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Preparation of polymer brush-type cellulose β-ketoesters using LiCl/1,3-dimethyl-2-imidazolidinone as a solvent

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Abstract

Cellulose β-ketoesters with branched alkenyl chains were prepared using cis-9-octadecenyl ketene dimer (OKD) and LiCl/1,3-dimethyl-2-imidazolidinone (DMI) 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. The results showed that 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 cellulose/OKD β-ketoesters with DS 2.1 behave like solid in chloroform owing to strong restriction on movement of cellulose chains by the long and branched alkenyl substituents introduced. Size-exclusion chromatographic analysis showed that little depolymerization occurred on cellulose during β-ketoesterification at room temperature, and that molecules of the cellulose/OKD β-ketoesters with DS 2.1 had semi rigid-rod conformation in tetrahydrofuran. Thus, cellulose β-ketoesters with densely substituents like polymer brushes or comb-shaped polymers were prepared in this study.

Keywords: Cellulose derivatives; Ketene dimer; Cellulose solvent

1. Introduction

Many aqueous and non-aqueous cellulose solvent systems have been developed so far, and some of them were used as homogeneous derivatization media of cellulose at laboratory levels. Non-aqueous cellulose solvent systems are often favorable in terms of efficient derivatizations with less reagents and controllability of degree of substitution in cellulose esterifications and etherifications [1,2]. Especially, lithium chloride/*N*,*N*-dimethylacetamide (DMAc) has some advantageous points in the preparation procedure of cellulose solutions and their stabilities compared with other systems, and many studies of homogenous derivatizations of cellulose have been carried out using this solvent system [2–8]. The combination of LiCl and 1,3-dimethyl-2-imidazolidione (DMI) also dissolves cellulose through the same cellulose pretreatments as those for LiCl/DMAc [9]. The LiCl/DMI cellulose solvent system is superior to the LiCl/DMAc system as reaction media in homogeneous derivatizations in terms of efficient reactions in both esterifications and etherifications [10]. Moreover, LiCl/DMI can dissolve most cellulose samples including tunicate cellulose, bacterial cellulose and softwood bleached kraft pulps, which are difficult to dissolve completely in the LiCl/DMAc system [10,11].

Numerous cellulose derivatives with various substituents, degrees of substitution, distributions of substituents and molecular mass values have been reported so far in terms of cellulose resources, preparation methods and conditions, chemical structures, properties, functionalities and end use. Some cellulose ethers and esters have been prepared with reagents having alkyl chains under homogeneous conditions using cellulose solvents, LiCl/DMAc and SO_2/amine/dimethylsulfoxide, and the obtained products have unique solution-state and solid-state properties [6–8,12–17]. Especially, cellulose derivatives having

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relatively long alkyl chains as substituents with high degree of substitution are included in the category of polymer brushes having worm-like conformations [18]. In polymer science, hyper-branched polymers, dendrimers, rod-like macromolecules and polymer brushes have recently attracted much attention in terms of their unique structures and functionalities [19,20].

Alkyl ketene dimers (AKD) are synthesized from mixtures of stearic and palmitic acid chlorides in the presence of triethylamine, and have been produced at industrial level and used as one of the most efficient paper sizing chemicals in alkaline papermaking for more than two decades. AKD has a unique four-membered ring with branched alkyl chains, and is possible to react with alcoholic hydroxyls to form β-ketoesters under specific conditions. β-ketoesters formed between AKD and either cellobiose or maltose with degrees of substitution lower than 0.9 were prepared using dimethylformamide as a solvent [21]. If one AKD molecule is introduced into one anhydroglucose unit of cellulose through the β-ketoester linkage, two alkyl chains are brought in at once. Cellulose/AKD β-ketoesters were prepared using LiCl/DMAc cellulose solvent system, but they had degrees of substitution of lower than 0.14, and thus were insoluble in any organic solvents [22]. Because AKD has a melting point of 50–60 °C, heating of the reaction mixture at more than 60 °C is required to maintain the homogeneous solution state during the reactions between cellulose and AKD in cellulose solutions. On the other hand, alkenyl ketene dimer, which is prepared from oleic acid chloride, is liquid at room temperature because of the presence of double bonds in the alkyl chains [23,24]. Thus, reactions between cellulose and alkenyl ketene dimer can proceed, maintaining homogenous solution state even at room temperature.

In this study, cellulose was dissolved in the LiCl/DMI system, and reacted with oleic ketene dimer (OKD) to prepare cellulose β-ketoesters with DS values as high as possible under non-aqueous and homogenous conditions to prepare cellulose polymer brushes. In this paper, relationships between reaction conditions and degree of substitution were studied in detail. Chemical structures and molecular mass values of the obtained products were analyzed by FT-IR, solution- and solid-state NMR, and size exclusion chromatography attached with a multi angle laser light scattering detector (SEC-MALLS).

2. Experimental

2.1. Materials

Microcrystalline cellulose produced from cotton linter (Cellulose Powder C, Advantec Tokyo Co., Ltd, Japan) was used as a cellulose sample after vacuum drying at room temperature for one day. Oleic ketene dimer (cis-9-octadecenyl ketene dimer: OKD), which was prepared from oleic acid chloride and triethylamine by the conventional method of preparing alkyl ketene dimmers [25], was kindly provided by NOF Corporation, Japan. OKD was light-yellow liquid at room temperature [23]. Purity of the OKD determined by ^{1}H-NMR was more than 90%. Anhydrous lithium chloride (LiCl), 1,3-dimethyl-2-imidazolidinone (DMI), 1-methylimidazole (MEI), phenyl isocyanate, pyridine and other reagents and solvents were of laboratory grade (Wako Pure Chemicals, Co. Ltd, Japan), and used without further purification. Tetrahydrofuran (THF) of liquid chromatographic grade (Wako Pure Chemicals, Co., Ltd, Japan) was used as an eluent of size exclusion chromatography. Methyl β-ketoester was prepared as a reference sample by heating an OKD/methanol mixture at 90 °C for 3 h in the presence of a catalytic amount of sodium acetate. Polystyrene standard (M_w 30,000; Pressure Chemical Co., U.S.A.) was used for MALLS calibration.

2.2. Preparation of cellulose solution

Two mass percentage cellulose solutions in 8 mass % LiCl/DMI were prepared on the basis of the reported method [9,10]. 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. After complete dissolution of cellulose, DMI (500 g) was added to the solution to reduce the viscosity, and thus 1 mass % cellulose solution in 4 mass % LiCl/DMI was obtained. The procedure to prepare cellulose/LiCl/DMI solutions used in this study is the same as that for preparation of cellulose/LiCl/DMAc solutions reported by McCormik et al. [26].

2.3. Reactions of cellulose with oleic ketene dimer

Desired amounts of oleic ketene dimer and 1-methylimidazole were slowly added to the cellulose solution stirred at room temperature. The molar ratios of oleic ketene dimer:1-methylimidazole:anhydroglucose unit of cellulose (OKD:MEI:AGU) varied from 3:3:1 to 10:10:1. In some experiments, 1-methylimidazole was not added at all. Being stirred at room temperature (20 ± 5 °C), 60 ± 5 °C or 100 ± 5 °C for 1–12 h, the mixture was poured into a large volume of 1-propanol. Precipitates thus formed were washed thoroughly with fresh 1-propanol. All the purified samples were dried in a vacuum oven at 40 °C for 1 day.

2.4. Preparation of cellulose triphenylcarbanilate

Carbanilation of the microcrystalline cellulose was carried out according to the method reported by Evans et al. [27,28]. Dry cellulose (50 mg) was suspended in a solution consisting of phenyl isocyanate (1 mL) and pyridine (10 mL), and the mixture was stirred at 80 °C for 48 h until a clear solution was obtained. Then methanol (1 mL) was added to the mixture to consume excess phenyl isocyanate, and the solution was poured into an aqueous methanol (100 mL, MeOH:water = 7:3 by volume). The precipitate thus formed was collected by centrifugation, washed successively with aqueous methanol and water by centrifugation, and dried in a vacuum oven at 60 °C for 1 day. No hydroxyl groups were detected at 3400 cm^{-1} in the IR spectrum of the obtained product.

2.5. SEC-MALLS analysis

Molecular mass values of the reaction products were measured by size exclusion chromatography (SEC) attached with a laser light scattering detector (MALLS) using THF as an eluent. The SEC-MALLS system consisted of an on-line degasser (DGU-12A; Shimadzu, Japan), a high-pressure pump (LC-10ADVP; Shimadzu, Japan), a stainless steel in-line filter with a 0.1 μm poly(tetrafluoroethylene) (PTFE) membrane (Millipore, U.S.A.), a manual injector (Model 7125; Rheodyne, U.S.A.), a column oven (CTO-10ACVP; Shimadzu), a SEC column packed with styrene-divinylbenzene copolymer gel (KD-806M; Shodex, Japan), a post-column filter with a 0.5 μm stainless steel frit (A-310; Upchurch Scientific, U.S.A.), a MALLS detector (DAWN EOS, $\lambda = 690$ nm; Wyatt technologies, U.S.A.) and a refractive index detector (RID-10A; Shimadzu, Japan). Data acquisition and processing were carried out using the ASTRA software (Wyatt technologies, U.S.A.). SEC conditions were as follows: the sample concentration of 0.02% (w/V), injection volume of 100 μL, flow rate of 0.5 mL/min and the column temperature of 40 °C. The detector cells of MALLS and RI were kept at ambient temperature. Before injection, the sample solutions were filtered through a 0.2 μm PTFE disposable membrane. The eluent was also filtered through a 0.2 μm PTFE membrane before use. The dn/dc values of cellulose derivatives in THF were determined using an interferometric refract meter (Optilab DSP, $\lambda = 690$ nm; Wyatt technologies, U.S.A.). The obtained dn/dc values were 0.169 and 0.080 mL/g for cellulose triphenylcarbanilate and cellulose/OKD β-ketoester with DS 2.1, respectively, and used for calculation of molecular mass values in the SEC-MALLS analysis. Another SEC column (Tosoh TSK gel G2500H_{XL}) was used in the SEC analysis for detection of non-cellulosic substances in the products.

2.6. Other analyses

FT-IR spectra of the reaction products were obtained using a Nicolet Magna 860 (Madison, WI, USA) by either the KBr disk technique or thin film method formed on a KRS-5 plate. Degrees of substitution (DS) of the reaction products were determined by elementary analysis, and expressed as average values of three measurements for one sample. Fluctuation ranges of the DS values were within ±0.1. Solution-state ^{1}H- and ^{13}C-NMR spectra of the reaction products were recorded on a Bruker AC-300 using deuterated chloroform and tetramethylsilane (both from Wako Pure Chemicals Co., Japan) as the solvent and internal standard, respectively. Some solution-state ^{13}C-NMR data of cellulose derivatives were accumulated for two days by the quantitative mode excluding the nuclear Overhauser effect at each pulse delay of 3 min. Solid-state ^{13}C-NMR spectra of cellulose derivatives were obtained on JEOL JNM-EX 400 (100.4 MHz) with cross-polarization and magic angle sample spinning under the following conditions: spinning rate 5 kHz, pulse delay 5 s and contact time 5 ms.

3. Results and discussion

3.1. Preparation and purification of cellulose β-ketoesters

Relationships between reaction conditions and degree of substitution of cellulose β-ketoesters were studied using oleic ketene dimer (OKD) and 1-methylimidazole (MEI) as the esterifying reagent and base catalyst, respectively, using the LiCl/DMI cellulose solvent system (Fig. 1). Oleic ketene dimer can be prepared from oleic acid chloride in the presence of triethylamine. Because OKD was liquid at room temperature (melting point −2.5 °C) due to the presence of double bonds in the chains, it was well mixed with the cellulose solution during the reaction. Molar ratios of the reagents to anhydroglucose unit of cellulose in the solution varied from 3:3:1 to 10:10:1 for OKD:1-methylimidazole:anhydroglucose unit of cellulose (OKD:MEI:AGU), respectively. Reactions were carried out at 20–100 °C for 0–12 h, and the reaction products were isolated as the precipitates formed by pouring the reaction mixtures into 1-propanol. Low-molecular-weight compounds originating from the solvent components and reagents were completely removed from the precipitates by washing them four times with 1-propanol through filtration. Purification by this washing method with 1-propanol was confirmed by SEC analysis of the products (Fig. 2(A)). When ethanol was used in place of 1-propanol as the precipitation medium and washing solvent, on the other hand, low-molecular-mass by-products and OKD remained more or less in the products even after washing four times (Fig. 2(B)). Details about the by-products are discussed in the latter section. The purified reaction products after drying were white gummy solids or powders, depending on DS values.

FT-IR spectra of the purified reaction products are shown in Fig. 3. Expectedly, the absorption band at about 3400 cm^{-1} due to the cellulose hydroxyls decreased with increasing the degree of substitution (DS), and inversely the absorption bands at 1740 and 1710 cm^{-1} due to the C=O stretching vibration of β-ketoester groups increased [21,22]. The bands at 2800–3000, 1470 and 720 cm^{-1} due to C–H

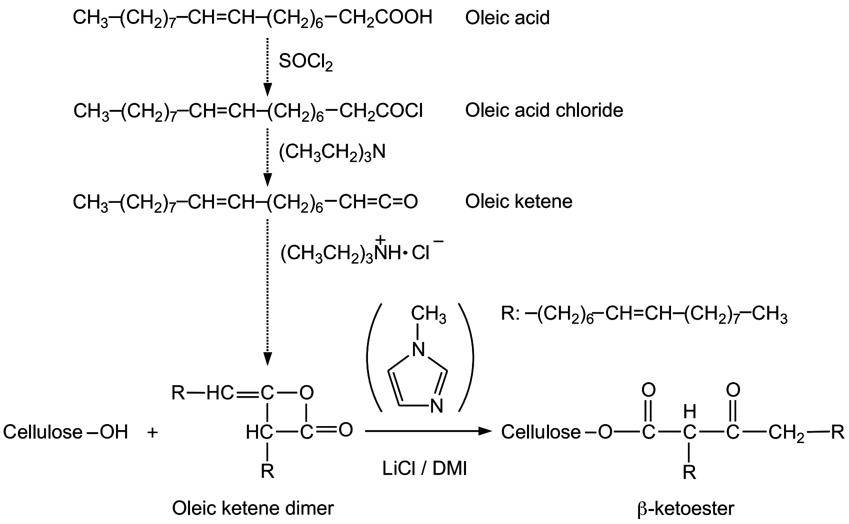

Fig. 1. Preparation of oleic ketene dimer (OKD), and reaction between cellulose and OKD using the LiCl/DMI cellulose solvent.

stretching and deformation vibrations of alkyl chains also increased with the β-ketoesterification. Thus, OKD was successfully introduced into cellulose hydroxyls through β-ketoester linkages by the homogeneous reaction using LiCl/DMI as the cellulose solvent.

3.2. Relationships between reaction conditions and degree of substitution

The relationships between the reaction time and DS of the cellulose β-ketoesters prepared under different conditions are shown in Figs. 4–6. In the case of the reaction at room temperature (Fig. 4), DS values increased with increasing the reaction time up to about 3 h, and then mostly reached plateau levels. When the molar ratios of oleic ketene dimer:1-methylimidazole:anhydroglucose unit of cellulose (OKD:MEI:AGU) were 3:3:1 and 6:6:1, the DS values of the products were only 0.2 and 0.5, respectively, even after the reaction for 12 h. The DS value reached approximately 2.1 at the OKD:MEI:AGU molar ratio of 10:10:1 after the reaction for 2 h. The extended reaction time, however, could bring about no clear increases in the DS value. Yields of the cellulose/OKD β-ketoesters, which were calculated from their recovered weights and DS values after the purification, were more than 95%, and thus

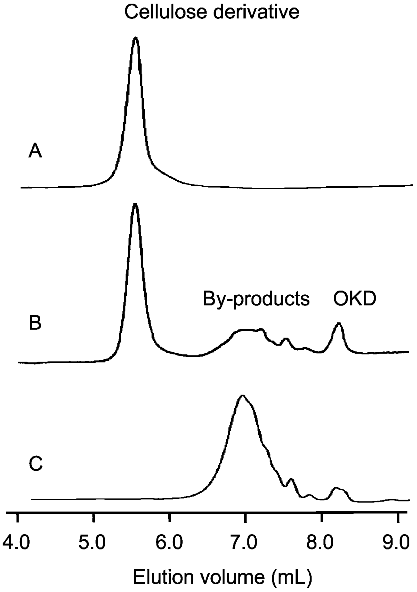

Fig. 2. SEC patterns of purified (A) and incompletely unpurified (B) reaction products, and by-products (C) formed from OKD in the products. The reaction products A and B were prepared at the molar ratio of oleic ketene dimer:1-methylimidazole:anhydroglucose unit of cellulose (OKD:MEI:AGU) of 10:10:1 and room temperature for 3 h.

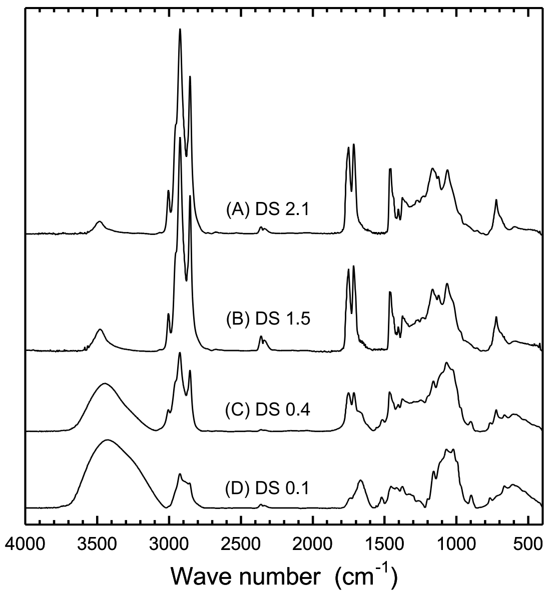

Fig. 3. FT-IR spectra of cellulose/OKD β-ketoesters with different degrees of substitution. The samples A was prepared at the molar ratio of oleic ketene dimer:1-methylimidazole:anhydroglucose unit of cellulose (OKD:MEI:AGU) of 10:10:1 at room temperature for 3 h.

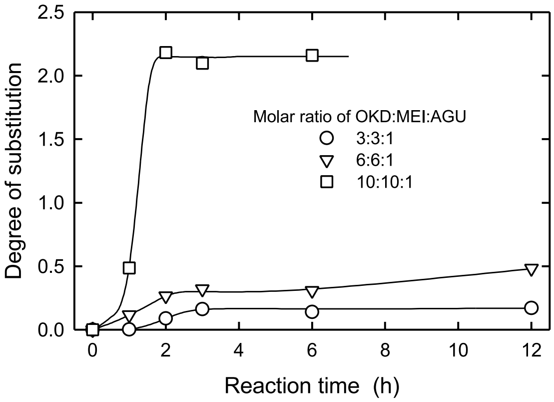

Fig. 4. Relationships between reaction time and DS of cellulose/OKD β-ketoesters prepared at room temperature. OKD: oleic ketene dimer, MEI: 1-methylimidazole, AGU: anhydroglucose unit of cellulose.

cellulose/OKD β-ketoesters can be obtained almost quantitatively.

More efficient introduction of OKD into cellulose hydroxyls was expected by reactions at higher temperatures. Nevertheless, as shown in Figs. 5 and 6, DS values of the products clearly decreased, when the reaction was carried out at 60 or 100 °C. The effects of reaction temperature on the DS values of the products are re-plotted in Fig. 7. It is clear that the higher the reaction temperature is, the lower the DS values of the products are. This result is inconsistent with normal reactions of alcoholic compounds with esterifying reagents such as organic acid anhydrides or organic acid chlorides. Some side reactions of OKD other than the introduction into cellulose as β-ketoesters must be taken into account to explain these anomalous phenomena. This subject of side reactions of ketene dimers is discussed in the latter section.

The effects of addition level of 1-methylimidazole on DS values of cellulose/OKD β-ketoesters are depicted in Fig. 8. These reactions were carried out at either room temperature or 100 °C for 3 h, where the molar ratio of OKD to anhydroglucose unit of cellulose was fixed to 10:1. In the case of the reaction at room temperature, the presence of 1-methylimidazole is necessary for the β-ketoester formation between cellulose and OKD. The DS value clearly increased with increasing the addition level of the amine catalyst. On the other hand, β-ketoester formation clearly occurred on cellulose hydroxyls even without the amine catalyst at 100 °C, where the optimum ratio exists around 10:4 for the OKD:MEI molar ratio.

Fig. 9 shows more detailed relationship between the OKD:AGU molar ratio and DS of the reaction products. Here, the OKD:MEI molar ratio was fixed to 1:1, and the reaction was carried out at room temperature for 3 h. The DS value remarkably increased between 6:1 and 8:1 for the molar ratio of OKD to anhydroglucose unit of cellulose. Thus, the amount of OKD added is critical to control the DS values of the cellulose/OKD β-ketoesters, and it is possible to introduce OKD into cellulose hydroxyls up to DS of approximately 2. However, it seems to be difficult to reach the DS value of 3 probably because of steric hindrance due to bulky alkenyl β-ketoester groups already introduced into cellulose hydroxyls. When ketene dimers with shorter alkyl chains like decanoic ketene dimer were used as the reagents for the homogeneous reactions, DS values of the

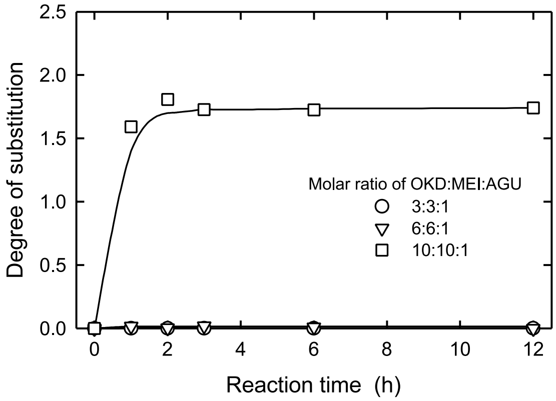

Fig. 5. Relationships between reaction time and DS of cellulose/OKD β-ketoesters prepared at 60 °C. See the footnote of Fig. 4.

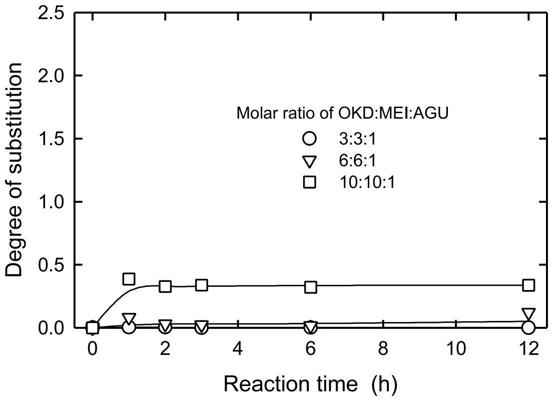

Fig. 6. Relationships between reaction time and DS of cellulose/OKD β-ketoesters prepared at 100 °C. See the footnote of Fig. 4.

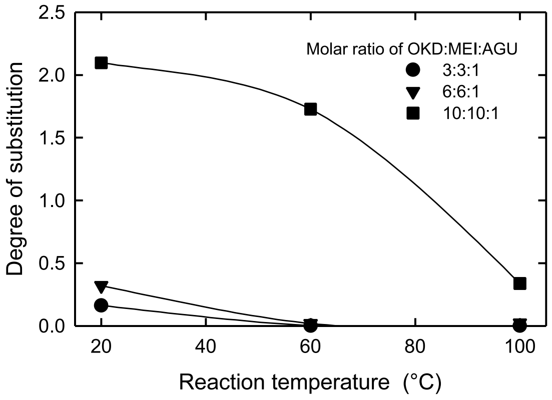

Fig. 7. Relationships between reaction temperature and DS of cellulose/OKD β-ketoesters prepared at various molar ratios of the reagents to anhydroglucose unit of cellulose for 3 h. See the footnote of Fig. 4.

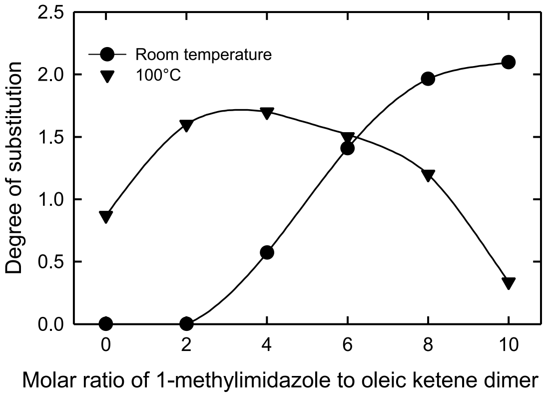

Fig. 8. Relationships between molar ratio of 1-methylimidazole to oleic ketene dimer and DS of cellulose/OKD β-ketoesters prepared at either room temperature or 100 °C for 3 h. Molar ratio of OKD:anhydroglucose unit of cellulose was fixed to 10:1.

corresponding cellulose β-ketoesters increased up to 2.7. Details will be presented in the following paper.

3.3. Side reactions and formation of by-products

When OKD/LiCl/DMI mixtures (without cellulose) with or without 1-methylimidazole were heated at 60–100 °C for 1–24 h, some oily by-products having molecular mass values ranging 1000–10,000 were formed (Fig. 2C). The higher the reaction temperature was, the more the by-products were formed. These by-products were also present in the incompletely purified cellulose/OKD β-ketoester products (Fig. 2(B)). When the molar ratio of OKD and 1-methylimidazole was 1:1, OKD was mostly converted to the by-products by stirring the mixture (without cellulose) at 100 °C for 3 h. Because the by-products once formed were no longer possible to react with cellulose hydroxyls, the formation of the by-products from OKD during the reaction hinders the formation of cellulose/OKD β-ketoester linkages. Thus, the anomalous relationships between the reaction temperature and DS values of cellulose/OKD β-ketoesters in Figs. 7 and 8 are explainable by the by-product formation and the corresponding decrease in the amount of OKD in the reaction media at higher temperatures. Because the molecular mass values of the by-products (ca. 1000–10,000) were far lower than those of cellulose/OKD β-ketoesters, it is possible to confirm the absence of the by-products in the purified cellulose/OKD β-ketoester samples from their SEC patterns (Fig. 2(A)).

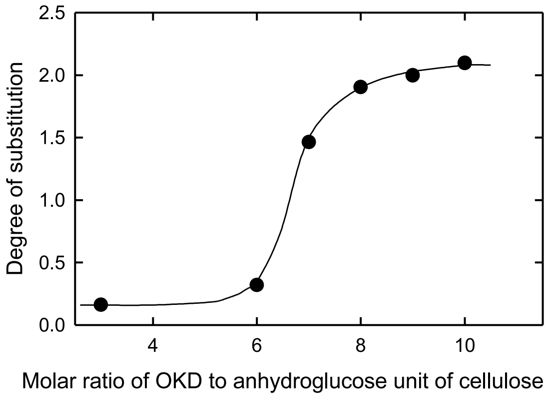

Fig. 9. Relationships between molar ratio of oleic ketene dimer to anhydroglucose unit of cellulose and DS of cellulose/OKD β-ketoesters prepared at room temperature for 3 h. Molar ratio of OKD:1-methylimidazole was fixed to 1:1.

We have been studying structural analyses of the by-products and their formation conditions. FT-IR, SEC and elementary analyses indicated that the by-products were mixtures of OKD oligomers, in which OKD molecules were linked each other through ester bonds. It was reported that oligomers of alkyl ketene dimer (AKD) were formed from stearic and palmitic acid chlorides in the yields of about 10% during the AKD wax production process in the presence of amine catalyst (generally triethylamine), and present as contaminants in commercial AKD wax [29–31]. Thus, the OKD oligomers formed as the by-products in this study are probably in the same category of the reported AKD oligomers. The OKD oligomers are preferably formed from OKD during the reactions in the presence of 1-methylimidazole especially at high temperatures rather than the formation of β-ketoester linkages with cellulose, and these side reactions are likely to have brought about lower DS values of cellulose/OKD β-ketoesters at high temperatures (Figs. 4–8).

3.4. NMR analyses of cellulose/OKD β-ketoester

The cellulose/OKD β-ketoesters with DS of more than 1.4 were gummy solids at room temperature due to the branched alkenyl chains introduced into cellulose hydroxyls. The cellulose/OKD β-ketoesters with DS of more than 1.4 were soluble in both chloroform and THF. In this and the next sections, the cellulose/OKD β-ketoester with DS 2.1 (Sample A in Figs. 2 and 3) was further characterized by NMR and SEC-MALLS, respectively.

Chemical structures of OKD, methanol/OKD β-ketoester and cellulose/OKD β-ketoester are shown in Fig. 10 for labeling each carbon position. Solution-state ^{13}C-NMR spectra of OKD, methanol/OKD β-ketoester and cellulose/OKD β-ketoester with DS 2.1 dissolved in $CDCl_3$ are shown in Fig. 11 together with solid-state ^{13}C-NMR spectrum of the cellulose/OKD β-ketoester. ^{1}H-NMR spectra of theses compounds dissolved in $CDCl_3$ were illustrated in Fig. 12. Alphabets and numbers in the spectra correspond to carbons or protons of each compound in Fig. 10.

When ^{13}C-NMR spectrum of the cellulose/OKD β-ketoester with DS 2.1 was recorded under normal proton-decoupling conditions, neither cellulose carbons nor at least the a–d carbons of β-ketoesters appeared at all in the spectrum. Moreover, almost the same ^{13}C-NMR spectrum was obtained, even though the ^{13}C-NMR analysis was carried out at the pulse delay of 3 min using the quantitative mode to exclude the nuclear Overhauser effect. In contrast,

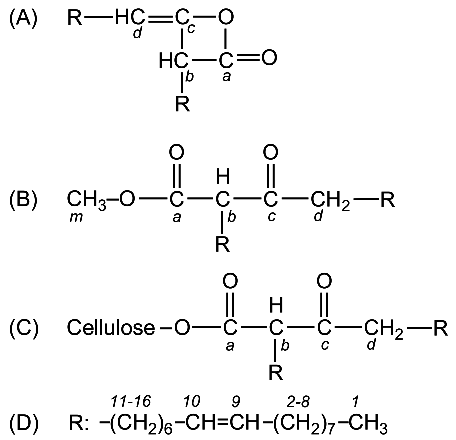

Fig. 10. Chemical structures of oleic ketene dimer (OKD), methanol/OKD β-ketoester and cellulose/OKD β-ketoester with alphabets and numbers for labeling each carbon position.

methanol/OKD β-ketoester showed all the corresponding carbon signals in the ^{13}C-NMR spectrum. This result indicates that the cellulose chains and at least the a–d carbons of β-ketoester groups behave like 'solid' even in the solution-state by strong restriction on movement of cellulose backbone due to the presence of flexible alkenyl chains of the substituents. On the other hand, cellulose and the *a-d* carbons of β-ketoester groups were detected in the solid-state ^{13}C-NMR spectrum; the β-ketoester linkages between OKD and cellulose hydroxyls are obviously formed in the product. Thus, the extremely restricted movement of cellulose carbons observed in the solution-state ^{13}C-NMR spectrum is characteristic for the cellulose/OKD β-ketoester. It is well known that comb-shaped copolymers with densely grafted side chains in a good solvent can adopt a worm-like cylindrical brush configuration, in which the side chains are stretched in the direction normal to the backbone owing to the excluded volume interaction [20].

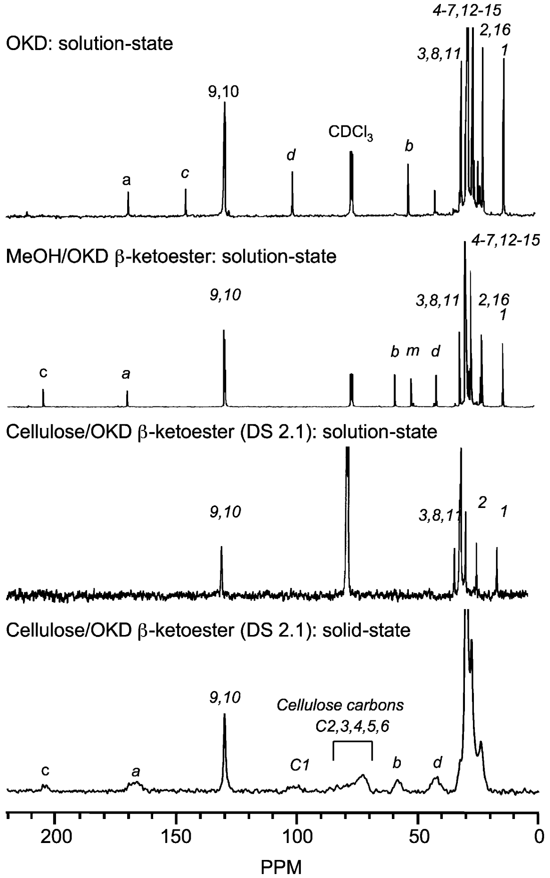

Fig. 11. Solution-state ^{13}C-NMR spectra of oleic ketene dimer (OKD) and methanol/OKD β-ketoester, and solution- and solid-state ^{13}C-NMR spectra of cellulose/OKD β-ketoester with DS 2.1. The solution-state ^{13}C-NMR spectrum of cellulose/OKD β-ketoester was recorded by the quantitative mode with pulse delay of 3 min.

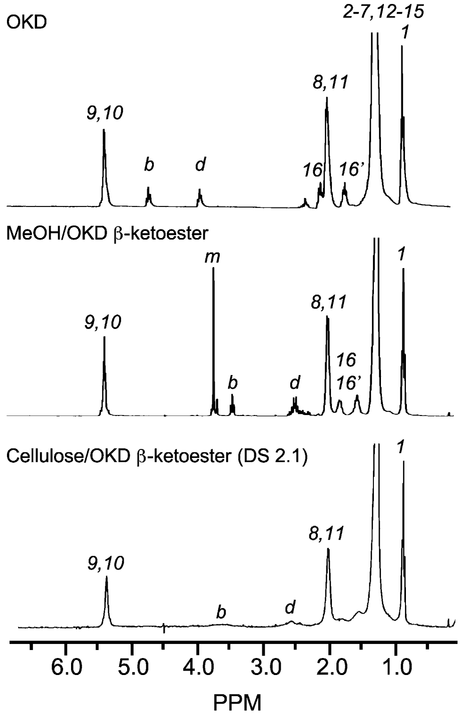

Fig. 12. ^{1}H-NMR spectra of oleic ketene dimer (OKD), methanol/OKD β-ketoester and cellulose/OKD β-ketoester with DS 2.1.

It is interesting to make clear distribution of the OKD substituent among C2, C3 and C6 hydroxyl groups of anhydroglucose unit for the cellulose/OKD β-ketoester with DS 2.1. ^{13}C-NMR analysis is often used to determine distribution of substituents in anhydroglucose unit for cellulose esters and ethers with DS values lower than 3 [32–34]. In the case of cellulose/OKD β-ketoesters, however, no information in terms of distribution of the OKD substituent could be obtained, because signals due to neither cellulose carbons nor carbonyl carbons of β-ketoesters appeared at all in the solution-state ^{13}C-NMR spectra. Further studies using other methods are then required to elucidate distribution of the substituent in the cellulose/OKD β-ketoesters.

^{1}H-NMR spectrum of the cellulose/OKD β-ketoester also supports the above hypothesis. The methyl protons of the substituent groups are well resolved to triplet like low-molecular-mass compounds, while the protons b, d, 16 and 16′ are broad and no cellulose protons are detected at all because of strong restriction on movement. The signal broadening is also observable for the protons 8–11 of cellulose/OKD β-ketoester.

3.5. SEC-MALLS analysis of cellulose/OKD β-ketoester

Molecular conformation or rigidity of the cellulose/OKD β-ketoester with DS 2.1 was then studied in comparison with cellulose triphenylcarbanilate by the SEC-MALLS method using THF as an eluent. Fig. 13 shows SEC elution patterns and the corresponding molecular mass (MM) plots of cellulose triphenylcarbanilate and cellulose/OKD β-ketoester. In both cases, the MM plots decrease with increasing the elution volume, showing that each molecule is properly separated according to its occupied volume by the SEC system. The peak position in the elution pattern of cellulose/OKD β-ketoester is higher than that of cellulose triphenylcarbanilate, and the MM value of the former is 2–3 times as much as that of the latter at the same elution volume. Because average mass values of one glucose residue in cellulose triphenylcarbanilate and cellulose/OKD β-ketoester with DS 2.1 were 519 and 1270.8, respectively, the difference in the MM plots between the two samples is quite reasonable.

Table 1 summarizes weight and number average molecular mass values of the original microcrystalline cellulose, cellulose triphenylcarbanilate and cellulose/OKD β-ketoester with DS 2.1. The cellulose/OKD β-ketoester has the highest molecular mass value because of the large OKD substituent introduced. However, the calculated degree of polymerization (DP) values are similar among the three samples, indicating that little depolymerization occurred on cellulose during the β-ketoesterification with OKD and 1-methylimidazole at room temperature in the cellulose solution. All the three samples have similar polydispersities of 1.4–1.6.

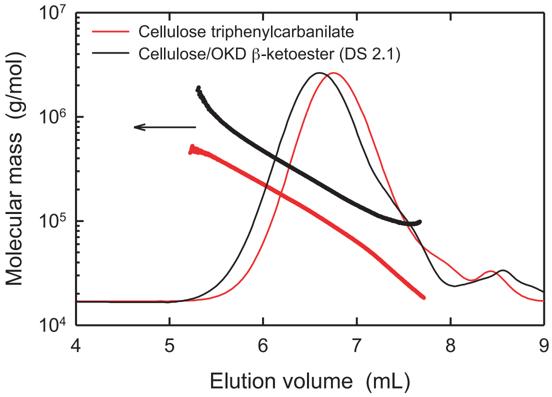

Fig. 13. SEC elution patterns and molecular mass plots of cellulose triphenylcarbanilate and cellulose/OKD β-ketoester with DS 2.1.

Fig. 14 depicts conformation plots, i.e. double logarithmic plots of radii of gyration ($\langle S^2\rangle^{1/2}$ or Rg) versus MM obtained by the SEC-MALLS analysis of cellulose triphenylcarbanilate and cellulose/OKD β-ketoester. According to the scaling concept of polymer solutions [35], relationships between $\langle S^2\rangle^{1/2}$ and MM of a polymer are expressed as follows;

$$\langle S^2\rangle^{1/2} \propto \mathrm{MM}^{\nu}$$

Where the scaling exponent ν is related to the molecular conformation of the polymer as well as interactions between the polymer and the solvent. When the exponent ν ranges from 0.5 to 0.6, the polymer molecules are regarded to have random coil or linear flexible conformation in a good solvent. When the exponent value ranges from 0.6 to 1.0, the molecules have rigid-rod conformation. As shown in Fig. 14, the slope of plots for cellulose triphenylcarbanilate gives $\nu = 0.59 \pm 0.01$, indicating that these molecules have random coil conformation in THF. On the other hand, the cellulose/OKD β-ketoester with DS 2.1 has the slope value of 0.71 ± 0.02, which corresponds to semi rigid-rod conformation.

This conformation of cellulose/OKD β-ketoester molecules is ascribed to the OKD groups introduced into cellulose hydroxyls. However, the unusual solution-state ^{13}C-NMR spectrum of this compound in Fig. 11 cannot be explained only by its semi rigid-rod conformation, because the difference in the slope value between 0.59 and 0.71 is not so remarkable. It is likely, therefore, that the cellulose backbones of the cellulose/OKD β-ketoester with DS 2.1 behave like solid in $CDCl_3$ due to the flexible long and blanched alkenyl substituents introduced into cellulose hydroxyls, while terminal alkyl carbons of the substituents behave like low-molecular-mass compounds well dissolved in $CDCl_3$. Thus, the polymer brush-type cellulose β-ketoesters having unique solution-state characteristics are prepared with oleic ketene dimer using the LiCl/DMI cellulose solvent system.

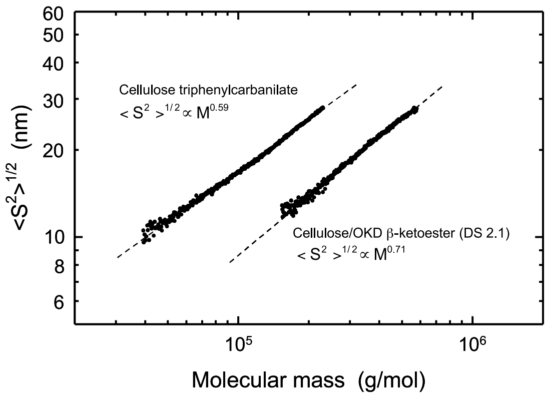

Fig. 14. Conformation plots of cellulose triphenylcarbanilate and cellulose/OKD β-ketoester with DS 2.1.

Table 1
Weight and number average molecular mass values (M_w and M_n, respectively) and the corresponding degrees of polymerization (DPw and DPn, respectively) of cellulose triphenylcarbanilate and cellulose/OKD β-ketoester

Sample	DS	M_w	M_n	(DPw)	(DPn)	M_w/M_n
Microcrystalline cellulose[a]	–	38,900	24,500	240	150	1.6
Cellulose triphenylcarbanilate	3.0	98,900	65,600	191	126	1.5
Cellulose/OKD β-ketoester[b]	2.1	256,000	188,000	202	148	1.4

[a] Cited from the previous paper [11].

[b] Prepared with oleic ketene dimer (OKD): 1-methylimidazole (MEI): anhydroglucose unit of cellulose (AGU) = 10:10:1 at ca. 20 °C for 3 h.

3.6. Stability of cellulose/OKD β-ketoesters

The stability of β-ketoester bonds was studied using cellulose/AKD β-ketoesters in the previous paper [22]; cellulose β-ketoester bonds are stable without cleavage even after treatments in water at 80 °C for 24 h or at 20 °C for 2 months. Thus, the cellulose β-ketoester bonds themselves are fairly stable at room temperature. Thermogravimetric analysis revealed that the cellulose/OKD β-ketoester with DS 2.1 was stable without degradation up to 250 °C in N_2 atmosphere. On the other hand, the cellulose/OKD β-ketoesters originally soluble in $CHCl_3$ became partly $CHCl_3$-insoluble by exposing the compound to air or by light-irradiation within one month. Some cross-linkages between the substituents must have occurred at the double bonds in the compound during these treatments. Thus, the cellulose/OKD β-ketoesters once prepared should be stored in dark under N_2 atmospheric conditions to avoid cross-linking.

4. Conclusions

Polymer-brush-type cellulose β-ketoesters with branched alkenyl chains with DS of up to 2.1 were prepared by homogeneous reaction between oleic ketene dimer and cellulose dissolved in the 4 mass % LiCl/DMI solution. The cellulose/OKD β-ketoester with the maximum DS was obtained, when the reaction was carried out at room temperature with the OKD:MEI:AGU molar ratio of 10:10:1, and the DS values were controllable by selecting the reaction conditions such as the amount of OKD added. Reactions at higher temperatures such as 60 and 100 °C resulted in decreases in DS of the products because of preferable formation of non-reactive by-products (mostly OKD oligomers) under these conditions. The cellulose/OKD β-ketoesters with DS 1.4–2.1 are gummy solid and soluble in both THF and chloroform. Solution-state ^{13}C-NMR analysis revealed that cellulose chains of the cellulose/OKD β-ketoesters with DS 2.1 behave like solid in chloroform owing to strong restriction on movement of cellulose chains, while terminal alkyl carbons of the OKD substituent do like low-molecular-mass compounds well dissolved in chloroform. SEC-MALLS analysis shows that molecules of the cellulose/OKD β-ketoesters with DS 2.1 have semi rigid-rod conformation in THF.

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