

Cellulose Esterification with Octanoyl Chloride and its Application to Films and Aerogels

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Homogeneous esterification of cellulose with octanoyl chloride (a long-chain fatty acid) was investigated in lithium chloride/N,N-dimethyl acetamide (LiCl/DMAc) medium. Cellulose was readily esterified by the octanoyl chloride, as shown by ¹H NMR analysis. The effects of the ratio of octanoyl chloride to cellulose hydroxyl groups, the reaction temperature, and the reaction time on the yield and degrees of substitution (DS) of cellulose esters (CEs) were investigated. CEs with high DS (2.2) were achieved after 8 h at 100 °C with a 1.6 to 1.8 of molar ratio of octanoyl chloride to cellulose hydroxyl groups. Furthermore, hydrophobic, fully transparent CE films and aerogels were prepared using CE tetrahydrofuran (THF) solutions. The CE aerogels exhibited high porosity and were formed with evenly distributed porosity, as revealed by scanning electron microscopy (SEM).

Keywords: Cellulose; Esterification; Cellulose ester; Cellulose ester film; Cellulose ester aerogel

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INTRODUCTION

Cellulose is the most abundant natural biopolymer on earth (Klemm *et al.* 2005). Apart from its conventional use in the pulp, paper, and fiber industries, cellulose is increasingly becoming important in other applications. In recent years, the effective utilization and variety of functions of cellulose have been investigated at length (Nagatani *et al.* 2005). Acylation of cellulose with short-chain carboxylic acids is well-understood (Glasser *et al.* 1994; Samaranayake and Glasser 1993). In recent years, some researchers have become interested in esterifying cellulose with higher-carbon fatty acids, but this process is more difficult to carry out (Satge *et al.* 2002). Fatty acid esters of cellulose can be synthesized in homogeneous media such as solutions in LiCl/DMAc ionic liquid. Several methods for the acylation of cellulose have been proposed, and different reagents have been used in both heterogeneous and homogeneous media (Marson and Seoud 1999; Sjöholm *et al.* 2002).

Research related to cellulose esters (CEs) has made great progress from the classical heterogeneous reaction (Wang and Tao 1994) and microwave radiation reaction models (Gourson *et al.* 1999) to a homogeneous reaction within a LiCl/DMAc system (Heinze and Glasser 1998) and a microwave system (Satge *et al.* 2002). CEs represent a class of commercially-important thermoplastic polymers with excellent fiber and membranous characteristics that have been recognized for nearly a century (Edgar *et al.* 2001). They can be synthesized from natural and renewable raw materials. Moreover, these bio-based products can be obtained through a “green” approach and they offer an

interesting alternative to petrochemical plastics, depending on the required physical properties (Lucie *et al.* 2011).

Shaped cellulosic aerogels are materials that have been recently developed (Fischer *et al.* 2006; Innerlohinger *et al.* 2006; Liebner *et al.* 2007, 2008, 2009, 2010). As of the time of this study, there appear to be no reports of any cellulosic aerogels being prepared from CEs with long carbon side chain.

In the present study, CEs were produced in the LiCl/DMAc system. CE films and aerogels were prepared using CE THF solutions, following the same procedure reported by a previous study (Wang *et al.* 2012). The characteristic films and aerogels were characterized using several physiochemical techniques.

EXPERIMENTAL

Materials

Microcrystalline cellulose, lithium chloride (LiCl), N,N-dimethylacetamide (DMAc), octanoyl chloride, and other chemicals were purchased from Nanjing Jianghua Chemical Co., Ind., China. All chemicals used were of laboratory grade and were used without further purification, except for DMAc, which was sieved through molecular sieves (Type-3 Å) for removing moisture and stored in dried condition prior to use.

Synthesis of CEs

A homogeneous cellulose solution (2%, w/w) in 8% LiCl/DMAc was prepared according to a previously reported method (Yanagisawa *et al.* 2004). CEs with different DS were generated by esterifying cellulose with octanoyl chloride in a homogeneous cellulose LiCl/DMAc solution under different reaction conditions. The product was precipitated by addition of methanol, washed with methanol, extracted with ethanol to remove any residual solvent, and finally dried under vacuum at 40 °C.

Preparation of CE Films and Aerogels

A clean CE solution was first prepared by dissolving cellulose in THF of different concentrations used for the preparation of films and aerogels. The CE films could be formed by evaporation of the CE THF solution. The CE solution was poured into a glass plate. The transparent, ductile films could be peeled away after the solvent THF had been evaporated completely by air-drying. The CE aerogels were produced by regeneration-gelation of the CE THF solution. The CE solution (14%, w/w) was poured into a glass plate to form a 1-mm-thick layer and immersed in ethanol for the regeneration-gelation. The gel was thoroughly washed with ethanol and tert-butyl alcohol and was subsequently freeze-dried to yield the aerogels, according to the previously reported procedure (Wang *et al.* 2012).

NMR and SEM Measurement

Proton nuclear magnetic resonance (¹H NMR) spectroscopy was performed in THF-D8 medium using a Bruker DRX-300 Spectrometer (operating at 300 MHz) to determine the degree of substitution (DS). The integration method used is described in a previous study (Joly *et al.* 2005). Observation of CE aerogels was carried out using a Hitachi S-4800 SEM.

RESULTS AND DISCUSSION

Esterification of Cellulose with Octanoyl Chloride

As shown in Fig. 1, cellulose was readily esterified by the octanoyl chloride–pyridine mixture. The CEs obtained in this medium showed a compact plastic consistency. The yield and DS of CE were greatly influenced by the ratio of octanoyl chloride-to-cellulose hydroxyl groups, the reaction temperature, and the reaction time. Practically, the weight increase of each cellulose sample was due to the grafting of fatty substituents. Consistent with its DS value, no extensive degradation of the polymer took place in the course of esterification when a DS value of 2.2 was achieved by reaction for 8 h at 100 °C with 1.6 to 1.8 of molar ratio of octanoyl chloride-to-cellulose hydroxyl groups, contrary to other synthesis methods (Thiebaud and Borredon 1995). The CEs were identified and quantitated by ^1H NMR spectroscopy (Fig. 2). Again, no significant mass loss due to degradation was detected for the samples. Acylation of the cellulose was confirmed to have occurred by integrating the characteristic signals of fatty acid protons from 0.89 to 2.34 ppm and of the cellulosic backbone from 3.00 to 5.50 ppm (carbohydrate protons).

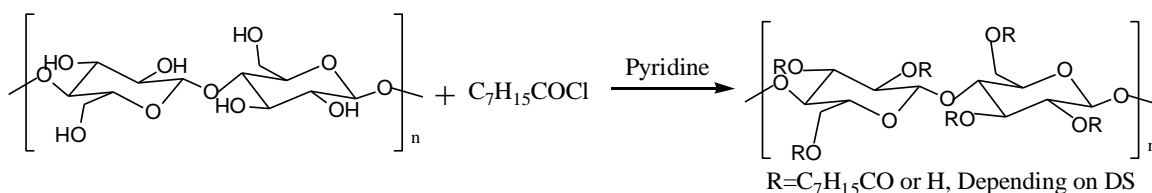


Fig. 1. Synthesis of cellulose esters (CEs) with octanoyl chloride in pyridine

Effects of Different Ratios of Octanoyl Chloride-to-Cellulose Hydroxyl Groups on the Yield and DS of CE

Esterification of cellulose with octanoyl chloride (a long-chain fatty acid) in homogeneous cellulose LiCl/DMAc solvent was achieved. The effect of the octanoyl

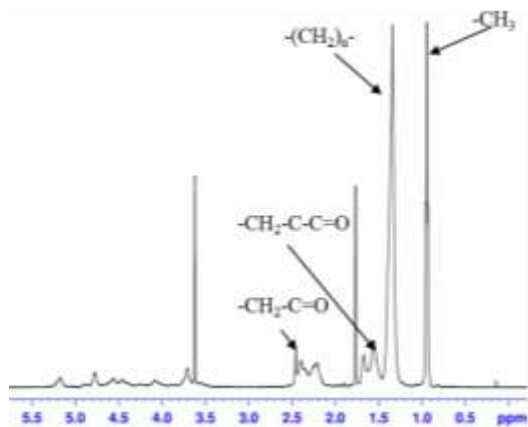


Fig. 2. ^1H NMR spectra of cellulose esters in tetrahydrofuran- d_8

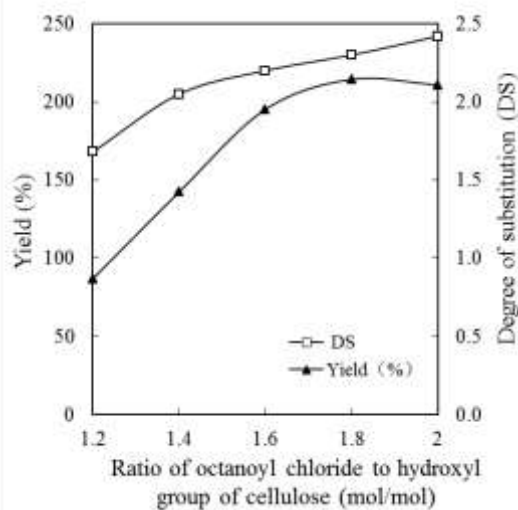


Fig. 3. Effect of octanoyl chloride content on the yield and DS of cellulose ester (reaction temperature: 100 °C; reaction time: 8 h)

chloride-to-cellulose hydroxyl group molar ratio on the DS of CE after 8 h at 100 °C is shown in Fig. 3. The yield and DS were greatly influenced by the amount of octanoyl chloride present. These parameters increased with increasing octanoyl chloride-to-cellulose hydroxyl group molar ratios. At higher relative octanoyl chloride contents, there were more opportunities for the hydroxyl groups of glucose units to have access to a fatty acid chloride. However, the increase in CE yield leveled off when the octanoyl chloride-to-cellulose hydroxyl group molar ratio increased beyond 1.6.

Effects of Reaction Temperature on the Yield and DS of CE

Esterifying cellulose was very difficult at lower temperatures. The DS of CE greatly increased with increasing reaction temperature. The effect of esterification temperature on the DS of the resulting CE is shown in Fig. 4. The molar ratio of octanoyl chloride-to-cellulose hydroxyl groups was 1.6, and the reaction time was 8 h. As the reaction progressed, esterified cellulose precipitated out of the DMAc/LiCl system and the long-chain group prevented free hydroxyl groups from being esterified. Thus, increasing the temperature can accelerate esterification, and CEs with higher DS can be obtained. However, the yield of CE exhibited a starkly different tendency compared to that of the DS. The yield of CE increased rapidly when reaction temperature rose from 40 to 80 °C, but it increased slowly with further increased temperature, and the yield even decreased when the temperature increased from 80 to 120 °C. This may have been due to HCl production during esterification. High temperatures led to acid degradation of cellulose.

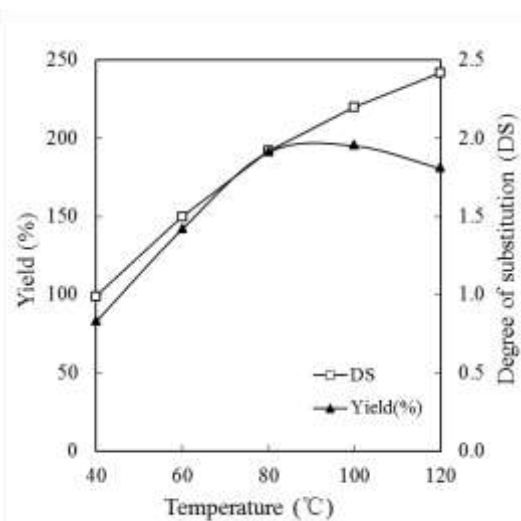


Fig. 4. Effect of reaction temperature on the yield and DS of cellulose ester (molar ratio of octanoyl chloride-to-cellulose hydroxyl group: 1.6; reaction time: 8 h)

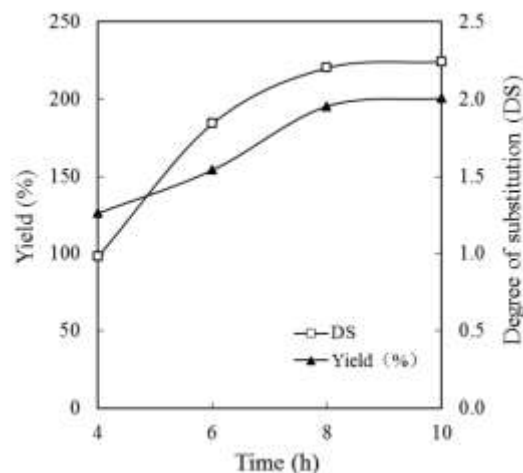


Fig. 5. Effect of reaction time on the yield and DS of cellulose ester (molar ratio of octanoyl chloride to cellulose hydroxyl group: 1.6; reaction temperature: 100 °C)

Effects of Reaction Time on the Yield and DS of CE

The effect of reaction time on the yield and DS of CE is shown in Fig. 5. The molar ratio of octanoyl chloride-to-cellulose hydroxyl groups was 1.6, and the reaction temperature was 100 °C. Both the DS and yield greatly increased as the reaction time increased. Due to the spatial steric effects of the long-chain substituents, the rate of

esterification was hindered and the DS and yield stabilized when the reaction time increased from 8 to 10 h.

Characterization of CE Films and Aerogels

The CE could be dissolved in THF completely at a concentration as high as 14%. Such behavior makes it possible to prepare CE films and aerogels easily. The CE film was presented simply by evaporating the solvent THF from the CE solution into a plate. A ductile film can be peeled as shown in Fig. 6. The film was completely transparent. The surface of the CE film was relatively flat and hard-packed. The features common to the membrane material are shown in Fig. 7A. Furthermore, the long-chain CE with high DS had strongly hydrophobic properties. There are broad prospective uses for this kind of film in the preparation of hydrophobic materials. Contact angle, which is also called the wetting angle, is formed at the liquid-solid contact zone and is determined by a thermodynamic equilibrium condition. The contact angle is a measure of the free energy of the interface as well as one of the important factors that determine the hydrophobic performance of materials (Xu *et al.* 2004; Pasquini *et al.* 2006). The contact angle of CE film reached up to 109° when the DS was increased to 2.2 (Fig. 6). The contact angle of cellulose without esterification was 0°. Strong water absorbency of cellulose was shown clearly, which was attributable to the large amounts of hydroxyl groups on the surface of cellulose. The hydroxyl number was reduced gradually with increasing DS, which resulted in the decreasing of hydrophilicity. It follows that such CE films can be used as full hydrophobic materials (Sami and Mohamed 2006). In contrast to the strong water absorbency of raw cellulose, the esterification of cellulose can improve the hydrophobicity of cellulose material significantly.

Cellulose aerogels can be prepared from the LiCl/DMSO system by a regeneration-gelation procedure, as shown previously by the authors (Wang *et al.* 2012). In this study, regeneration of CE from the THF solvent via immersion in ethanol yielded translucent gels. The gels were transferred to tert-butyl alcohol and then freeze-dried to create aerogels. The inside observation on fractured cross sections of CE aerogel shows networks of unique porous structure (Fig. 7B). The SEM images show that the bulk of CE aerogel was composed of long and fairly straight fibrils interconnected with one another to form three-dimensional networks with large interstitial spaces.



Fig. 6. Contact angle of cellulose ester film with water (A) and photograph of cellulose ester film (B)

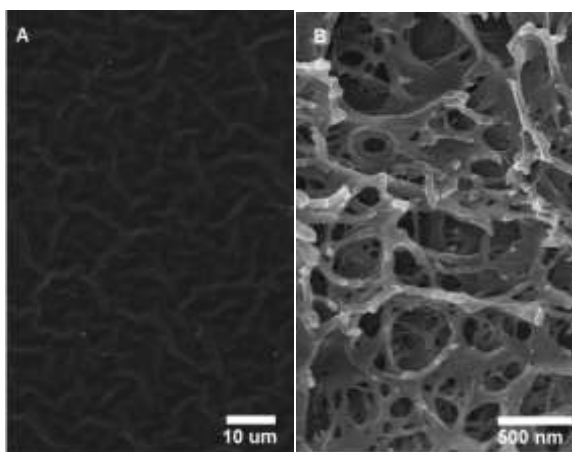


Fig. 7. SEM images of the surface of the cellulose ester film (A) and a cross section of the cellulose ester aerogel (B)

In comparison with the CE, the CE aerogel material had higher porosity, larger aperture, and higher adsorption performance. A future study should investigate the adsorption performance of CE gel materials in more detail.

CONCLUSIONS

1. Fully substituted cellulose fatty ester derivatives were readily synthesized with octanoyl chloride in a homogeneous LiCl/DMAc medium, as shown by ^1H NMR analysis. CE samples with high DS (2.2) were achieved after 8 h at 100 °C with 1.6 to 1.8 of molar ratio of octanoyl chloride-to-cellulose hydroxyl groups.
2. Both of the yield and DS of CE esters increased with increasing of the ratio of octanoyl chloride to cellulose hydroxyl groups, the reaction temperature, and the reaction time. However, the increase in CE yield leveled off when the octanoyl chloride to cellulose hydroxyl group molar ratio was increased beyond 1.6 after 8 h at 100 °C. In particular, the yield increased slowly with further increased temperature, and the yield even decreased when the temperature increased from 80 to 120 °C due to the degradation of cellulose.
3. A hydrophobic, fully transparent CE film was prepared using CE THF solutions. The contact angle of CE film were able to reach 109 degrees when the DS was 2.2. Porous CE aerogels were prepared by regeneration-gelation of CE THF solutions. The SEM images of aerogel revealed that the bulk of CE aerogel was composed of long and fairly straight fibrils interconnected with one another to form three-dimensional networks with large interstitial spaces.

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