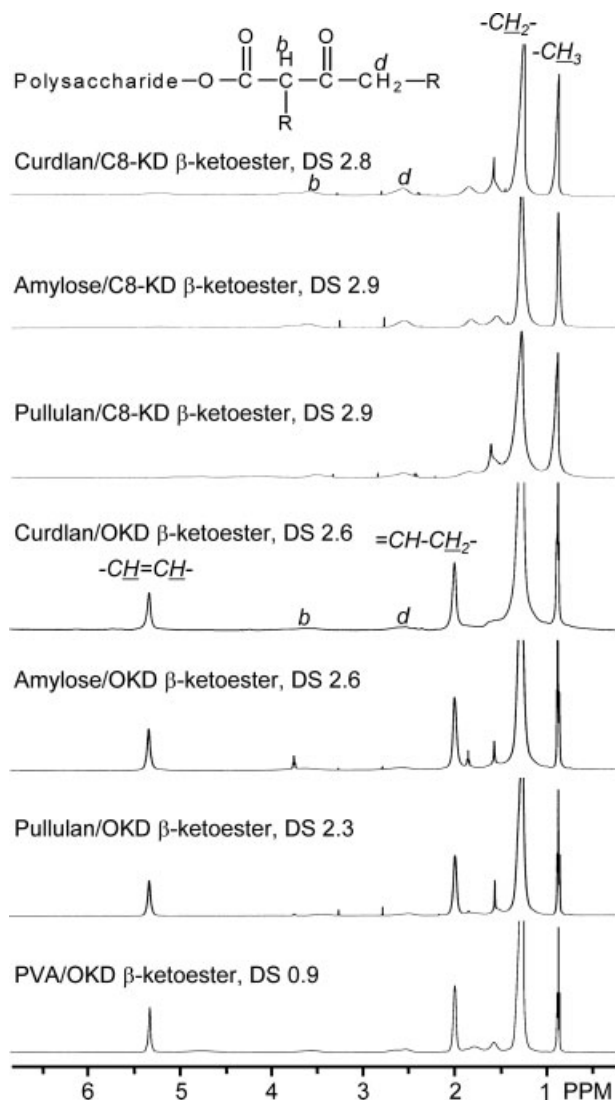
## SEC-MALLS analysis of polysaccharide and PVA β-ketoesters

The SEC elution patterns of the polysaccharide/OKD and PVA/OKD β-ketoesters are depicted in Figure 5. The β-ketoesters prepared from amylose, pullulan, cellulose, and PVA had elution patterns of mostly normal distribution. Because the curdlan sample used in this study was prepared by partial acid hydrolysis of commercial curdlan, the corresponding β-ketoester had a bimodal SEC elution pattern, a small high-molecular-mass fraction at 8–9 mL and a main fraction at 9–11.5 mL. The conformation plots of the β-ketoesters in Figure 5 are shown in Figure 6. All the polysaccharide/OKD and PVA/OKD β-ketoesters were roughly on the same line, although the slop value of the amylose β-ketoester was different from others.

Figures 7 and 8 show SEC elution patterns and the corresponding conformation plots of the polysaccharide/C8-KD β-ketoesters, respectively. Because the substituent chain length of these β-ketoesters is shorter than that of the polysaccharide/OKD β-

**TABLE II**
**Molecular Mass Parameters of Polysaccharide and PVA β-Ketoesters[a]**

| Polymer | DS | $M_w$ | $DP_w$ | $M_n$ | $DP_n$ | $M_w/M_n$ | Slope of conformation plot |
|---|---|---|---|---|---|---|---|
| β-Ketoesters prepared with OKD | | | | | | | |
| Cellulose | 2.1 | 203,000 | 160 | 123,000 | 100 | 1.7 | 0.57 |
| Curdlan | 2.3 | 368,000 | 270 | 219,000 | 160 | 1.7 | 0.57 |
| Amylose | 2.6 | 1,670,000 | 1,100 | 1,180,000 | 770 | 1.4 | 0.49 |
| Pullulan | 2.6 | 982,000 | 640 | 849,000 | 550 | 1.2 | 0.57 |
| PVA | 0.9 | 1,160,000 | 2,200 | 992,000 | 1,900 | 1.2 | 0.50 |
| β-Ketoesters prepared with C8-KD | | | | | | | |
| Cellulose | 2.9 | 230,000 | 260 | 186,000 | 210 | 1.2 | 0.57 |
| Curdlan | 2.9 | 217,000 | 240 | 135,000 | 150 | 1.6 | – |
| Amylose | 2.9 | 754,000 | 840 | 438,000 | 490 | 1.7 | 0.55 |
| Pullulan | 2.8 | 479,000 | 550 | 329,000 | 380 | 1.5 | 0.55 |

[a] THF was used as the eluent for the SEC-MALLS analysis.

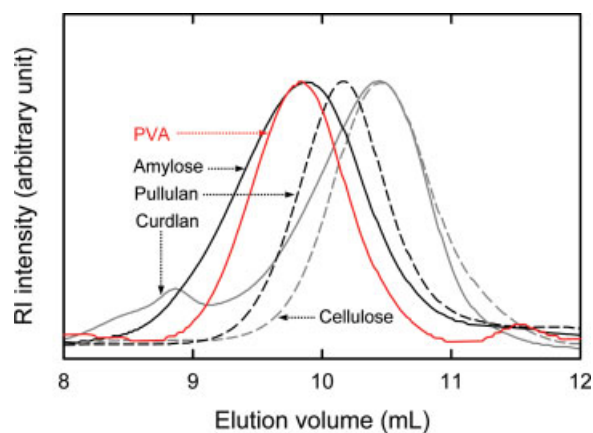**Figure 3** Solution-state $^1$H-NMR spectra of polysaccharide and PVA β-ketoesters.

Molecular mass parameters of the polysaccharide and PVA β-ketoesters obtained from the SEC-MALLS data are summarized in Table II. In the case of curdlan and its β-ketoesters, the small high molecular-mass fractions were excluded in the calculation. Weight and number average degrees of polymerization ($DP_w$ and $DP_n$, respectively) were calculated from $M_w$, $M_n$, and DS values, and are also listed in Table II. Because the SEC elution peak areas were almost equal to one another, the DP data in Table II calculated on the assumption of 100% mass recovery are enough to be reliable.

Clear depolymerization during the β-ketoesterification was observed for amylose and pullulan, which originally had the high DP values. The slope values of the β-ketoesters in Table II, which are related to conformations of the polymers in solutions, are similar to those of the original polysaccha-
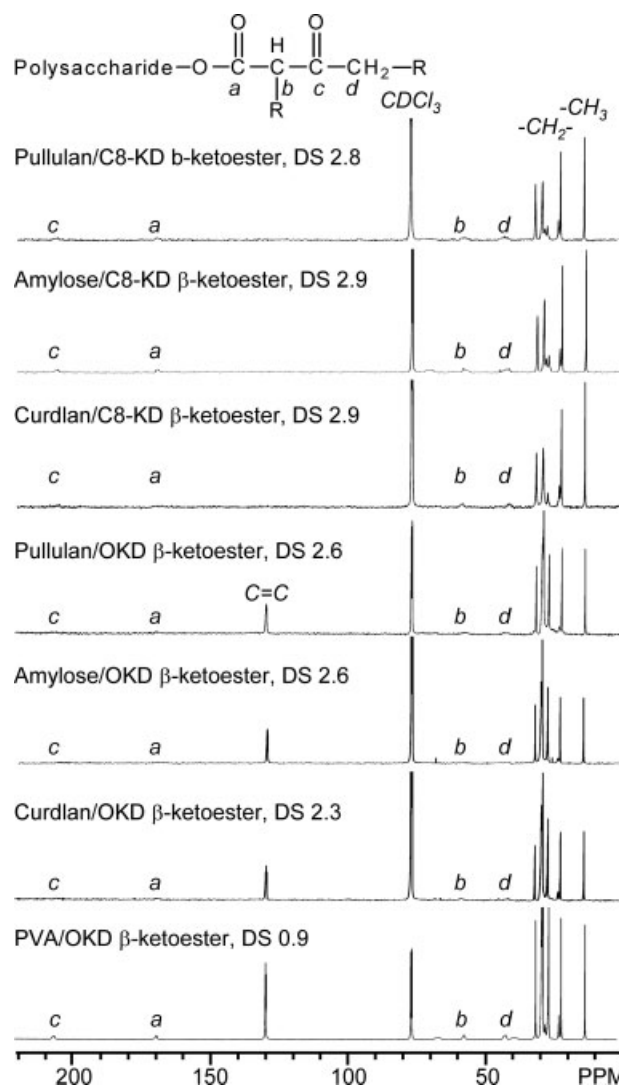


**Figure 4** Solution-state $^{13}$C-NMR spectra of polysaccharide and PVA β-ketoesters.

ketoesters, the SEC elution pattern of, for instance, the amylose β-ketoester was shifted to higher elution volume or lower molecular mass direction, compared with the SEC elution pattern in Figure 5. The conformation plots of curdlan/C8-KD β-ketoester was extremely scattered probably because of the presence of a trace amount of aggregates. Other three β-ketoesters had linear or slightly curved conformation plots. Based on the Benoit–Dotty theory,[16,17] the shorter the polymer chains, the more rigid they are. Thus, the conformation plots of these three β-ketoesters were slightly curved. In the case of the polysaccharide/OKD β-ketoesters, long and bulky substituents might have no or a little influence on the chain stiffness irrespective of the DP values, whereas the polysaccharide/C8-KD are influenced more.
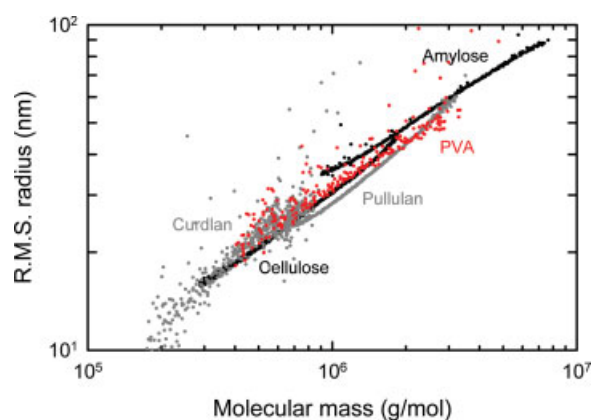
**Figure 5** SEC elution patterns of polysaccharide/OKD and PVA/OKD β-ketoesters. THF was used as the eluent. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
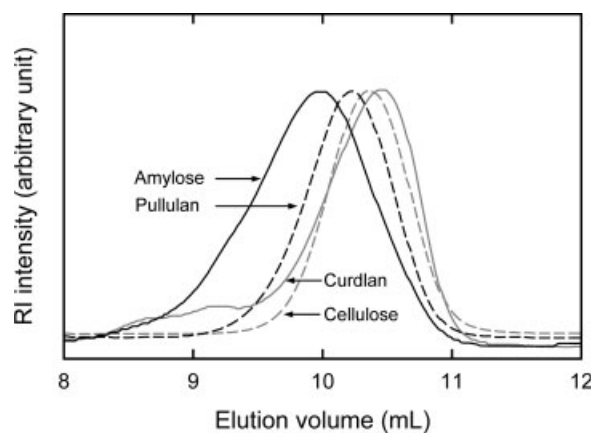


**Figure 7** SEC elution patterns of polysaccharide/C8-KD β-ketoesters. THF was used as the eluent.
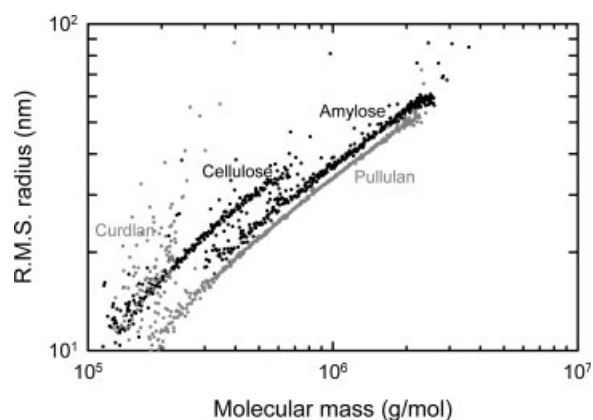
rides or PVA in Table I. All polysaccharides and PVA except amylose and the corresponding β-ketoesters have random-coil or flexible conformations in 1% LiCl/DMI and THF, respectively. Thus, no significant changes in the conformations occur before and after the β-ketoesterifications of the polysaccharides and PVA; the solid-like behavior of polymer chains in the β-ketoesters observed in NMR spectra (Figs. 3 and 4) could not be explained by the conformation analysis using SEC-MALLS not only for cellulose β-ketoesters[8,9] but other polysaccharide and PVA β-ketoesters. Again, the specific polymer-brush-type chemical structures of polysaccharide and PVA β-ketoesters having substituents with long and branched alkyl or alkenyl chains may have brought about such anomalous solution-state ^{1}H- and ^{13}C-NMR spectra in Figures 3 and 4.

## CONCLUSIONS

PVA and four glucans, cellulose, curdlan, amylose and pullulan, were reacted with either OKD or C8-KD under homogeneous conditions in 4% LiCl/DMI to prepare PVA and polysaccharide β-ketoesters with high DP values. The isolated and purified reaction products had chemical structures of polysaccharide β-ketoesters with DS 2.1–2.9. The polysaccharide/C8-KD β-ketoesters had DS values higher than those of the polysaccharide/OKD β-ketoesters, when prepared under the same conditions. In all polysaccharide and PVA β-ketoesters, nearly no or quite small carbon or proton signals due to polymer chains and substituents close to the polysaccharide chains were observed in the solution-state NMR spectra, indicating that the polymer chains of the β-ketoesters behave like solid in solutions. The specific chemical structures of the substituents having long and branched alkyl or alkenyl chains may have brought about such anomalous solution-state NMR patterns,



**Figure 6** Conformation plots of polysaccharide/OKD and PVA/OKD β-ketoesters. [Color figure can be viewed in the online issue, which is available at www.interscience. wiley.com.]



**Figure 8** Conformation plots of polysaccharide/C8-KD β-ketoesters.

irrespective of the chemical structures of the polymer chains. Conformation analysis of the β-ketoesters in solutions by SEC-MALLS could not explain the unique NMR patterns; most of the β-ketoesters had flexible or random-coil conformations in THF.

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