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NMR characterization of cellulose acetate: Mole fraction of monomers in cellulose acetate determined from carbonyl carbon resonances

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ABSTRACT

Cellulose acetate (CA) samples with varying degrees of substitution were prepared via homogeneous acetylation in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) and by the acid-hydrolysis of cellulose triacetate in acetic acid. Quantitative analysis of the ^{13}C NMR spectra facilitated the assignment of the carbonyl carbon shifts of the 2-mono-, 3-mono-, 6-mono-, 2,3-di-, 2,6-di-, 3,6-di-, and 2,3,6-tri-substituted anhydroglucose units (AGUs), and the determination of the mole fraction of 7 AGUs and unsubstituted AGU in the CA chains. This shed some light on the mechanism of CA production in homogeneous reaction systems. In addition, comparison of the mole fractions of the 8 AGUs suggested that the acetone solubility of CA strongly related to the AGU composition.

1. Introduction

Cellulose acetate (CA) is a cellulose ester that is widely used in various materials (Bifari, Bahadar Khan, Alamry, Asiri, & Akhatar, 2016; Fisher et al., 2008). CA is generally produced by the esterification of the hydroxyl groups at the 2-, 3-, and 6-positions of the anhydroglucose units (AGUs) of cellulose with acetic anhydrides. The degree of substitution (DS), i.e., the average number of acetyl groups per AGU, is related to the physicochemical properties of CA. Commercial CA is produced through two-step reactions involving the acetylation of cellulose and partial hydrolysis of CA (Wu et al., 2004). First, the hydroxyl groups of cellulose are acetylated by acetic anhydride in the presence of acetic acid and concentrated sulfuric acid to form cellulose triacetate (CTA, DS = 3). Next, the acetyl groups of CTA are partially hydrolyzed upon addition of water to give products with the desired DS. The DS of commercial CAs is generally 1.9–2.5, because such samples are soluble in acetone (Fisher et al., 2008). On the other hand, CAs produced by one-step acetylation processes are not soluble in acetone, even if the DS is 1.9–2.5 (Heinze, Schwikal, & Barthel, 2005). Therefore, the substituent distribution at the 2-, 3-, and 6-positions of CA prepared by two-step reactions differs from that prepared by the one-step procedure, and these differences affect the solubility of CA.

Important properties of CA which could influence their structure-property relationships include DS, substituent distribution, and monomer composition (Fisher et al., 2008). Quantitative ^{13}C NMR is commonly used to estimate the DS and substitution distribution of CA (Kamide & Okajima, 1981; Buchanan, Edgar, Hyatt, & Wilson, 1991; Tezuka, 1993; Tezuka & Tsuchiya, 1995; Kono, Hashimoto, & Shimizu, 2015). DS can be determined from the integral values of the methyl and/or carbonyl carbon resonances of the substituent acetyl groups (Kamide & Okajima, 1981). To determine the substituent distribution of CA, perpropionated CA derivatives can be analyzed following the complete propionation of unsubstituted CA hydroxyl groups (Tezuka & Tsuchiya, 1995). The ^{13}C NMR spectrum of perpropionated CA exhibits two sets of three carbonyl carbon resonances, which correspond to acetyl groups at the 2-, 3-, and 6-positions and propionyl groups at the 2-, 3-, and 6-positions. Quantitative evaluation of the acetyl and propionyl triplet resonances permits the determination of the DS at the 2-, 3-, and 6-positions (DS_2, DS_3, and DS_6, respectively) of CA.

The composition of eight monomers comprising CA, i.e. un-, 2-mono-, 3-mono-, 6-mono-, 2,3-di-, 2,6-di-, 3,6-di-, and 2,3,6-tri-substituted AGUs, has been determined by acid or enzymatic hydrolysis of the polymeric CA chains followed by chromatographic separation and quantification (Glasser, McCartney, & Samaranayake, 1994; Saake, Horner, & Puls, 1998: Chap. 15). This approach can be used to estimate the mole fraction (χ) of the monomers, but the chemical heterogeneity of CA in the intact poly-

Abbreviations: AGUs, anhydroglucose units; [BMIM]Cl, 1-butyl-3-methylimidazolium chloride; CA, cellulose acetate; CMC, carboxymethylcellulose; CTA, cellulose triacetate; DS, degrees of substitution; EDA, electron donor–electron accepter; FWHM, full width at half maximum; HSQC, heteronuclear single quantum coherence; INEPT, Insensitive nuclei enhanced by polarization transfer; χ, mole fraction; MC, methylcellulose; NOE, nuclear Overhauser effect; ROE, rotaing frame Overhauser effect.

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meric chains is generally lost. In addition, the acid-hydrolysis of glucoside bonds is generally accompanied by the hydrolysis of the acetyl groups, and the complete depolymerization of CA to the monomer units is generally difficult. Thus, methods for the quantitative estimation of AGUs in CA are required to elucidate structure-property relationships in CAs and for quality control in industrial CA production.

Notably, we previously reported the two-dimensional (2D) NMR of a series of sodium carboxymethyl cellulose (CMC) samples with DS = 0.68–2.86 (Kono, Anai, Hashimoto, & Shimizu, 2015; Kono, Oshima, Hashimoto, Shimizu, & Tajima, 2016a; Kono, Oshima, Hashimoto, Shimizu, & Tajima, 2016b) as well as those of methylcellulose (MC) samples with DS = 0.66–2.44 (Kono, Fujita, & Tajima, 2017). The ^{1}H and ^{13}C chemical shifts of eight AGUs could be assigned using correlation spectra. The chemical shift of each AGU was unaffected by the neighboring substituents or the DS. In addition, quantitative ^{13}C NMR of the samples provided the χ of the eight AGUs comprising these cellulose ethers. The χ of the eight AGUs revealed the reaction mechanism of CMC and MC production (Kono et al., 2016a Kono et al., 2016b; Kono et al., 2017). For CA, a similar 2D NMR approach was applied to samples with DS values ranging from 0.92 to 2.92 prepared from CTA (DS = 2.92) by acid-hydrolysis; the ^{1}H and ^{13}C chemical shifts of the eight AGUs were assigned (Kono, Hashimoto et al., 2015), and were unaffected by the neighboring substituents and the DS. However, the χ of the eight AGUs of CA could not be determined by ^{13}C NMR because the changes in chemical shift of C2, C3, and C6 of CA upon substitution with acetyl groups were smaller than CMC and MC (Kono, Hashimoto et al., 2015). For example, substitution of the methyl groups at the 2-, 3-, and 6-positions caused a downfield shift in the signals of the directly attached C2, C3, and C6 of cellulose (β-effect, i.e. through two bonds from the substituent) to 9.6–10.1 ppm. The large β-effect caused a separation in the ^{13}C chemical shifts of the ring carbons of CMC and MC, which permitted the estimation of χ of the eight AGUs in these cellulose ethers. On the other hand, β-effects caused by the acetyl substituent groups at the 2-, 3-, and 6-positions of cellulose were only 0, 0.2, and 2.8 ppm for the directly attached carbons, and γ-effects, i.e., through three bonds from the substituent, ranged from −4.3 to +0.2 ppm. Moreover, the chemical shifts of the ring carbons of eight AGUs of CA overlap, which complicates their quantitative estimation (Kono et al., 2016a; Kono et al., 2017).

In the present study, in order to quantify the eight AGUs in CA chains, CA samples (DS = 1.26–2.70) were prepared from cellulose in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) via esterification with acetic anhydride (Schlufter, Schmauder, Dorn, & Heinze, 2006). Quantitative ^{13}C NMR spectra of the CA samples were measured, and lineshape analysis of the carbonyl carbon regions was performed to assign the chemical shifts of the carbonyl carbons and to determine the change in χ for each AGU against the DS. In addition, a similar analysis was applied for CA samples (DS = 2.31–1.28) prepared from CTA in acetic acid by hydrolysis with sulfuric acid (Kono, Hashimoto et al., 2015). Based on these results, the mechanisms for the acetylation of cellulose and the hydrolysis of acetyl groups in CA in homogeneous reaction systems are discussed.

2. Experimental

2.1. Materials

Purified pulp (97% α-cellulose) was provided by Daicel Co., Japan. [BMIM]Cl and CTA (DS = 2.92) were purchased from Sigma-Aldrich Inc. (USA). Other chemicals employed in this work were of a chemically pure grade and were used as received without further purification.

2.2. Preparation of CA samples

CA samples (CA **1**–**3**) were prepared from purified pulp dissolved in [BMIM]Cl, according to a previous report (Schlufter et al., 2006). The cellulose pulp (0.45 g, 2.8 mmol for AGU) was dissolved in 7.5 g of [BMIM]Cl with stirring at 353 K for 15 min. After complete dissolution of cellulose, acetic anhydride (0.85 g, 8.4 mmol) was added to the solution. After heating at 353 K for 1 h, the solution was poured into 100 mL of water to precipitate CA. The precipitate was filtered on a sintered crucible, suspended in water (∼50 mL), dialyzed against a stream of distilled water for 3 d, and lyophilized to obtain CA **1**. Similarly, CA **2** and CA **3** were prepared by setting the feed amount of acetic anhydride to 1.4 g (13.9 mmol) and 2.0 g (19.5 mmol), respectively.

HCA **1**–**3** were prepared from commercial CTA by acid-hydrolysis with sulfuric acid, according to a previously reported procedure (Kono, Hashimoto et al., 2015). Briefly, 1.0 g of CTA was dissolved in 15 mL of acetic acid. Sulfuric acid (0.40 g) was added, followed by water (1.5 mL). The mixture was allowed to react at 358 K for 10, 40, and 70 min to obtain HCA **1**–**3**, respectively. At the end of the reaction, 20% aqueous solution of magnesium acetate was added to neutralize the sulfuric acid. The precipitate was washed in ethanol. The precipitates were suspended in water, dialyzed against water for 3 d, and lyophilized. All samples were stored in a desiccator under vacuum until use.

2.3. NMR experiments

Each CA sample (∼35 mg) was dissolved in 700 μL of dimethyl sulfoxide-d_6 (DMSO-d_6) containing 0.03% tetramethylsilane (TMS, isotropic purity 99.9%, Sigma-Aldrich Inc.) and transferred to an NMR tube (diameter; 5 mm, Wilmad-LabGlass Co., USA). NMR data were acquired on a two-channel 500 MHz Bruker AVIII spectrometer equipped with a Bruker *z*-gradient dual-resonance BBFO probe (Bruker BioSpin, GmbH, Germany) at 363 K. ^{1}H NMR spectra were obtained by setting the ^{1}H flip angle and number of scans to 30° and 32, respectively. Quantitative ^{13}C NMR spectra were obtained using the ^{1}H inverse-gated decoupling method (Kono, Hashimoto et al., 2015) with a ^{13}C flip angle, repetition time, and scan number of 30°, 30 s, and 6144, respectively. ^{1}H–^{13}C heteronuclear single quantum coherence (HSQC) data were acquired on a 1024 × 256 point matrix for the full spectrum, with 64 scans per increment. The interpulse delay and repetition time in the HSQC experiment were set to 3.44 ms (corresponds to $1/4J_{CH}$) and 2 s, respectively, and a sine-squared window function was applied along both dimensions prior to the Fourier transform. All ^{1}H and ^{13}C chemical shifts were referenced to the methyl resonance of TMS at 0 ppm.

Lineshape analysis of the quantitative ^{13}C NMR spectra was performed using a simulation software package (“Solaguide” in TopSpin ver. 3.1, Bruker BioSpin) and a nonlinear least-squares method to fit a Lorentzian function to the spectra (Noll and Pires, 1980). The baselines of the ^{13}C spectra were precisely subtracted prior to each fit. The fit was performed using an initial Lorentzian line with a full width at half maximum (FWHM) of 5–15 Hz, and the chemical shift and amplitude of the line were manually adjusted to fit the experimental spectra to achieve a coefficient of determination (r^2) above 0.85. In addition, the FWHM, chemical shift, and amplitude of the Lorentzian lines were fit using the simplex algorithm to minimize the least-squares difference between the experimental and simulated spectra (Kono et al., 2017). In the lineshape analysis, the quality of the fits was set to $r^2 > 0.96$.