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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